INVESTIGATION OF THE VOLGA RIVER SEDIMENTS COMPOSITION

– INORGANIC POLLUTANTS OF POTENTIAL CONCERN –

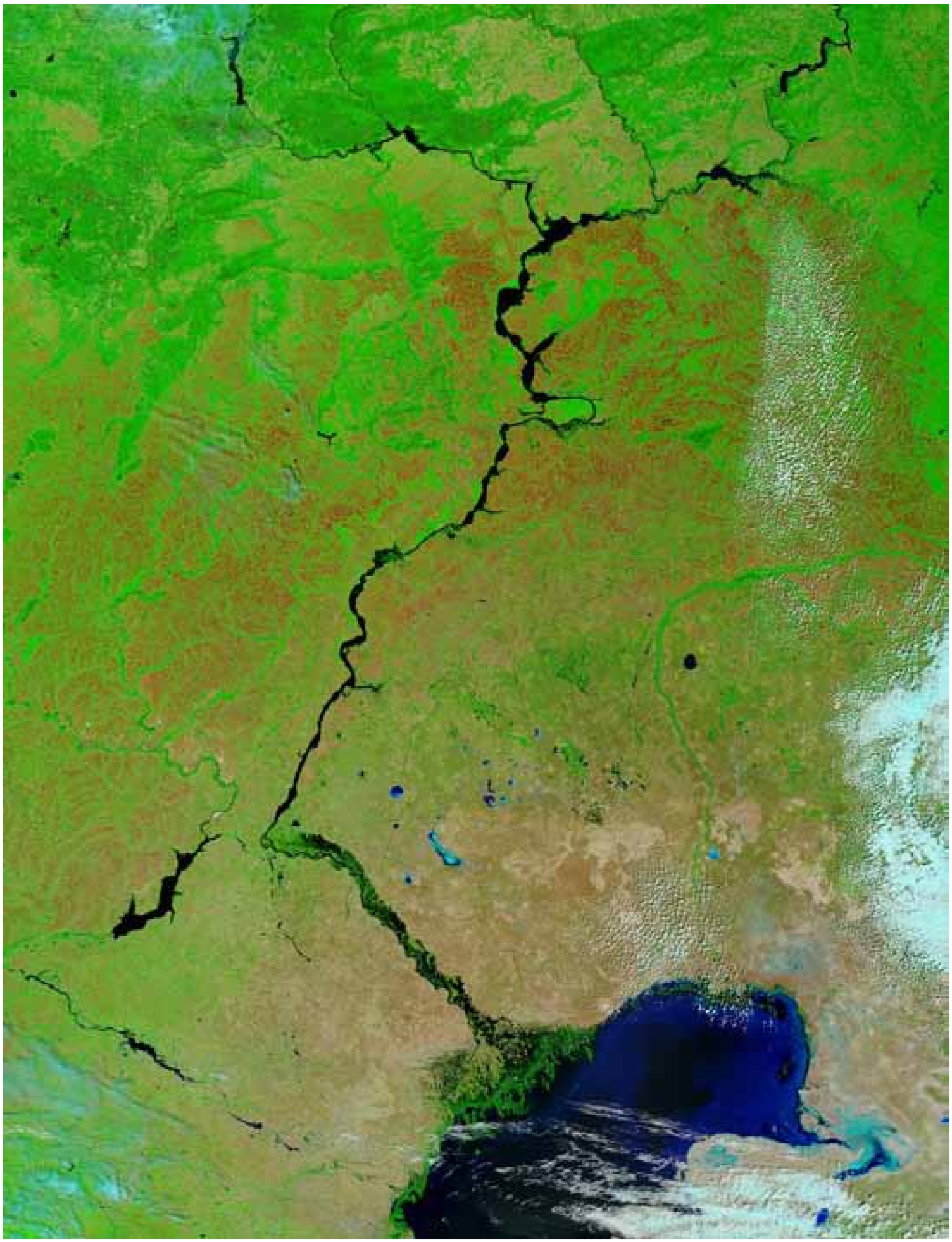

Image courtesy MODIS Rapid Response Project at NASA/GSFC

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Thema

INVESTIGATION OF THE VOLGA RIVER SEDIMENTS COMPOSITION

– INORGANIC POLLUTANTS OF POTENTIAL CONCERN –

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	Prof. Dr. Heinz Friedrich Schöler

Abstract

Within the framework of the joint Russian-German research project “Volga-Rhine”, a continuation of the scientific-technical cooperation started with the “Oka-Elbe”-project in 1992, investigations of the inorganic (this report) and organic pollution (conducted by the working group of Prof. H.F. Schöler) of the Volga rivers aquatic sediments were carried out.

Starting with the work of Züllig (1956) sediments have been recognized and used extensively as an almost ideal compartment for the description of the current condition of an aquatic system. Acting as a buffer (sink and source) with respect to heavy metals, nutrients, and major groups of organic pollutants, especially fine grained sediments (< 20µm) are appropriate to reflect the manifold factors determining the status of a water body – at the same time avoiding the time and effort needed to describe these (highly) fluctuating systems by the use of water analysis.

Originally intended as a geochemical description of the Volga system, with respect to (heavy) metals and phosphorous, already a cursory error estimation regarding the entire measurement process (chemical analysis as well as sampling itself) changed the intention of this work drastically. Applying the widely accepted guidelines to the expression of uncertainty in measurement (GUM, 1993), as well as adopting basic principles of Gy’s Theory of Sampling (Gy, 1998) eventually disproved the validity of numerous geo-chemical approaches towards an interpretation of – not only – sediment data sets, mainly due to shortcomings in the sampling-scheme and thus lacking proof of representativeness. Although, ‘*there is an understandable lack of enthusiasm for rousing the sleeping dogs of sampling when there is a fair chance of being severely bitten*’ (Thompson, 1999) it is the only way that will lead to justifiable interpretations and decisions within the framework of any sampling scheme.

Making a sample demonstrably representative for anything but itself, inevitably leads to uncertainty-budgets typically in the range of 20%-100%. This in fact leaves little more opportunities than:

- return to robust classification systems (like the I_{geo}-classes (Müller, 1979)),
- group multiple samples in order to achieve the desired precision (this report), or
- change the methodology (e.g. the US-EPA TRIAD-approach (Crumbling, 2001)).

Kurzfassung

Im Rahmen des gemeinsamen, russisch-deutschen Forschungsvorhabens “Wolga-Rhein”, einer Fortsetzung der wissenschaftlich-technischen Zusammenarbeit, welche im Jahre 1992 mit dem “Oka-Elbe“-Projekt begann, wurden die Wolga-Sedimente in Bezug auf anorganische (diese Arbeit) und organische (Arbeitsgruppe Prof. H.F. Schöler) Schadstoffe untersucht.

Ausgehend von der Arbeit Zülligs (1956) wurden Sedimente als geradezu ideales Kompartiment zur Beschreibung des Gewässerzustandes (an-) erkannt und eingesetzt. Insbesondere feinkörnige Sedimente (< 20 µm) fungieren als Puffer (Quelle und Senke) für (Schwer-) Metalle, Nährstoffe und wichtige organische Schadstoffe und sind daher besonders geeignet die vielfältigen Einflussfaktoren auf Gewässersysteme zu bestimmen – während sie gleichzeitig den Aufwand und die Kosten, die zur Beschreibung dieser fluktuierenden Systeme mittels Wasseranalytik nötig würden, deutlich reduzieren.

Ursprünglich als geo-chemische Beschreibung der Wolga in Bezug auf (Schwer-) Metalle und Phosphor geplant, änderte schon eine oberflächliche Fehlerbetrachtung des gesamten Meßvorgangs (chem. Analytik und Probennahme) die Ziele vollständig. Die Anwendung der weithin akzeptierten Grundlagen zur Beschreibung von Messunsicherheiten (GUM, 1993) und Grundprinzipien von Gy’s Theorie der Probennahme (Gy, 1998) schließlich, widerlegte die Stichhaltigkeit zahlreicher geo-chemischer Ansätze zur Interpretation von Sediment-Datensätzen – und nicht nur diesen – im wesentlichen aufgrund unzureichender Probennahmepläne und der daraus resultierenden mangelnden Representativität. Obwohl es, wie Thompson (1999) anmerkte, *‚verständlicherweise wenig Begeisterung dafür gibt, die schlafenden Hunde der Probennahme zu wecken, da die Chancen gebissen zu werden hoch sind’*, ist es doch die einzige Möglichkeit nachprüfbare Interpretationen und Entscheidungen im Rahmen eines Probennahmeplans zu treffen.

Das Unsicherheits-Budget einer Sedimentprobe, die nachweislich nicht nur sich selbst repräsentiert, liegt typischerweise im Bereich von 20%-100%. Tatsächlich lässt dies kaum mehr Möglichkeiten als:

- die Rückkehr zu robusten Klassifizierungssystemen (z.B. I_{geo}-Klassen (Müller, 1979)),
- das Zusammenfassen mehrer Proben um die gewünschte Präzission zu erreichen (diese Arbeit), oder
- die Methodik zu ändern (z.B. TRIAD-Ansatz der US-EPA (Crumbling, 2001)).

1 The Volga River Basin

1.1 General description

Figure 1 **The Volga River Basin (all maps © by UNEP)**

The Volga River in European Russia – part of the larger East European Plain – is Europe's largest river in length (approx. 3500 km, 3200 of which are navigable[1]), watershed basin (approx. 1.35 million km[2]) and annual mean discharge (200-255 km³/year near Volgograd[2]).

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[1] One can find almost any length for the Volga in the literature and in tables; starting from 3370 km (http://disc.gsfc.nasa.gov/geomorphology/GEO_5/GEO_PLATE_D-8.HTML) up to 3692 km (http://www.wetlands.org/programs/RussiaCD/eng/VOLGA-10.HTM).

Numerous reasons are conceivable for the differences: different lengths of the fairway pre- and post-damming (diminishing the winding of the original channel, due to the risen water-level); different fairways, for different classes (size) of ships; different 'endpoints' of the Volga (sea-level-fluctuations of the Caspian Sea; where does the river-delta end?) and different 'starting-points' of the Volga (The most humorous description of the latter problem is provided by Sochurek (1973): "Finding the headwaters of the Volga in that wide sweep of forest and lake, each connected by stream or rivulet, seems to be an arbitrary exercise. The state places the source to the west of Ostashkov at a place called Volgoverkhovye." (While this 'state' was not necessarily the 'evil' USSR, since Behning (1928) places the headwater of the Volga underneath a chapel close to the village 'Wolgino-Werchowje' (in German: 'Wolga-Anfang' (i.e. 'Beginning of

Its basin stretches from the Valdai Hills (Valdayskaya Heights) and Central Russian Upland in the west to the Ural Mountains in the east and narrows sharply near Saratov in the south, flowing generally southeastward, to empty into the Caspian Sea – the Earth's largest landlocked water body – approx. 28 m below sea level. More than 55 million people (approx. 40% of the total Russian population) live in the Volga Basin and almost 50% of Russia's industrial and agrarian production is located here – while it accounts for only about 8% of the area of the Russian Federation.

The Volga plays an important role in Russia's transportation system[3], carrying more than 70% of the country's river transport, as well as providing water for irrigation, industrial and domestic use

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the Volga'), which should be the same place; and it's not very likely, that the early soviet-government was eager to place a chapel (!) on a reckoned source of the Volga…))

[2] This may be one of the few figures with an uncertainty **not** owed to the lack of information.

Regular instrumental observations of the Volga-runoff in the Caspian region were started in 1876 and all data are available (of course with the exception of the years of WW II). The underlying problem in this case is the natural and man-made fluctuation of the Volga-discharge (which can be seen in the sea-level fluctuations of the Caspian Sea – to which inflow the Volga accounts for about 80%)), and the resulting differences, when averaging different time-periods (highest run-off near Volgograd (1926): 383 km^3; lowest run-off near Volgograd (1937): 161 km^3.)

The discharge of selected (Russian) Rivers is provided by the *State Hydrological Institute* (SHI) in St. Petersburg – including 6 stations on the River Volga; 4 stations on the River Oka, and 3 stations on the River Kama – and can be obtained through (http://espejo.unesco.org.uy/part`4/7_fussr/russia/index.htm). Or, in more detail (!) by the *National Center for Atmospheric Research* (NCAR) (http://dss.ucar.edu/datasets/ds553.2/) – including different data sources (not only SHI), more stations and longer (more complete) time-series).

See also Polonskii (1995) who subdivides the Volga runoff in several low and abundant water periods within the natural and anthropogenic impacted flow of the Volga.

[3] This statement is part of almost every description of the River Volga – and without question valid up to the first half of the 20th century – while it may not be true today:

"*Even the Volga that was formerly a transportation pivot of the Central and Southern Russia is losing its freightage importance to an increasing extent. The transit traffic from the Trans-Siberian route enters directly the marine "flanks", i.e. St. Petersburg and Novorossisk. The Volga and its tributaries are almost not operating but they are forming allegedly annoying "water obstacles" which need the bridges to be built over them.*"

(*New East, 3/4 2000*; http://segodnya.spb.rus.net/3-4-00/eng/28_e.htm)

The *Russian-American chamber of commerce* published data about the inland-water transport on their web-site, talking about 4.8% of the total freightage in the Samara-Region (with 73.2 million tons one of the biggest transport centers of Russia) being carried by water. (http://www.russianamericanchamber.org/regions/samara.html)

The *US Department of Commerce* published data citing the Minister of Transport of the Russian Federation Sergei Frank in December 2002, which indicate an even less proportion of freight being transported by inland waterways throughout the Russian Federation as a whole.

(http://buyusainfo.net/info.cfm?id='115755'&keyx='270179400'&loadnav= - link reachable through *BISNIS* (Business Information Service for the Newly Independent States) http://www.bisnis.doc.gov/bisnis/isa/isa-transp.cfm).

They report 115.7 Million tons of cargo transported by river – compared to a total of 11,795.0 Million tons (cargo turnover being: 80,238.5 Million tons-kilometer – compared to a total of 3,001,168.9 Million tons-kilometer).

(in contrast to many other countries, most drinking water in Russia is derived from surface water, not groundwater – the figures reaching from 68% (Astrakhan Oblast – southern part of the Volga-basin) to more than 98% (Moscow)[4]. Cf. Hamburg: 100% groundwater based, or Amsterdam: 50/50.).

The *United Nations Economic Commission for Europe – Inland Transport Committee* stated that the volume of goods traffic on the Volga-Baltic Waterway (from and to St. Petersburg) grew 2.5 times between 1997 and 2001 reaching 15 Million tons in 2002 – resulting in capacity limits during peak load periods.

On the other hand an "*extremely difficult situation*" due to low water-depths in the section Gorodets-Balkhna (near Nizny Novgorod) with '*the need to operate vessels significantly under-loaded and, practically, a complete standstill for large passenger vessels*' is reported (http://www.unece.org/trans/doc/2003/sc3/TRANS-SC3-2003-11E.pdf).

To make a long story short: even if the Volga would (still) carry 70% of the country's river transport, the amount would be just about 80 Million tons – 15 Million of which would be on the Volga-Baltic Waterway; and about the same amount on the Volga-Don-canal. The remaining 65 (or 50) Million tons for the rest of the Volga sound a bit less impressive (i.e. approx. 0.6% of the total transported cargo in Russia), c.f. Greater River Rhine area 175.3 M t (2001)), especially as there are substantial problems in several sectors (navigational, as well as administrational) which make even these reduced figures at least questionable (c.f.: BAW (2002) or various (online-) reports of the above mentioned *UNECE-Transport division* (http://www.unece.org/trans/main/sc3/sc3.html)).

[4] One could carry out the same comparison of sources as above for the freight-transport – and almost any figure from (Russian) statistics. It's nearly impossible to decide, which one is closer to reality, and as we will see later, sometimes there are different numbers within the same data-set and/or publication. There are several reasons; one of them is surely the sheer size of the country. What holds true, for say the European part of Russia is not necessarily true for the Asiatic part of the country. This also holds true for a north-south comparison of the European part. Of course, there are other possible reasons, and one can easily figure them out, but it would be less polite to discuss them… or, as de Melo and Ofer (1999) with regard to economic data annotated, '*For those who know Russia, a cautionary word about the reliability of data may not be necessary.*'

Any approach to derive a single (meaningful) figure for the whole region is doomed to fail – and individual numbers for different regions are hard to obtain, unless one is willing to spend money…

1.2 *Physical geography of the Volga basin*

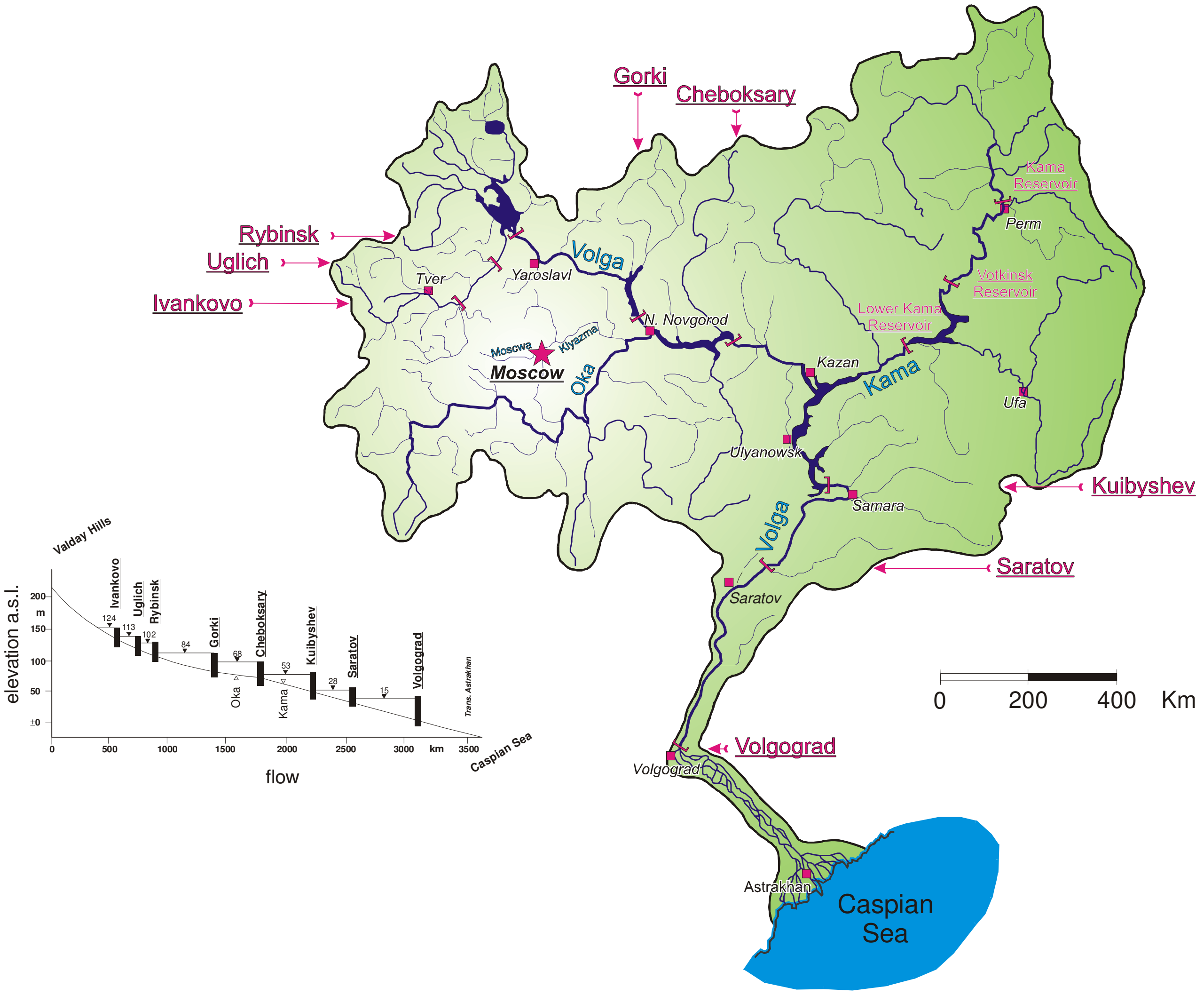

Figure 2 **Volga river catchment and main hydrotechnical constructions of the Volga-Kama-Cascade.**

Rising 228m a.s.l. in the Valday Hills northwest of Moscow, the Volga flows southeast through a chain of small lakes towards Moscow, past the cities of Rzhev and Tver, before bending northeast. Near the bend, the Volga is connected to the Moscow Canal, which flows south, to join the River Moscwa north of the Russian capital Moscow.

After passing the reservoirs of Ivankovo and Uglich, the river flows through the Rybinsk Reservoir, which is fed by the rivers Mologa and Shecksna in the north, rather than the Volga itself. The Reservoir is also served by the Volga-Baltic Waterway, reaching the Baltic Sea at St. Petersburg; and the White-Sea-Baltic Waterway, which flows north into Lake Onega and the White Sea.

From the Rybinsk Reservoir the river flows southeastward through a narrow valley between the Uglich Highlands to the south and the Danilov Upland to the north continuing its course along the Unzha and Balakhna plains to Gorodets, to form the Gorky reservoir.

Passing through the next reservoir in line, the Cheboksary reservoir, the Volga receives the headwaters of its second largest tributary, the River Oka near Nizhny Novgorod (formerly Gorky).

Between the confluence of the Oka River and the city of Kazan, where the Volga turns south, it doubles in volume before its major tributary the River Kama joins within the upper/middle part of the Kuibyshev reservoir. From this point the Volga becomes a mighty river, which, after a sharp loop (‘Samara Bend’ at the Zhiguli Mountains) – at the beginning of which the (former) ‘Lenin’-dam near Togliatti marks the end of the Kuibyshev reservoir – flows south until reaching Volgograd (formerly Stalingrad – there before Zarizyn).

On this way, it passes through the Reservoirs of Saratov and Volgograd. It is only on this part of the river, where the pre-damming distinction between the high and steep right bank (‘hilly side’, or ‘Bergufer’) and the low left bank (‘plains side’, or ‘Wiesenufer’) remains intact. Especially within the Saratov reservoir, which in contrast to the other reservoirs of the ‘valley-type’ has a riverine character raised only a little above the natural level of the Volga, this dissimilarity, caused by the Coriolis Effect (Einstein, 1926), was preserved, whereas in other reservoirs both banks were flooded.

Just downstream the Volgograd reservoir, the Volga’s main distributary, the Akhtuba, branches southeastward to the Caspian Sea, running parallel to the main course of the river for about 500km through the Caspian Depression. At Volgograd, the River is connected to the Volga-Don Canal, which facilitates transportation to the Sea of Azov and the Black Sea. The ‘unregulated’[5] floodplain of the Volga-Akhtuba is characterized by numerous interconnecting channels, old cutoff courses and loops, where natural conditions are pretty much different from the surrounding semi-desert and desert zone, since temporary (spring-) flooding secures excessive moisture.

Shortly before Astrakhan a distributary of the Akhtuba, the Buzan, marks the beginning of the river-dominated Volga delta of more than 10,000 km².

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[5] Two parts of the Volga are often referred to as unregulated: the part upstream the Ivankovo reservoir and the part downstream the Volgograd reservoir. In fact they are influenced by the Verkhenevolzhskoe Reservoir (on the Upper Volga-lakes – see[9]) and the Volgograd reservoir respectively, since the flow from/to these parts is controlled by man.

1.3 Geology and formation of the Volga basin

The greater part of the catchment area of the Volga is in the middle of the Russian (or East European) plain – a part of the East European Shield – only a small part within the catchment area of the Kama belongs to the Ural Mountains. The base rocks are ancient crystalline rocks from the Precambrian, covered extensively with a thick layer of sedimentary rocks.

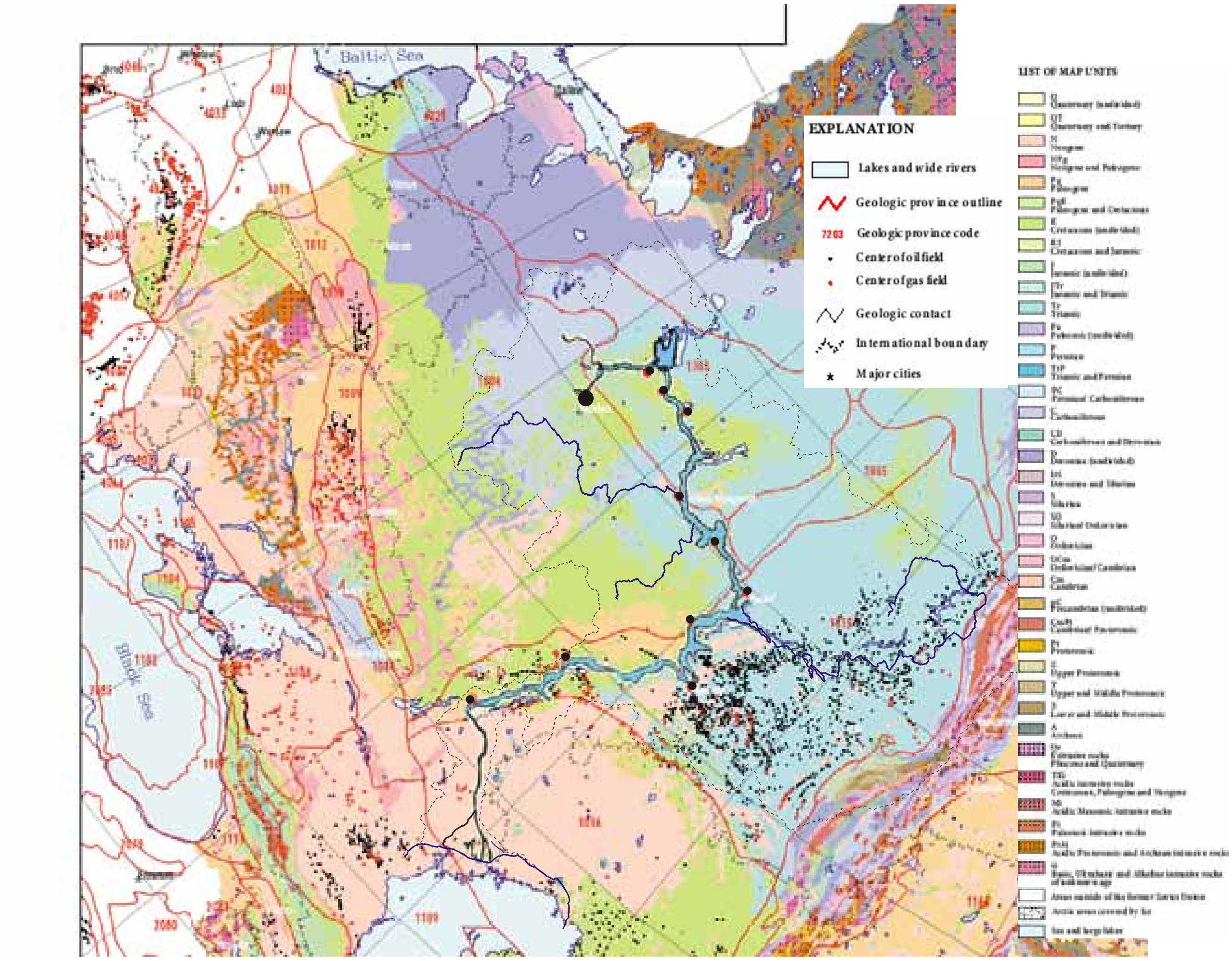

Figure 3 **Map showing geology, oil and gas fields, and geological provinces of the Former Soviet Union (Persits et al. (1998) – because of different projections, the inserted Volga basin (not in the original map) is only a rough estimate.**

Within the Volga basin, the thickness of this layer exceeds about 3000 m in the area of the Moscow syncline, and reaches 8000 m in the Glasov (near-Ural) syncline and more than 10000 m in the near-Caspian. The adjacent basins bear deposits of brown coal (Moscow basin), as well as oil/gas (Volga-Ural province and North-Caspian basin) and salt (North-Caspian basin).

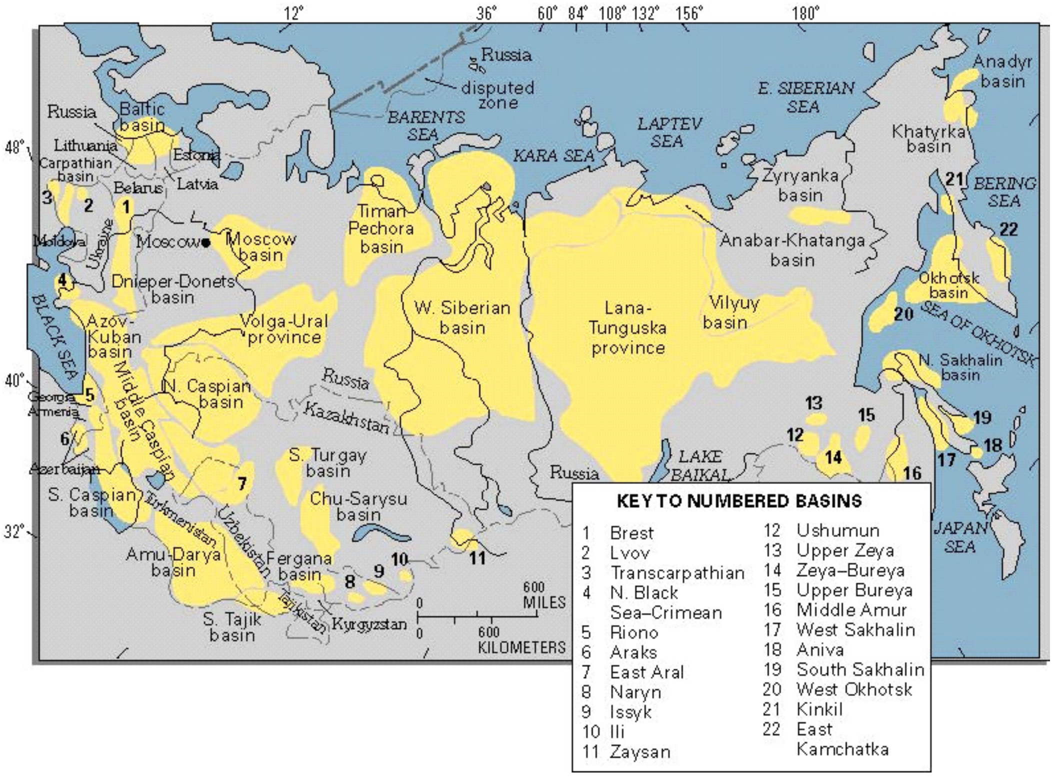

Figure 4 **Map showing the location of basins in the former Soviet Union (© USGS-Energy Resource Surveys Program)**

Approximately 65% of the Volga catchment area is occupied by lowlands with a height under 200 m a.s.l., about 35% by uplands hardly exceeding 200-250 m; resulting in a mean elevation of about 170 m. These uplands are the watersheds separating the Volga from the adjoining basins, as well as dividing it into the sub-basins of its tributaries.

The Valdai Hills (highest peak 346 m), show imprints of the last glaciation (the Valdai (Würm) glaciation) which ended 10.000-15,000 years ago, with many lakes filling the depressions left behind and rather stony soils, as well as 'erratic blocks' typical for terminal moraines. Having left the Valdai Hills, the River enters the Upper Volga lowland, crosses the southern part of the Mologa-Sheksna depression (Rybinsk reservoir) and flows over several interconnected lowlands – the Yaroslavl-Kostroma, Unzha, Balakhna, Mari, Zavolzhye and the near-Caspian. Only in a few places does the river cut through the near-Volga uplands, e.g. near Plyos (south-east of Kostroma – well known for Isaak Levitan, the landscape painter who recorded local scenes) and in the Samara Bend, where the Volga divided the Zhiguli massif of ancient limestones and dolomites into the Zhiguli (right bank) and Sokolii Hills. These hills (highest point 368 m) – the only mountains of tectonic origin in the East European Plain – are situated in the intermediate zone between the forest and the steppe, and remained uncovered by glaciation, as well as the so-called Akhchagyl Sea formed at the end of the Pliocene (approx. 1,000,000 years ago). Because of a deep down-fold of the earth's crust, extending from the area now occupied by the Caspian Sea to the middle course of the Paleokama

River, the lake expanded to more than three times the present Caspian Sea area and established the first of a series of connections with the Black Sea and Lake Aral. Later (Quaternary) transgressions, linked to the glaciation cycles starting with the Oka glaciation (simultaneous with the Günts and Mindel glaciation in the Alps – starting about 700,000 years ago), caused the sea level to sink within a series of high and low stands, from then 50 m a.s.l. to its present level of approx. -28 m. At the end of the Dnieper (Riss) glaciation (about 300,000 years ago) – the glaciation which covered the largest part of the Volga catchment area of all glaciations – the (Paleo-) Volga captured the (Paleo-) Kama, almost doubling its catchment area, flowing along the large fold in north-south direction sometimes called the 'seam' of the Russian platform and once covered by the Akhchagyl Sea.

1.4 Geographic subdivision

1.4.1 Climatic zonation

Four geographic zones lie within the Volga basin (Figure 5):

- the boreal forest of the Taiga in the north up to Nizhny Novgorod (formerly Gorky), with 800-600 mm precipitation
- the forest steppe from there to Samara (formerly Kuibyshev)
- the steppe from there to Volgograd (formerly Stalingrad) with 350-250 mm precipitation
- the (semi-) desert lowlands northwest of the Caspian Sea (down to 175 mm precipitation).

Especially in the Lower Volga region – downstream Samara – the precipitation decreases sharply when moving south, and the entire catchment area is characterized by warmer winters and cooler summers in the west than at the same latitude in the east (east of 40°E), due to the moderating influence of the Atlantic in the west. The climatic conditions in the steppe belt (14^a in Figure 5-II) as well as the desert region (18 in Figure 5-II) are highly continental, and differ considerably from those in the Atlantic-Continental forest climate regions (9^a, 9^b, 9^c, and 9^d in Figure 5-II) of the Volga basin, while the moderating influence of the Caspian Sea is negligible. With winter temperatures comparable to the NW part of the catchment area – the mean average temperature in January in Volgograd is approx. the same (-9.6°C), as in Tver, 8°N of Volgograd – and much hotter summers than even the eastern parts – e.g. the mean temperature in July in Astrakhan is 25.1°C cf. 20.6°C in Samara.

The Volga is generally free of ice for about 200 days each year (about 265 days at Astrakhan) –with icebreakers extending the navigational period particularly in the Volga-Don-Canal and the Volga-Baltic waterway. It is fed by snow (60% of its annual discharge), groundwater (30%), and rainwater (10%).

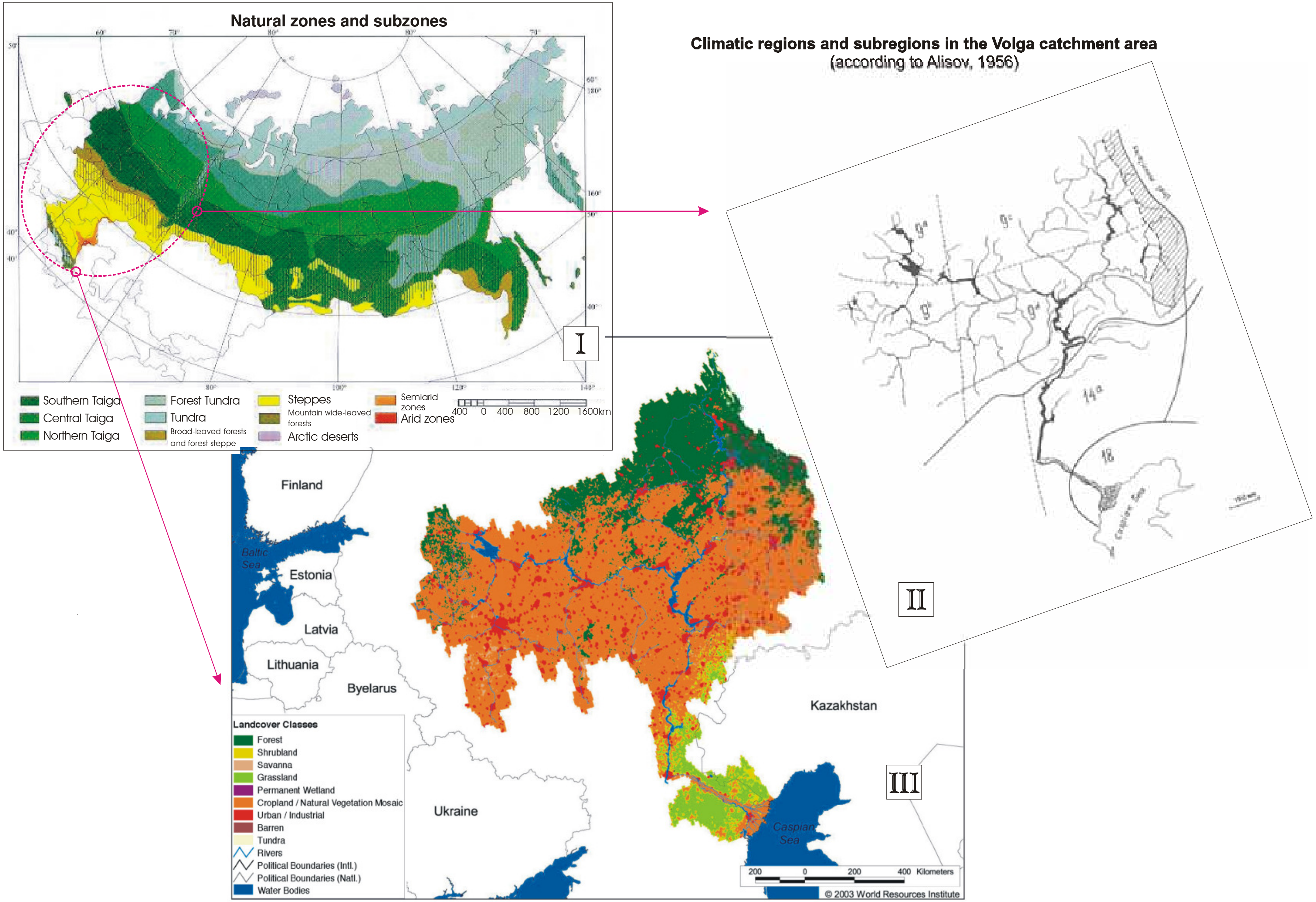

Figure 5 Climatic zonation and landcover of the Volga River basin
(map I: Stolbovoi and McCallum, 2002; map II: WRI, 2003; map III: Fortunatov, 1979).

1.4.2 Major soil groupings

Due to the almost homogenous deposits covering the Volga catchment area and the East European plain, the soil characteristics in this area essentially follow the above geographic and climatic zonation.

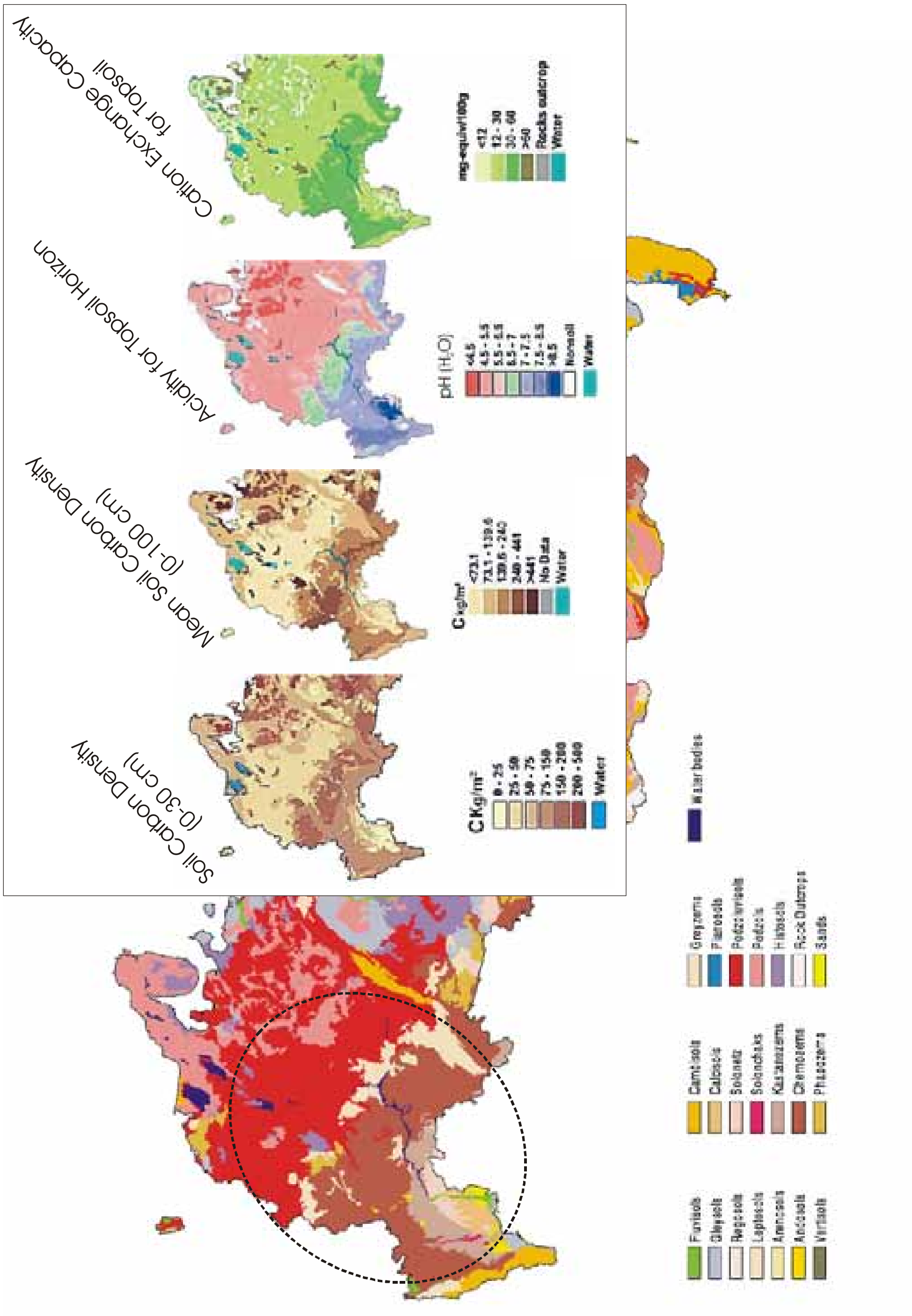

Figure 6 Major soil groupings of European Russia and key-characteristics controlling their behavior towards water-soil interaction (Stolbovoi and McCallum, 2002).

Podzoluvisols (sod-podzolic and light grey forest soils formed from fine-textured deposits) and **Podzols** (formed from coarse-textured deposits) are widely spread in the boreal forest zone. The more widespread Podzoluvisols show some features of Podzols (a strongly bleached horizon) and of

Luvisols (an accumulation of clay). These soils are formed from unconsolidated clay and loam parent material; the soil is acid with the pH increasing downward; texture and total chemical composition are usually differentiated down the profile; and the humus content varies from 3–7% (increasing from the west to the eastern part of the country) for undisturbed soils and from 1–2.5% for cultivated soils. Fulvic acids, rather than humic acids dominate the humus composition.

Greyzems (grey forest soils), formed from calcareous parent rocks can be found in a relatively small area of the forest-steppe zone around Cheboksary, Kazan and the mouth of the Kama River. They differ from the light grey forest soils by the darkness and thickness (15-25 cm) of the humus horizon; the reaction of the topsoil is slightly acid or acid, and neutral or alkaline in the subsoil; the humus content is 5-12%. Humic acids linked with Ca^{2+} dominate the humus composition.

Chernozems, the agriculturally most valuable soil grouping – although frequently affected by droughts – are formed under the more continental climate conditions of the steppe and forest-steppe zones and are characterized by a mollic A-horizon (of about 30-100 cm) that contains and/or overlies a calcic horizon or concentrations of soft powdery lime within 125 cm of the surface, directly on the parent material. The soil reaction is nearly neutral, becoming alkaline downward and the cation exchange capacity – dependent on the humus content (3-12 %) – is 30–60 cmol/kg (SI unit equivalent to milliequivalents per 100 g of soil in Figure 6). The humus composition is identified by a high content of humic acids (up to 50 %); the distribution of clay and sesquioxides in the profile is mostly undifferentiated.

Due to the narrowing of the Volga basin near Saratov the **Kastanozems** (soils with a thick, dark brown topsoil, rich in organic matter and a calcareous or gypsum-rich subsoil) up to Volgograd, **Solonetzes** (soils with subsurface clay accumulation, rich in sodium) and **Calcisols** (soils with accumulation of secondary calcium carbonates), predominant in the Kalmykia Republic, cover only small areas of the catchment, while in the Volga floodplain south of Volgograd up to the Delta region is the only occurrence (left) of **Fluvisols** (young soils in alluvial deposits).

1.4.3 Natural and man-made subdivision

There are several ways to subdivide the Volga (e.g. according to geographic zones; discharge, etc.), each of them arbitrary to a certain extent. The most widely used is a subdivision into three parts: Upper, Middle and Lower Volga[6] (Figure 7).

- **Upper Volga:**

From its source to the confluence of the Oka River, where the Volga is a relatively small river, or *From its source to the former confluence of the River Sheksna – now the outlet of the Rybinsk Reservoir.*

- **Middle Volga:**

From the confluence of the Oka to the confluence of its main tributary, the Kama River, on which way it doubles in size, or
From the confluence of the River Sheksna to the confluence of the Kama.(Since this subdivision would need to draw a border-line across the Kuibyshev reservoir, Fortunatov (1979) suggests extending the middle Volga up to the dam of this reservoir)

- **Lower Volga:**

From the confluence of the Kama (*or the end of the Kuibyshev reservoir*), where the Volga becomes a mighty river, to the delta.

This subdivision also roughly matches the Volga runoff, which doubles on the conjunction with the Oka and Kama respectively (Figure 8); more than 90% of the annual runoff occurs above the confluence of the Kama and the Volga loses about 2% of its water in evaporation below Volgograd.

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[6] This subdivision is used by all (available) Russian authors and has probably been introduced by Alisov (1956) since he is sometimes cited in this context. The second subdivision (*in italic*) is used by Behning (1928) - the only pre-damming publication available to me – and Fortunatov (1979) (with the modification for the Middle Volga).

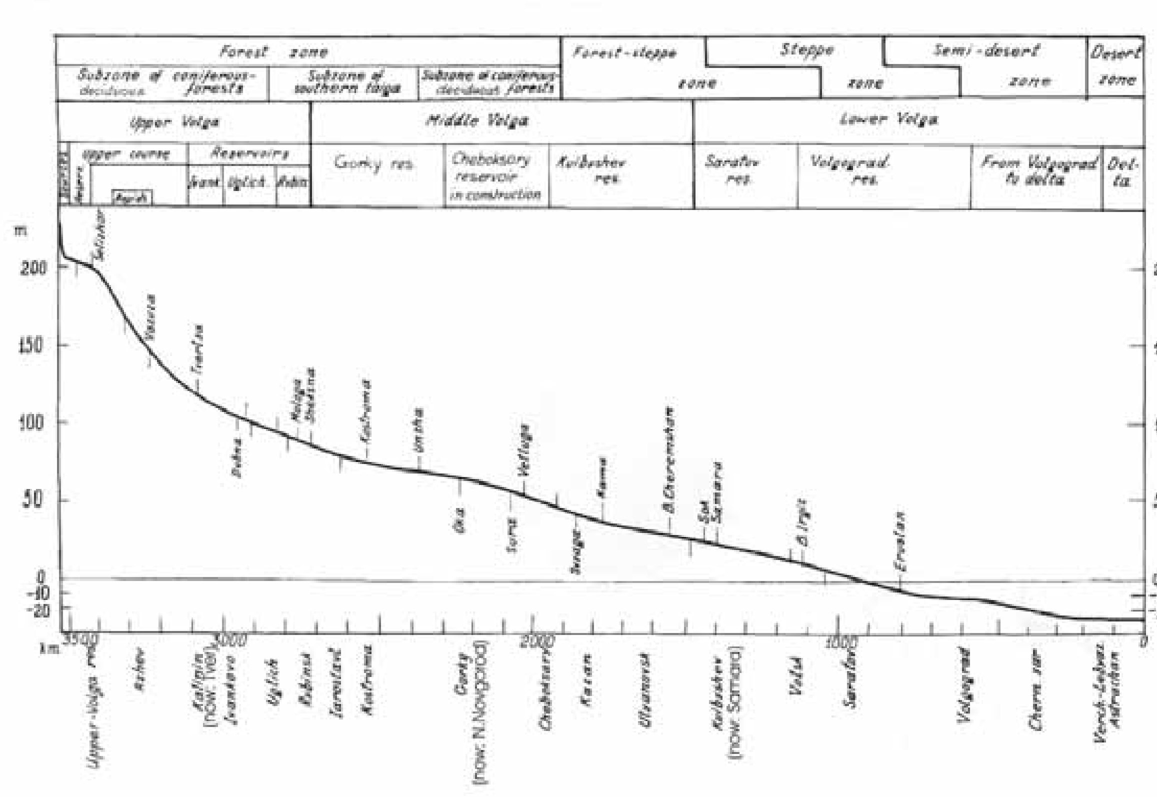

Figure 7 Longitudinal profile of the Volga and its division into districts (after Fortunatov (1979))

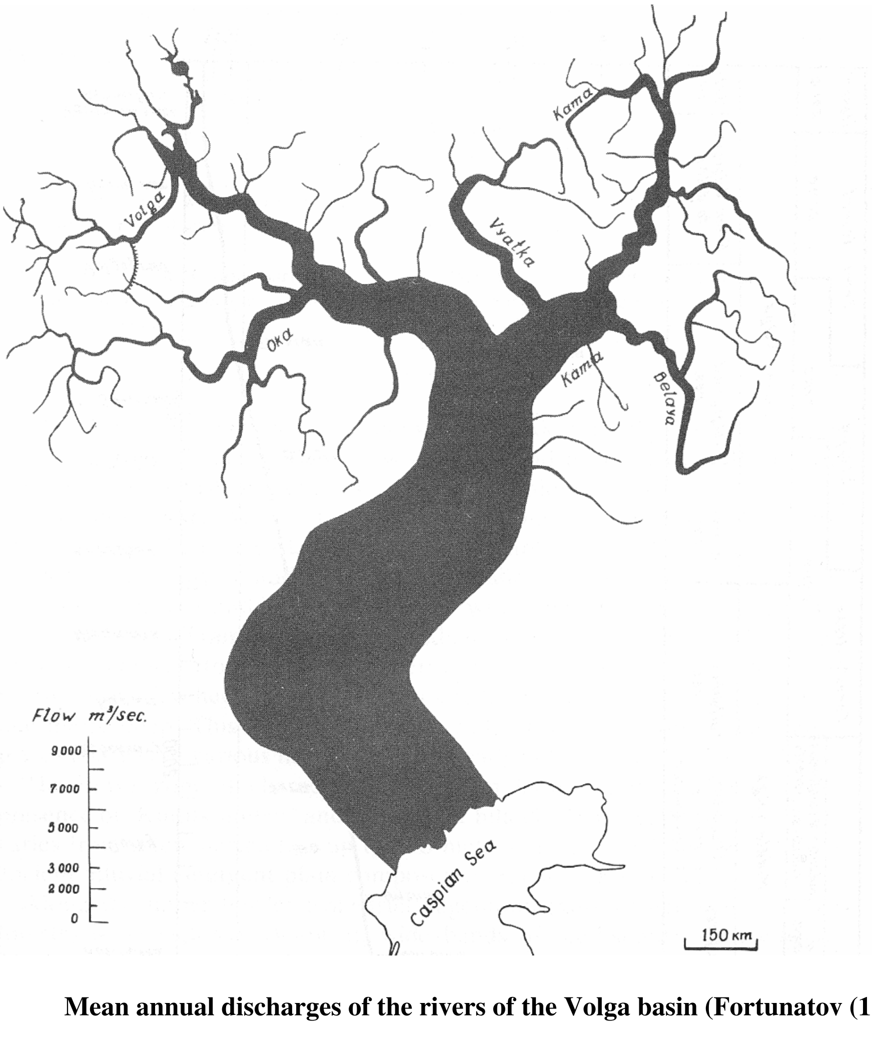

Figure 8 Mean annual discharges of the rivers of the Volga basin (Fortunatov (1979))

1.5 Economic development

Since the 1930s, the Volga Basin – as the economic and strategic heartland of Russia – has been drastically influenced by anthropogenic factors. After replacing Lenin's market socialist '*New Economic Policy*' with a system of centrally-ordained Five-Year Plans under Stalin, the USSR was transformed from a backward peasant society to an advanced industrialized state – even though at a terrible cost now and then.

Table 1 Growth of urban population in Russia* in Millions – after Piterski (2001)

	Population [millions]			
Year	**Total**	**Urban Population**	**Rural Population**	**% Urban**
1897	67.5	9.9	57.6	**14.7**
1914	89.9	15.7	74.2	**17.5**
1926	92.7	16.4	76.3	**17.7**
1939	108.4	36.3	72.1	**33.5**
1959	117.5	61.6	55.9	**52.4**
1970	130.1	81.0	49.1	**62.3**
1991	148.5	109.8	38.7	**73.9**
2000	145.9	106.5	39.4	**73.0**

* Present Territory of Russia

Throughout Stalin's '*revolution from above*' the foundation of the Soviet Union's (military-) industrial complex as well as the collectivized agrarian complex was laid, and despite several efforts towards reformations in the post-Stalinist area it remained basically unchanged until the breakdown of the USSR on December 25, 1991.

This revolution started in 1928 and was markedly influenced by the Russian experience in 1941, of being invaded for the second time within less than half of a century by the German aggressors. In particular, by the resulting necessity to move thousands of factories from the war zone to the interior of the country during the '*Great Patriotic War*', as WWII is called in Russia).

Seven of Russia's 13 cities with more than 1 million inhabitants are situated in the Volga basin, four of which (N. Novgorod, Kazan, Samara and Volgograd) are directly on its bank, two (Perm and Ufa) are in the Kama catchment. The largest city of Russia, the capital Moscow, is connected to the Volga via a canal and the River Moscwa, a tributary of the Oka, which empties into the Volga. Furthermore at least nine additional cities on the Volga bank could, and still can be, regarded as major industrial centers, each with a population above 250,000[7].

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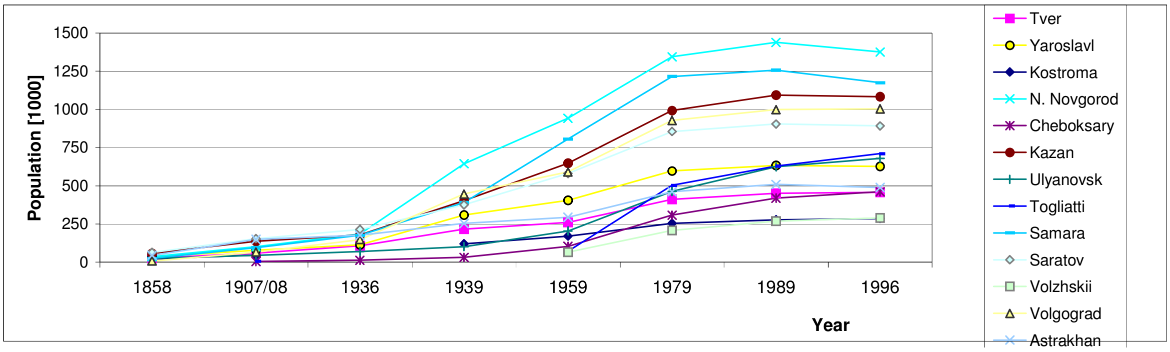
[7] The limitation to cities larger than 250,000 inhabitants is arbitrary and can only be rationalized with the difficulties to obtain (economic) data at the city level – with the exception of Moscow and St. Petersburg – not to speak of smaller cities.

Table 2 Vital statistics of the major Volga riparian cities
(data: © 1999/2005 "populstat" site: Jan Lahmeyer POPULATION STATISTICS: historical demography of all countries, their divisions and towns: http://www.library.uu.nl/wesp/populstat/populframe.html).

	population [1000] in:									
City	**1996**	**1989**	**1979**	**1959**	**1939**	**1936**	**1907/08**	**1858**	**particulars**	**founded**
Tver	458	451	412	261	216	108	60	25	formerly Kalinin	12th cent.
Yaroslavl	628	633	597	406	309	114	79	35	other year of foundation: ca. 1024	1010
Kostroma	286	278	255	171	121		46	22		1152
N. Novgorod	1376	1438	1344	942	644	185	100	36	formerly Gorky	1221
Cheboksary	462	420	308	104	31	12	4.8			1551
Kazan	1085	1094	993	648	402	179	137	58		1401
Ulyanovsk	680	625	464	205	102	70	44	25	renamed after the original name of Lenin in 1924	1648
Togliatti	710	630	502	72			6.6		formerly Stavropol; rebuilt in 1957	1957
Samara	1175	1257	1216	806	390	176	96	25	seat of the Soviet government from 1941-1943	1586
Saratov	892	905	856	581	376	215	155	64		1590
Volzhskii	290	269	209	67					agglomeration of Volgograd	1954
Volgograd	1003	999	929	591	446	148	67	7.0		1589
Astrakhan	488	509	461	294	254	177	149	45	ancient capital of khanate of Tatars, conquered by Russia in 1556	



With the exception of Togliatti (near Samara) and Volzhskii (near Volgograd) these cities along the Volga (as the north-south trade route for many centuries) are old cities with historical roots going back, up to the beginning of the 11th century. Furthermore, they are still the capitals of their respective region (Oblast, or autonomous Republic – as the 'subjects' of the now Russian Federation[8]), typically accounting for about one third of the regions population. They profited from the process of urbanization and centralization on a regional level during soviet times, as they did from the construction of the eight[9] complexes combining dams, reservoirs and hydropower stations (HPS) on the Volga – although to different extents.

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[8] The Russian Federation consists of seven federal districts (or 10 (12) so called 'economic regions') that are divided into 89 'subjects'. These 'subjects' (21 autonomous Republics, 1 autonomous oblast, 10 autonomous districts, 6 Krais (territories, regions), 49 Oblasts and 2 federal cities) are of equal federative rights in the sense that they have equal representation (2 delegates each) to the Federative Council of Russia, while there are numerous differences amongst them with respect to their (socio-economic) relations and dependence towards the capital Moscow.

[9] The first Reservoir on the Volga (Verkhenevolzhskoe Reservoir; constructed 1843 / reconstructed 1947), a system of regulated lakes (the Upper Volga-lakes – Sterzh, Vslug, Peno and Volgo), is usually 'ignored' – with the missing of a hydropower plant and lack of importance for the water and energy supply of the Russian capital as the only 'rational' reasons, since its size with respect to surface area (approx. 180 km^2) and Volume (0.8 km^3) is comparable to the Ivankovo and Uglich Reservoirs respectively.

With respect to contaminants entering the Volga, these cities should represent the major point sources, and cover with their adjective regions virtually the whole course of the River Volga. The sole exceptions are the Ivanovskaya oblast (and its capital Ivanovo) and the Respublika Mariy El (and its capital Yoshkar-Ola), both of which lack cities with more than 250000 inhabitants along the Volga bank, and will thus merely act as diffuse sources, as will the cities of Moscow, Perm and Ufa – if at all.

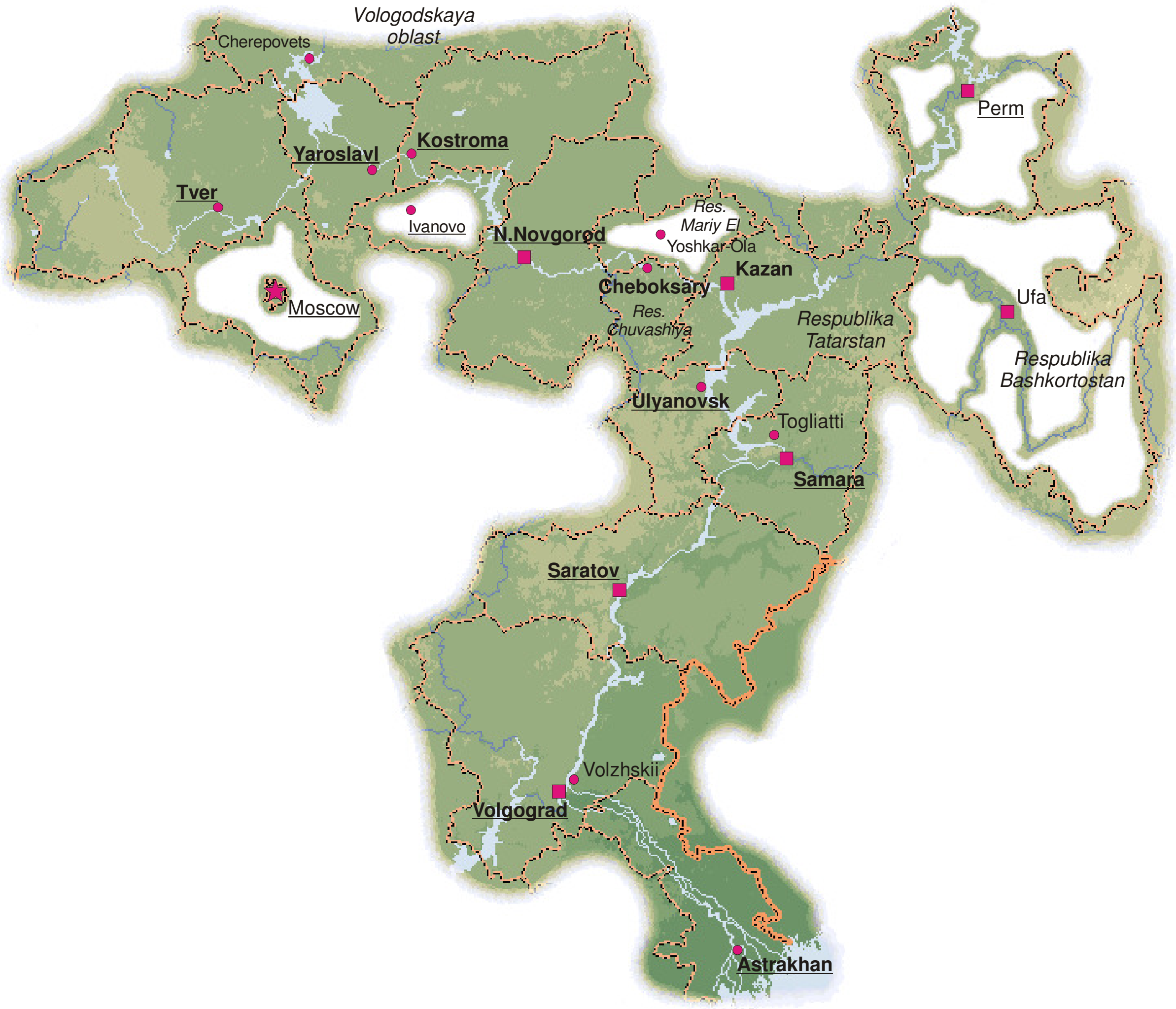

Figure 9 Volga riparian regions and major industrial centers
(regions with industrial centers not directly situated on the Volga banks are bleached out. Basic map: © Microsoft Encarta, 1999).

It is also **not** considered in this study. The only reason being a lack of initial information.

Since there are no major anthropogenic activities within the catchment area of this reservoir, and the Upper Volga lakes have been sampled, the resulting loss of information is however considered to be negligible. The only information missing are the measurements of a series of samples along a transect of the dam, which, as will be shown for the other reservoirs, is less important, than initially assumed.

While information about the industrial and agrarian sector of these regions is available[10], information about their spatial distribution (along the Volga) or even the Capital of the region is hardly available – whereas in the CTEC (2003) publication a map for each of the 89 regions is provided, giving at least a rough overview of the spatial distribution of economic activities.

Table 3 Shares of Industrial Sectors by Volume of Sales as of 1989
(data: deMelo and Ofer, 1999; Tver: 2002-data from BISNIS: http://www.bisnis.doc.gov).

Industrial Sectors of **Capital Cities**	**Tver (2002)**	**Yaroslavl**	**N. Novgorod**	**Cheboksary**	**Kazan**	**Ulyanovsk**	**Togliatti**	**Samara**	**Saratov**	**Volgograd**	**Astrakhan**
Chemical and petrochemical	5.2	**47.7**	4.3		**31.6**	0.1	**12.5**	**15.4**	**26.9**	**26.2**	6
Metallurgy		0.3	2.4	3.6	0.3	0		4.9	0.4	**25.8**	0
Machinery and metal-working	**27.5**	**25.8**	**57.7**	**48.2**	**20.2**	**60.5**	**83.4**	**39.5**	**27.9**	**26.4**	**15.2**
Forest products	7.2	1.9	2.3	0.9	1.6	3.8		2.3	5	3.6	9.7
Construction materials	5.7	2.3	2.3	2	3.8	7.7		4.4	7.3	4.5	6.8
Light industry	8.3	**10.4**	**11**	**32.6**	**24.2**	6.5	0.5	5.3	8	2.6	**28.1**
Food industry	**14**	9.7	**18.6**	**12.6**	**13**	**17.4**	2.3	**27.3**	**23.3**	9.8	**32.7**
Other	2.9	2.1	1.4		5.3	4.1		0.8	1.2	1.2	1.6
Energy	**23.9**						1.3				
Total	94.7	100	100	100	100	100	100	100	100	100	100

Furthermore the available information is often outdated by the dramatic changes in the industrial (and agrarian – although to a much lesser extent) sector due to the ongoing transition. Table 4 and Table 5 highlight both problems: the difference between the capital and its region, as well as the changes during transition.

Table 4 Shares of Industrial Sectors
(data 1989: deMelo and Ofer 1999; data 1999: OECD 2003).

	City of **N. Novgorod** **1989**	Region of **N. Novgorod** **1999**	City of **Samara** **1989**	Region of **Samara** **1999**
Electrical energy		10.3		12.7
Fuel industry		2.7		7.1
Metallurgy	2.4	5	4.9	2.3
Chemical and Petrochemical industry	4.3	7.8	15.4	9.3
Machine-building industry and metal working industry	57.7	51.9	39.5	53.3
Timber industry, woodworking industry, Pulp and paper industry	2.3	5.1	2.3	0.4
Construction Materials producing industry	2.3	2	4.4	3.1
Light industry	11	1.6	5.3	0.3
Food industry	18.6	9.3	27.3	9.9
Total	98.6	95.7	99.1	98.4

While one can for example rationalize the differences in ‘machine-building industry and metal working industry’ between the city of Samara and its region with the sole existence of the car-industry center of Togliatti, the drop in ‘timber industry’ makes no sense, unless this industry would have faced a tremendous breakdown – since it most probably was not situated in the city itself. There are numerous examples like this – e.g. the ‘statistical absence’ of an ‘electrical energy’ and/or

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[10] Provided by e.g. “BISNIS” (the ‘*Business information Service for the Newly Independent States*’ by the U.S. Department of Commerce; http://www.bisnis.doc.gov) – detailed industrial and agrarian information, although with a focus on investor relations, or CTEC (2003) – basic data on Russia’s regions from 1997 up to the year 2002, although with a $395 price tag.

fuel industry in the city of N. Novgorod, while there sure is one – and all of these figures are once again questionable. Different sources report different figures; there are vast differences within the same source for consecutive years; the region and its capital are often 'mixed-up', or treated as if they would be equal, and so on...

Table 5 Shares of industrial output in N. Novgorod according to the US Department of Commerce (BISNIS, http://www.bisnis.doc.gov) and the OECD (OECD, 2003).

US Department of Commerce	% of total output of Industries January-September 2002	output as % of total industrial output 1999	OECD 2003
Fuels and Energy	0.1	10.3	Electrical energy
		2.7	Fuel industry
Ferrous metals	2.6	4.6	Ferrous Metallurgy
Non-ferrous metals	1.0	0.4	Non-ferrous Metallurgy
Chemical & petrochemical industry	1.2	7.8	Chemical and Petrochemical industry
Machine building	70.6	51.9	Machine-building industry and metal working industry
Wood & paper	1.5	5.1	Timber industry, woodworking industry, Pulp and paper industry
Construction materials	1.5	2.0	Construction Materials producing industry
Cloth-making	1.7		
Foods & Food processing	15.0	9.3	Food industry
Flours and cereals	1.2		
Medical industry	3.3		
Printing & publishing	0.3		
		1.6	Light industry
total	100.0	95.7	

No matter what the reasons for these differences and uncertainties may be – lack of information; various data-sources; rapidly changing shares of industrial sectors and/or their output[11]; or any other

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[11] Changing shares of industrial sectors and/or their respective output is of course a big variable in Russia's post-soviet economy – albeit not the only one. After a disastrous decline of Russia's GDP after the collapse of the FSU – once again source-dependent, but about 45% (cumulative) between 1991 and 1996 seems to be a 'fair' average (cf. the cumulative output decline during the 'Great Depression' (1930-34) of 27% for the US and 16% for Germany!) – and another big drawback due to the Asian financial crisis in 1998 – resulting in a sharp decline in Russia's earnings from oil exports and an exodus of foreign investors – Russia's economy grew steadily from its low around 1996 by an average of more than 6% annually in 1999-2002; although by riding on the back of higher oil prices and a weak ruble. So besides the fact, that this growth was/is once again accompanied by huge costs for most Russians – with e.g. inflation rates up to 90% in 1999, and falling wages and pensions of about 30% and 45% respectively in the same year – and is very much dependant on the type of industry (roughly speaking: light industry and machinery/metal-working as the least competitive sectors; raw-materials as the 'winner' - particularly oil, natural gas, metals, and timber, which account for over 80% of exports) and region. However, as one can easily see from the tables above, this is just a rule of thumb, since e.g. in N. Novgorod, especially the machinery/metal working industry, seems to have faced a considerable growth – or at least has consolidated. Another prominent example – against the trend – is the Volga Automobile plant (AutoVAZ) in Togliatti, which profited from the financial crisis in 1998, since the demand for cheap Russian cars increased, in relation to the demand for cars from more expensive foreign competitors. As a result, the output in 1999 increased 13% over 1998.

After all, there's a high uncertainty bound to Russian statistical data:

"*The transition from the centrally planned system to a market-based one severely disrupted the economy and the collection of data. The imperatives of plan fulfillment tended to ensure that Soviet-era statistics exaggerated actual output. When enterprises began to switch from net subsidy recipients to net taxpayers, it was an incentive for them to understate output. The post-Soviet production collapse, although real, was therefore milder than appears in official statistics. In addition, because of tax avoidance, much private-sector activity goes unrecorded. Goskomstat (the State Statistics Committee) estimates that 25% of production is "informal", and adjusts GDP figures upwards on this basis; some calculations put informal production at 40% of GDP or more. Partly as a result of efforts to improve them, statistical series are created, altered, and discontinued frequently, and methodological changes often go unexplained.*" (The Economist Intelligence Unit – Country Profile Russia:
http://www.economist.com/countries/Russia/profile.cfm?folder=Profile%2DEconomic%20Structure
and/or: http://store.eiu.com/index.asp?layout=show_sample&product_id=30000203&country_id=RU)

"*The official data describing the composition of GDP in Russia are puzzling. Goskomstat statistics show that Russia is a service economy, where the production of services (60 percent) exceeds the production of goods (40 percent). Moreover, it is a service economy dominated by market services (49 percent) that exceed the public sector (11 percent) by more than suggested by employment (which, in turn, makes the market service sector appear extremely productive by international standards). Perhaps most important, it is not clear from the official accounts why many observers worry about the country's dependence on oil and gas – in the official statistics, the share of oil and gas is less than 9 percent of GDP, although export revenues from oil and gas are said to account for 20 percent of GDP. The solution lies in transfer pricing. Many companies avoid taxes by selling their products to trading companies at below-market prices; these trading companies then sell the product to the final customer at market prices, and pocket the difference. Typi-*

possible factor – it is clear, that this kind of information is far from being reliable enough, to make any sound estimate about the amount and/or even kind of pollutants entering the Volga through these point-sources, let alone through diffuse sources. While one could of course also criticize the underlying popular idea of linking different kinds of industries and their respective size to its most likely emitted pollutants and their amount, for being far to simplifying; especially in the case of Russia, or other economies in transition, where the variation in production facilities (e.g. with respect to the means of production) should be huge in each and every respect. Several joint-ventures with (western) trusts resulted in production facilities fully up to par with international standards (e.g. Volga paper mill in N. Novgorod, *DuPont-Khimprom* chemical plant in Chuvashiya, *Mineral-Knauf* gypsum extraction and processing in Astrakhan) in respect to quality (ISO 9000/9002-certified) and ecological standards (ISO 14000-certified). At least the same standards of quality are also fulfilled by several (export-oriented) Russian holdings, namely but not limited to, industries of the former defense sector (which shifted production or already produced double-use products) while many other facilities are undoubtedly rather outdated and in no way comparable with 'state-of-the-art' facilities. Without knowing their share in industrial output – and not even the industrial output itself (cf. footnote[11]) – leave alone the implications on the release of COPC's, at best a qualitative impression of possible influences (on the aquatic system) can be given.

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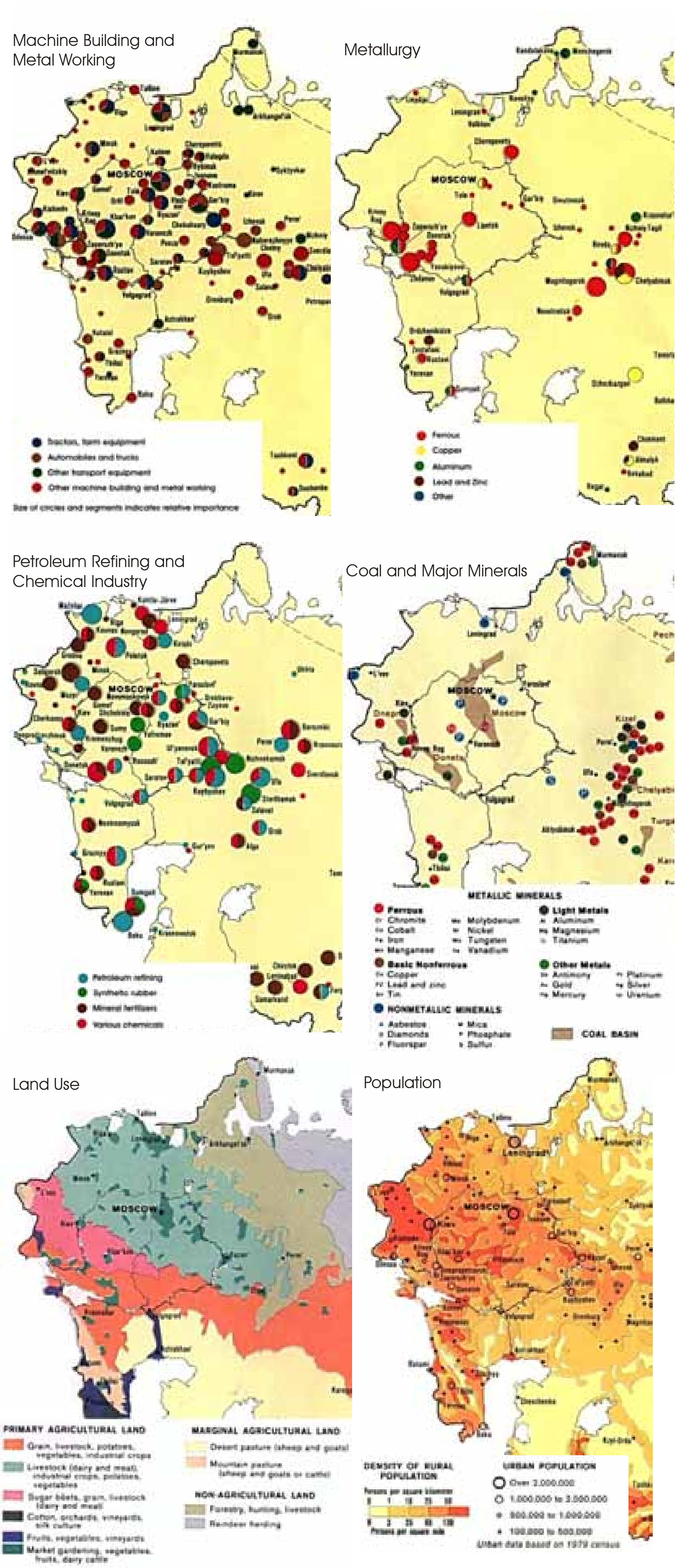
cally, the trading company would be registered in a region where it can get tax relief on the profits it earns or can avoid effective taxation by other means. Transfer pricing thus cuts tax payments for the production companies by artificially lowering their profits; but by so doing, it also distorts the national accounts, blows out of proportion value-added generated in the trading sector, and hence in the service sector, and artificially underestimates the contribution of industrial production, in particular of oil and gas, to GDP." … "Taken together, the exercise demonstrates that the statistics showing an increase in the share of services (a) reflect mostly relative prices, not quantity, with the service sectors becoming more expensive, just as one would expect in a natural resource based economy; and (b) indicate that structural changes, observed in the economy during the last 5 years, are rather more limited than one would conclude from a cursory glance at the statistics." (The World Bank, Russia Country Department: Russian Economic Report - February 2004.
http://www.worldbank.org.ru/ECA/Russia.nsf/0/0CF40EF2E501A275C3256CD1002B7D90/$FILE/RER7_eng.pdf)

Despite the former Soviet Union's reliance on and promotion of machine building and metal working industries – and an often-assumed uniformity amongst Russian industrial centers –, variations in the importance and structure of industry did exist, as did the chances during transition.

Figure 10 depicts the situation according to the United States CIA in 1982 – a qualitative overview of (even then) unknown accuracy, most of which probably underwent (major) changes regarding the relative importance of industrial sectors since its publication. On the other hand there should be only minor alterations with respect to land-use and population density – a view that is backed up by more recent maps on land use (e.g. Stolbovoi and McCallum, 2002) and population density (e.g. WRI, 2003). The first due to the natural conditions and only very little success in transforming the agrarian sector, the latter despite the general decline in population in Russia since about 1994 and the depopulation of some regions, which used to be much less pronounced in the Volga-region than e.g. in Russia's Far East.



Machine Building and Metal Working

Metallurgy

Petroleum Refining and Chemical Industry

Coal and Major Minerals

Land Use

Population

Figure 10 **Industrial activities, land use and population density in the Former Soviet Union (European Russia) according to the US-CIA 1982 (UT Library, 2003)**

The changes with respect to industrial structure, share and output may however be remarkable. Especially regions with oil and gas resources face a markedly higher share of petroleum refining and petrochemical enterprises than they used to. E.g. according to reports of the above mentioned US Department of Commerce (BISNIS: http://www.bisnis.doc.gov) the petrochemical industry accounted for about 60% of Astrakhans GDP in 2000, while the often strongly reported shipbuilding-industry contributed just about 6%.

Other branches and companies like *RUSAL* – Russia's biggest producer and exporter of aluminum semi products established in Samara in 1960; ISO 9001/9002 and 14001 certified – or major producers of fertilizers and agrochemicals e.g. in Togliatti (*TogliattiAzot* founded in 1981 – a pipeline of 2,500km connects the plant with the port of Yuzhnyy on the Black Sea[12]) and Volgograd are not considered in Figure 10, for what reason so ever.

Two other characteristics show substantial differences between the regions, but their implications are less clear: the share of the (former) defense industries in the regions, and the role of agricultural production for the regional economy. On the one hand, defense industries – whose share was high in N. Novgorod, Kazan, Samara and Volgograd – means a huge task for restructuring; on the other hand it's usually associated with a high level of human and technological capital.

Agriculture – whose share was high in Tver, Mariy El, Cheboksary, Saratov and Astrakhan – remained generally unreformed and cash poor, adding additional pressure on public revenues, but because of high inter-regional transport costs also helped to keep food prices low, and thus promoted lower industrial wages.

Comparing Table 6 with Figure 10 reveals changes during the process of transformation and/or a different point of view – none of which are fully quantifiable.

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[12] This fact emphasizes a quite important point: although a specific kind of industry may be situated directly on the Volga bank, it's impact on the aquatic system may be neglectable, since the 'dangerous' processes – in this case stockpiling and shipping – are (at least partly) situated somewhere else.

E.g. our Russian partners reported the effluents of the chemical plant(s) in the city of Dzerzhinsk – 'known' as one of the most polluted cities in Russia, situated on the Oka bank - NOT to be entering the Oka, but instead the Volga near Kstovo (downstream N. Novgorod) . There is virtually no way to proof this information, but it makes sense in several ways:With respect to heavy metals, we found no elevated concentrations within the vicinity of Dzerzhinsk and there are (hardly explainable) elevated concentrations of heavy metals near Kstovo (although the sampling-density is too low for a comprehensive description).

No matter, what one might think about the former Soviet Union; the idea of a centrally planned system, knowing about its needs and ways of water-supply (mostly surface-water!), as well as its industry and the respective pollutants, in a land of virtually unlimited space; deliberately polluting the drinking-water resources of major cities is almost ridiculous. Therefore, the idea of effluents at least in some cases entering the environment not necessarily at the point where they arise does not seem too far-fetched.

Table 6 Natural resources and industrial activities in the Volga riparian regions (data: Stolbovoi and McCallum, 2002; US Department of Commerce (BISNIS http://www.bisnis.doc.gov); OECD (OECD 2003); and "RA expert, a Russian rating agency, http://www.raexpert.ru/).

''subject' of the Federation (Oblast or Republic)	**Tver**	**Yaroslavl**	**Ivanovo**	**Kostroma**	**N.Novgorod**	**Chuvashiya**	**Mariy El**	**Tatarstan**	**Ulyanovsk**	**Samara**	**Saratov**	**Volgograd**	**Astrakhan**
natural resources	peat (mainly for combustion)	sands	clays and loams	clays and loams	sands	gypsum	sands	oil and gas	oil	oil	oil and gas	oil and gas	oil and gas
	brown coal	peat	gypsum	gypsum	clay	sands	clay	gypsum	quartz			phosphates	fish
	gravel	clay	dolomites	sands	peat	clay	peat	oil asphalt	diatomite		sand	bishofite salts	gypsum
	construction and silicate sands	mineral water	sands		mineral salt		timber	peat	peat		clay	mason's sand	salt
	kaolin clay		phosphorite		timber			building stone	chalk		limestone	limestone	sands
	limestone		mineral water					clay	marlstone		dolomites	mineral water	clay
	sapropel							limestone	clay		chalk		
	mineral water							dolomite	spring water				
industry	energy (Kalinin Nuclear Power Station and Konakovo Hydro Electric Station)	fuel, chemical and petrochemical	light industry (cotton, wool, shoe)	fuel, chemical and petrochemical	machine building (AutoGAZ - Volga sedans, light commercial vehicles), buses, motors, railroad wheels)	machine building (tractors, avionics)	power generation	oil production and petrochemistry	aircraft-building (Aviastar manufactures Antonov and Tupolev air planes)	automobile (AutoVAZ (brand-name: Lada) - produces about 70% of all Russian cars)	oil/gas and energy generating sectors; oil and gas extraction and processing, Balakovo Nuclear Power Plant, Saratov Hydro Electric Plant	chemical and petrochemical (lubricants, motor, hydraulic and aircraft oil, tires, chemical fibers, caustic soda, fertilizers)	fuel production
	machinery building (passenger train cars, excavators, tower cranes, metal-cutting machinery)	machine building (automotive, ship-building, electrotechnical cables)	power generation	light industry (cotton, wool)	chemical and petrochemical (fuel, light hydrocarbons)	food processing	machine building	automotive (Kamaz-trucks)	automotive (UAZ - cross country vehicles, small trucks, mini-buses	chemical and petrochemical (large, export oriented enterprises - synthetic ammonia (TogliattiAzot is the worlds biggest exporter of ammonia and one of the leading manufacturers of fertilizers), phosphorus and derivates, fertilizers, rubber)	machine building (navigation systems, telecommunication, radar), diesel generators, aircraft, equipment for energy, chemical and oil industry, trolley-buses, bearings)	metallurgy (ferrous and non-ferrous)	food production (mostly fish and salt - Baskunchak salt-lake supplies 25% of the salt in Russia)
	food processing	food processing	food processing	machine building	food processing	power generation	radio electronics	aerospace (helicopters, aircraft-engines)	electronic engineering	metallurgy (Samara is the center of Russia's aluminum processing)	chemicals and petrochemicals (rubber, chemical filaments and fibers, acrylic acid, methyl acrylate, phenol, sulphric acid, fertilizers	machine building and metal-working (special grades of steel, tractors, ships, pipes, equipment for oil and gas-industry, medical equipment)	construction materials (gypsum, cement, bricks, reinforced concrete)
	construction material		machine building (tools, motors)	timber industry	construction materials	petrochemical (caustic soda, chlorine dyes, rubber, polymers)	lumber	power generation	textiles		building sector	food processing	machine building (mostly shipbuilding)
	food catering and trade enterprises			food processing	glass (Bor Glassworks is the largest producer of automobile and construction glass in Russia)		food processing				light industry (fabrics, footgear)		
	chemical (polyester)												
	building sector										(LITIY-ELEMENT is the only Russian supplier of lithium batteries)		
	tourism sector												
peculiarity					In the soviet era, N. Novgorod was closed to foreigners, due to the high share of the military industrial complex					Togliatti is the economically predominant city in the Samara region (approx. 60% of the regions industrial output). While Samara was closed to foreigners in the soviet era, Togliatti wasn't.	In the soviet era, Saratov was closed to foreigners.	Volgograd City stretches nearly 100 km along the Volga River, but is often no more than 5km wide. Volgograd was closed to foreigners in the soviet era	
Investment potential in 2003 according to '*RA expert*' (ranking from 1 to 89 for Russia's regions)	55	**33**	66	70	**7**	50	71	**10**	48	**6**	**20**	**25**	56

Despite the changes in the industrial sector, and to a much lesser extent the agrarian sectors and structure, some basic facts and trends remain unchanged. The industrial sector is still skewed towards heavy industries, but the fuel and energy sector as well as the chemical and petrochemical industry are of almost equal importance, and in some regions are now the leading sectors. Moreover, the economy is still dominated by large industrial enterprises, while the share of small and medium-sized enterprises is still below 15% of the GDP, compared with typically 50% or more in developed market economies. Especially the large oil-companies of Russia – the industrial enterprises with the highest export-volume, and thus a surplus of investment capital – were quite acquisitive since 1999, buying out major parts of other industrial sectors. By now, the acquisition has moved beyond the industrial sector, with conglomerates buying into insurances, agriculture, and the food industry – according to some estimates, 20 large conglomerates account for about 70% of Russia's GDP. On the other hand, this leaves little chances for small- to medium-sized businesses, and the idea of just a few industrial centers – and thus point sources – along the Volga is an apt description. This is supported by the 'investment potential' ranking of the regions according to *RA expert* (one of the leading Russian rating agencies evaluating the investment climate throughout Russia: http://www.raexpert.ru/), which should approximately reflect the potential for economic development, as well as the initial economic situation of the regions.

The ranking amongst the Volga-regions remained virtually unchanged between 1999 and 2003 with N. Novgorod, Samara and Tatarstan as the distinct leaders of the cities/regions taken into consideration– and so it seems reasonable that at least the **relative** importance of the regions with respect to industrial and agrarian production in the Volga-region can be roughly described even with formally outdated statistics; while keeping the considerable uncertainty bound to every Russian statistical figure and a distinct drop in industrial output in mind.

1.6 Industrial and agricultural intensity in Volga riparian regions

Nevertheless even ‘secure’ facts are worth a second look. It is frequently said that five regions on the Volga – Tver, Mariy El, Chuvashiya, Saratov and Astrakhan – have a strong, if not dominating agricultural base. This may be true from an economic point of view, taking the ratio between agricultural and industrial production – and thus the income-structure of the region – as indicator; with respect to possible influences of the industrial and/or agrarian sector towards the aquatic system of the Volga, it is at least misleading. Table 7, as well as the accompanying Figure 11, Figure 12 and Figure 13 reveal some inconsistencies connected with this simple division into predominantly agrarian and industrial regions.

Table 7 Natural and socio-economic conditions in the Volga riparian regions (data: Stolbovoi and McCallum (2002); ISN (‘International Relations and Security Network’, Russian Regional Reports: http://www.isn.ethz.ch/news/rrr/); Nupi (‘Norwegian Institute of International Affaires’ – The Centre of Russian Studies (CRS): http://www.nupi.no/English/Research/Russian_studies/)

	'subject' of the Federation (Oblast or Republic)												
	Tver	**Yaroslavl**	**Ivanovo**	**Kostroma**	**N.Novgorod**	**Chuvashiya**	**Mariy El**	**Tatarstan**	**Ulyanovsk**	**Samara**	**Saratov**	**Volgograd**	**Astrakhan**
Area [1000km^2]	84.1	36.4	23.9	60.1	74.8	18.3	23.2	68	37.3	53.6	100.2	113.9	44.1
Population 2000 (est.) [1000]	1602.2	1413.9	1222.3	786.3	3657.7	1356.7	758.9	3778.6	1467.9	3297.4	2712.1	2693	1024.1
Capital population (2000) [1000]	457.9	631	475.6	303.8	1453.1	460.1	276.2	1094.9	690.9	1255.1	905.4	1058.2	512
Urban population [%]	72.2	80.4	82.9	66.3	77.6	60.4	62.1	73.4	72.6	80.6	73.4	74	67
Population density [persons/km^2]	19.1	38.8	51.1	13.1	48.9	74.1	32.7	55.6	39.4	61.5	27.1	23.6	23.2
	sod-podzolics	sod-podzolics	sod-podzolics	sod-podzolics	sod-podzolics	grey forest	sod-podzolics	grey forest	leached chernozems	chernozems	dark chestnuts	southern chernozems	solonetzic and solonchacous browns
soils	podzols	light grey forest	light grey forest		light grey forest	sod-podzolics	light grey forest	chernozems	sod-podzolics	dark chestnuts	solonetzes	meadowish solonetzes	meadow alluvials
	peats					left bank: low plain with bogs and peat bogs							sands
agricultural land	24000 km^2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	37000 km^2	n.d.	85000 km^2	86000 km^2	n.d.
Average personal income index in July 1995 (Russia=100)	66	85	54	73	75	50	60	71	59	100	62	60	66
Agricultural production as percentage of all Russian production (1995):	**1.24**	**1.09**	**0.8**	**0.69**	**1.89**	**0.92**	**0.76**	**3.51**	**1.19**	**2.72**	**2.53**	**2.29**	**0.52**
total anual output (1998) [1000 tons]													
grains	252.2	141.6	132.6	116.6	811.1	458.7	287.1	1940.0	461.7	647.5	1229.3	998.6	43.5
yield [tons/ha]	0.90	1.04	1.18	0.88	1.09	1.38	1.13	1.64	0.82	0.86	0.44	0.56	0.67
cultivated Area [km^2] calc.	2802	1362	1124	1325	7441	3324	2541	11829	5630	7529	27939	17832	649
[%] of total Area calc.	3.3	3.7	4.7	2.2	9.9	18.2	11.0	17.4	15.1	14.0	27.9	15.7	1.5
grains [tons/km^2] of total Area (calc.)	3.0	3.9	5.5	1.9	10.8	25.1	12.4	28.5	12.4	12.1	12.3	8.8	1.0
potatoes	587.9	307.0	163.6	273.3	932.2	839.0	581.7	1245.9	263.7	400.3	139.4	209.6	87.1
yield [tons/ha]	15.5	14.3	12.6	17.3	13.6	14.6	17.6	14.1	8.8	7.6	9.3	7.6	5.8
cultivated Area [km^2] calc.	379	215	130	158	685	575	331	884	300	527	150	276	150
[%] of total Area calc.	0.5	0.6	0.5	0.3	0.9	3.1	1.4	1.3	0.8	1.0	0.1	0.2	0.3
potatoes [tons/km^2] of total Area (calc.)	7.0	8.4	6.8	4.5	12.5	45.8	25.1	18.3	7.1	7.5	1.4	1.8	2.0
vegetables	229.7	116.8	53.7	130.6	251.0	111.7	84.0	226.5	105.6	170.4	164.3	251.7	153.2
yield [tons/ha]	26.3	32.8	13.7	25.5	17.8	11.8	27.4	19.0	9.9	10.8	22.5	10.7	9.1
cultivated Area [km^2] calc.	87	36	39	51	141	95	31	119	107	158	73	235	168
[%] of total Area calc.	0.1	0.1	0.2	0.1	0.2	0.5	0.1	0.2	0.3	0.3	0.1	0.2	0.4
vegetables [tons/km^2] of total Area (calc.)	2.7	3.2	2.2	2.2	3.4	6.1	3.6	3.3	2.8	3.2	1.6	2.2	3.5
meat	57.8	35.4	28.6	34.1	88.1	66.7	46.2	186.4	49.1	95.3	128.7	127.3	19.6
cattle, total livestock [1000 heads]	417.3	284.6	190.8	193.0	663.9	356.8	222.3	1178.0	342.0	471.7	716.6	567.7	153.6
meat [tons/km^2] of total Area (calc.)	0.7	1.0	1.2	0.6	1.2	3.6	2.0	2.7	1.3	1.8	1.3	1.1	0.4
milk	550.6	354.4	257.3	263.2	931.0	536.0	312.0	1490.0	425.8	669.8	972.2	597.6	106.0
cows [1000 heads]	216.0	136.3	95.6	95.5	303.7	186.4	106.7	517.8	168.9	230.3	343.4	263.6	69.0
milk [tons/km^2] of total Area (calc.)	6.5	9.7	10.8	4.4	12.4	29.3	13.4	21.9	11.4	12.5	9.7	5.2	2.4
Percent of land occupied by forest	50	50	43	60	40	32	>50	16	25	12	5	4	-
Industrial production as percentage of all Russian production (Jan.-Aug. 1994)	**0.66**	**1.44**	**0.54**	**0.31**	**3.22**	**0.52**	**0.21**	**3.21**	**0.98**	**4.48**	**1.09**	**1.57**	**0.31**
Percent of population working in (1993)													
Industry	32.8	39.4	39.9	30.7	38.3	31.9	30	31.2	34.9	25.6	26.7	27.7	22.8
Agriculture	14.6	9.3	10	12.6	10.6	20	18.8	14	16.1	9.6	19.6	19	14.2
Trade	8.8	8.6	8.3	9.7	7.5	8.3	7.7	8.6	7.9	9.5	11	9	10.3
Culture	11.3	11.7	11.4	11.8	14.4	12	13.8	12.5	12.2	11	11.5	10.5	11.7
Management	2.6	2.3	2.5	3.1	2.1	1.9	2.3	1.4	2	1.8	2	2.1	2.8
Intensity of agricultural production [%share/1000km^2 (*100)]	1.5	3.0	3.3	1.1	2.5	5.0	3.3	5.2	3.2	5.1	2.5	2.0	1.2
Intensity of industrial production [%share/1000km^2 (*100)]	0.8	4.0	2.3	0.5	4.3	2.8	0.9	4.7	2.6	8.4	1.1	1.4	0.7

While the share of the industrial production of all Russian production of the regions is little surprising – with N. Novgorod, Tatarstan and Samara as the leading regions (Figure 11-a) – the share of the agricultural sector (Figure 11-a), as well as the respective intensities (i.e. industrial and agricultural shares of the Russian production normalized to the regions area – Figure 11-b) are unexpected, when considering most descriptions of the Volga basin.

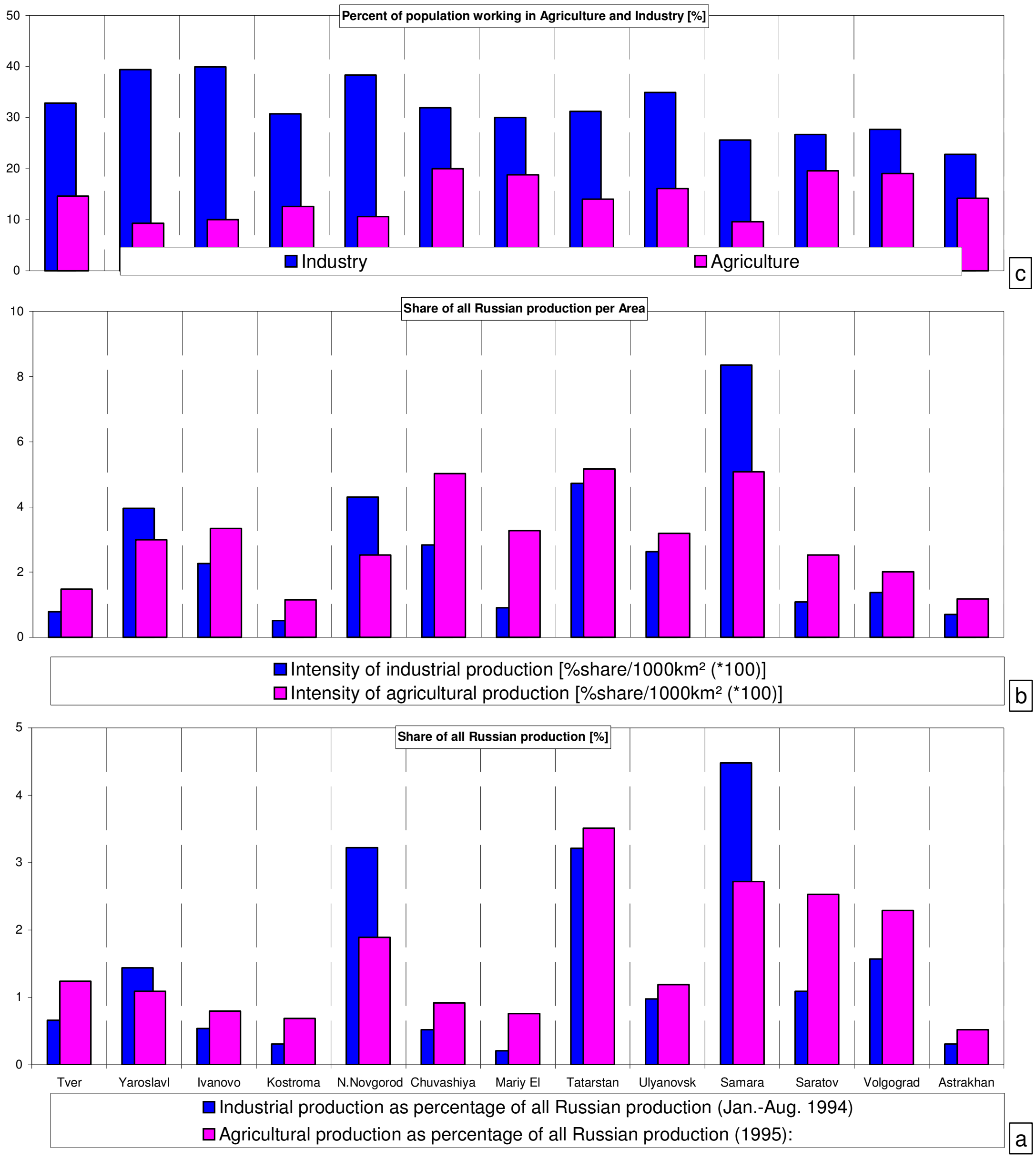

Figure 11 Industrial and agrarian production of the Volga riparian regions – total output, intensity and percent of the population working in the respective sector (based on data of Table 7).

That is, the regions of Tatarstan and Samara have (perhaps unexpectedly for some) to be looked upon as major agricultural centers, even with respect to the intensity of the agrarian sector. Additionally, the industrial output of presumed industrial regions like Ulyanovsk, Saratov and even Volgograd appear less impressive, especially when comparing the output per Area with the region of e.g. Yaroslavl and even the presumed agrarian Republic of Chuvashiya. The fact that the industrial and agricultural output – and intensity – is NOT reflected by the share of people working in the respective sector and region (Figure 11-c), is less astonishing since other factors like size, structure and efficiency of the respective sectors are generally more important – especially when considering the average personal income (i.e. approx. the average cost of workforce) in the regions[13] (Table 7).

Talk of the intensity of agrarian production, e.g. the myth of Astrakhan having an outstanding intense agrarian sector in the Volga delta, may be just that – a myth. While the Volga delta accounts for about ¼ to ½ of the regions area (10,000 km² – 20,000 km² depending on how the area is calculated – length*width as a square, or as a triangle – both versions are used in the literature) the output is below (grains, potatoes, meat, milk) or just comparable (vegetables) with e.g. the Upper Volga regions of Ivanovo or Yaroslavl – let alone Chuvashiya (Figure 12). On the other hand, when accounting for the area of these regions covered by forests (Table 7), and thus not cultivated (nor industrialized), less land remains for agricultural purposes than in the Volga delta – which in turn would mean a more intense and/or efficient agricultural sector – even in the case of vegetables and fruits, which are generally reported to be a major area of production of Astrakhan[14].

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[13] One might of course find a discrepancy between the (later on) claimed importance of the industrial sector – which normally has higher wages than the agrarian sector – for the regions and the reported average personal income index, since a higher industrial share should also be reflected in a higher average personal income. I am not able to fully explain this discrepancy, as little as I am claiming the drawn conclusions to be correct – I would be fully satisfied, if they were reasonable and not completely wrong…

One plausible explanation has been given – the role of agriculture in the regions, and its implications – due to high inter-regional transport costs, a strong agricultural base can help to keep food prices low, and thus promote lower industrial wages. Another hint might as well be once again the way at least some Russian statistics are derived: '*According to the official statistics, the purchasing power of Volgograd's population must be low. The share of the population whose income is below the so-called living minimum is 55 percent. However, it's well known that the majority of the people do not declare their real incomes and their real purchasing power is usually higher.*' (BISNIS-report on Volgograd: http://bisnis.doc.gov/bisnis/bisdoc/010105ovvolgagd.htm)

[14] On the other hand at least part of this explanation is backed up by solely economical reports, like the several times cited US Department of Commerce – BISNIS reports; who rarely mention any agricultural activities in the Astrakhan region and only talk about fish and salt as agricultural products of economic importance, while declaring the agricultural output of the Samara region as substantial for Russia. Unfortunately, the reported data throughout the regions is too sparse, to allow a general comparison.

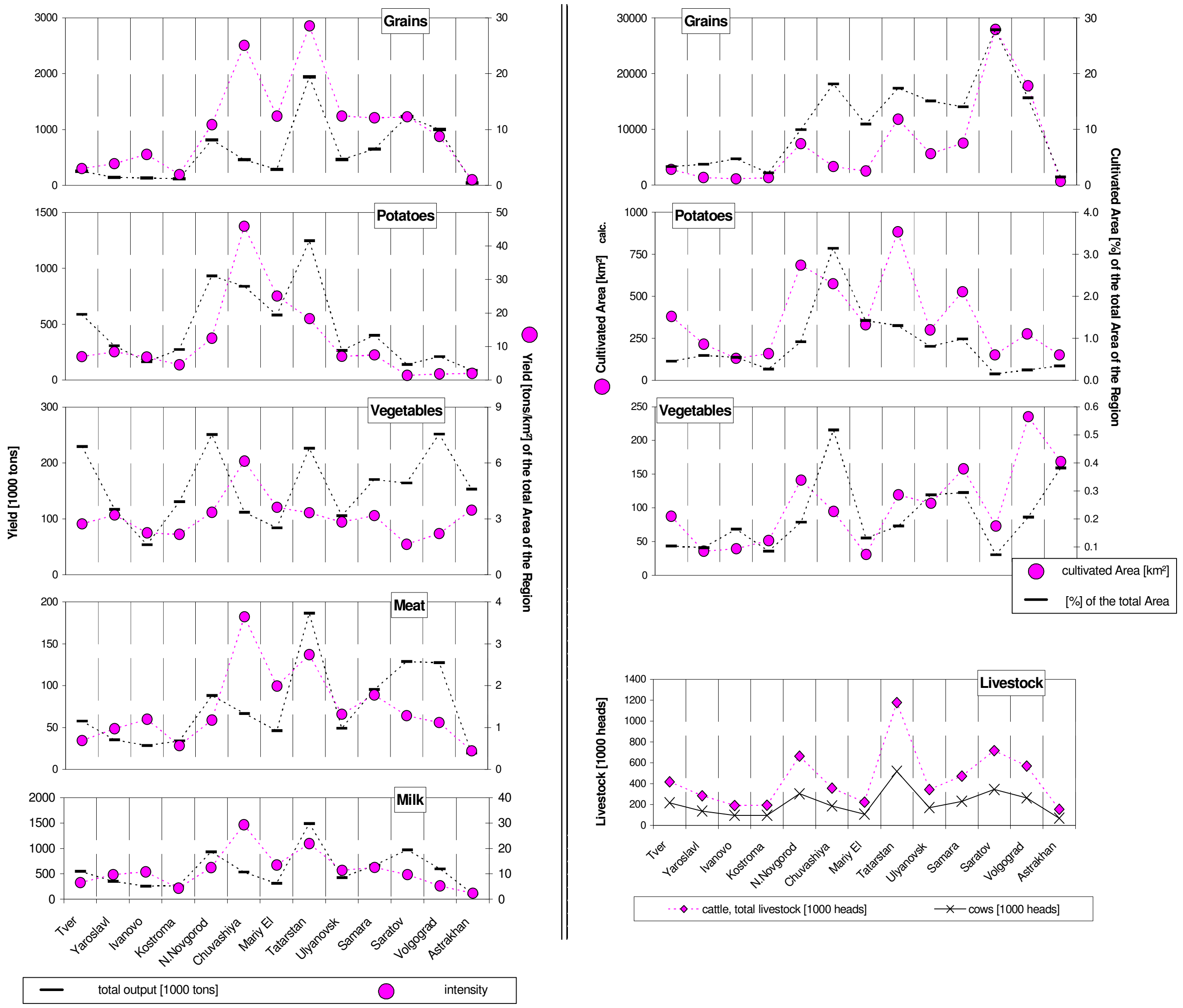


Figure 12 **Agrarian output and intensity (output per area) in the Volga riparian regions (based on data of Table 7).**

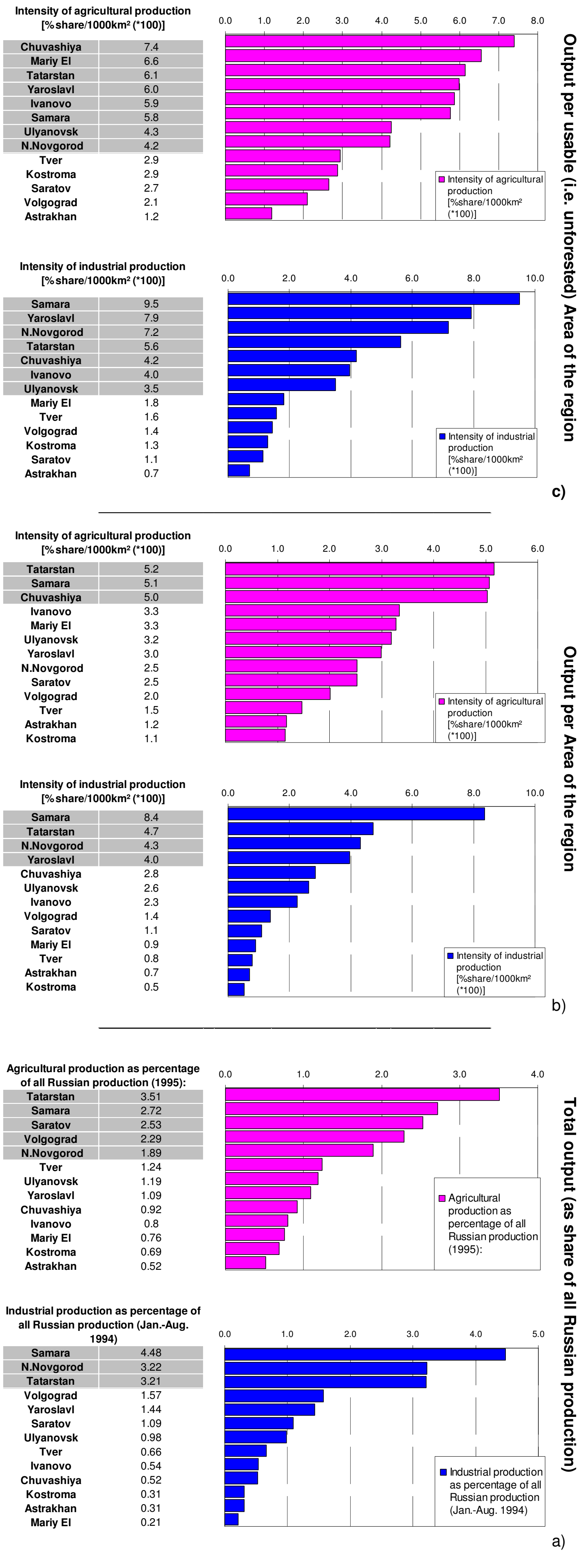
Nevertheless, all this is just an attempt to overcome the lack of more precise and relevant data, for example the exact distribution of industrial and agricultural businesses along the Volga with their output (of products and waste). A high uncertainty quotient remains bound to the conclusions, since neither the quality of the underlying data, nor the changes over the past 10 years can be accurately judged, at least some prejudice about the economic structure in the Volga basin can be disproved – making some of the later results less peculiar than they were at first sight.

Of course, there are several shortcomings and pitfalls, and no one would even try any sort of rationalization let alone interpretation of the later results on this basis, if more comprehensive data would be available – while it is believed to be more reliable, and closer to reality, than a lot of generalized descriptions of the Volga basin's economical structure available.

The overall ranking of the regions industrial and agricultural **intensity** (Figure 13 (b and c)) is quite different from many other descriptions.

While there is little discrepancy with respect to the overall industrial/agricultural output of the regions (Figure 13a) and the importance of the industrial/agricultural sector for the respective region (Figure 11a), the conclusions drawn from these data are quite different to those drawn from the data normalized with respect to area (Figure 13 (b and c)).

With respect to contaminants, potentially entering the aquatic system of the Volga, the intensity of human activities in the respective region is much more relevant, than their total extent. Of course, the total amount of contaminants would remain unchanged, while the concentrations – our main interest – are among other things dependent on the intensity, and the industrial or agricultural output per area is just used to approximate the intensity.



Intensity of agricultural production [%share/1000km² (*100)]

Chuvashiya	7.4
Mariy El	6.6
Tatarstan	6.1
Yaroslavl	6.0
Ivanovo	5.9
Samara	5.8
Ulyanovsk	4.3
N.Novgorod	4.2
Tver	2.9
Kostroma	2.9
Saratov	2.7
Volgograd	2.1
Astrakhan	1.2

Intensity of industrial production [%share/1000km² (*100)]

Samara	9.5
Yaroslavl	7.9
N.Novgorod	7.2
Tatarstan	5.6
Chuvashiya	4.2
Ivanovo	4.0
Ulyanovsk	3.5
Mariy El	1.8
Tver	1.6
Volgograd	1.4
Kostroma	1.3
Saratov	1.1
Astrakhan	0.7

Intensity of agricultural production [%share/1000km² (*100)]

Tatarstan	5.2
Samara	5.1
Chuvashiya	5.0
Ivanovo	3.3
Mariy El	3.3
Ulyanovsk	3.2
Yaroslavl	3.0
N.Novgorod	2.5
Saratov	2.5
Volgograd	2.0
Tver	1.5
Astrakhan	1.2
Kostroma	1.1

Intensity of industrial production [%share/1000km² (*100)]

Samara	8.4
Tatarstan	4.7
N.Novgorod	4.3
Yaroslavl	4.0
Chuvashiya	2.8
Ulyanovsk	2.6
Ivanovo	2.3
Volgograd	1.4
Saratov	1.1
Mariy El	0.9
Tver	0.8
Astrakhan	0.7
Kostroma	0.5

Agricultural production as percentage of all Russian production (1995):

Tatarstan	3.51
Samara	2.72
Saratov	2.53
Volgograd	2.29
N.Novgorod	1.89
Tver	1.24
Ulyanovsk	1.19
Yaroslavl	1.09
Chuvashiya	0.92
Ivanovo	0.8
Mariy El	0.76
Kostroma	0.69
Astrakhan	0.52

Industrial production as percentage of all Russian production (Jan.-Aug. 1994)

Samara	4.48
N.Novgorod	3.22
Tatarstan	3.21
Volgograd	1.57
Yaroslavl	1.44
Saratov	1.09
Ulyanovsk	0.98
Tver	0.66
Ivanovo	0.54
Chuvashiya	0.52
Kostroma	0.31
Astrakhan	0.31
Mariy El	0.21

Figure 13 Ranking of the agricultural and industrial output and intensity in Volga riparian regions (based on data of Table 7).

As mentioned above, this is a very crude approach and in order to work perfectly, the industrial and agrarian structure would have to be identical in all regions. E.g., the output of contaminants per product, the spatial distribution of enterprises relative to the Volga and the fate of the contaminants on their way to the Volga would have to be identical. This is undoubtedly far from reality – and the fact that much worse approaches exist in the literature is just a weak apology for using it anyway…

Moreover, subtracting the forested area of the regions total area in order to calculate a measure of intensity (Figure 13-c) may overestimate the intensity of the 'northern' regions, since it doesn't account for unused areas (e.g. steppe and desert) in the south, nor for e.g. mountainous areas in other regions and Figure 13-b avoids this correction.

However even using Figure 13-b to asses the impact of human activities, one should e.g. not be surprised to find as much, if not more pollutants contributable to industrial activities in the Republics of Mariy El and Chuvashiya, as in the Volgograd oblast, or considerably higher amounts of agricultural pollutants in the Republic of Tatarstan than in the oblasts of e.g. Tver or Astrakhan, while other descriptions would rather suggest the opposite.

1.7 The ‘Volga chain of reservoirs’ and possible implications

1.7.1 Overview

Part of the industrial and agricultural development in the Volga basin was accompanied and supported by large hydrotechnical constructions. A series of eight[9] complexes combining dams, reservoirs, and hydropower stations, changed the rivers regime drastically – as did three of these constructions on the largest tributary, the Kama, whereas the second largest tributary, the Oka, remained unregulated. While they improved navigation, flood control, irrigation and facilitated hydroelectric power supply, the task of operating these dams in order to provide for the necessities of the different sectors proved (and still proves) to be difficult – generating conflicts at an interbranch and interterritorial level, especially due to the absence of a legislative and normative base (cf. GCI, 2003 or Kosarikov[15] et al., 2001). Moreover, the Volga was converted from a free-flowing lowland river to a chain of man-made lakes – with the risk of adverse effects on self-purification, bacterial and algal pollution and additional evaporation from their surfaces[16].

Selected characteristics of the Volga reservoirs are given in Table 8 – highlighting once again the difficulties in data-acquisition. Most of the differences concerning the Cheboksary reservoir in the Republic of Chuvashiya can be explained by the fact, that this reservoir still has not reached its projected dimensions – and probably never will. Projected in the 1970’s, the end of its construction fell into a time were the adverse effects of large-scale hydrotechnical constructions on rivers flowing through flat areas – especially their excessive land-use – became obvious, as well as the social impacts of necessary resettlements. Filling the reservoir to its projected level of 68m would mean a further loss of land in the Republic of Mari-El and the N. Novgorod oblast, a rise in ground-water, and the necessity to resettle several villages in these regions; while the now reached 63m[17] prevent the HPS from working at full capacity (using only about 10-20% at present) – one of numerous administrational conflicts mentioned before, since the current absence of cooperation and/or compensation between upstream and downstream regions prevents strict solutions.

The differences with respect to the length of the reservoirs of Rybinsk and Kuibyshev are explained by their geometry, and the distance reported (largest distance, or distance along the Volga), while

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[15] The Ecology Committee Deputy Chairman of the Russian Federation Duma (Parliament)

[16] Very detailed reports about the dams on the Volga (and the rest of the Former Soviet Union), the historical development and their general implications on the adjacent ecosystems are provided by WCD (2000) and UNEP (1999) (Chapter 7.2 – “Management of Water Reservoirs: The Russian Experience” – with special emphasis on phosphorus and nutrients), as well as the more general reports on the impacts of (large) dams and HPS by WCD (2000-1) and IEA (2000).

[17] This would imply, the preferential use of the ‘smaller’ figures reported in Table 8 for the Cheboksary reservoir.

other differences (esp. the flooded area and the number of resettled people) can only be quoted, with no way to prove or disprove them. Even in the case that no differing values are reported – like in the case of geographical position and some morphometrical characteristics – differences exist in the literature, but were considered less interesting and/or relevant. Finally, the ‘Year of construction’ or ‘filling’ of the reservoirs provides at least some sort of humor, with some reservoirs being filled, before they were constructed – once again outlining the necessity to handle all the figures with some care and doubt[18]. Of course this leaves the validity of most information untouched; e.g. the Kuibyshev reservoir is and will be the largest reservoir on the Volga in each and every respect, the water exchange rates are highest in the Cheboksary and Saratov reservoir, the electrical energy output of the Ivankovo and Uglich HPS are almost neglectable, and so on. On the other hand a discussion e.g. about the (mean) depths of the reservoirs after their construction and/or some years after operation, in order to speculate about the sedimentation processes and/or the amount of shore-line erosion, or even the amount and kind of inundated land – things, that would affect this work considerably – would be quite unreliable because of the sometimes large variation of the reported values.

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[18] One could use the solomonic words of CEP (2002), used for a table regarding the biodiversity in the Caspian Sea, for each and every number: “***Note: numbers approximate since literature does not agree on values***”

Table 8 Some characteristics of the Volga reservoirs

		Reservoir									
	Source	Verkhene-volzhskoe *(Ryanzhin 2002)*	Ivankovo	Uglich	Rybinsk	Gorki	Cheboksary	Kuibyshev	Saratov	Volgograd	Sum
Year of construction	**Ryanzhin 2002**	1843	1933-37	1937-40	1937-41	1955-57	1982-85	1955-57	1967-68	1958-60	
Year of construction and filling	**Fortunatov 1979**	1843 (1943-47 reconstr.)	1937	1940	1941-47	1955-57	-	1955-57	1967-68	1958-60	
Year of filling	**WCD 2000**		1936-40	1936-40	1946-50	1951-55	1976-80	1956-60	1966-70	1956-60	
Latitude	**Ryanzhin 2002 / UNEP 1999**	57° N	56.50 N	57.26 N	58.30 N	57.00 N	56.19 N	54.35 N	52.10 N	49.00 N	
Longitude	**Ryanzhin 2002 / UNEP 1999**	33° E	36.54 E	38.08 E	38.30 E	43.20 E	46.34 E	48.30 E	48.00 E	45.00 E	
Elevation a.s.l. [m]	**Ryanzhin 2002**		124	113	102	84	(68)	53	28	15	
Dam height [m]	**WCD 2000**		28	27	30	17	42	45	40	47	
Storage height [m]	**Zimm et al. 1980**		18	12	18	18	-	27	-	26	
Max. Depth [m]	**Fashchevsky 2003**	16	14	23	30	22	20	32	30	37	
Mean depth [m]	**Fashchevsky 2003**	4.4	4	5.5	6	6.4	6.1	9.4	7	10	
Shallows less than 2m deep [%]	**Fortunatov 1979**		48	36	21	23	-	16	18	12	
Shallow area with depth less 2m [%]	**Fashchevsky 2003**		47	36	21	23	-	16.5	18.5	37	
Seasonal Water level fluctuation [m]	**Ryanzhin 2002**		-	-	2	2.3	-	6.2	2	2.5	
Length [km]	**Mineeva 2003**	92	120	146	110	430	321	484	348	546	2597
Length [km]	**WCD 2000**		120	146	360	430	330	650	350	540	2926
Length of shoreline [km]	**ILEC 2001**		-	-	-	2168	-	2500	865	1678	
Surface [km^2]	**Ryanzhin 2002**	183	327	249	4550	1591	2270	6450	1830	3120	20570
Watersurface area [km^2]	**Shubin 2003**		327	249	4550	1591	1080	6150	1831	3117	18895
Surface area [km^2]	**WCD 2000**		327	249	4550	1570	1055	6448	1831	3117	19147
Total storage [km^3]	**Zimm et al. 1980**	0.8	1.12	1.25	25.42	8.82	14.2	58	12.9	32.1	155
Volume, total [km^3]	**Shubin 2003**		1.12	1.25	25.42	8.82	4.6	57.3	12.87	31.45	143
Capacity (full) [km^3]	**WCD 2000**		1.12	1.25	25.42	8.82	9.5	58	12.37	31.45	148
Effective storage [km^3]	**Zimm et al. 1980**	0.52	0.81	0.81	16.67	3.91	5.7	34.5	1.75	8.65	73
Volume, effective [km^3]	**Shubin 2003**		0.81	0.81	16.67	3.9	0	33.9	1.75	8.25	66
Capacity (active) [km^3]	**WCD 2000**		0.81	0.8	16.67	2.78	5.7	34.6	1.75	8.25	71
Rated flow [m^3/s]	**HPI**		7350	11600	9150	11800	18000	67000	64000	59500	
Discharge Q$_{max}$ [m^3/s]	**Shubin 2003**		7400	13000	9000	15100	40800	70800	53000	63060	
Average annual flow [km^3]	**Fashchevsky 2003**	0.94	9.65	13.6	35.2	52.5	112	239.7	247	251	
Discharge [km^3]	**WCD 2000**		9.63	10.8	35.2	52.5	112.7	241	247	251	
Hydropower plant capacity [MW]	**HPI**		30	110	330	520	1404	2300	1360	2563	8617
Mean annual electricity produced [10^9 kWh]	**Zimm et al. 1980**		0.13	0.24	1.10	1.51	3.50	10.90	5.40	11.10	33.88
Energy production [10^9 kW per hour]	**WCD 2000**		0.08	0.18	0.92	1.49	1.6	9.44	5.3	10.92	29.93
Reservoir per unit of power [ha/MW] calculated	**based on Ryanzhin 2002 Area data**		1090	226	1379	306	162	280	135	122	
Reservoir per unit of power [ha/MW] calculated	**based on Shubin 2002 Area data**		1090	226	1379	306	77	267	135	122	
Residence time [yr]	**ILEC 2001**				0.27	0.43		0.24	0.50	0.40	
Residence time [yr]	**UNEP 1999**		0.12	0.11	0.79	0.18	0.04	0.24	0.06	0.13	
Water exchange [yr-1] calculated	**calculated from UNEP 1999 data (1/Residence time)**		8.3	9.1	1.3	5.6	25.0	4.2	16.7	7.7	
Water exchange [yr^{-1}]	**Mineeva 2003**		7.9	9.8	1.4	6	20.9	4.2	19.1	8	
Area of flooded lands [km^2]	**Naydenko 2003**		292	137	4340	1292	1675	5039	1169	2693	16637
Flooded area [km^2]	**WCD 2000**		150	183	3177	836	610	2957	704	1623	10240
including [%]											
arable land	**Naydenko 2003**		34	41	13	16	5	14	6	11	
grass lands	**Naydenko 2003**		27	39	27	36	28	41	39	40	
forests and shrubbery	**Naydenko 2003**		24	11	56	32	58	32	41	26	
other lands	**Naydenko 2003**		16	9	4	16	10	12	13	23	
including [%]											
Agric.	**WCD 2000**		20	31	18	25	6	24	11	19	
forest	**WCD 2000**		80	63	76	61	77	55	67	43	
other	**WCD 2000**		0	7	6	14	17	21	22	38	
Resettled population [10^3 people]	**Naydenko 2003**		19.5	24.6	116.7	47.7	42.6	150.0	25.3	50.0	476
Resettled population [10^3 people]	**WCD 2000**		30	25	117	48	42	150	25	15	452
Mean Biomass of Phytoplankton in the vegetation period [g/m^3]	**UNEP 1999**		5.47	2.46	3.3	5.86	6.3	5.1	5.74	2.97	
Max. Biomass of Phytoplankton in the vegetation period [g/m^3]	**UNEP 1999**		20.8	6.5	12	63	-	80	-	8	
Average annual phosphorus load to the reservoir [mg/m^3]	**UNEP 1999**		781	776	83	245	652	34	5	20	
Concentration of total phosphorus [µg/l]	**UNEP 1999**		86	87	80	42	60	84	61	60	
Maximum concentration of chlorophyll-a [µg/l]	**UNEP 1999**		23.9	12.2	24	17.1	17	11.9	11.6	6.1	
Trophy according to chlorophyll a	**Mineeva 2003**		Eutrophic	Mesotrophic	Meso-eutrophic	Eutrophic	Eutrophic	Meso-eutrophic	Mesotrophic	Mesotrophic	
Purposes	**Naydenko 2003**	flow regulation	power engineering	power engineering	**flow regulation (upper Volga and Sheksna)**	power engineering	power engineering	**flow regulation (middle Volga))**	power engineering	power engineering	
		Improvement of navigation conditions on the upper Volga	water transport	water transport	power engineering	water transport (**navigation flashes to the downstream side**)	water transport	power engineering	water transport	water transport (**navigation flashes to the downstream side**)	
			water supply		water transport	water supply	water supply	water transport	**irrigation**	**irrigation**, water supply	
					water supply	fish breeding		**irrigation**	water for fisheries	fish industry (**flashes for flooding the sturgeon spawning grounds**)	
								water supply			

1.7.2 Historical development

The large-scaled 'reconstruction' of the Volga, which was closely associated with the construction of canals – for transport, water-supply and irrigation – started in the mid-30's of the last century in the Upper Volga – mainly serving the needs of the capital Moscow in this phase. These constructions were part of the *GOELRO plan* (Gosudarstevennaja Elekrofikacija Rossii – or the State Electrification of Russia), Lenin's famous plan for the electrification of Russia in 1920 which emphasized the need to use entirely local raw material and energy-resources. This program of providing energy for the country and drastic reconstruction of the economy on the basis of electrification – the significance of which was defined by Lenin as: "*Communism is Soviet power plus the electrification of the whole country*" – affected the whole country, and a total of 19 Hydropower Stations (**HPS**) were built up to 1941. Although the plan was not limited to HPS, their manifold advantages – high efficiency and flexibility, as well as their relative simplicity with low maintenance costs and a high reliability – often made them the 'power-source of choice', leaving virtually no region in the country, which did not use the hydropower resources available within its territory in some way.

The Ivankovo reservoir and the adjacent 'Moscow-Canal' – a deep waterway linking the river Moskva, the tributary of the Oka, with the Volga – were the first large-scaled hydrotechnical constructions on the Volga in 1937, swiftly followed by the reservoirs of Uglich and Rybinsk – the latter of which is responsible for the flow-regulation of the Upper Volga. The 'Moscow-Canal', as well as the five smaller man-made reservoirs it passes on its way to the Volga, is fed by the Ivankovo reservoir, providing a major part of the water supply for industrial and domestic use of the capital and connecting the city via the reservoirs of Ivankovo, Uglich and Rybinsk and the Volga-Baltic waterway (namely the Mariinsk waterway – opened in 1810 and partly reconstructed in 1960-64 to permit the transit of ships of larger capacities) with St. Petersburg and the Baltic Sea, as well as via the North Dvina Canal (built in 1829) with the White Sea.

During WWII the construction of HPS shifted to regions outside the war-zone, namely the Urals and Central Asia – as did part of the industrial production –, while after the liberation of the country the reconstruction of damaged HPS (5 large HPS, totaling about half of the HPS capacity of the USSR in 1940 had been destroyed) were the priority issues.

In the mid- to late 1950's the reservoirs of Gorki, Kuibyshev and Volgograd (as well as the first reservoir on the Kama river – the Kama Reservoir near the city of Perm) were constructed almost simultaneously. The Kuibyshev reservoir, responsible for the flow-regulation of the Middle Volga, as well as the Volgograd reservoir have a more pronounced irrigation focus, since they are situated in climatic zones that are liable to droughts (with drops in the yield of crops on the average once every three years in the 1980's – and the Great (Soviet) Famines of 1921 and 1932-33 were at least provoked by such droughts, while there's still a vast propaganda concerning further implications).

Nevertheless, they are also the most important and powerful HPS on the Volga, since after receiving the headwaters of the Kama (resulting in an approx. doubling of the Volga runoff) the conditions for HPS become much more favorable. The Kuibyshev reservoir (and HPS) energized parts of the Samara region – to which a lot of production facilities were moved during WWII – and gave rise to its (now) most important and most well known industrial centre Togliatti[19].

After the construction of the second reservoir on the Kama – the Votkinsk-reservoir (around 1965) – the Volga-Kama chain of reservoirs was completed with the reservoirs of Saratov and the Lower Kama reservoir, as well as the (up to now 'unfinished') Cheboksary reservoir. In the following 1980's projects for further reservoirs and HPS – like the Nizhne-Volzhskaya (Lower Volga) HPS – were turned down[20], as were plans on the transfer of Siberian river flows to the Volga basin in order to compensate for the increased water-consumption especially in the agrarian sector. "*There were also what were considered to be extreme suggestions for environmental restoration, such draining some reservoirs (Rybinskoye on Volga* (i.e. Rybinsk reservoir – R.O.)*, Tsimlianskoye on Don etc.).*" (WCD, 2000)

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[19] The former, resettled Stavropol – 1964 named after the Italian communist leader Palmiro Togliatti who spent part of his exile-years from 1926-44 in Moscow – and ironically, with his theory of 'polycentrism' denying the predominant role of the Soviet party, can be looked upon as one of the precursors of Eurocommunism. In 1966, the construction of the AUTO-VAZ-works in cooperation with the Italian car manufacturer FIAT laid the foundation for the rapid rise of the city – which since 1991 has a city-partnership with Wolfsburg, home of the VW-group.

[20] It is often stated in environmentally based reports that this happened due to adverse ecological effects, but it also occurred in a time of increasing use of nuclear power in the FSU (by the mid 1980's 25 units were in operation – 18 of them in the European part) as well as the exploitation of large natural gas deposits. The share of hydropower on electricity production in European Russia (2002) is about 8% (20% for Russia on the whole), the share of nuclear power about 30% (16% for Russia on the whole), while most electricity is produced by thermal power stations (>60% fueled by gas). Especially the widely used Combined Heat Power Plants (CHPP) offered some advantages over HPP's, which in combination with the quite unfavorable conditions for HPP's in European Russia (East European PLAIN) further reduced the need for new ones – reflected by the above figures.

1.7.3 General implications

With the exception of the Cheboksary reservoir – downstream the city of Cheboksary (near Novocheboksary, the center of the chemical industry in Chuvashyia) – all the reservoirs are situated upstream of major cities, and as can be seen from Table 8 differ considerably in a number of basic indices (area, area of shallows, length (of shoreline), volume, residence time, etc.), as well as the industrial and agrarian infrastructure within their catchment (Table 6 and Table 7) and their main purpose. In conjunction with their probable sediment trapping efficiency (see Table 9), consequently the reservoirs should remain unaffected by pollution due to the adjacent major city, while being considerably influenced by the upstream regional structure and effluents.

It was the Volgograd reservoir particularly, which draw a wider attention to adverse ecological effects. It is frequently reported, that 'immediately' after its construction, the catch of sturgeon species in the Lower Volga decreased by about 30% – due to lost spawning grounds upstream from the Volgograd reservoir, altered river flow patterns disrupting natural signals for spawning migration, and other factors – but then could be increased again, to reach its peak in the mid-to late 1970's through the establishment of fish-breeding farms and measures to regulate harvesting[21]. Another measure frequently reported to be aimed at the improvement of the fish habitat in the Lower Volga was the construction of a water divider in the head of the Volga Delta (around 1973 or 1976) to increase the share of water flowing to spawning areas in the eastern part of the delta, but which was only used a limited number of times due to different interests of fishery and agriculture in the volume and timing of flooding[22].

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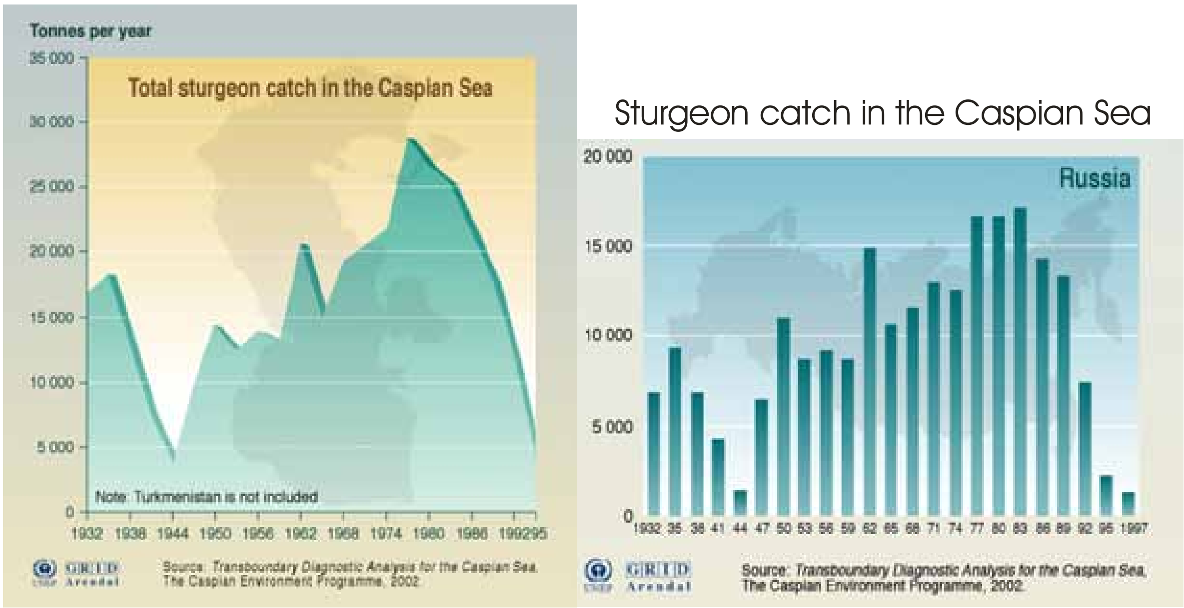
[21] This popular explanation has some inconsistencies. The legal catch size of the (slow-growing) sturgeons is achieved with about 10 years (the larvae of most sturgeons migrate to the Caspian Sea, where they live for 6-20 years until they're mature; for which reason they simply cannot be caught in a river – and the USSR banned open-sea catch of sturgeon around 1962), which would have been the period of time after which a reduction in catch could have occurred. It seems more reasonable, that the catch declined (dramatically) in the regions upstream the Volgograd reservoir, since the fish couldn't pass the dam – and later installed fish 'ladders' are reported to be quite ineffective – but remained untouched downstream the reservoir – resulting in a net decrease. What could have been realized is a (sharp) decline in young sturgeons-population because of the lost spawning grounds. That is supported by the fact that the peak in sturgeon harvesting in the mid-1970's linked to the fish-breeding farms also could not be achieved until they worked for about 10 years. This doesn't negate the negative effects of the dam, but outlines the fact, that measures against the diminishing of this economical important fish were most probably also taken 'immediately'. However Figure 14 tells a different story, and Poddubnyi (1979) reports artificial sturgeon breeding to have started in the Lower Volga in 1916, "*and since 1940 it has become a routine matter*".

[22] Another reason for the construction of this water-divider could have been to ensure water-supply to the canals in the eastern delta, e.g. for ships and irrigation, under the conditions of an at this time declining sea-level in the Caspian Sea, which in conjunction with a deepening of the 'Volgo-Kaspiiskii-Canal' (in the western branch of the delta)

Moreover, it is reported (Schoor et al., 2002) that every year a six weeks flood in the delta region through the Volgograd reservoir is allowed in May/June of about 25,000 m³/s (mean annual flow ≈8,000 m³/s). Alike, Avakyan (1999) reports, that every year from 70 km³ to 130 km³ of water are annually discharged in spring or early summer (depending on whether the year is dry or wet) in the Lower Volga (through the Kuibyshev reservoir) in order to supply water for fishery in the delta-region below Volgograd[23].

Despite these efforts, the commercial catches of sturgeons have declined dramatically in recent years. Especially after the collapse of the Soviet Union, when large-scale organized poaching developed, which is nowadays considered as the major threat to the sturgeon-population. However, none of the influences are quantifiable; neither the effect of the Volgograd reservoir or a potential overexploitation in the 1980's, nor the effectiveness of the fish-breeding farms – whose output also declined – let alone the poaching.



Source: *Transboundary Diagnostic Analysis for the Caspian Sea*, The Caspian Environment Programme, 2002

Source: *Transboundary Diagnostic Analysis for the Caspian Sea*, The Caspian Environment Programme, 2002

Figure 14 Total and Russian sturgeon catch in the Caspian Sea-region (graphics prepared by UNEP-GRID allegedly based on CEP 2002-data[24])

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redistributed the flow in the delta to the benefit of the western branch, lowering the water-level in the eastern branch and giving rise to siltation of the canals there (Polonskii, 1995). This would also explain the limited times it has been used as good as the above version. Because of a rising sea level (since about 1977 – and Polonskii (1995) reports the water divider to have been operational since 1973) and abundant water from the Volga (see[2] – average annual flow 1978-93: 270 km³), the need for this construction should have ceased.

[23] These two statements are not necessarily inconsistent, since the (bigger) Kuibyshev reservoir and the Saratov reservoir must be 'synchronized' with the Volgograd reservoir in order to allow the flooding, otherwise the excess flow of 17000 m³/s would consume the effective storage of the reservoir within about 6 days.

[24] There are however some differences between Figure 14 and the reported CEP (2002) data, as well as within the CEP (2002)-report itself, who states: "*Although the numerical values differ from those of Table…, the decreasing trends are similar*" – while this table simply omits the years between 1980 and 1991... The crucial point is that while the de-

"*The variations between 1932 and 1950 are explained by the reduction of fishing during war and the gradual rehabilitation of the industry after the war. Two important events took place in the early 1960s, the construction of the Volgograd dam, which cut off access to upstream sturgeon spawning grounds, and a parallel ban on fishing with nets at sea to protect juvenile sturgeon. The fishery was transferred to the mouths of the rivers, which resulted in an initial substantial increase in annual catch that peaked in 1977 at 28,900 tonnes before declining rapidly to 12,000 tonnes in 1992. … High catches during the period immediately following the construction of the dam were based largely on year-classes from before the damming of the Volga, as sturgeon mature very late. (Sturgeon reaches spawning maturity between the ages of seven and 16 years, depending on the species.) It is estimated that poachers take about 12 times the volume of the officially recorded catch.*" (CEP, 2002)

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creasing trends may be similar, the implications can be quite different. Judging from the Russian sturgeon catch according to Figure 14 the recent dramatic decline in sturgeon catches is in compliance with the idea of increased poaching in the post-Soviet era as the main culprit. On the other hand, already the depicted 'Total sturgeon catch in the Caspian Sea' of the littoral states (Russia, Iran, Azerbaijan, Kazakhstan, Turkmenistan) backs up the idea of a more or less steady breakdown – for what reasons soever – since about 1980.

Things get even worse, when using other sparse information, like Poddubnyi (1979): "*The catch of sturgeon species, which in 1910 made up 27.000 tons in the Volgo-Kama region, now does not exceed 4-6.000 tons. This decline is, however, a result of fishing regulations and not of low abundance of commercial stocks (Vovk, 1966).*"

(Vovk, F.I. 1966. Reproduction of the sturgeon fish stock in the tail waters of the dam of the Volga power station after the name of the 22nd congress of the CPSU. Trudy Volgograd. Otd. GasNIORH 2: 3-78. – not available to me – R.O.)

No matter, when this 'now' may have been (1966 or 1979) the catches are markedly below the above reported figures for this time , supporting reports of an 'immediate' breakdown in sturgeon catches after the Volgograd reservoir became operational – albeit claiming other reasons, confirming at least some sort of problem in fish stocks; and so the simple idea of failed regularities and overexploitation in the 1970's and early 1980's, not compensated for by the breeding-farms, as the main reason for the rapid decline appears to be as liable as any other.

1.7.4 Implications affecting sedimentation processes

1.7.4.1 Overview

It is far beyond the scope of this work to qualify the beneficial and adverse effects of the Volga reservoirs. Most of them are almost unquantifiable already with respect to the sparse data available, and even much more elaborate studies on this topic, like the before cited WCD (2000) report, had to state in their Conclusions: "*The material listed … provides only a fragmentary picture of a very extensive problem of interaction of dams and reservoirs with human economic activities and environment.*"

Solely the main effects of the reservoirs directly affecting this work will be addressed; omitting e.g. the social implications of resettlements, as well as possible impacts on biodiversity, but also the benefits of cheap power generation, water-supply and improved water-transport[25]. What is also missing is a description/consideration of the more than 200 small reservoirs (<1 km³) along the Volga, mostly used for drinking water supply. On the one hand, none of these reservoirs was sampled, and thus any speculation about their (environmental) conditions would be meaningless. On the other hand, their stored water is consumed in one way or another, eventually entering the Volga as a form of wastewater, influencing the parameters measured.

All reservoirs affect hydraulic and hydrologic characteristics. The risen water level upstream of a dam changes parts of the fluvial environment to a lacustrine one. Shallows (i.e. areas with depths less than 2 m – or in general, depths less than the water-level fluctuations in the reservoir) are (partly) lost for agricultural use and/or are turned into areas with excess bio-production once they are submerged[26]. The risen water-level causes a rise in groundwater level, resulting in increased moisture circulation in the zone of aeration, possibly leading to underflooding, water logging, and salinization, soil transformation (gleying and peat formation) and additional leaching of the affected soils. The upstream currents are less strong; while downstream, the flows are generally less strong during high discharge season and greater during low discharge season than under natural conditions. Waves in the upstream parts are usually higher, because of the flattened relief – the 'lost' valley of

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[25] An overview/review of Russian (USSR) studies conducted on the problems of reservoir construction and their impact on socio-economic, as well as environmental issues starting in the 1930's is provided by Avakyan (1999).

[26] The excess bio-production of shallows is not necessarily negative, but could instead be used to control the trophic state of a 'valley-type'-reservoir if prevented from complete drying (cf. UNEP, 1999) or else can be regarded as a (temporarily) regained area for agricultural production (Avakyan, 1999) – e.g. 'flood recession agriculture' (crops are planted on floodplains at the end of the wet season to exploit the moisture left behind by the retreating floods (IEA, 2000-1)).

the reservoir – and a longer wind fetch of the enlarged water surface than under pre-damming conditions.

The initial conditions for dams and reservoirs – at least with respect to the consequences – were quite unfavorable in the Volga basin. As an (at least nowadays) frequently used and accepted rule of thumb, the environmental impacts of dams (reservoirs) are roughly proportional to the area inundated, and the gentle slope of the river (a mean about 7 cm/km throughout its whole course, and just about 4.5 cm/km downstream the Ivankovo reservoir – cf. Figure 7) causes the HPS's to be quite ineffective with respect to land use per Unit of Capacity – which of course also holds true for the water storage per area. So beyond the 'small' versus 'large' dams debate – 'small' dams (and reservoirs) cause smaller human interventions and less impact on a specific site, while based on the energy and power produced their cumulative impact might be larger, since they are less effective[27] – and in principle the Volga reservoirs combine the disadvantages of both, and have changed the rivers regime drastically.

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[27] Average Size of Hydro Reservoir per Unit of Capacity (IEA, 2000):

Size of plants (MW)	Number of plants in category	Average size of reservoir per unit of power (ha/MW)
3000 to 18200	19	**32**
2000 to 2999	16	**40**
1000 to 1999	36	**36**
500 to 999	25	**80**
250 to 499	37	**69**
100 to 249	33	**96**
2 to 99	33	**249**

Source: Goodland 1995.

The reasons for this correlation are merely geometrical. A small object has more surface area in proportion to its volume, than a large object (e.g. doubling the Volume of a cube, increases its surface area only by a factor of 1.59). So in order to obtain the same amount of storage volume and/or hydropower capacity the landmasses inundated by a multitude of small reservoirs or HPS would be considerably larger, than by a single large reservoir or HPS – while this is not necessarily true for their cumulative impact on the environment (IEA, 2000).

1.7.4.2 Hydrology

The natural (pre-dammed) discharge showed an expressed seasonal course, characterized by two maxima: due to snow and ice melting in spring (April-May/June; ≈ 60% of the total annual runoff) and autumn raining (October/November; ≈ 30% of the total annual runoff). The dams and reservoirs have reduced the volume and duration of these floods, broken the seasonal dynamics, given rise to winter floods – now about 30% of the annual flow, because the hydrological regime (i.e. runoff control) of the reservoirs is mainly dominated by the interests of hydropower generation, although without changing the mean annual flows or the inter-annual fluctuations. In conjunction with the fact, that only the Rybinsk reservoir is large enough for a 'year-to-year' regulation – i.e. a very large reservoir with a storage capacity equal to, or more than 50% of mean annual river inflow; able to eliminate seasonal, as well as (most) inter-annual fluctuations, guaranteeing a steady outflow – while the other reservoirs are of the 'seasonal'-regulation type, this gave again rise to spring-floods (in April/Mai) in recent water abundant years, especially in the Volgograd oblast[28]. It is also this kind of 'seasonal'-regulation – characterized by frequent spilling during heavy flooding – that led our Russian partners to the idea of large amounts of (contaminated) sediments to be transported downstream every once in a while.

Flushing is frequently reported for some Russian reservoirs in Siberia, where low-level outlet gates with a large discharge capacity were included in the dams at construction. Besides the fact, that for the pre-damming Volga as a relatively slow-flowing lowland-river («1 m/sec during low-water level in the summer) the risk of deterioration of the reservoirs due to siltation should have been considered as minimal, and so – although unknown – it is not very likely that low level outlet gates were installed, and desiltation should be quite ineffective since some of the criteria for (the rarely) successful flushing (e.g. narrow, steep-sided reservoir, requirement of the reservoir to be emptied, etc. (cf. Atkinson, 1996)) are not met in the Volga reservoirs, even if these outlets were included. It seems more reasonable that some sort of 'drawdown' – i.e. lowering of the water levels in a reservoir for a few weeks or months during flood season – is conducted, in order to pass the higher sediment loads in this period through the reservoirs[29], which in fact would be at best as effective as

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[28] Another explanation is that the warmer winters during the last decade resulted in earlier snowmelt of parts of the snowcover. The (over-)moistening of the upper soil, especially in the steppe-zones, entails a more rapid runoff, leading to floods – without the need of higher precipitation and/or annual runoff,

[29] This would correspond to the sometimes-made distinction between sediment flushing and sediment sluicing. While sediment flushing is trying to remove the sediments that have already settled in the reservoir, sediment sluicing is used only to prevent them from settling during times of flood. Moreover flushing is aimed particularly at sands and gravels, which determine the sustainable volume of a reservoir, while sluicing 'removes' only the finer fractions.

the (spring)-floods in the pre-dammed era – while the interests of HPS should prevent even this from being done extensively, since it would mean a loss in profit[30].

With the exception of the artificial flooding of the delta region (see Chapter 1.7.3; p.48 ff.) at present regular spring floods are only observed in the area of N. Novgorod, due to the unregulated Oka discharge, although their volume (duration and water level) decreased considerably, since the excess spring-discharge of the Volga is no longer contributed, but is used for the filling of the Gorky reservoir instead.

The amplitudes of annual water level fluctuations have also been decreased[31] – although at a higher water level[32] – while on the other hand in the tail waters of the dams weekly and daily fluctuations have become characteristic[33] due to the work of the HPS. These changes are also reflected in the current velocities. In general a HPS (dam) slows down the upstream current velocities – reducing the stream's sediment carrying capacity – while altering the downstream currents according to its operation (working regime) and the river, carrying a reduced sediment load show high channel erosion in order to restore the sedimentation balance. The main purpose of the Volga HPS's is to compensate for peak loads, resulting in rapid changes in current velocities within wide limits in the tail

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[30] "*Today a flood is a source of unexpected and absolutely unregulated profits by the Joint Stock Companies 'Unified Electric Systems of Russia' (RAO EES). Energy barons will always be tempted to make money by passing water through turbines of power plants rather than discharging water from overfilled reservoirs*." (Kosarikov et al., 2001). (The 'Unified Energy System of Russia' (RAO UESR) (http://www.old.rao-ees.ru/en/) –another name for the above 'RAO EES', and currently the largest energy monopoly in the world (the 'Federal wholesale electricity market' (FOREM) is in fact a subsidiary of the 'UESR') - which was set up by Decrees of the Russian Federation President in 1992, aimed at providing reliable power supply, is a holding company owning controlling stakes in 72 (out of 74) regional energy supply companies (AO-Energos) and 32 large federal level power plants, and controls about 70% of the Russian electric power market (based on installed generating capacity – approx. 80% based on actual sales) – as well as the principal backbone transmission lines. RosEnergoAtom (http://eng.rosatom.ru/) - a state-run association also created in 1992, to oversee the operation and construction of nuclear power plants – controls another 10% (16% of actual sale) of this market. All NPPs in Russia are under its jurisdiction, with the exceptions of the Leningrad NPP, which was privatized in 1992, and the South Urals NPP, which is considered a military installation.)

[31] These fluctuations were quite significant under natural conditions, reaching from about 15 m near Samara and Saratov, to more than 10 m in Tver and Volgograd, and still exceeding 4m at Astrakhan (Butorin, 1979).

[32] The water level in the impounded zones rose considerably: e.g. approx. 15 m in the Gorky reservoir and more than 26 m in the Kuibyshev reservoir respectively (Butorin, 1979).

[33] Daily fluctuations are about 2 m in the tailwaters of the Rybinsk, Gorky and Kuibyshev reservoirs – maximum values may reach up to 6 m (in the Volgograd reservoir), while annual fluctuations in the reservoirs are well below 6 - 7 m (Butorin, 1979)

waters – i.e. pulsations on a daily, as well as a seasonal basis[34] – even leading to reverse currents, in the case of a (sudden) cessation of the HPS operation. As a net effect, the flow regulation decreases the current velocity[35], resulting in a regime far more complex than in an un-dammed River. While general regularities remain unchanged (e.g. lowest velocities are found near the banks and the bottoms; highest are midstream near the surface), the morphology of the reservoirs, the activities of the HPS, as well as wind-induced currents in the shallow Volga reservoirs makes them difficult to describe – and subject to unforeseeable changes[36].

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[34] E.g.: Butorin (1979) reports a change in the surface currents of the Rybinsk reservoir tailwaters from 0.17 to 1.37 m/s within 24 h (on July 29-30, 1957) – a value close to the velocities reached during the spring-floods in the pre-damming era (≈1.5 m/s) – while the velocity fluctuations in "a near-bottom layer" reached just 0.56 m/s.

This points out the major problem bound to the description of – not only – this (four-dimensional) parameter. Unless one does not conduct some sort of 'over-sampling' of fluctuating parameters, the results will be a more or less meaningless approximation of reality (cf. e.g.: EN 25667-1: 1993 Water quality -Sampling - Part 1: Guidance on the design of sampling programmes (ISO 5667-1: 1980 – containing a description of the connection between the (known) variability of a parameter and the necessary sampling density/frequency to describe it – resulting in numbers of samples usually way too high to be (monetarily) feasible, except for e.g. authorities.

In fact the same problem that had to be solved when changing from analog to digital media; a 1:1 transcription is practically impossible and there will always be a loss of information; but it will go by unnoticed at a specific bit-rate… so will the fluctuations – depending on the precision needed to address a question statistically soundly.

[35] In fact, this is just an effect of the increased surface (i.e. width of the 'riverbed') since the net-discharge of the Volga – after filling of the reservoirs – did not change. The usually reported figures for the slow-down of the Volga are, that it took about 30 days before the damming for the water to flow from Rybinsk to the Volga delta (or Volgograd), now it takes (more than) one and a half years – which would correspond to current velocities dropping from about 1 m/s to 0.05 m/s – approx. the time achieved by summing up the residence times of the reservoirs (cf. Table 8). With respect to the fluctuations reported by Butorin (1979) – cf. [34] – this information is not very valuable…

[36] This goes without saying for almost any fluctuating parameter bound to the natural and/or manmade regime of a water body. There is no way to describe such a system by single numbers, or single measurements. Only extended time-series (not available) along with a measure of spread would be sufficient.

1.7.4.3 Sediment 'balance'

Trap efficiencies of reservoirs for sediments tend to fall into the range of 80-98% (Colby, 1963). This figure is reasonable for the Volga reservoirs, but not provably. Brune (1953) describes the sediment-trapping efficiencies of reservoirs as a function of their capacity-to-annual-inflow ratio (C/I) – the higher the ratio, the more effective the sediment-trapping, mainly because of slower currents, resulting in decreased sediment carrying capacity, and higher detention time.

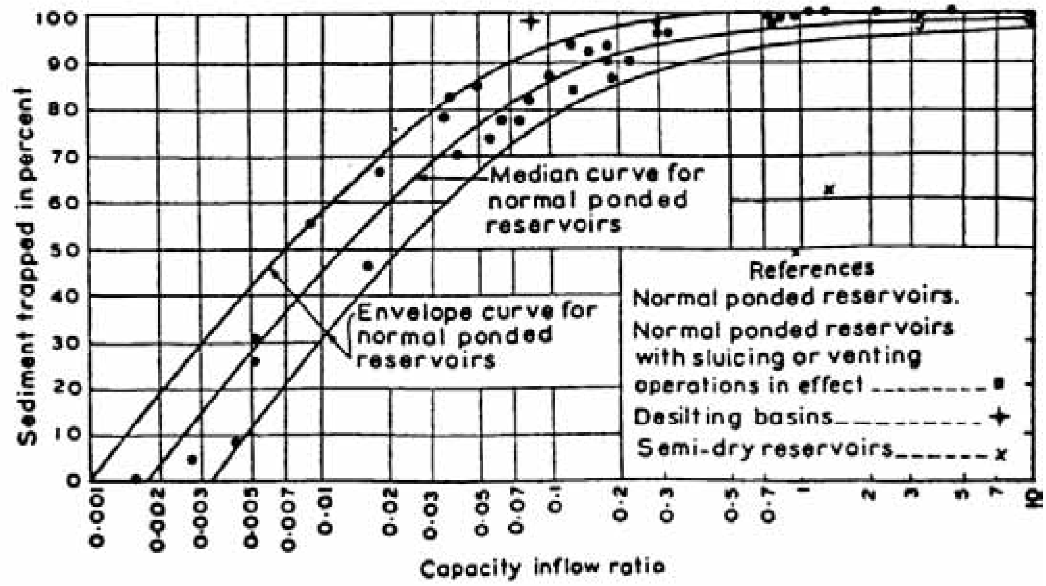

Figure 15 **Sediment-trapping efficiency curve (Brune, 1953)**

Applying his Sediment-trapping efficiency curve (Figure 15)[37] on the Volga reservoirs, shows that, potentially with the exception of the Saratov reservoir, their sediment-trapping efficiency should be well above 70% (Table 9)[38] – supporting the idea of the eventual sedimentation of almost all suspended solids within each reservoir, leaving the respective downstream reaches virtually unaffected by pollutants bound to them.

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[37] Alternatively, based on Brune's plot: trapping efficiency $E[\%] = 100(0.97^{0.19^{\log(C/I)}})$ (Dendy, 1974).

[38] Of course, it is not so easy. Sediment trapping efficiency is a very important parameter for the construction and maintenance of a reservoir, since it determines its (useful) service life. It is far more complex to be described by such a simple model, but with flow-velocity and detention-time – of which the capacity-to-inflow ratio is just a measure – as the most important factor(s), it seems to work quite efficiently and, with other methods, is widely used (e.g. USACE, 1997).

Table 9 Presumed sediment-trapping efficiencies of the Volga reservoirs (calculated according to Dendy (1974)[37]).

				Capacity/Inflow		**Sediment-trapping efficiency**	
Reservoir	Maximum Volume [km^3]	Useful Volume [km^3]	Average annual flow [km^3]	Max. Volume / Average Flow	Useful Volume / Average Flow	Max. Volume / Average Flow	Useful Volume / Average Flow
Ivankovo	1.12	0.81	9.65	0.12	0.08	**>85%**	**>80%**
Uglich	1.24	0.81	13.6	0.09	0.06	**>85%**	**>80%**
Rybinsk	25.42	16.67	35.2	0.72	0.47	**>95%**	**>95%**
Gorky	8.81	2.78	52.5	0.17	0.05	**>90%**	**>75%**
Cheboksary	13.85	5.70	112	0.12	0.05	**>85%**	**>75%**
Kuybyshev	58.00	34.60	239.7	0.24	0.14	**>90%**	**>85%**
Saratov	12.86	1.75	247	0.05	0.01	**>75%**	**>40%**
Volgograd	31.45	8.25	251	0.13	0.03	**>85%**	**>70%**

As mentioned above, the creation of a large water body flattens the topography, reducing air flow resistance, which in conjunction with the larger wind fetch compared to the un-dammed river gives rise to higher and more frequent waves: "*With the impounding of the Rybinsk reservoir, frequency of strong winds near the reservoir increased 25 fold at night and threefold during the day*"[39] (IEA, 2000-1).

According to Butorin (1979) the waves on the Volga did not exceed 0.5-0.75 m in height before the damming, while now they may reach more than 3 m in the Kuibyshev reservoir and more than 2 m in the Rybinsk reservoir – presumably lower on the smaller reservoirs. This indicates an increased shore abrasion within the reservoirs – albeit to different extents (depending e.g. on the height and type of waves and the morphology of the banks). Although shoreline erosion is not a new phenomenon in the Volga catchment – as in any other catchment – and led to the above mentioned distinction between the high and steep right bank ('hilly side', or 'Bergufer' – erosion) and the low left bank ('plains side', or 'Wiesenufer' – deposition), human impact markedly influenced this natural processes. Deforestation first took place in the Upper Volga virtually with the establishment of the first settlements. Beginning in the 17th century the agricultural use of the Volga banks spread from Kazan downstream and in the 18th century clearing of vast forest areas in the middle and lower Volga took place – giving rise to sheet and gully erosion and landslides, especially in the vulnerable karst regions between Kazan and Volgograd, where up to 80% of the land was in agricultural use at this time. At the beginning of the 20th century, already 10-12% of the agricultural cropland had been lost due to erosion; in the most severely affected region between Kazan and Saratov up to 30% – corresponding to a loss of 1-5t per hectare and year (Weigt, 1978). According to the *World Resources Institute* 52% of the original forest in the Volga catchment has been lost and 11% of the area is affected by water-erosion (WRI, 1998).

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[39] The report also points out the possibility of changes in climatic conditions and atmospheric stability – although often minimal and difficult to distinguish from normal fluctuations – generated by large reservoirs.

There seems to be agreement in the literature, that the least extent of shoreline erosion takes place in the (relatively small) Ivankovo reservoir – explained by a smaller windfetch, and thus smaller waves, and its age, and thus matured water-body and shoreline; having reached some sort of steady state[40]. Butorin (1979) reports the extent of eroded shorelines to be 3% in the Ivankovo reservoir, 13% in the Uglich reservoir, and 9% in the Rybinsk reservoir, as well as "*similar processes of shore transformation … in the other Volga reservoirs*", but notably two-thirds of the Gorky reservoir shoreline[41]. Additional information can be found e.g. in: (Stolbovoi and McCallum, 2002) – based on the 'International Soil and Reference Information Centre' (ISRIC[42]) project on '*Global Assessment of Soil Degradation*' (*GLASOD*), as well as later publications). According to their large-scale maps, water-erosion only takes place in the Rybinsk reservoir and on the Lower Volga between Kazan and Astrakhan![43]

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[40] In some cases, shoreline erosion may form a littoral shallow, which decreases the intensity of waves and shore transformation, leading to stabilization. However, this explanation does not describe the Uglich reservoir (comparable size and age, but more eroded shorelines than the Ivankovo reservoir) and it may also be an effect of a differences in bank-morphology:
low, partly boggy banks in the Upper Volga, up to the **Ivankovo** reservoir;
higher right banks composed of clay and black limestone in the **Uglich** reservoir;
lower banks of sand and sandy loams in the **Rybinsk** reservoir;
higher right banks (reaching from 10m up to 130m) and precipices composed of sandy and muddy rocks till the junction of the Kama (Reservoirs of **Gorky**, **Cheboksary** and the upper part of the **Kuibyshev** reservoir);
uplands of various heights on the right bank, with outcrops of hard limestone (Samara bend) up to Samara (lower **Kuibyshev** reservoir);
lower, easily damaged right banks (karst) and low, sandy left banks up to Volgograd (**Saratov** reservoir and **Volgograd** reservoir);
Caspian deposits and low banks up to the **delta region** – i.e. supply limited erosion and sediment transport, since the coarser particles (i.e. sands approx. > 0.5 mm) usually cannot be carried by slow-flowing rivers.
It would be just a speculation – although backed up by our observations during sampling (see[43]) – to infer an increasing erosion downstream, e.g. from reports of retreating shorelines up to 50 m within 27 years (1937-194) near a village in the Ivankovo reservoir – without further destruction in the following 3 years – (Butorin, 1979), compared to 10 m within one year for a village within the Volgograd reservoir in 1960 (and additional 30 m in the following 5 years (Weigt, 1978)), since this is neither representative, nor quantifiable. On the other hand, who would expect a thoroughly and quantitative monitoring of 7000+ km of shoreline, in cases where neither villages, nor shipways are affected?

[41] Cf. BAW (2002), which reports navigational problems in the section Gorodets-Balkhna (near N. Novgorod) to be the result of the shoreline erosion, causing the river to become wider and shallower. This is NOT an effect of siltation! The fairway is not affected and dredging is impossible, since it would lower the fairway beneath the sluice-level. See also:[3]

[42] http://www.isric.org/

[43] From an unscientific approach, our observations during the sampling suggest an increasing extent of shoreline erosion downstream. While we hardly recognized any erosion in the Reservoirs of Ivankovo, Uglich and Rybinsk (the

With respect to sediments and sedimentation-processes, available information is sparse, if not absent. In general, there is only a poor correlation between sediment yield and erosion rates, making it difficult to estimate the sediment load entering the reservoir based on erosion rates within its catchment (Morris and Fan, 1998). Additionally, with e.g. reported volumes of collapsed ground per meter shoreline for the Rybinsk reservoir varying within a factor of 10 for different points (Butorin, 1979), and no one should expect any sort of quantification.

A minimum of trustworthy data on sedimentation processes for the River Volga is available. In the *International Lake Environment Committee Foundation* (ILEC) database, a sedimentation rate of 4 mm/year for the Kujbyshev Reservoir is reported.[44] Selivanov (1977) reports the same low sedimentation rate (3-4 mm/year) for the Volga-Delta, while Gapeeva et al. (1997) used sedimentation rates of about 10 mm/year for the interpretation of the vertical heavy-metal-distribution in core-samples of the Ivankovo Reservoir – therein referring to Zakonnov (1993). Butorin (1979) easily explains these differences, recalling self-evident facts:

"*A characteristic feature of sedimentation is, however, that it differs greatly from place to place. Thus in the Rybinsk reservoir the thickness of the secondary deposits in some places is more than 1m, while in others it does not exceed several millimeters*."

He reports the mean annual sedimentation rates to be 2 mm for the Ivankovo reservoir, 1.7 mm for the Uglich reservoir and 2.5 mm for the Rybinsk reservoir – pointing out that these rates do not give rise to any problems according to siltation of the reservoirs.

Most other data about the sediment runoff of the Volga seem to reflect the pre-damming period, with a mean annual sediment runoff to the Caspian Sea between 14 million tons/year (Polonskii, 1993) and 25.5 million tons/year[45]. Polonskii (1993) also reports the **post-damming** sediment runoff to the Caspian Sea to be 6-7 million tons/year – which matches the figures about sediment-runoff by Selivanov (1977) and Weigt (1978) – while the CEP (2003) reports: "*The flow of pileups*

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latter we sampled only in the southern 'Volga-part'), shoreline erosion was remarkable in the other reservoirs - especially in the case of occasionally higher and steeper right banks (various places between Yaroslawl and the Samara bend) and almost the whole course between Samara and Astrakhan (albeit much less pronounced after the city of Volgograd), with nearly every sign of a problematic situation (large areas of bare soil on steep, high shoreline banks; leaning and downed trees with exposed roots on the shoreline; muddy waters near the shoreline; excessive deposits of sediment near the shoreline resulting in shallows). Bank reinforcements were absent – with the exception of in the large cities – and/or of a more or less provisional kind in smaller cities. Of course, this is only a subjective snapshot, not allowing any quantification.

[44] http://www.ilec.or.jp/database/eur/eur-54.html

[45] http://disc.gsfc.nasa.gov/geomorphology/GEO_5/GEO_PLATE_D-8.HTML

of Volga river is estimated in the period till 1995 as 15 millions tons a year, and after 1961 it is 13.6 millions tons a year."[46]

The *UN Environment Program* (UNEP) through its *General Environment Monitoring System* (GEMS/Water) claims in their *Digital Atlas of Global Water Quality* (for the years 1976-1990) total suspended solids for the River Volga to be 117 mg/l (calculated from an annual load of 25 million tons/year and a discharge of 214 km³/year)[47]. At the same time, one can download triennial water quality statistics from the same program, starting from 1979-1981 to 1997-1999, that do not at all correspond with the above data (Figure 16)[48].

Judging from the low sampling density (a maximum of 47 samples for three years, i.e. statistically more than three weeks in-between the sampling) the figures are merely a clue, far from telling much about the real sediment transport of the Volga – although much more reliable than other one-time only measurements[49]. Even a superficial look at Figure 16 reveals the above addressed problems of fluctuating (or event-driven) parameters. E.g., at best a tenfold concentration of suspended matter could go by unrecognized for three weeks (at N. Novgorod, as well as in the delta-station) while most of the time the (statistical) sampling density is even much lower. The maxima are necessarily arbitrary, and even the median-values for a single station or throughout a river transect (N. Novgorod stations) vary within a factor greater than two. So any attempt to balance the sediment load on this basis is highly questionable – which in fact is not an exclusive problem of the Volga, since river load is the least studied hydrological element due to its complexity and difficulties in measurement (cf. Milliman and Meade, 1983).

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[46] C.f. e.g. Jaoshvili (2002) – reporting uncertainties in river sediment load balances for the Black Sea, as well as to the world oceans: "*Despite the fact that the Danube is one of the most studied rivers in Europe, figures for the amount of sediment load brought down it to the sea vary considerably.*" (Sediment load for the Danube after its damming varies between 42.2 and 55 million t/year – and between 67.7 and 87.8 million t/year before damming). So in fact the differing figures for the Volga are not surprising at all; it's just the methodological uncertainty bound to any approach balancing complex systems.

[47] http://www.gemswater.org/atlas-gwq/table5-e.html

[48] http://www.gemswater.org/publications/index-e.html

[49] One of the possible reasons that reported figures match quite well with the GEMS/Water-medians could be because investigations (at least on the Volga) are most probably conducted under more or less comparable conditions. Sampling campaigns predominantly take place within the relatively short summer-season – avoiding possible extreme conditions, e.g. water high- and low-stands, and thus producing 'average' results under 'average' conditions. No one likes too hot, too wet or too cold… That is one of the problems pointed out by Milliman and Meade (1983) which eventually lead to errors in the rates of sediment delivery, especially since rivers are rarely studied during flood-stage, when sediment yields are much greater and bed loads (typically 5-10% for large rivers) are often neglected, partly also due to the (inadequate) sampling well below the water surface.

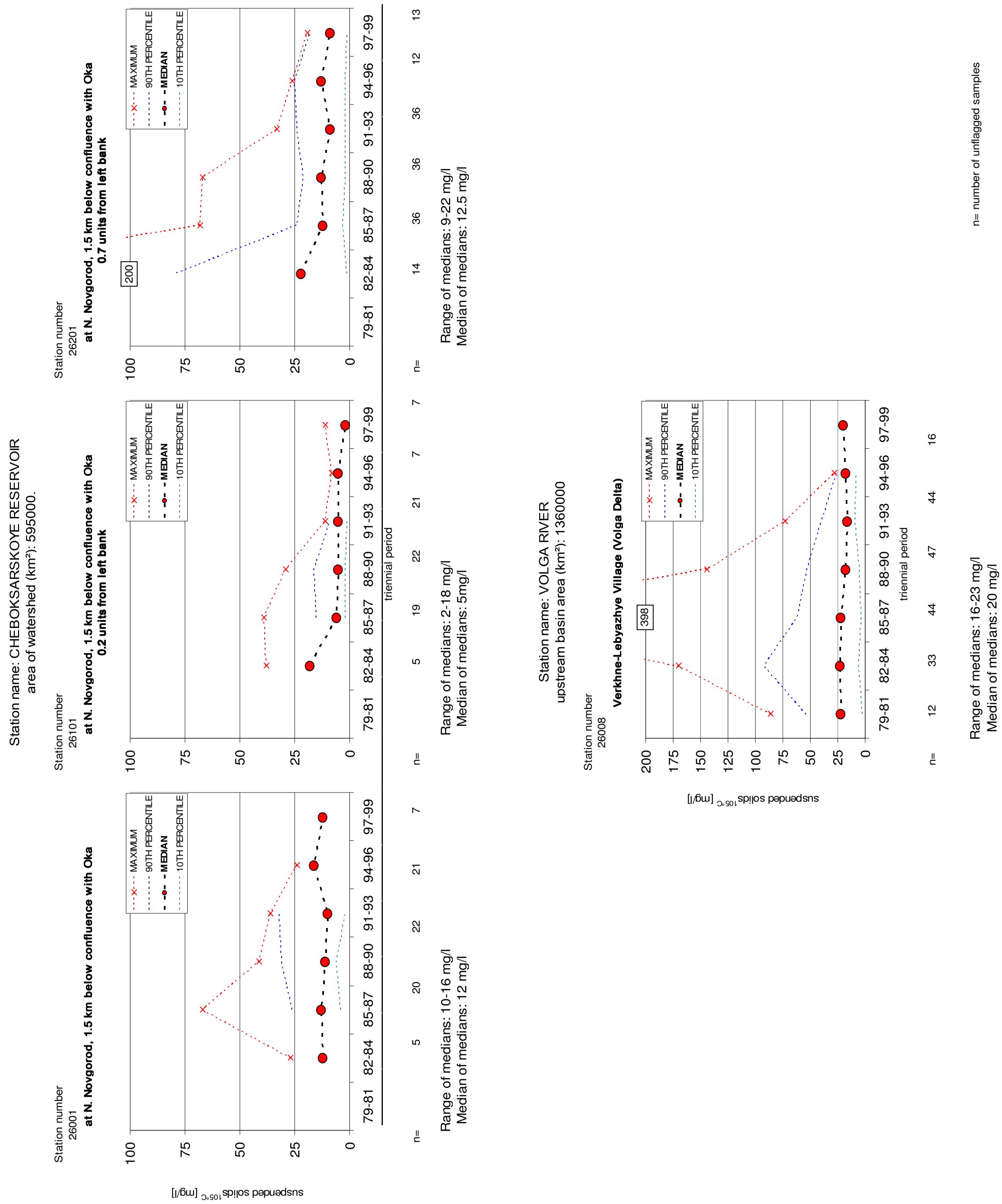

Figure 16 **Triennial time-series of suspended solids of the Volga (data, station number and description from GEMS/Water – see footnote[48])**

However, the GEMS dataset is the only easily available dataset covering a greater space (stations near N. Novgorod and Volga-Delta) and time (1979-1999). Since 1979 the median of the suspended solids for the stations on the River Volga are reported to be well below 25 mg/l – corresponding approx. with Golubkov et al. (2000) (11.3-22.3 mg/l for the Delta-Region) and Winkels et al. (1998) (19 mg/l for the Delta-Region) – identifying the Volga as river of low sediment carrying capacity and low sedimentation rates.

1.8 Summary

On the basis of the size of the Volga catchment (compromising about the cumulative area of France, Spain and Italy), the general confusion and chaos after the collapse of the Soviet Union, as well as the multitude of authorities involved in decision making and data collecting on a regional and national level in the Soviet and post-Soviet era, not to forget the still existent Russian disposition to label data as classified, the incompleteness and uncertainties bound to most data about the basin are little surprising.

Although it may be easier to describe river basins in western European countries, the results would be about as uncertain as the ones given for the Volga – a more or less reliable, rough overview with unavoidable significant errors on a smaller-scale level and high uncertainties due to non-standardized methodologies of different (statistical) agencies. Some of the uncertainties are of a principal nature – e.g. sediment load and sedimentation rates – while others are merely due to a lack in (reliable) data – e.g. in the economic overview. Nevertheless, the data should be sufficient for a generalized description of such a vast area, and reliable enough to describe at least the major trends along the Volga River with respect to human influences, as well as the natural subdivision.

In this section some of the data of the previous tables is ranked according to the percentiles of the respective parameter, and the adjacent colors were assigned to the respective region within diagrams showing the natural subdivision, as well as the reservoir dams, major tributaries (Oka and Kama), and the spatial distribution of the sampling points of our monitoring – in order to give an idea of, where interesting details and changes might take place, and where we might have missed them during sampling.[50]

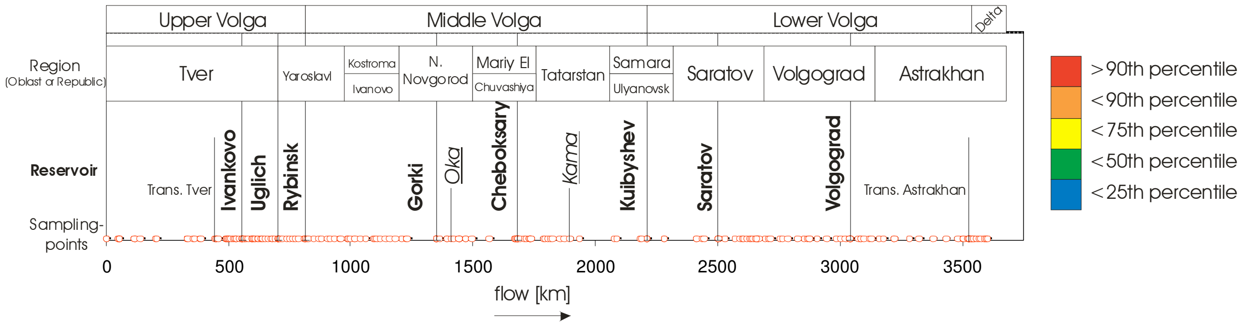

Figure 17 General scheme and colors assigned to percentiles for the following figures (circles indicate sampling points).

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[50] The included transects near Tver and Astrakhan, were chosen more or less arbitrarily during sampling. Very little human (industrial) activity took place between the source and the transect in Tver, as did from Volgograd to the transect in Astrakhan, which on the one hand could qualify these stretches to be used as ‘background’ areas (see later discussion), on the other hand is not fully accounted for in the various ‘intensity’ indices.

Figure 19 depicts some basic characteristics of high certainty of the Volga riparian regions mainly based on Table 7, while the 'probable degree of shoreline erosion' – i.e. erosion within the Volga reservoirs, which because of their respective dimension in fact means along the entire Volga bank – suffers from the uncertainties reported in the chapter about the sediment 'balance' (p.56) and is mainly based on our observations during the sampling campaigns (see footnotes[43 and 40]) – is believed to be close to reality, but cannot be quantified.

Figure 20, based on Table 7 and the adjacent Figure 11 and Figure 13 depicts indices of industrial and agricultural production (intensity) on the regional level during the years of 1994 and 1995. Therefore they should reflect partly the breakdown of the Russian industry and agriculture after the collapse of the Soviet Union – and a potential shift within the regions output during that time – while completely omitting the further substantial regression in 1998 (see footnote[11]), as well as the distinct economic rebound in the last years and their implications; namely the higher share of the energy and petrochemical sector in regions with oil and gas resources (see p.34 and Table 6).

The overall importance of different industrial sectors in major **cities** along the Volga – i.e. the product of the share of the total industrial production of a region (Table 7) and the share of the specific industry in the respective city (Table 3) – depicted in Figure 21 is the most uncertain of all indicators and the only one explicitly dealing with probable 'point-sources'. However, due to the predominance of large industrial enterprises, in fact every classification figure not accounting for the regions area is determined by the (potential) 'point-sources'.

While an almost constant ranking of the regions according to their industrial potential (output) throughout the years can be rationalized (see below), and relative changes in the kind and amount of agrarian output between the regions are not very likely (due to the structural stability in the agrarian sector (see below) and the natural conditions determining the means of production as well as its products), the operation of a specific company cannot be assured, and thus a once prominent 'point-source' may have vanished, although judging from the Russian industrial structure– a clear dominance of large industrial enterprises bought together to conglomerates in recent years – and economic development would suggest most of them to be still operational and little to no chances for new (different) companies to be established (see footnote[11] and p. 35f.). However, this remains speculative and cannot mask the need for more precise information and data.

At last Figure 22 provides the most generalized – and least uncertain – view on the overall human impact on the Volga River after its damming – combining population (density), industrial and agricultural activities, as well as the Volga discharge and thus the dilution of potential effluents, and as long as one's not clung to idea of being able to anticipate the kind and amount of COPC's entering an aquatic system or any other adverse effects, in case he just knows the kind and dimension of industry and/or agriculture it is also the most useful. Funny as it may seem, the results are approx.

comparable to the depicted ‘investment potential’ (see also Table 6), while in fact its relative high constancy throughout the years is only used as a justification to use sometimes formally outdated numbers to describe the present status, insinuating that the **relative** economic potential (and thus **relative** industrial output, as well as **relative** impact on the (aquatic) environment) changed very little during transition. This should also hold true for indices concerning agricultural activities, whose transformation, i.e. structural change with respect to ownership, means of production and/or agricultural output was, and still is very slow (e.g. Kwiecinski, 1998) – albeit (initially) suffering from about the same extent of dramatic fall in production as the industry (cf. OECD, 2000).

Any implications concerning human influences on the (aquatic) environment going further than the stated relative ones can hardly be rationalized. Even the popular idea that the (presumed) drastic decline in industrial and agricultural output could have lead to an instant, identical decline in e.g. COPC’s entering the Volga is – if not all wrong, since most economic reports cautiously just report dramatically declining proceeds, which are not necessarily contributable to a decline in production (see ‘The Economist Intelligence Unit’11); non-profitable state-run companies were prevented from being closed for social reasons, regardless of whether the products were sold; and so on – at least in isolated cases highly questionable. Apart from the aforementioned prominent example of AutoVAZ in Togliatti who profited from the crisis – and thus increased its production and output – a more general example will be given, using FAOSTAT 2004 data[51] (Table 10 and Figure 18):

Table 10 **Fertilizer production, consumption, and export (Russian Federation) – data: FAOSTAT 2004**

Fertilizers [10^6t]	year	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
Production	**Total Fertilizers**	12.28	9.94	8.34	9.60	9.09	9.35	9.28	11.03	11.49	12.15
Export		5.53	5.41	5.96	7.21	6.72	7.01	7.69	8.50	9.62	9.46
Consumption		5.51	3.85	1.51	1.75	1.58	1.55	1.26	1.36	1.42	1.60
Production	**Nitrogenous Fertilizers**	5.83	4.81	4.13	4.86	4.90	4.09	4.14	4.97	5.45	5.49
Export		2.16	2.59	2.71	3.56	3.65	2.85	3.31	3.49	4.34	4.04
Consumption		2.62	2.05	0.90	1.00	0.98	0.95	0.83	0.96	0.96	1.09
Production	**Phosphate Fertilizers**	3.00	2.51	1.72	1.93	1.58	1.85	1.69	2.02	2.32	2.40
Export		1.18	1.29	1.27	1.33	1.13	1.34	1.48	1.76	2.08	1.83
Consumption		1.54	0.90	0.26	0.35	0.38	0.32	0.28	0.22	0.28	0.31
Production	**Potash Fertilizers**	3.45	2.63	2.50	2.81	2.62	3.40	3.46	4.05	3.72	4.26
Export		2.18	1.53	1.97	2.32	1.95	2.83	2.89	3.25	3.21	3.58
Consumption		1.35	0.90	0.35	0.40	0.22	0.28	0.15	0.18	0.18	0.20
Crude Fertilizers											
Production	**Natural Phosphates**	13.97	10.38	8.02	9.07	8.68	10.00	10.05	11.22	11.06	10.53
Exports - Qty							4.59	4.85	4.68	4.09	3.38

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[51] http://apps.fao.org/default.jsp

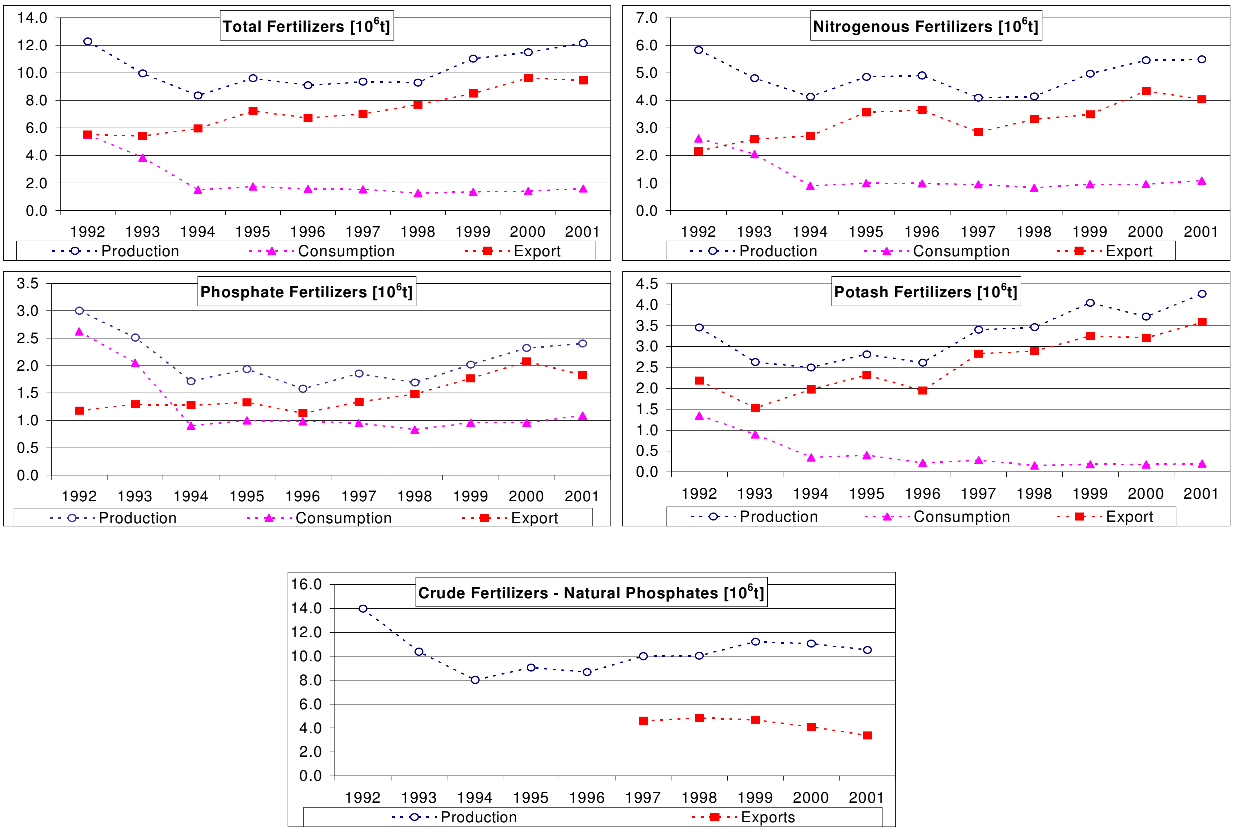


Figure 18 Fertilizer production, consumption, and export (Russian Federation) – data: FAOSTAT 2004.

While increasing exports (almost) completely compensated for declining sales on the domestic market – i.e. the fertilizer production started to recover in 1995 and in 2001 reached about the level in 1992 – the consumption is reported to have dropped about one third. Even though declining yields per ha for the Russian agriculture in this period are also reported by the FAO[51], they could have been provoked by a multitude of reasons – a potentially reduced use of fertilizers is just one of them. No figures about the use of organic fertilizers (compost, manure) as well as crude fertilizers – like Thomas slag (from steel production) or the mentioned natural phosphates – is available, while already the difference between produced and exported natural phosphates could (over-)compensate the drop in consumed phosphate fertilizers – therefore I wouldn't e.g. bet large amounts on drastically reduced phosphorous run-off from agricultural land.

1.8.1 The Volga in brief

- Europe's largest river with approx. 3500km length, 1.35 million km^2 watershed basin and more than 250 km^3 annual mean discharge.
- Slow-flowing Lowland River of thus little sediment-carrying capacity and low sedimentation-rates – several mm/year on average.
- Two major tributaries, Oka and Kama, each doubling the Volga discharge at the respective confluence.
- Under a natural regime, the River could have been divided into three parts. The Upper Volga (from its source, to the confluence of the Oka River), were the Volga is a relatively small river. The Middle Volga (from the confluence of the Oka to the confluence of its main tributary, the Kama River), on which way it doubles in size, and the lower Volga (from the confluence of the Kama to the delta), where the Volga becomes a mighty river.
- Eight big dams on the Volga (and three on its biggest tributary, the Kama) changed the rivers regime drastically, moreover decreasing sediment-carrying capacity and most probably increasing shoreline-erosion.
- Basin lies within four geographic zones, though the River is usually divided into three stretches according to its discharge – Upper, Middle and Lower Volga.
- Basin has a uniform cover of sedimentary rocks; only the Kama drains parts of the Ural Mountains, with its richer geology.
- Major natural resources in the basin are oil and gas (Middle Volga and Caspian region), coal and phosphate (Moscow basin).
- The banks are occupied by Russia's two major cultivable soils – Podzols in the forest zone of the Upper and Middle Volga and highly fertile Chernozems ('black earth') in the steppe and wooded steppe regions of the Lower Volga.
- The catchment is entirely situated on the European Plain – Russia's region with the highest population density, as well as industrial and agrarian production.
- The industrial structure is characterized by large conglomerates situated mainly in about 13 (regional) centers along the Volga banks – which should represent the major threats to the aquatic environment.
- With respect to industrial and agrarian production, three regions – N. Novgorod, Tatarstan and Samara – outperform the other regions by far. They are followed by the regions of Yaroslavl, Saratov and Volgograd, while the industrial and agrarian activities in the other regions are relatively low.

Figure 19 Basic characteristics of the Volga and riparian regions (color code see: Figure 17).

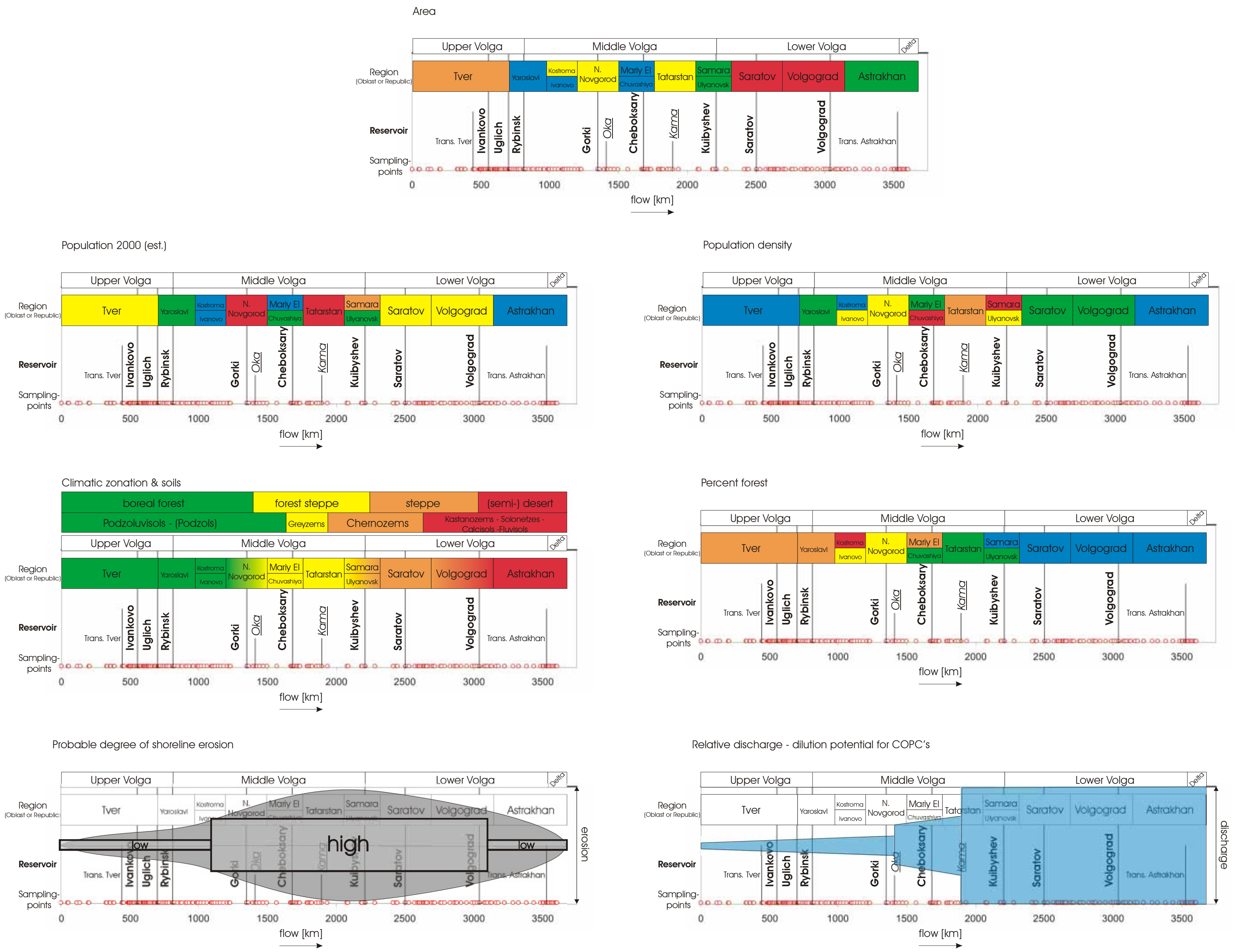
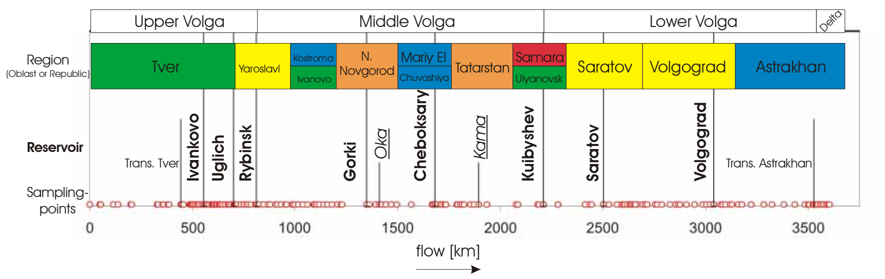
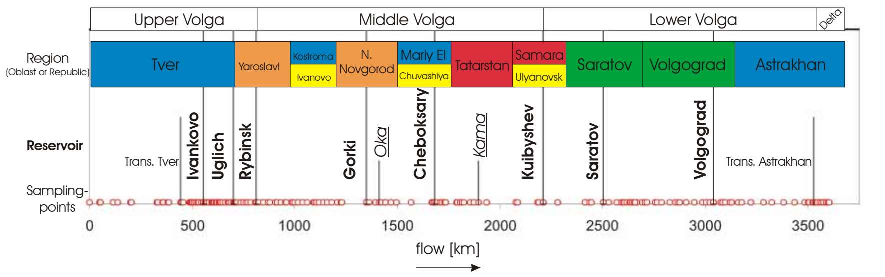


Figure 20 Industrial and agricultural activities in the Volga riparian regions and indices of their respective intensity – i.e. overall human impact (color code see: Figure 17).

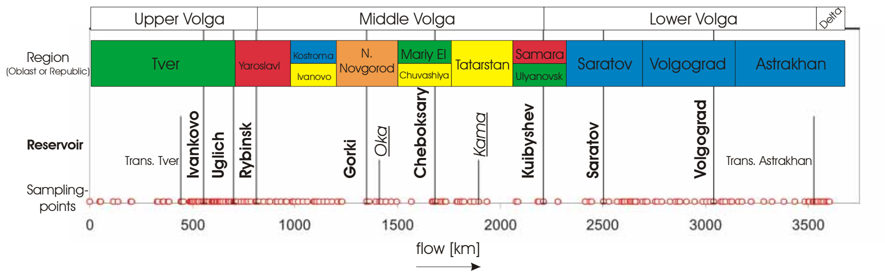
Industrial production as percentage of all Russian production (Jan.-Aug. 1994)



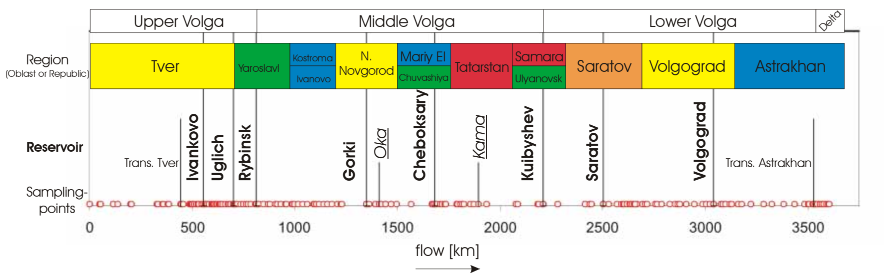
Industrial output per area



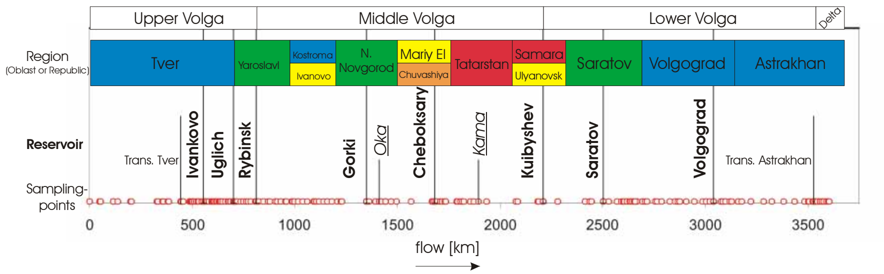
Industrial output per usable (i.e. unforested) area



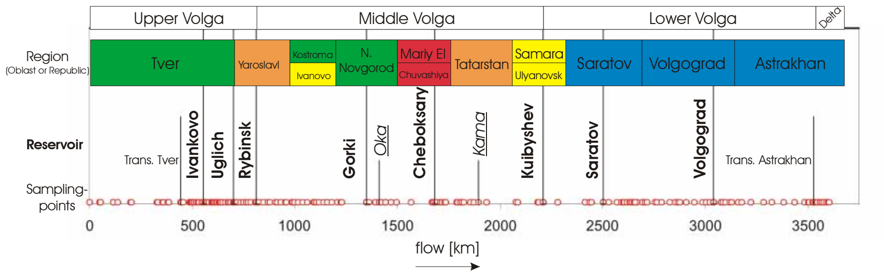
Agricultural production as percentage of all Russian production (1995):



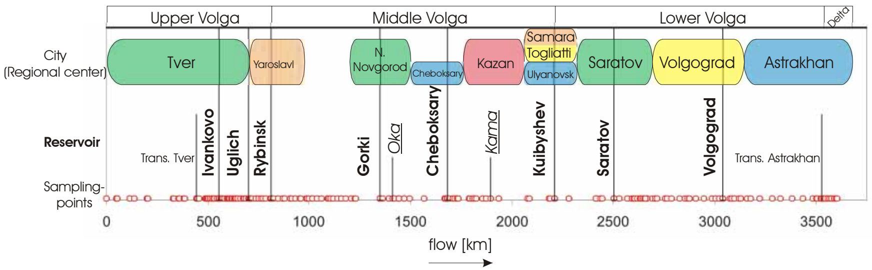
Agricultural output per area



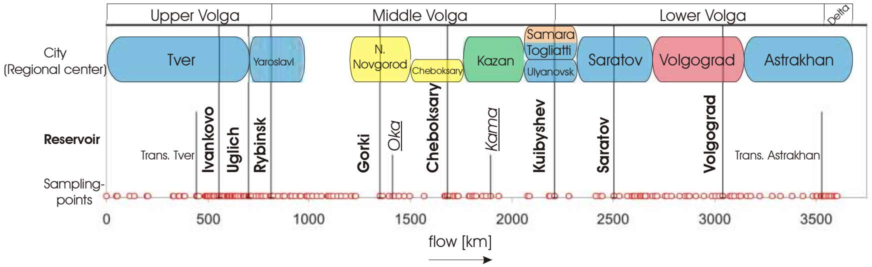
Agricultural output per usable (i.e. unforested) area



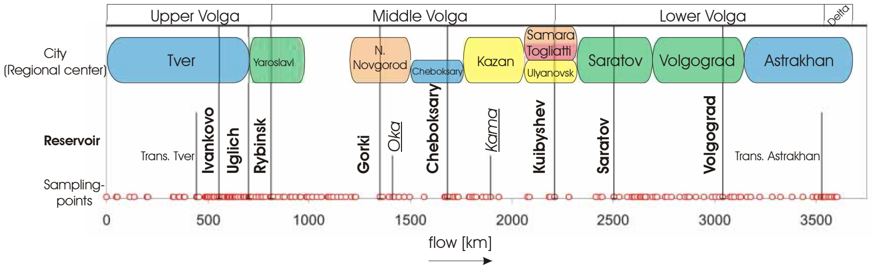
Overall importance of chemical and petrochemical industry of **major cities**



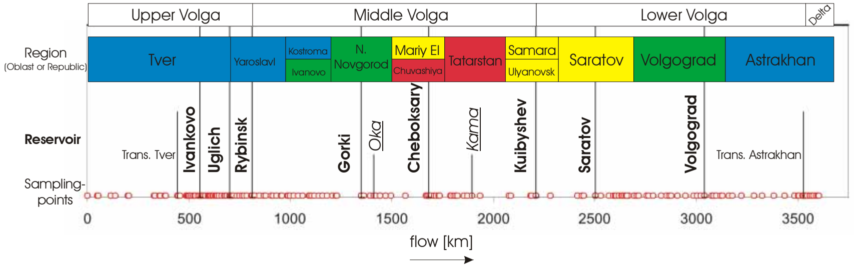
Overall importance of metallurgy of **major cities**



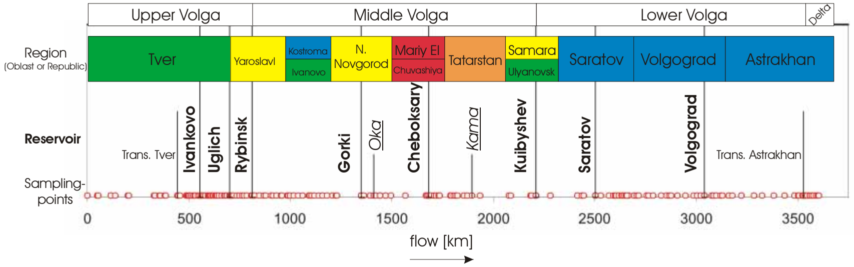
Overall importance of machinery and metal-working industry of **major cities**



Grain-yield per total area



Potato-yield per total area



Cattle, total livestock per total area

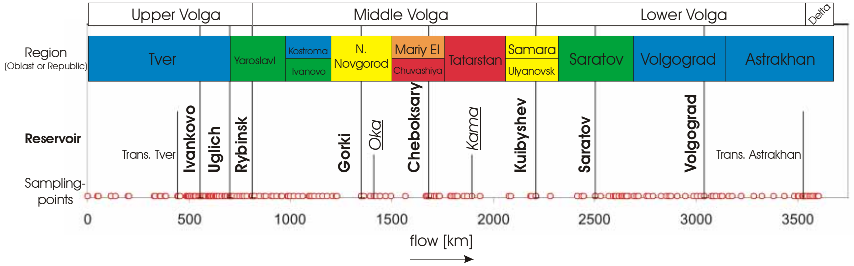
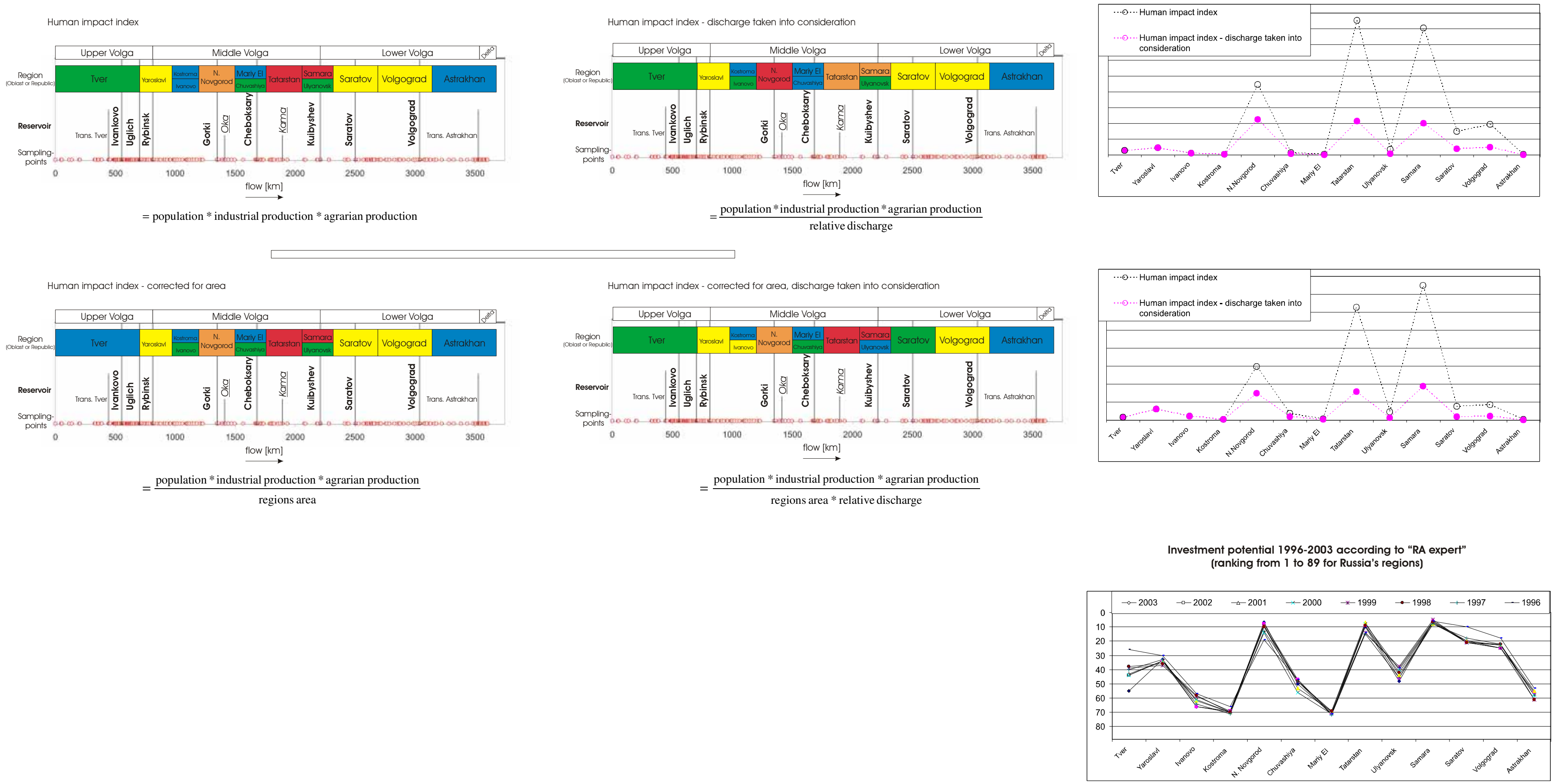


Figure 21 **Industrial structure in the Volga riparian centers (as available) – i.e. human point-sources - and agrarian structure in the riparian regions (color code see: Figure 17).**



$$= \text{population} * \text{industrial production} * \text{agrarian production}$$

$$= \frac{\text{population} * \text{industrial production} * \text{agrarian production}}{\text{relative discharge}}$$

$$= \frac{\text{population} * \text{industrial production} * \text{agrarian production}}{\text{regions area}}$$

$$= \frac{\text{population} * \text{industrial production} * \text{agrarian production}}{\text{regions area} * \text{relative discharge}}$$

Figure 22 Human activity indices for the riparian regions (accounting and not accounting for the regions area) compared to investment potential (color code see: Figure 17).

2 Materials and Methods

2.1 Sampling-scheme

The initial sampling-scheme proposed by Prof. Dr. Müller in 1997 – the planning-phase of the Volga-Rhine-Project – stipulated a sampling of the River Volga within approx. one month. Starting at its source and going down to the Caspian Sea by boat, with a sampling density of at least one sample every 10km (being somewhat denser near known and assumed hot-spots). This would have been a combination of a grid and a judgmental sampling-scheme (i.e. 'informative judgmental sampling[52]'), combining the benefits of both worlds. Due to reasons beyond our control, this was impossible to organize. So the resulting sampling scheme and sampling density is merely a compromise between 'our' wishes, and the circumstances, which in fact holds true for (most) sampling schemes:

"*In most monitoring and assessment studies, the number of samples to be collected usually results from a compromise between the ideal and the practical. The major practical constraints are the costs of analyses and logistics of sample collection.*" US-EPA (2001)

As it turned out, the sampling took five years and only the Upper Volga reservoirs of Ivankovo, Uglich and Rybinsk were sampled within a single 'expedition'/year. The other reservoirs were sampled on a one-each-year base.

The sampling-campaigns throughout the years were designed to obtain preferably equally spaced samples 'as dense as possible' – dependent on the time at our disposal for sampling, and the length of the sampled stretch. Additional samples were taken near known, or assumed 'areas of interest', like towns or industrial areas (<5% of the samples) – even though with important shortcomings discussed later.

Our knowledge of the 'areas of interest' of the Volga was, and to be frank, still is (very) limited. Most of it arose from, not very precise, publicly available CIA-maps about military, industrial and agricultural land-use in the former USSR (see Figure 10) and economic reports like the *World Bank Working paper* about the regional capitals along the Volga River and their major industries (de Melo and Ofer, 1999). Other sources were the report of the *British Foreign & Commonwealth Office* (FCO, 2000) on environmental problems in the Russian Federation, the report of the *State Committee of the Russian Federation for Environmental Protection and Hydrometeorology* on environmental problems of the Caspian region (UNDP-GEF, 1998), and of course the information pro-

---

[52] "*Sampling in which locations are chosen according to the judgment of an expert and partly in accordance with the statistical principles of sampling*" (IUPAC, 2003)

vided by our Russian partners, based on known land-use and assumed ‘areas of interest’. No further information was (or is) available at the time. Neither from the literature, nor from our Russian partners, since no such thing as a discharge-register for industrial businesses or cities seems to exist in Russia – although there are some approaches towards it on the oblast-level.

So the sampling was biased in several ways:

- More than 70% of the samples are from the right bank of the Volga, owed to the fact, that the sampling was (mostly) carried out from vessels (going downstream) and crossing the river (up to 38 km in width in the Kujbyshev reservoir) would have been to time-consuming – a compromise between the number of samples (representativeness) and completeness of information (also representativeness).
- There are several not, or less than sufficient sampled stretches of the Volga (especially in the Middle Volga).
- There are several not, or less than sufficient sampled assumed areas of interest (hot-spots) on the Volga (especially around the major cities).

This resulted in altogether 343 sediment samples of the Volga and its tributaries, including six cores, 270 samples of which are from the Volga itself. From these 270 samples, 62 samples were taken close to the eight reservoir retention dams as transects.

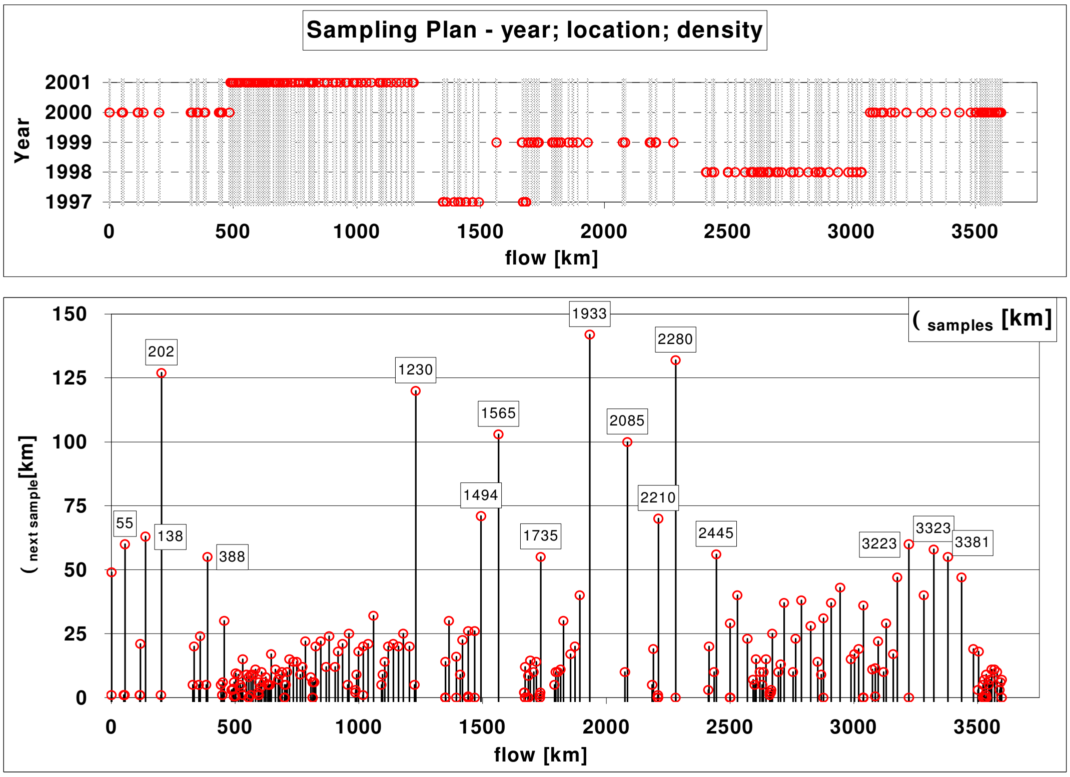


Figure 23 **Sampling Plan – year; location; density and location of samples with distances > 50 km between consecutive sampling points.**

2.2 Sampling, preparation, measured parameters and methods

The sediments were sampled with a ‘van Veen’-type grab, which penetrates and collects the uppermost 15-20 cm of a sediment body. By wet sieving, the < 0.02 mm (< 20 µm) grain-size fraction was removed – the reason to use this fraction is discussed elsewhere (Müller et al., 2001)) – and dried at < 40°C, to avoid the loss of volatile metal-species. Sub-samples of this fraction were digested by aqua regia (DIN EN 13346).

This ‘digestion’, which is merely an extraction, is not a ‘rational method’ (resulting in the total concentration of the analyte in the sediment), but instead an ‘empirical method’ (resulting in concentration of the analyte that can be measured in the sediment by the specific procedure applied). The extraction with ‘aqua regia’ is widely used throughout Europe and its results can be interpreted as ‘maximum potential of endangerment’ – i.e. maximum amount of an element which can be released by natural processes in a reasonable timeframe –, but it is not fully comparable with e.g. the North-American EPA-standards (EPA 3050(B)).

Table 11 Used materials and methods – shaded cells indicate the method used to report the results

used material	Parameters [mg/kg] (unless otherwise noted)	ICP-OES (wavelength)	FI-AAS	GF-AAS	other method	comment
aqua regia digested subsample of the fraction < 20µm	**Ag**	328.068		X		ICP more reliable
	Al [%]	396.152				
	As	193.696			FIAS	ICP more reliable
	B	249.678				
	Ba	455.403				
	Ca [%]	315.887				
	Cd	228.802	X	X		sensitivity of ICP comparable to GF-AAS, but much more stable and reliable
	Co	228.615	X			
	Cr	267.716	X			
	Cu	324.754	X			
	Fe [%]	258.588	X			ICP too sensitive
	K [%]	769.897				
	Li	670.783	X			
	Mg [%]	383.829				
	Mn [%]	257.610	X			
	Mo	204.598				
	Na [%]	588.995				
	Ni	231.604	X			
	P [%]	213.618			photometric $^{b)}$	results fully comparable, but ICP much more convenient
	Pb	220.353	X			
	Sc	361.383				
	Sr	407.771				
	V	292.401				
	Y	371.029				
	Zn	206.200	X			
dried subsample of the fraction < 20µm	Hg	194.164			AMA 254 $^{a)}$	AMA 254 and CV-AAS
	C_{total} [%]				▨	thermal combustion and IR-measurement of the resulting CO_2
	S_{total} [%]				▨	thermal combustion and IR-measurement of the resulting SO_2
	CO_3 [%]				"Karbonatbombe"	Müller et al. 1971
	moisture content$^{105°C}$ [%]				DIN EN 12880	difference in weight after drying at 105°
	loss on ignition$^{550°C}$ [%]				DIN EN 12879	difference in weight after combustion of dried sample at 550°

2.3 Quality assurance/quality management

At first sight, the QA/QM used, is a little bit confusing. This is owed to the use of two different methods (AAS and ICP-OES) for the determination of the metals and metalloids. In the beginning of this work, only AAS-techniques (Fl-AAS, GF-AAS, and CV-AAS) were available in our institute. From long-time in-house-studies the precision of the (than) used methods and measurements was known to be approx. ± 10% (depending somewhat on the analyt of interest and its concentration in the sediment). The QA/QM-procedures were fixed at first for the AAS-techniques, while the ICP-OES-measurements were used in case of better performance, without putting up new procedures.

Most samples (> 80%) were digested twice, including one blank and one **laboratory reference material** (LRM) for each series of digestion (10 samples). Therefore, any deviations of the measurements for any analyt in the duplicates, and/or the measurement of the LRM significantly greater than 10% lead to the repetition of the measurement. In case the deviation remained, the digestion was repeated until the deviation was ≤ 10%.

When ICP-OES became available in our institute, it could be shown that the precision (expressed as **relative percentage deviation** (RPD) of duplicates) improved (sometimes drastically) for most elements – while achieving at least the same accuracy (relative to LRM's) – with the exception of Hg and Fe. Mercury because of the low sensitivity compared to CV-AAS, and iron because of its high concentrations in the samples, which would have required the calibration to be outside the linear-range or a dilution of the samples. The already digested samples were re-measured with ICP-OES and the 'precision' was calculated by averaging the RPD of all duplicates – with 270 samples (resulting in up to 221 duplicates) at least a close approach to a 'precision' derived from a regular validation.

During a short 'validation'-period – consisting of 30 duplicates of three different LRM's – spike-recovery between 80% and 120% could be assured for all elements except Hg, where no such study was conducted and B, where recovery was biased (between 110% and 180%)[53].

Two spiked samples were measured with every batch (approx. 50 samples including reagent-blank and LRM). Since spike-recovery was 100% (± 20%) throughout the batches, no further action was necessary. No significant contamination of the reagent-blank was observed throughout the series – except for B.

---

[53] This is one of the reasons for **NOT** using the B-measurements for an in-depth interpretation. The most important reason is of course the use of glassware for digestion and the preparation of calibration-solutions, making both unreliable.

According to IUPAC (1999), "*Quantitative analytical results should be corrected for recovery unless there are specific reasons for not doing so*."

However, following their argumentation **against** correction[54] – and keeping in mind, that the recovery-information from spiked LRM's is based on only three matrices and showed no bias (except for boron) for which reason a calculated correction factor would be close to '1' – no action was taken to correct the results.

---

[54] Most problems and uncertainties of the measurement of digested sediment-samples are matrix-related (e.g. signal-enhancement or suppression due to matrix-effects). In case one cannot assure the matrix of the sample and the reference to be 'identical' (matrix-mismatch) the correction factors may vary between the two matrices.

2.4 'Uncertainty'

2.4.1 Analytical Measurement

"*Analytical measurements generally strive to estimate the measurand, that is, the true value of the concentration of the analyte, with an uncertainty that is fit for purpose. It is only on that basis that results can be completely comparable.*"

"*Uncertainty of measurement does not imply doubt about the validity of a measurement; on the contrary, knowledge of the uncertainty implies increased confidence in the validity of a measurement result.*" (EURACHEM/CITAC, 2000)

Glancing at the literature, most articles in the field of environmental-geochemistry are mentioning the precision of the measurement – if any – which is far away from stating the true 'error' of the data or the 'uncertainty' of it, to be more precise.

Although the concept of measurement uncertainty has been recognized in the field of natural science – especially in physics – virtually since the days of the first measurements, it was the publication of the *Guide to the Expression of Uncertainty in Measurement* (usually referred to as GUM) in 1993 (GUM, 1993) which formally established general rules for their evaluation and expression. The approach used here, is based on the EURACHEM/CITAC (2000) guide that demonstrates how the concepts of the GUM may be applied to chemical measurements – as well as on worked out examples in this guide and the forum on their web site (http://www.measurementuncertainty.org).

(a) **Definition of Uncertainty**

"*A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand",* with the note that *"The parameter may be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.*" (VIM, 1993)

(b) **Stating uncertainty**

'Uncertainty' is not to be mixed up with the 'error' of the measurement – that is the difference between the result and the 'true value' – which would be a single value, and cannot be known. 'Uncertainty' takes the form of a range and according to the GUM (1993) should be reported as an 'expanded uncertainty' (U), which is obtained by multiplying the calculated 'standard uncertainty' (u) by a 'coverage factor' (k).

The reported result is a confidence interval, in which the 'true value' is believed to lie in with a certain level of confidence (usually that of 95%):

$$\bar{x} \pm U \equiv \bar{x} \pm k \times u$$

$$- - -$$

$$\begin{aligned} \bar{x} &= \text{arithmetic mean of the measurements} \\ U &= \text{expanded uncertainty} \\ k &= \text{coverage factor} \\ u &= \text{standard uncertainty} \end{aligned}$$

Equation 1 Confidence interval (of a measurement)

(c) Calculating measurement uncertainty

Every single source of ‘uncertainty’ of the measurement-process has to be taken into account – precision is only one of them. The (main) sources of ‘uncertainty’ in the case of measuring digested sediment-samples by the means of ICP or AAS are:

- ***Uncertainty of the calibration-standards (not the calibration itself!)***

That is, how ‘uncertain’ is the internal reference-system.

- ***Uncertainty of digestion and sample-measurement (an already combined uncertainty)***

That is, how ‘uncertain’ is the measurement relative to the internal reference system .

- ***Uncertainty of the QC-measurement***

That is, how ‘uncertain’ is the measurement relative to an external reference-system.

- ***Uncertainty of the LRM/SRM itself***

That is, how ‘uncertain’ is the external reference-system.

The analytical result of an AAS or ICP-measurement of a digested sediment sample can be expressed as:

$$c_{sample} = \left(\frac{\left(R_{sample} - R_{blank}\right)}{R_{calib}} \right) \times \frac{V_{digest}}{m_{sample}} \times c_{calib} \times f_{RM}$$

– – –

c_{sample} = Calculated concentration of the sample

R_{sample} = Response of the digest solution of the sample

R_{calib} = Response of calibration - solution

R_{blank} = Response of a blank sample

V_{digest} = Volume of digest solution of the sample

m_{sample} = Mass of the sample

c_{calib} = Concentration of the calibration solution

– – –

$$f_{RM} = \text{Correction factor of the QC - measurement} \equiv \frac{1}{\text{Recovery}}$$

$$f_{RM} = \frac{c_{conv}}{c_{QCt}}$$

c_{conv} = (Certified) content of the (certified) reference material (conventional true value)

c_{QC} = Determined content of the (certified) reference material (QC - measurement)

Equation 2 Model equation for the quantitation of a measurand by AAS or ICP-OES

This model equation assumes the direct comparison of the response of the sample and the calibrant, which corresponds to a ‘one-point-calibration’. In the case of a linear calibration with zero intercept the resulting uncertainty contribution is comparable to that using the regression data of the actual calibration, but much easier to calculate (Kurfürst et al., 1996).

The model equation can be further simplified, when combining all the terms attributable to the sample-measurement[55]:

$$c_{sample} = RR_{sample} \times c_{calib} \times f_{RM}$$

$$---$$

$$\begin{aligned} RR_{sample} &= \text{Relative response of the digest solution of the sample} \\ c_{calib} &= \text{Concentration of the calibration solution} \end{aligned}$$

$$---$$

$$f_{RM} = \text{Correction factor of the QC - measurement} \equiv \frac{1}{\text{Recovery}}$$

Equation 3 Simplified model equation for quantitation of a measurand by AAS or ICP-OES

Based on this equation one can account for all the above mentioned uncertainty contributions for the measurement of digested sediment-samples:

$$\frac{\Delta RR_{sample}}{RR_{sample}} = \text{Uncertainty of digestion and sample measurement}$$

$$\frac{\Delta c_{calib}}{c_{calib}} = \text{Uncertainty of the calibration standard(s)}$$

$$\frac{\Delta f_{RM}}{f_{RM}} = \text{Uncertainty of the QC - measurement AND the LRM/SRM itself (combined uncertainty)}$$

---

[55] This simplification is only justifiable when, like in this study, the experimental standard deviation of multiple measurements is used to estimate the standard uncertainty of the relative response of the samples – since, it will include the uncertainty contributions of the combined terms (u(R_{calib}), u(V_{diges},) and u(m_{sample})).

2.4.1.1 Catastrophe and how to soundly avoid it

In order to achieve realistic estimates for the uncertainty-budget, the approach of 'pooling' the sample-RPD's and the QC-measurement-RPD's respectively is used (Kurfürst 1998). The underlying idea of this approach is that the strict calculation of the uncertainty-budget of a (single) measurement would lead to (formal) catastrophe in routine analysis – although the method itself might have been proven acceptable ('*fit-for-purpose*') during validation.

Equation **1** – used to calculate the expanded uncertainty – is of course nothing but another way to express the confidence interval of the Student's t-distribution (i.e. a normal distribution with n < ∞):

$$\bar{x} \pm (t_{df,\alpha/2} \times \frac{\sigma}{\sqrt{n}})$$

$$---$$

$$\bar{x} = \text{Arithmetic mean}$$

$$t_{df,\alpha/2} = \text{Student's t - factor (function of degrees of freedom and probability of error)}$$

$$\sigma = \text{Standard deviation}$$

$$n = \text{Number of observations}$$

Equation 4 Confidence interval for Student's t-distribution

The two variables we can influence to some extent are the number of observations (measurements) and the standard deviation (precision). Using a level of confidence of 95% (and the appropriate t-value) for different numbers of duplicates and an assumed standard deviation of the measurements (between multiple digestions!) of 5% – a realistic value for the ICP-OES for most elements – leads to confidence intervals [%] shown in Table 12.

Table 12 Confidence interval [%] for different number of duplicates

Precision (σ)	5%		
Samples (n)	1	**2**	3
$\frac{t_{df,\alpha}}{\sqrt{n}}$ (95%)	8	**9**	2.5
Confidence interval	8	**45%**	12%

Since more than two digestions of a sample are rarely measured in routine analyses, there would be an expanded uncertainty of at least 45%, just for the combination of digestion and sample measurement – assuming a 95% level of confidence and an approved precision of 5%. Things get even worse when using a (certified) reference material for quality control, because this will introduce two additional uncertainty contributions; the uncertainty of the (certified) reference material, and the uncertainty measuring it. Since nobody is interested in ‘our’ precision, but instead in ‘our’ performance according to the ‘real world’ (i.e. a ‘conventional true value’) these contributions are unavoidable – although generally not considered.

While the uncertainty contribution of the (certified) reference material is known – the producer states its expanded uncertainty, and the coverage factor can most of the times considered being near two – the QC-measurement is as uncertain as that of the samples.

At best, the uncertainty of the measurement, the QC-measurement, and the reference material – representing the ‘state-of-the-art’ – are in the same range. Combining these uncertainties would result in confidence intervals beyond any acceptable range. While being mathematically correct, these intervals are inconsistent with everyday lab-experience, where one can expect a measurement to be close to the performance achieved during validation and/or long-time experience.

The crucial point of all measurements in routine analyses is the lacking degrees of freedom (replicates), and the resulting large t-value.

The performance of the analytical process cannot be proven for the single measurement, but this also holds true for a single validation-measurement. Nevertheless, the validation-experiments are used to calculate the method-uncertainty. Turning back this argumentation, one can use the approved performance of the validation AND than achieved degrees of freedom (replicates) to calculate the uncertainty of a measurement – resulting in the coverage factor to be near two.

In fact, this is frequently done tacitly, when an expanded uncertainty is stated – irrespective of the number of duplicates – although the GUM (1993) and EURACHEM/CITAC (2000) propose to use the value obtained from the t-statistics[56].

---

[56] Nevertheless, even in the Eurachem/Citac (2000) -guide one can find examples, where a coverage factor of two is used, without calculating the effective degrees of freedom (e.g. Example A1 in the guide).

Used on Equation 3 the combined uncertainty (*u*) can be estimated according to the rule of the addition of variances:

$$c_{sample} = RR_{sample} \times c_{calib} \times f_{RM} = RR_{sample} \times c_{calib} \times \frac{c_{conv}}{c_{QC}}$$

$$---$$

combined uncertainty:

$$u_c = \sqrt{\left(\left(\frac{s_1^2}{n_1}\right) + s_2^2 + s_3^2 + \ldots + s_n^2\right)}$$

$s_1 =$ Standard deviation of the arithmetic mean of independent measurements, with

$n_1 =$ Number of independent measurements

$s_2 - s_n =$ Calculated or estimated Standard deviations

$$---$$

here:

$$u_{sample} = \sqrt{\left(\left(\frac{s_{RR_{sample}}^2}{n_{sample}}\right) + \left(s_{c_{calib}}^2\right) + \left(s_{c_{conv}}^2\right) + \left(\frac{s_{c_{QC}}^2}{n_{QC}}\right)\right)}$$

expanded uncertainty:

$$U_{sample} = k \times u_{sample} = 2 \times u_{sample}$$

Box 1 Estimation of the (expanded) measurement-uncertainty

However, this may be too optimistic. The replicates of the samples and QC-measurements were already considered during the ‘pooling’, in order to justify the use of a coverage factor of two.

Measuring duplicates of (QC-) samples during routine-analysis would though be merely to prove the validity of the assumed standard deviation, rather than stating it[57].

---

[57] Hence many QA/QM-plans rely on just measuring ‘some’ duplicates (and QC and/or spiked samples) for a given number of samples to prove validity, instead of trying to assure it for every single measurement. First of all, because it cannot be assured by duplicates of one sample (see above discussion).

Following Example A4 of the EUROCHEM/CITAC-guide, which also does not consider the replicates, leads to the formulas for the calculation of the (expanded) uncertainty shown in Box 2.

$$c_{sample} = RR_{sample} \times c_{calib} \times f_{RM} = RR_{sample} \times c_{calib} \times \frac{c_{conv}}{c_{QC}}$$

– – –

standard uncertainty :

$$u_{sample} = \sqrt{s^2_{RR_{sample}} + s^2_{c_{calib}} + s^2_{c_{conv}} + s^2_{c_{QC}}}$$

expanded uncertainty :

$$U_{sample} = k \times u_{sample} = 2 \times u_{sample}$$

Box 2 Calculation of the (expanded) uncertainty

Although there is some controversy whether the raw result of a sample should be corrected according to an experimental recovery (f_{RM}, which is actually the inverse of the recovery) it is clear, that its uncertainty contributes to the overall uncertainty of the measurement process (i.e. f_{RM} is considered, or 'proven' to be 1±k*u). Otherwise, no relation of the measurement to a 'conventional-true-value' (i.e. the 'real' content of the sample) can be established. Moreover, the use of an 'uncertain' RM would be advantageous because the range for acceptance would be wider[58].

---

[58] According to the GUM (1993) the measurement of a RM is acceptable (i.e. unbiased by definition), when:

$$\left| c_{conv} - c_{QC} \right| \leq 2 s_{sample}$$

– – –

$$s_{sample} = \sqrt{s^2_{bl} + \frac{s^2_{RR_{sample}}}{n_{RR_{sample}}}}$$

s_{sample} = Standard deviation in the measurement process

s_{bl} = Standard deviation between laboratories - stated by the producer

$s_{RR_{sample}}$ = Standard deviation within the laboratory - estimate for the own measurement

This was 'proven' to be valid for the used RM's during 'validation' and the QC-samples in the measurement process of the actual samples and no correction was applied. Still, this is no strict proof, and in fact, it is virtually impossible. The matrix composition of sediment SRM's and the samples can only be similar, not totally identical, so the interferences due to matrix concomitants can be different – leading to the unsolved questions of whether any non-primary chemical analysis can be traceable at all and the resulting implications... (cf. Pauwels and Squirrel, 2000)

2.4.1.2 Measurement-uncertainty-budget for this study

The calculation of the uncertainty of the ICP-OES measurements, as well as that of Hg (CV-AAS), and the C_{total} and S_{total}-measurements (IR-photometric), were conducted according to Box 2 and are depicted in Figure 25.

- Depicted in Figure 24 are the RPD’s of the duplicates measured, which were used to estimate the precision ($\mathbf{u}(\boldsymbol{RR}_{sample})$).
- The standard uncertainty of the calibration-solutions was taken from the literature (e.g. O’Donnell, 2000) to be approx. 1% (mainly from temperature and volumetric effects) ($\mathbf{u}(\boldsymbol{c}_{calib})$).
- The standard uncertainty for the QC-measurements is the same as for the samples ($\mathbf{u}(\boldsymbol{c}_{QC})$).
- The standard uncertainties for RM’s can be taken from Figure 25 ($\mathbf{u}(\boldsymbol{c}_{conv})$).

RPD [%]	*Ag*	*Al*	*As*	*B*	*Ba*	*Ca*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	***Hg***	*K*	*Li*	*Mg*	*Mn*	*Mo*	*Na*	*Ni*	*P*	*Pb*	*Sc*	*Sr*	*V*	*Y*	*Zn*	***C***	***S***
Mean	9	4	6	14	2	2	5	2	2	2	2	2	5	3	2	1	5	5	2	2	2	3	3	3	2	3	3	9
Median	5	3	4	11	1	1	2	1	2	1	1	1	4	2	2	1	3	4	1	1	1	2	2	2	1	1	2	9
Standard Deviation	11.6	3.8	5.9	12.4	2.6	2.3	10.1	2.2	3.0	3.6	2.8	0.9	4.4	3.0	2.5	2.2	7.9	5.1	4.8	2.4	2.6	2.8	2.8	2.9	2.1	3.0	3.5	7.5
Count	221	221	221	221	221	221	221	221	221	221	221	**25**	221	221	221	221	221	221	221	221	221	221	221	221	221	221	**50**	**50**
Confidence Level(95.0%)	1.5	0.5	0.8	1.6	0.4	0.3	1.3	0.3	0.4	0.5	0.4	0.4	0.6	0.4	0.3	0.3	1.0	0.7	0.6	0.3	0.3	0.4	0.4	0.4	0.3	0.4	0.5	1.1

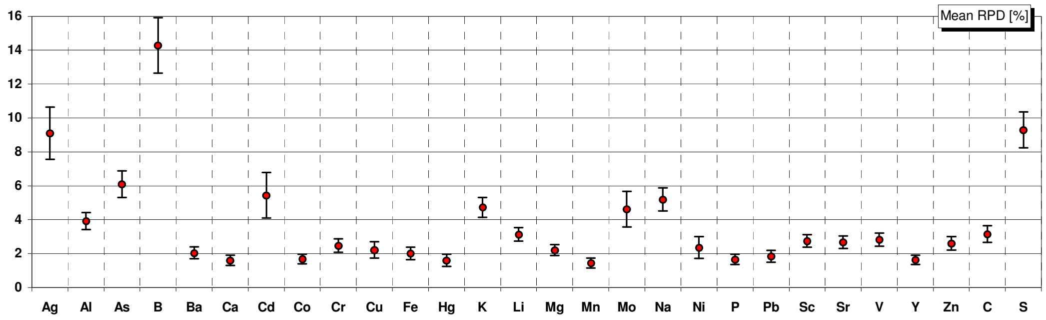


Figure 24 **Mean RPD for the measurements (error bars indicate 95% confidence interval)**

Figure 25 Calculated (expanded) uncertainty [%] - valid for measurements > limit of quantitation (LOQ)

		Ag	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg a)	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sc	Sr	V	Y	Zn	C b)	S c)
I)	Uncertainty of the Calibration [%]	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	***1.5***	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	***0***	**1**
II)	Mean RPD Sample [%]	**9**	**4**	**6**	**14**	**2**	**2**	**5**	**2**	**2**	**2**	**2**	***1.6***	**5**	**3**	**2**	**1**	**5**	**5**	**2**	**2**	**2**	**3**	**3**	**3**	**2**	**2**	**3**	**9**
III)	Uncertainty QC-Measurement [%]	**9**	**4**	**6**	**14**	**2**	**2**	**5**	**2**	**2**	**2**	**2**	**2**	**5**	**3**	**2**	**1**	**5**	**5**	**2**	**2**	**2**	**3**	**3**	**3**	**2**	**2**	**3**	**9**
IV)	Mean uncertainty (V_R [%]) of the used RM	n.d.	51	17	n.d.	n.d.	11	19	n.d.	16	8	8	18	n.d.	n.d.	13	7	n.d.	n.d.	15	7	11	n.d.	n.d.	n.d.	n.d.	8	n.d.	31
IV')	Mean Uncertainty CRM (extractable) [%] e)	11	6	6	-	5	2	4	3	5	2	3	d) 10	6	8	3	2	7	8	3	2	3	-	2	5	-	2	n.d.	n.d.
	Max. Uncertainty CRM (extractable) [%]	13	10	15	-	16	3	9	10	27	13	4	40	10	9	4	3	7	9	14	2.5	12	-	3	8.5	-	11.5	n.d.	n.d.
IV")	Mean Uncertainty CRM ('total') [%] e)	12	6	8	11	6	3	11	8	6	5	3	10	4	6	3	4	13	4	7	10	7	9	7	7	12	5	2	10
	Max. Uncertainty CRM ('total') [%]	32	32	25	35	27	17	39	39	30	27	12	40	11	32	8	12	44	19	49	76	25	17	39	26	21	16	4	42

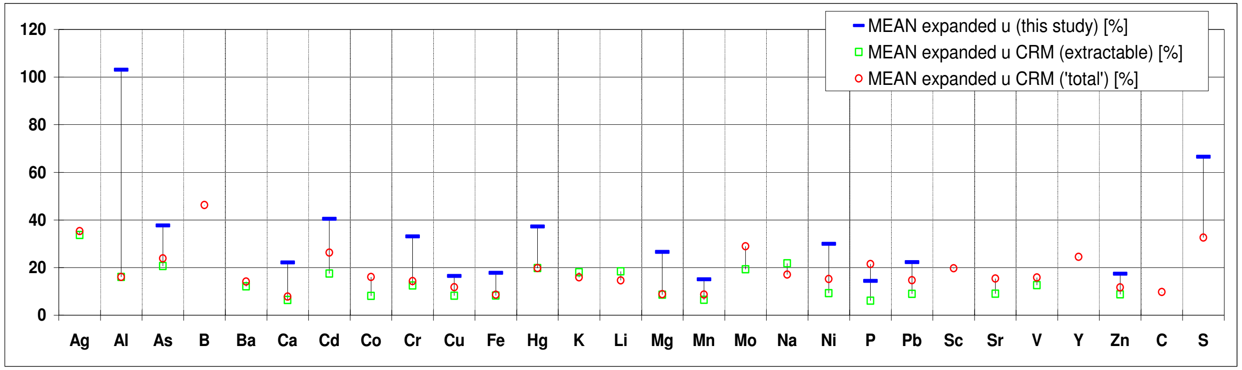
const.

calculation of the expanded measurement-uncertainty using the uncertainty of the RM (**IV**) as variable

$$u = \sqrt{(I)^2 + (II)^2 + (III)^2 + (\overset{IV}{\quad})^2}$$

$$\text{expanded uncertainty} = U = k * u$$

		Ag	Al	As	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sc	Sr	V	Y	Zn	C	S
	MEAN u (this study) [%]		52	19			11	20		17	8	9	19			13	8			15	7	11					9		33
(k=2)	**MEAN expanded u (this study) [%]**		**103**	**38**			**22**	**40**		**33**	**16**	**18**	**37**			**27**	**15**			**30**	**14**	**22**					**17**		**67**
	MEAN u CRM (extractable) [%] e)	17	8	10		6	3	9	4	6	4	4	10	9	9	4	3	10	11	5	3	4		5	6		4		
(k=2)	**MEAN expanded u CRM (extractable) [%]**	**34**	**16**	**21**		**12**	**6**	**17**	**8**	**12**	**8**	**8**	**20**	**18**	**18**	**9**	**6**	**19**	**22**	**9**	**6**	**9**		**9**	**13**		**9**		
	MEAN u CRM ('total') [%] e)	18	8	12	23	7	4	13	8	7	6	4	10	8	7	4	4	14	9	8	11	7	10	8	8	12	6	5	16
(k=2)	**MEAN expanded u CRM ('total') [%]**	**35**	**16**	**24**	**46**	**14**	**8**	**26**	**16**	**14**	**12**	**9**	**20**	**16**	**15**	**9**	**9**	**29**	**17**	**15**	**22**	**15**	**20**	**15**	**16**	**24**	**12**	**10**	**33**



Rem.:

a) The calibration was conducted with CRM NIST-SRM 2711 (Montana soil) with an stated **expanded** uncertainty of 3%

b) The calibration was conducted with $CaCO_3$ from LECO$^{®}$ without stated uncertainty (but presumably with a purity >99.9x%)
assuming a triangular or quadratic distribution would result in a standard uncertainty below 0.06%

c) The calibration was conducted with LECO$^{®}$ "Calibration Sample Sulfur in Coal" part.-No. 501-005 ... 1% ± 0.02% (no further information about the (kind of) uncertainty was available)
assuming a quadratic distribution (worst case) result in a standard uncertainty of 1.15%

d) The CRM LGC-6187 in the IAEA-database with an stated expanded uncertainty of 321% was excluded for the calculation of the mean uncertainty

e) 'CRM' refers (only) to CRM's listed in the IAEA-database (with their stated uncertainty)

n.d. = no data, i.e. not measured
- = without stated uncertainty

The grey shaded lines in Figure 25 indicate the standard uncertainty of the measurement, while in the blue shaded lines the stated uncertainty of the used RM and the calculated expanded uncertainty of the reported results are given. In the green and red shaded lines the mean uncertainties for CRM's (extractable, and 'total content'), as derived from the '*IAEA Database of Natural Matrix Reference Materials*' (IAEA, 2003), are given, as well as the (expanded) uncertainty that would have been achievable using an average CRM.

The same calculation has been conducted for measurements below the **limit of quantitation** (LOQ) (but above the **limit of detection** (LOD)):

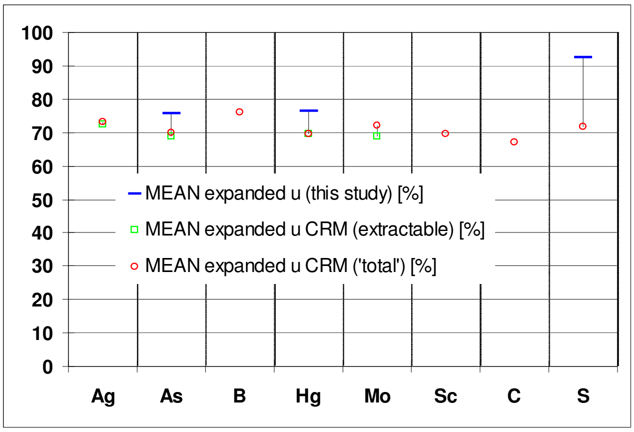
		Ag	**As**	**B**	**Hg** a)	**Mo**	**Sc**	**C** b)	**S** c)
I)	Uncertainty of the Calibration [%]	**2**	**2**	**2**	***1.5***	**2**	**2**	***0***	**1**
II)	**Standard deviation [%]**	**33.3**	**33.3**	**33.3**	**33.3**	**33.3**	**33.3**	**33.3**	**33.3**
III)	Uncertainty QC-Measurement [%]	**9**	**6**	**14**	**2**	**5**	**3**	**3**	**9**
IV)	Mean uncertainty (V_R [%]) of the used RM	n.d.	17	n.d.	18	n.d.	n.d.	n.d.	31
IV')	Mean Uncertainty CRM (extractable) [%] e)	11	6	-	10 d)	7	-	n.d.	n.d.
	Max. Uncertainty CRM (extractable) [%]	13	15	-	40	7	-	n.d.	n.d.
IV")	Mean Uncertainty CRM ('total') [%] e)	12	8	11	10	13	9	2	10
	Max. Uncertainty CRM ('total') [%]	32	25	35	40	44	17	4	42
	MEAN u (this study) [%]		38		38				46
(k=2)	**MEAN expanded u (this study) [%]**		**76**		**76**				**92**
	MEAN u CRM (extractable) [%] e)	36	34		35	34			
(k=2)	**MEAN expanded u CRM (extractable) [%]**	**73**	**69**		**69**	**69**			
	MEAN u CRM ('total') [%] e)	37	35	38	35	36	35	34	36
(k=2)	**MEAN expanded u CRM ('total') [%]**	**73**	**70**	**76**	**69**	**72**	**69**	**67**	**72**

$$u=\sqrt{(I)^2+(II)^2+(III)^2+(\overset{IV}{\quad})^2}$$

$$\text{expanded uncertainty}=U=k*u$$

const.

calculation of the expanded measurement-uncertainty using the uncertainty of the RM (IV) as variable



Rem.:

a) The calibration was conducted with CRM NIST-SRM 2711 (Montana soil) with an stated expanded uncertainty of 3%
b) The calibration was conducted with $CaCO_3$ from LECO® without stated uncertainty (but presumably with a purity >99.9x%)
c) The calibration was conducted with LECO® "Calibration Sample Sulfur in Coal" part.-No. 501-005 ... 1% ± 0.02% (no further information about the (kind of) uncertainty was available)
d) The CRM LGC-6187 in the IAEA-database with an stated expanded uncertainty of 321% was excluded for the calculation of the mean uncertainty
e) 'CRM' refers (only) to CRM's listed in the IAEA-database (with their stated uncertainty)

Figure 26 Calculated (expanded) uncertainty [%] – valid for LOD < measurement < LOQ.

The LOD and LOQ were calculated from the calibrations according to DIN 32645 with the program **dintest** (2003) as the mean of all calibrations, with a probability of error (α) of 5% and a result uncertainty for the LOQ of 33.3%. This was done in order to get a realistic estimate for these limits, instead of reporting results obtained during the 'validation', which were naturally lower in most cases (cf. Burrows, 1997).

The expanded uncertainty for the **loss on ignition** and the **moisture content** were calculated using the propagation of error on the weighing of differences to be approx 10% (not considering any uncertainties of the method).

The uncertainty of the **carbonate**-measurements was estimated to be approx. 2% absolute (not relative like the rest) due to limitations in the readability of the scale of the 'Karbonatbombe'.

In conjunction with the 'validation'-results, there are at least two problematic elements: Al and B. Aluminum because of its high level of expanded uncertainty in the results (owed to the high uncertainty of the used RM) and Boron because of its biased results (owed to the use of standard lab-glassware for critical operations like the digestion-procedure).

Although one can presume the performance of the measurements to be slightly better, because of data derived from the 'validation' (i.e. spike-recovery), this can be neither assured, nor proven. The spike-recovery was calculated based on three RM's (matrices) only, and the experiment was conducted as a 'surrogate recovery'[59], for which reason the digestion was not considered.

Hence, in case there is no stated value/uncertainty for the used RM, the (expanded) uncertainty, which would have been derived using a CRM, is assumed, and considered the lower bound of the reported (expanded) uncertainty. This seems more reliable and justifiable, than using 'better' results from an (incomplete) validation-process.

Apart from that procedure, the results for Boron are not considered, because they are uncontrollable biased (see above).

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[59] This definition is used by IUPAC (1999): "*Recovery of a pure compound or element specifically added to the test portion or test material as a spike. (Sometimes called 'marginal recovery'.)*"

The resulting analytical limits as well, as the affected results and their uncertainties are depicted in Table 13. The color code of the expanded uncertainty refers to their calculation, as described above (Figure 25).

Table 13 LOD, LOQ and respective expanded uncertainty – including number of affected measurements

		N	**LOD**	**LOQ**	No. of flaged		expanded uncertainty [%]	
					<LOD	LOD<x<LOQ	x>LOQ	LOD<x<LOQ
[mg/kg]	**Ag**	266	0.06	0.27	**1**	**125**	🟥 35	🟥 73
[%]	**Al**	266			-	-	🟦 103	
[mg/kg]	**As**	269	0.8	3.4	0	6	🟦 38	🟦 76
[mg/kg]	**B**	264	9	39	**8**	**242**	🟥 46	🟥 76
[mg/kg]	**Ba**	266			-	-	🟥 15	
[%]	**Ca**	266			-	-	🟦 22	
[mg/kg]	**Cd**	269	0.03	0.13	0	0	🟦 41	
[mg/kg]	**Co**	266	0.3	1.4	0	0	🟥 16	
[mg/kg]	**Cr**	270	0.2	1.3	0	0	🟦 33	
[mg/kg]	**Cu**	270	0.2	1.0	0	0	🟦 17	
[%]	**Fe**	270			-	-	🟦 18	
[mg/kg]	**Hg**	270	0.03	0.10	**4**	**91**	🟦 37	🟦 76
[mg/kg]	**K**	266			-	-	🟩 18	
[mg/kg]	**Li**	268	0.4	2.3	0	0	🟩 19	
[%]	**Mg**	266			-	-	🟦 27	
[%]	**Mn**	270			-	-	🟦 15	
[mg/kg]	**Mo**	266	0.2	1.0	0	1	🟥 29	🟥 72
[%]	**Na**	266	0.003	0.015	0	0	🟩 22	
[mg/kg]	**Ni**	267	0.2	1.0	0	0	🟦 30	
[%]	**P**	270	0.005	0.021	0	0	🟦 15	
[mg/kg]	**Pb**	270	0.4	1.6	0	0	🟦 23	
[mg/kg]	**Sc**	266	0.3	1.3	0	1	🟥 20	🟥 69
[mg/kg]	**Sr**	266	0.3	2.0	0	0	🟥 16	
[mg/kg]	**V**	266	0.5	2.8	0	0	🟥 16	
[mg/kg]	**Y**	266	0.2	1.0	0	0	🟥 25	
[mg/kg]	**Zn**	270			-	-	🟦 18	
[%]	C_{total}	263	0.36	1.29	0	6	🟥 10	🟥 67
[%]	S_{total}	263	0.10	0.36	**63**	**182**	🟦 67	🟦 92
[%]	CO_3	174		5.0	-	**148**	**2% absolute!**	
[%]	$LOI^{550°}$	260		1.0	-	-	10	

The amount of uncertainty may appear to be quite high for most parameters. In fact, this uncertainty is widely accepted – but rarely taken into account or even stated – and even more sophisticated studies are dealing with at least the same amount of uncertainty (e.g. the “*Great Lakes Assessment and Remediation of Contaminated Sediment (ARCS) Program*”. Talking about metals in sediments their measurement quality objectives (MQO) accepted a precision (derived from analytical duplicates!) of ≤ 20% and an accuracy (determined from CRM’s) of 20%).

Using the above calculation would result in an “expanded uncertainty” of more than 50%!

Of course, there are ways to reduce this uncertainty: 'simply' measure more duplicates and/or measure more precise. The first is prohibited by the costs and the second by the matrix, we are measuring in. Talking about sediments, the matrix-problem can be seen in round-robins and even in the stated 'uncertainty' of CRM's: Sometimes 'we' – meaning everybody in the field of environmental geochemistry, because this problem is not exclusive to our laboratory or used methods – are able to measure quite 'precise'/'correct', sometimes 'we' aren't – depending on the matrix. Unless 'we' do not want to (or are not able to) spend huge amounts of money and time on analysis, we have to live with a certain amount of 'uncertainty' and consider it when dealing with the data.

Not only is the calculation of the uncertainty the only way to make results comparable as mentioned above, it is also the only way to make them interpretable. Talking about differences between single-values of say 20%, when there is an expanded uncertainty of about 30% would be obscene and a complete waste of time and paper.

2.5 Uncertainty revisited – Sampling; the real catastrophe

No matter what question a study addresses, the most important question is:
'How reliable are the answers?'

This cannot be answered by the reliability or reproducibility of the analytical process – i.e. the above calculated measurement uncertainty accounting for any bias that might influence the **analytical result of the sample**[60] – since the question aims at **the target of the study** – i.e. in this case the composition of the Volga sediments.

Unfortunately the sample is not the target – and '*field studies show that matrix heterogeneity severely limits the confidence with which analytical results can be justifiably extrapolated beyond the tiny sample analyzed*' (Crumbling, 2001).

Figure 27 shows the cause and effect diagram of the (main) uncertainty sources in the measurement process of sediment (soil) samples – leading to the combined uncertainty of a reported result (u_{tot}) for the target, and thus the reliability of the answers.

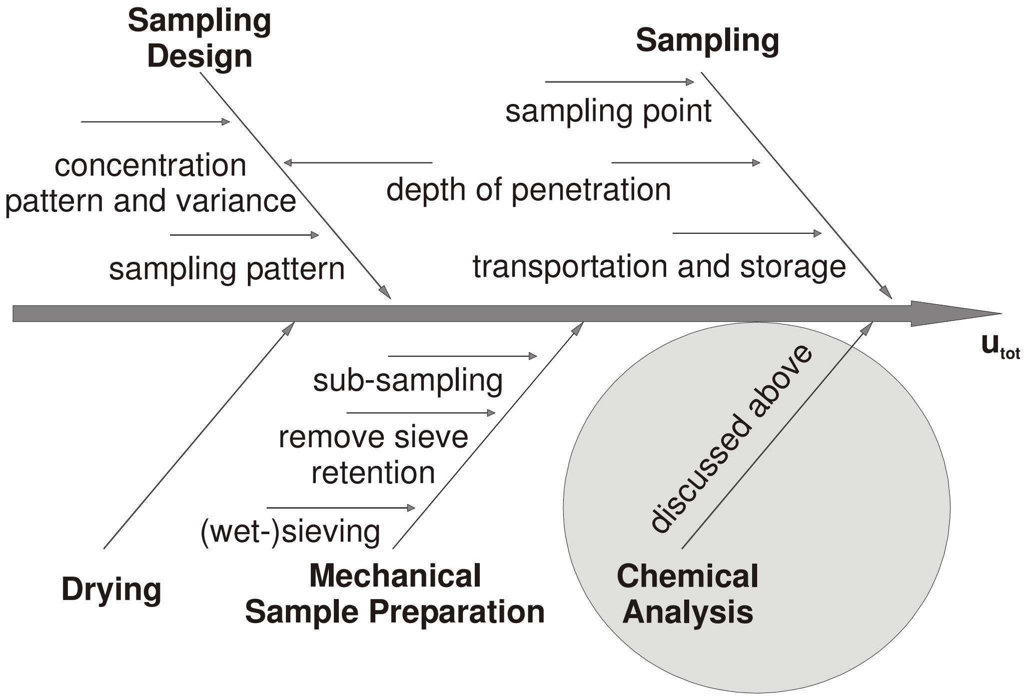

Figure 27 Cause and effect diagram showing (main) sources of uncertainty for the measurement-process of soil (sediment)-samples (after Kurfürst et al., 2004)

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[60] Here: a sub-sub-sample of the field-sample!

Target → field-sample → sub-sample for wet-sieving → sub-sample for digestion.

In other words, the (chemical) analysis of the sample is only the last – and often least – important step in a chain of uncertainties, which includes the sampling design, the sampling and the sample-preparation. Therefore, beside the basic, but not trivial question whether the target is suitable to address the question, two issues need to be considered – preferably before (chemical) analysis:

- **The field sample (primary sample) must be representative of the sampling target.**
- **The analytical sample (secondary sample) must be representative of the field-sample.**

If any of these steps fails to be 'fit for purpose' the results are suspect – and one can go as far, as to state: '*If the sampling uncertainty is not known it is questionable whether the sample should be analyzed at all*' (Minkkinen, 2003).

On the other hand '*there is an understandable lack of enthusiasm for rousing the sleeping dogs of sampling when there is a fair chance of being severely bitten*' (Thompson, 1999). As a result, very little information on the performance of sampling is available; since the validation of sampling – at least in environmental geo-chemistry – is far less developed than that of analytical methods and the underlying major reason for (sub-) sampling uncertainties – the heterogeneity of the target – is unknown a priori.

Neglecting the drying-process and the mechanical sample preparation – due to their low uncertainties[61] (taking for granted no (systematic) contamination to have occurred) and their partial consideration in the uncertainty-budget of the chemical analysis[62] – the first and most important steps in almost any (chemical) measurement will be addressed: the sampling (-design) and the sample reduction (sub-sampling).

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[61] This is a very optimistic assumption – to say the least. In fact they are only considered to be quite low compared to the other uncertainties – which is most probably correct for the drying-process and the sub-sampling of fine-grained sediments, while very little is known e.g. about the implications of wet-sieving.

Again, a pettifoggers approach would be to state that there are no uncertainties, but systematic errors (e.g. carbonates dissolved during wet-sieving, hence passing the sieve; agglomerations of (organic) particles, hence not passing; volatile species being lost during drying and so on) leading to biased results – which are accounted for, since the resulting sub-sample is empirically defined as 'the' sample, with no way to overcome and/or correct for these sample- and process-specific systematic errors. See also the discussion on sampling-'error'…

[62] E.g. variations/uncertainties in the sub-sampling of 'the' sample – i.e. the sub-sampled, wet-sieved and dried field-sample – influences the sample presented to the digestion/measurement procedure, and is accounted for when calculating the RSD (RPD) of duplicates.

2.5.1 Principal problem of addressing sampling-uncertainty

The traditional approach of sampling is to conduct the sampling according to a ‘correct’ – i.e. accepted – protocol and eliminate sampling bias by definition – i.e. the equivalent to regarding an analytical method as ‘empirical’. Unlike with ‘empirical’ analytical methods – like the here used digestion with aqua regia – who have ‘known’ limitations, which cannot be overcome[63] – e.g. several minerals/substances cannot be dissolved by aqua regia, no matter how often one will try – the uncertainties of sampling can be overcome: **Just sample everything!**

While this approach may not be too practical, it highlights the inanity of this concept – even if bias is eliminated by definition the uncertainty remains, and would have to be accounted for, just like in the case of the (chemical) measurement.

Although sampling-uncertainty is widely accepted – e.g. within the US-EPA TRIAD-Approach[64] (Crumbling, 2001)[65] – and approaches towards a rigorous validation of sampling procedures exist –

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[63] It is important to realize, that in the case of a chemical measurement this is not necessarily a weakness. In contrary: the (amount of) uncertainty of ‘empirical’ methods is usually lower than that of ‘rational’ methods (cf. e.g. Figure 25) since they are defined; with no need to be proven (i.e. being traceable), even though their bias (relative to the never known ‘real total’) may be higher – i.e. they redefine the analyte in terms of a method and without a framework the ‘total’ amount of a measurand is as meaningless as an ‘empirically’ defined one.

In fact, this was the idea when implementing ‘empirical’ methods: the objective of a chemical measurement is to determine the concentration of the measurands of interest, not the total composition of the sample. The total composition will always remain unknown, so the environment of the measurement is unknown and in contrast to e.g. physical measurements there’s no way to make the results fully traceable, while in case all laboratories used a single ‘correct’ (empirical) method, the results would be true and comparable – eliminating e.g. any uncertainty related to the underlying chemistry.

[64] The TRIAD Approach (Systematic Planning – Dynamic Work Plans – Real Time Analyses) largely relies on (cheaper) on-site analysis with their usually higher uncertainties when compared to lab-methods. The additional uncertainty of the measurements is outweighed by measuring more samples, and thus decreased sampling-uncertainty, sought to result in a scientifically sounder site-description than traditional approaches.

[65] This is not to say, that US-EPA recognized the problem first – it is just one of the wider known approaches to account for, and trying to overcome it. E.g. Rasemann and Herbst (2000) (in German) describe sampling-models for heterogeneous lots, pointing out that already Agricola in 1556 laid down guidelines on how to obtain a representative sample from geological material – unsurprisingly using the same principles as are used today.

As with measurement-errors, sampling-errors have been around since the first sampling and were recognized by many – while seldom taken into account in case no commercial interests made it necessary. Namely in mining (industries) – just to stay within about the same compartment – sampling-errors during prospection soon attracted attention, since it can lead to the loss of large amounts of money – while e.g. a less uncertain site characterization in environmental geochemistry became only necessary in recent years, when erroneous decisions based on improper site-characterization became obvious, violating the need for more (cost-) effective cleanup due to increasing financial restrictions in this field (Crumbling 2003). Nevertheless, still any amount of uncertainty can go by unnoticed in a study due to a lack of interest in it or the consequences of its results.

like the SOILSAMP-project[66] (de Zorzi et al., 2002) – no generally accepted guidelines to its expression exist to date; and are difficult (and costly) to establish:

The uncertainty of a (chemical) measurement can be estimated by summing up the contribution of a random component (i.e. analytical precision – expressed as RSD of duplicates) and a systematic component (i.e. analytical bias – e.g. expressed as recovery of a CRM).

However, the application of this concept to sampling bears some obstacles. Besides the (not 'just' philosophical) problem of being unable to sample the same target twice (unless it is completely homogenous and stable within time and space), i.e. stating sampling precision, usually no such thing as a 'Reference Sampling Target' (i.e. the equivalent of a CRM) exists – and thus the bias usually remains unknown/undefined. Even studies accounting for sampling errors, mostly using an 'in-between-sample'-variance as estimator for the sampling-uncertainty don't deal with sampling-bias, due to these difficulties (for a further discussion including possible ways to overcome this point by applying different sampling-protocols and/or 'Collaborative Trial in Sampling' (CTS) or 'Sampling Proficiency Tests' (SPT) see: Ramsey (2002)). However, already these studies usually show the primary sampling to be the largest source of uncertainty in measurement (for an overview see e.g. Ramsey (2002), Crumbling et al. (2003)).

On the other hand this should make procedures used in the 'real world' the best starting-point, and in fact the sampling of sediments to describe an aquatic system and its hinterland is an idea basically 'stolen' from mining and prospecting – as will be described later…

[66] This project, funded by the National Environmental Protection Agency (ANPA) of Italy is aimed at assessing sampling-uncertainties of soils in various environments, based on the traditional 'bottom-up' approach of adding all of the separate components of uncertainty together.

2.5.2 Gy's Theory of Sampling

Sampling errors are nothing new to a measurement-process and within the framework of Chemometrics a complete ***Theory of Sampling*** exists – namely starting with Pierre Gy's works in the 1950's. Originally developed for the mining-industries (i.e. search for, and exploration of mineral resources) it seems to be the only comprehensive sampling theory for particulate matter and implicitly addresses (almost) every aspect of sampling particulate environmental matrices[67].

He addresses seven types of sampling error and ways to overcome them (Gy 1998; Pitard 1993):

1. Fundamental Error (***FE***): resulting from compositional (constitutional) heterogeneity – e.g. a difference in concentration between the particles in the sample; namely particle size. The ***FE*** is the minimum sampling error achievable and the only error that can be calculated in advance.
2. Grouping and Segregation Error (***GE***): resulting from distributional heterogeneity – i.e. a nonrandom distribution of particles in the segregation; namely due to gravity.

(These two errors can be combined to the *short-range heterogeneity error* CE_1 *(= FE+GE)*)

3. Long-Range Heterogeneity Fluctuation Error (***CE_2***): resulting from spatial heterogeneity – e.g. a trend.
4. Periodic Heterogeneity Fluctuation Error (***CE_3***): resulting from temporal or spatial heterogeneity – i.e. (small-scale) fluctuations.

(Together with the short-range heterogeneity error these two errors can be combined to the *Continuous Selection Error CE* (= $CE_1+CE_2+CE_3$))

5. Increment Delimitation Error (***DE***): resulting from inappropriate sampling design or equipment – e.g. failure to sample all strata of the target.
6. Increment Extraction Error (***EE***): resulting from failures to precisely extract the intended increment – e.g. loss of strata during sampling due to inappropriate devices.

(These two errors can be combined to the *Materialization Error ME (= DE+EE)* and together with the *Continuous Selection Error* make up the *Sampling Selection Error SE (= CE+ME)*)

7. Preparation Error (***PE***): resulting from alterations of a sample; loss or contamination.

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[67] There may be limitations of this theory for volatile and semi-volatile measurands. One of the key-problems addressed by this theory is the grain-size distribution of a matrix; its implications towards sampling-errors and how to overcome them. This usually involves homogenization-steps like grinding, which may be inappropriate for these substances – but should be a minor problem with regard to heavy metals in sediments.

The outcome of the resulting *Total Sampling Error* (*TE* (= *PE*+*SE*)) together with the *Total Analytical Error* (*AE*) is the *Overall Estimation Error* (*OE*):

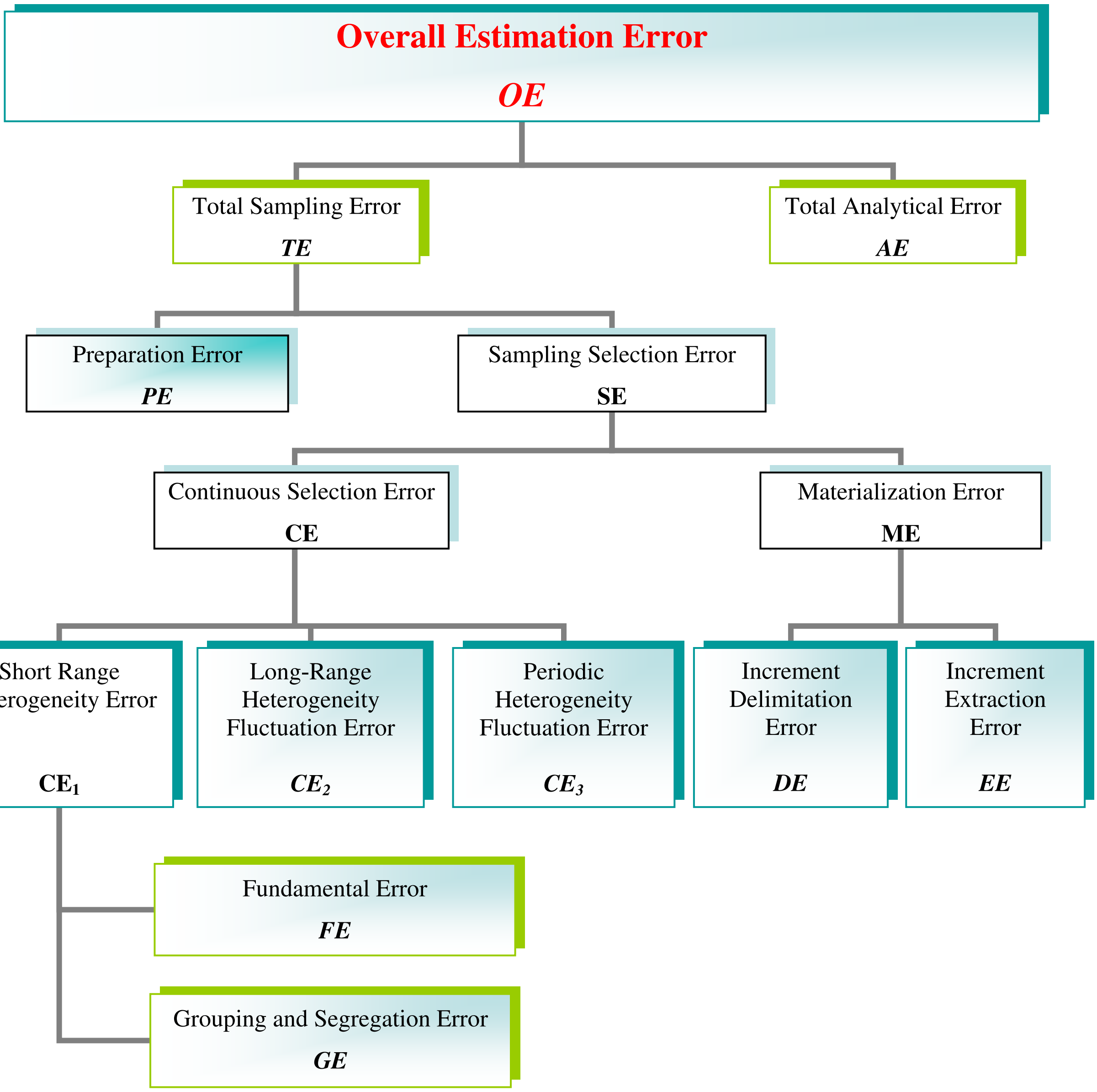

Figure 28 Relationships between different types of errors, according to Pierre Gy (after Back, 2001)

Apart from a different terminology[68], the ***Overall Estimation Error*** is equivalent to the ***uncertainty of the measurement process*** u_{tot} ($u_{tot}^2 = u_{analytical}^2 + \sum_{n=1}^{N} u_{(sub-)sampling}^2$) in Figure 27 and is calculated in the same way (sum of variances):

$$\mathrm{OE} = \mathrm{AE} + \sum_{n=1}^{N} (\mathrm{PE_n} + \mathrm{FE_n} + \mathrm{GE_n} + \mathrm{CE_{2n}} + \mathrm{CE_{3n}} + \mathrm{DE_n} + \mathrm{EE_n})$$

$$\sigma_{\mathrm{OE}}^2 = \sigma_{AE}^2 + \sum_{n=1}^{N} (\sigma_{PE_n}^2 + \sigma_{FE_n}^2 + \sigma_{GE_n}^2 + \sigma_{CE_{2n}}^2 + \sigma_{CE_{3n}}^2 + \sigma_{DE_n}^2 + \sigma_{EE_n}^2)$$

N = number of sampling or preparation stages

Equation 5 Global Estimation Error of a measurement process (Pitard 1993)

Realizing that each, the Fundamental Error as well as the Grouping and Segregation Error can easily reach 50-100% in a single sub-sampling step (e.g. in case of grab-sampling; cf. Gerlach et al., 2002), that usually repeated sub-sampling (or sample-splitting) is necessary (each producing an additional sampling error), and natural – let alone man-made – heterogeneity is at least of about the same magnitude, one knows he's potentially in big trouble[69].

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[68] Although there are important differences between (the concepts of) 'uncertainty' and 'error' (see Chapter 2.4 'Uncertainty' (p.77) these terms are often used synonymously.

The idea of sampling theory is that in principle a (sufficiently simple) target can be described without any error. E.g. a jar with red and green balls; a 'correct' sample would represent the jar without any bias and could be checked for correctness by counting the whole lot. I.e. in contrary to a (chemical) measurement the target can be known completely – just sample everything! Although impossible for most sampling targets, this holds true in principle for the Total Sampling Error of every target – hence the use of the term 'error' is justified, while for 'real-world'-targets at best the 'uncertainty' of the sampling and the Overall Estimation (or u_{tot}) will be known. Since within the framework of sampling theory the term 'error' is used, it has been kept.

[69] The numbers are of course arbitrarily chosen from the literature, and I would not claim them to be representative – albeit much closer to reality, than a presumably error-free sampling…. One can easily find much higher numbers for any step – as well as much lower ones, under idealized conditions. Without a doubt, there is a thin line between creating hysteria and trying to be honest about possible limitations and shortcomings regarding the results of sampling natural matrices. The studies accounting for sampling errors – for what reasons so ever – usually find about >90% of the data uncertainty to be contributed by sampling considerations, while most studies simply ignore them – for what reasons so ever – one of the reasons, why representative numbers are unknown.

Gy (1998) reports bias in primary sampling easily to be about 1000% and about 50% in secondary (i.e. sub-) sampling, there are humorous descriptions of analytical equipment turned '*into a random number generator if sample material has not been prepared correctly*' (Flatman and Yfantis, 1996), most of 'us' are familiar with the measurement of artifacts entering 'our' samples one way or another (hopefully finding them, instead of interpreting them…), not to speak about 'known' inappropriate sampling at least in the past – e.g. water-samples analyzed for heavy-metals in the oceans being contaminated by the anti-fouling paint of the ship – and so on. All this is of little help. One can learn from it, and try to avoid 'old' errors, while what holds true for the sampled matrix, as well as the individual sample, also holds true

2.5.2.1 Basic concept

2.5.2.1.1 Sampling Selection Error

A key word and issue in sampling theory is sampling ***correctness***. Unlike with the above-mentioned 'traditional' definition of a 'correct sample', correctness here means an unbiased sample – i.e. all constitutive elements of the sampling target will have exactly the same probability of being selected.

The deviation from this idealistic case is quantified as the sampling error – the fundamental theoretical unit is the ***relative error***; i.e. the above ***Sampling Selection Error (SE)***:

$$E = \frac{(a_S - a_L)}{a_L}$$

$E = \text{relative Error} \equiv \text{Sampling Selection Error (SE)}$

$a_S = \text{analyte concentration in sample (S)}$

$a_L = \text{analyte concentration in lot (L)}$

E is a fixed value for a single sample and can be described by its distribution and the value of its moments (mean, variance, mean square) for a series of samples.

- A sample is considered ***accurate***, if the expected value of E (*m(E)*) is below an accepted bias (*m_0*):
  $$|m(E)| \leq m_0$$
- It is considered ***reproducible***, if the variance of E (*$\sigma^2(E)$*) is below a accepted variance (σ_0^2):
  $$\sigma^2(E) \leq \sigma_0^2$$
- It is considered to be ***representative*** – i.e. ***accurate and reproducible*** – if the mean square error of the sample selection error (*$r^2(E)$*) is below an accepted level:
  $$r^2(E) \equiv m^2(E) + \sigma^2(E) \leq r_0^2 \equiv m_0^2 + \sigma_0^2 \,.$$

Hence, accuracy, reproducibility, and representativeness are a matter of definition, not virtues within themselves – allowing the amount of error (uncertainty) one is willing or able to accept to address a question, to be defined by one.

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for any study concerned with sampling errors derived from actual measurements – every case is different; and without sampling-validation, any attempt to address the problem is doomed to fail…

However, **oftentimes representativeness is loosely defined in qualitative terms**, while it is virtually impossible to demonstrate representativeness – at least without the complete knowledge of the intrinsic heterogeneity of the sampled lot: '*in fact, "representative samples" are often used to make decisions even though no real evidence is presented to verify that the sample represents anything but itself*' (Back, 2001). All sampling errors are the result of heterogeneity and "*almost everything that is worth analyzing is actually or potentially heterogeneous.*" (Thompson, 1999).

Sampling theory instead demands the independent analysis of heterogeneity of the sampled lot as a fundamental step in advance of any sampling operation, providing information going far beyond the sole purpose of sampling – since only the hypothesis of considering a lot as homogenous allows solving all sampling problems; by oversimplifying them.

2.5.2.1.2 *Classification of lots – Heterogeneity Fluctuation Error*

To make things worse one important concept in sampling theory is the ***dimension of the sampling target***. It can be classified as zero-, one-, two-, and three-dimensional depending on the spatial dimension of its heterogeneity (Pitard, 1993) – irrevocably of its physical dimension:

- **Zero-dimensional**: E.g., the above-mentioned randomly distributed colored balls in a jar – i.e. a statistical population – any 'correct' sample will describe the target unbiased.
- **One-dimensional**: e.g. a stream of water – i.e. a statistical population with a linear **or** chronological behavior – a series of 'correct' samples, proportional to the number of strata or the periodicity, will describe the target unbiased.
- **Two-dimensional**: e.g. a piece of contaminated land, where the depth of the lot is small to its areal extent – a series of 'correct' samples, proportional to the number of strata, will describe the target slightly biased (depending e.g. on how severely the assumption of two-dimensionality is violated).
- **Three-dimensional**: e.g. piles of material or soils where the thickness is not negligible.

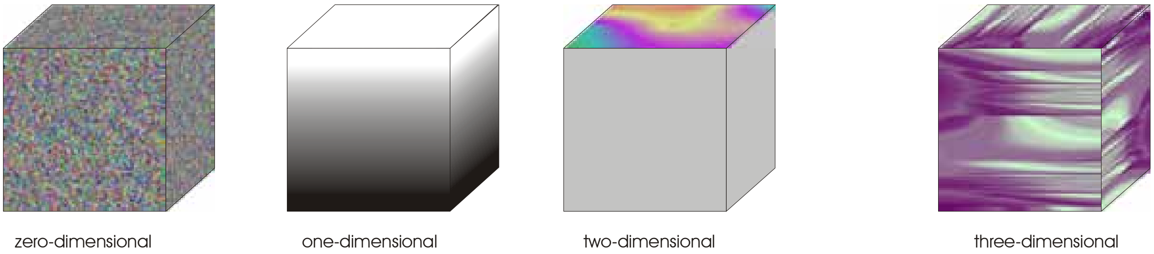

Figure 29 Dimension of sampling-targets – colors represent different strata.

Statistically ***correct*** sampling is only possible from zero- and one-dimensional targets; under favorable conditions, acceptable sampling is possible for two-dimensional targets, but it is practically impossible for three-dimensional lots. However they can (and have to) be divided into a series of one-dimensional strata, at the cost of an additional sampling-plan for every dimension.

The bad 'news' is of course: environmental lots are rarely zero- or one-dimensional and the more dimensions a lot has/the more heterogeneous it is, the more difficult the sampling operation. '*Theoretically all sampling problems are solvable; however, in a great number of cases, the notion of solvability is closely related to the notion of cost-effectiveness*' (Lischer, 2001) – or feasibility.
Having to accept the classical '**a study of one is a study of none**' for any non-zero-dimensional lot, the implications with respect to many popular sampling-strategies and attempts toward data-analysis and interpretation could be tremendous.

Oftentimes at least one dimension of heterogeneity is ignored – at best for one of the above reasons –, making the representativeness – as a qualitative term! – of the sample and any derived result questionable. E.g. core-samples – i.e. interpretation of a series of single samples to explain vertical heterogeneity of a measurand, often without the faintest idea about its horizontal heterogeneity and/or physical properties of the samples influencing the measured parameters, like grain-size distribution. As a matter of course, the same holds true for longitudinal profiles of river-sediments – i.e. interpretation of a series of single samples to explain spatial heterogeneity, often without accounting for variations over a river transect and/or depth, etc.

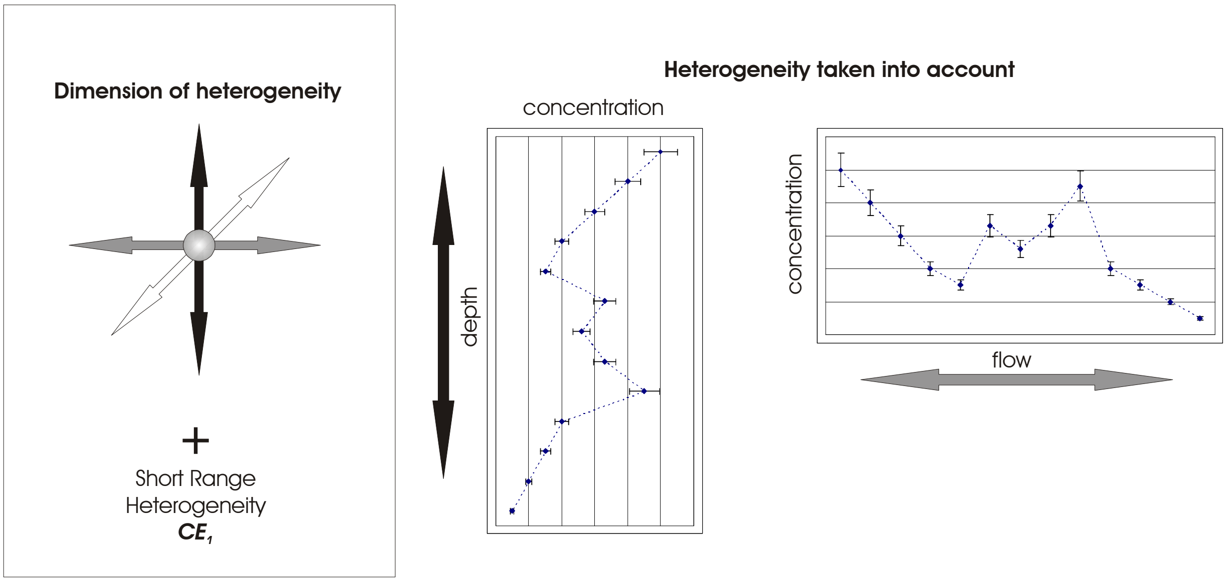

Figure 30 **Overall heterogeneity of a soil/sediment lot and (fraction of) heterogeneity taken into account, when interpreting solely horizontal/vertical profiles (error bars indicate analytical error/uncertainty).**

In other words, the chance of obtaining a single meaningful sample in a sampling-scenario is limited to the – often-unproved – case that the ignored dimensions of heterogeneity are well below the one under investigation.

2.5.2.1.3 Sample Support – Materialization Error

Closely related to the dimension of a lot is the sample support – i.e. the volume, shape, and orientation of a sample in a continuous lot.

In contrast to discrete (discontinuous) sampling targets – e.g. people, housing units – where a sampling unit is clearly defined by the investigated fragments, which are entirely independent from their neighbors, (most) environmental sampling lots have to be described by a continuous model, where neighboring fragments are statistically correlated, and the sampling units must be defined in terms of support. Because of the heterogeneity, '*changes in support not only change the means of distribution, they also change the variances of concentrations and the correlations of concentrations between sampling units*' (US-EPA, 1989). E.g. when sampling sediments or soils where the concentration of a measurand decreases with depth, then the deeper the sample, the lower the mean concentration will be. I.e. in order to define any kind of action level, or to draw conclusions from varying concentrations the sample support has to be defined – e.g. the upper 10 cm for a given area.

For heterogeneous lots – such as soils and sediments – samples with small support volume vary considerably more than larger samples of the same target – again the limit case being the whole lot taken as a sample, and without prior information no appropriate sample support can be chosen.

The Representative Elementary Volume (REV), used in soil physics and hydrogeology, illustrates this.

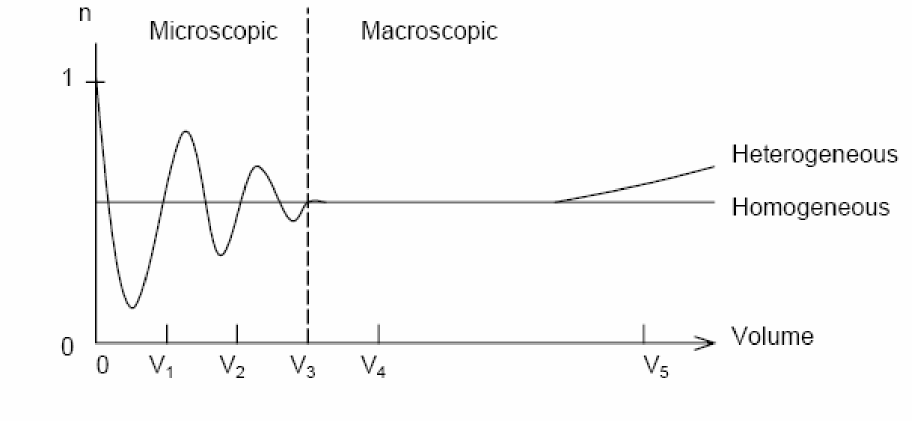

Figure 31 ***Representative Elementary Volume*** **(REV) as the minimum volume (V_3) at which a measurand or measured parameter (here porosity) becomes constant (after Hubbert in Freeze and Cherry, 1979 as cited in Back, 2001).**

The REV is thus the minimum sample volume needed to eliminate short-range heterogeneity, while in case of a – macroscopically – heterogeneous lot it is the minimum volume to represent one stratum of the lot, and an upper bound exists beyond which multiple strata are mixed – i.e. long-range heterogeneity is envisioned (cf. Chapter 2.5.6.1.1, p. 151 ff.).

2.5.2.1.4 Short Range Heterogeneity

Two fundamental types of heterogeneity can be distinguished: *Compositional* (or *Constitutional*) and *Distributional* Heterogeneity.

Compositional heterogeneity occurs when there is a difference e.g. in concentration in-between the particles of a lot – i.e. the heterogeneity in composition of each particle. This heterogeneity can only be reduced by comminution – e.g. grinding –, which changes the properties of the particles, while homogenization has no effect on it. The sampling error caused by these fundamental properties of the particles is the Fundamental Error (FE).

Distributional heterogeneity occurs in case of a nonrandom distribution of particles – e.g. vertical segregation due to gravity, with the lighter/larger particles on top of the finer/denser particles. It depends on the compositional heterogeneity, the spatial distribution of the particles and the shape of the lot, and is thus closely related to the above sample support. The distributional heterogeneity and the resulting Grouping and Segregation Error (GE) is reduced with homogenization, increasing increments (i.e. composite sampling) and increasing sample support and is always smaller or equal to the compositional heterogeneity.

2.5.3 Implications

Traditionally sampling is aiming to obtain (sub-) samples as representative as possible for the target and some of the techniques to assure this are composting and grinding – the first delimitates in-between sample variance, the second within-sample variance – i.e. the Short Range Heterogeneity Error (CE_1).

On the other hand, decisions about risk are usually based on the average concentration of the target, while decisions about risk reduction (remedial action) are usually based on the distinction between zones with concentrations above or below a regulatory limit. A hypothetical perfect composite sample of e.g. the section of a floodplain could thus address the question about risk, while it would be unsuitable to address questions concerning risk-reduction, distribution, etc.

In other words: **the 'perfect' sample depends on the question** and in case one or more of the possible 'errors' in sampling is the subject of the study – e.g. spatial distribution – it cannot be treated as an error.

Some of the most frequently addressed sampling objectives are (Back, 2001):

1. **to determine the average site contamination level (mean concentration)**
2. **to classify the soil in different concentration classes during, or prior to, remediation**
3. **to locate "hot spots"**
4. **to delineate the contaminated area/plume**
5. to create a contour map (isopleth) over contaminant concentrations
6. to forecast the contamination level during excavation (i.e. the concentration that can be expected as excavation proceeds)
7. to determine which chemical substances are present
8. to monitor concentration changes over time

The sampling-requirements can be quite different for the above objectives and the following discussion will be limited to the initial objectives of this study (in bold), while one implication of sampling-theory remains universal: Without knowledge of the heterogeneity of the sampling target no scientifically sound – i.e. statistically correct – sampling plan to address any objective can be established, since the number/location of samples necessary to achieve a needed/desired level of representativeness remains unknown.

In other words, **at best, an a posteriori evaluation of heterogeneity is conducted/possible and it remains unknown up to the last stage of a study, whether an objective can be addressed at all!**

2.5.3.1 Sediment Sampling

One of the first broader applications of sediment sampling was for prospection and geochemical mapping purposes, on search for the ‘perfect’ sampling target in which nature has already performed part of the sampling procedure – namely comminution and homogenization.

Geological (geo-chemical) sampling aiming for representative rock samples is one of the least favorable scenarios one can think of, due to the shear size and the inaccessibility of the sampling-lot. Sediments on the other hand – as a result of weathering, having undergone extensive comminution and mixing during their transport to the aquatic system – are easily accessible, inherently more homogenous, and their composition reflects the sum of all natural and man-made influences in the catchment area of the sampled aquatic system.

However there may be tremendous bias, especially in larger catchments, when trying to draw conclusions from the sedimental composition towards (the composition of) the parent rock material and/or soil in the catchment. The most obvious limitations being the nature of weathering as a superficial process, not accounting for deeper layers; overrating of areas closer to the aquatic system due to transportation-phenomena; segregation due to different weathering-rates; and so on.

Fortunately, none of these problems affects the use of sediments for **monitoring the condition of the aquatic environment**, since the questions and targets addressed are quite different. Geochemical mapping has to assure that the sampled sediment is suitable to describe the catchment area unbiased – i.e. the sediment isn’t the target of the question –, while this is irrelevant for monitoring the condition of the aquatic environment, where the sediment itself is the target of the study[70].

Simplified, sediments can be divided into two fractions: an ‘inert’ fraction, with little or no ion exchange and sorption capacity that is therefore (almost) not involved in any (ionic) water-sediment-exchange, and an ‘active’ fraction. Mineralogically the ‘inert’ fraction is identical with the ‘coarse’ (or sand) fraction (i.e. approx. > 63 µm), consisting of the most resistant minerals like quartz, feldspar (if freshly weathered), and occasionally mica and other silicate minerals with low metal levels in their matrix. The ‘active’ fraction corresponds to the ‘fines’, containing variable amounts of so-called ‘clay minerals’ (phyllosilicates of the illite-, kaolinite-, chlorite-, and smectite families) with higher metal levels in their matrix, a large surface and corresponding ion exchange and sorption capacity (Müller et al., 2001).

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[70] It won’t affect prospection either, since in the worst case an anomaly – i.e. in this case an elemental content worth exploiting – goes by unregistered, while no ‘artificial’ anomaly will be produced, but it could cause considerable bias and problems if any conclusions beyond these relatively simple tasks are drawn.

Additionally to this natural subdivision between a 'coarse' fraction with low metal-levels and a 'fine' fraction with higher metal-levels it is almost exclusively the 'active', 'fine' fraction, which is affected by changes in (trace-) element contents due to natural and/or man-made changes in the aquatic environment – the processes we are interested in[71]. Inevitably, a strong dependence between the metals under investigation, as well as other trace elements, and the grain-size distribution of sediment-samples is observed, since the 'coarse' fraction mainly acts as a thinner[72]. This already led Förstner and Wittman (1979) to the conclusion: *"One can even go as far as to state that without a correction for grain-size effects, a mutual comparison of metal data in fluviatile deposits would be impossible."* An alternative way of addressing the problem is to look at grain-size as a normalizer that represents several underlying geochemical relationships, since Al, Fe, TOC and grain-size tend to co-vary in many cases, making it '*often a simple compromise that works well enough in many cases*' (NAVFAC, 2003).

No strict border-line can be drawn between 'coarse' and 'fine' fractions – as well as between 'inert' and 'active' – leaving little more than a rule of thumb for monitoring and assessment of trace-elements: 'the finer, the better', with the fraction < 20 µm presumably a good compromise between expenditure of separation and remaining grain-size-effects (Müller et al., (2001)).

So an additional variable susceptible for large errors – especially in a fluviatile environment and its usually large variations with respect to sedimentation conditions – is introduced to the sampling scheme: grain size.

If measuring bulk sediment, one would have to assure additionally, the grain-size distribution of the samples to be representative for the sampled sediments – or follow the assumption, that the heavy-metal content of the 'fines' only depends on their nature (background-concentration, ion-exchange-capacity) and the environmental conditions (e.g. natural and man-made offer of ions for exchange), but not – or to a much lesser content – on sedimentation-conditions, and use them. Although this will not fully eliminate grain-size-effects, as they will remain no matter how 'fine' the fraction

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[71] This may not be correct in case of particulate pollutants, or pollutants bound to particulate matter, since in principal they can be of any size – e.g. metal fillings. Irrevocably of the (non-) effects of this kind of pollution to an aquatic environment the products of their decomposition will be found in the 'fine' fraction, and their presence in the here sampled sediments can be ruled out almost completely since for about 2/3 of the samples the fraction < 2 mm has been analyzed also, exclusively resulting in lower metal-contents than in the fraction < 20 µm.

[72] Things get a bit more complicated, with respect to the organic share of the sediment, which can act as an 'inert' thinner, or take an 'active' part in ion exchange and accumulation, depending on its nature. Without knowledge about the kind of organic substances in the 'fine' fraction, no statement is possible, which in turn makes normalization with respect to the organic content quite uncertain.

might be, they are considerably delimited compared to the coarser fractions – and so are the requirements of the sampling-scheme.

In order to overcome these problems, there are numerous ways to normalize the results of studies based on bulk sediment, e.g. with respect to Li, Al, Fe, TOC, the grain-size itself. Besides the fact that none of these 'normalizers' is of general applicability (NAVFAC, 2003) and the underlying assumptions would have to be checked at background samples (Louma, 1990), an additional amount of uncertainty will be introduced to the data-set (division of two measurements and thus propagation of error)[73].

The only advantage of measuring bulk sediment, besides its ease of 'separation', namely to know what amount of (trace-) metals are stored in a specific sample at a specific place with a specific grain-size distribution would only be useful for balancing the element load and, to a limited extend, the element fluxes in the sediments along the river; tasks with a complexity and expenditure far beyond the scope of this study, as well as any known study on the River Volga. For any other purpose, especially for the monitoring and assessment of (trace-) elements, the use of 'finer' fractions – like the < 20 µm fraction used here – is not only equivalent, but superior with respect to methodological uncertainties (e.g.: no necessity for representative sampling with respect to grain-size distribution, less expenditure for homogenization and preparation (grinding) of the samples) as well as being more sensitive to potential natural and/or man-made changes, since only the 'active' parts of the sediment are considered.

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[73] This only holds true for an a posteriori normalization for grain-size, where the measurement result of the bulk-sediment for a given parameter is corrected with the measurement result of the share of a grain-size fraction. In this case both measurement-uncertainties add up, while when only analyzing this specific fraction the target is redefined and the measurement result of the parameter of interest is independent of the fractions share in the bulk sediment. On the other hand, in case the (wet-) sieving causes any change in the properties and/or contents of the fraction under investigation, and/or the fraction can not be separated quantitatively an (unknown) amount of bias will be introduced in the latter case, and as mentioned in footnote[61] very little is known about the implications of (wet-) sieving on the (chemical) properties of a fraction – although they are considered to be small in most cases.

2.5.3.2 Fundamental Error (FE) of Sediment Sampling

Assuming that the sediment-particles are rounded in shape[74] the **FE** for a particular mass of the sample, and vice versa, can be calculated using the formula (Ramsey and Suggs 2001):

$$FE^2 = \frac{10 * \lambda * d^3}{M_{sample}}; \qquad M_{sample} = \frac{10 * \lambda * d^3}{FE^2}$$

FE = (tolerable) Fundamental Error
λ = Density of material $[\mathrm{g/cm^3}]$
d = Size of largest particles $[\mathrm{cm}]$
M_{sample} = Mass of sample $[\mathrm{g}]$

Further assuming an approximate density of the sediment of about 2.5 g/cm³ – presumably an upper bound (cf. density of quartz: 2.65 g/cm³) – this results in the following sample masses necessary to achieve a given tolerable error of the (sub-) sampling (Table 14).

Table 14 **Sample masses (dry weight) for different maximum particle sizes and FE's – λ: 2.5 g/cm³**

Maximum Particle Size [mm]	(Tolerable) FE expressed as RSD [%]					
	15	10	5	2	1	
5	139	313	1250	7813	31250	Sample mass [g]
2	9	20	80	500	2000	
1	1	3	10	63	250	
0.063	0.28	0.63	2.5	16	63	Sample mass [mg]
0.0200	0.01	0.02	0.08	0.50	2	

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[74] Any approach addressing the question of the minimum sample mass (m_p) needed, can be reduced to the formula suggested by Brunton (1895) (as cited in Rasmann and Herbst, 2000): $m_p = k_0 * d^3$, where k_0 accounts for all deviations of the sampled particles from an ideal cube with the length d – pointing out the outstanding importance of grain-size (as long as the geometry isn't too different from a cubic one). This also holds true for the calculation of the FE according to Gy, which involves several empirical factors, geometry being one of them. Although the 'finer' the grain-size fraction will get, the more it will violate the assumption of a simple geometry (cube, sphere) the implications are very limited, since the necessary geometrical corrections are small and there's still a lot of scope, before the FE of the sub-sampling step would influence the results, while the coarser fractions can be described unanimously by a spherical model.

These simplifications are however not applicable to (biological) samples, where already the primary sample violates the above assumptions, no diameter is defined, and the geometrical factor becomes much more important (e.g. needles, (de-composed) plants, etc.) and already the Fundamental Error makes sampling questionable (cf. Pitard, 1993).

So in our case, where we sampled fine-grained sediments with a maximum particle size of about 2 mm and primary sample masses well above 2 kg; wet-sieved sub-samples of this primary sample of about 100g and analyzed sub-samples of the < 20 µm fraction of about 0.5 g; the secondary sampling-step (sub-sampling the primary sample) introduces by far the highest FE, while it is still below 5% RSD. To assure a FE this low when analyzing the fraction < 2 mm would require efforts in grinding and homogenization of this fraction at least comparable to the effort of wet-sieving, while simply analyzing 1g (500mg) of the fraction < 2 mm without any further treatment would result in FE's of > 40% (> 60%)[75].

Omitting the more complex calculation of the Grouping and Segregation Error (GE) and instead using the aforementioned relationship (chapter 2.5.2.1.4; p.103) between GE and FE (GE≤FE) the ***short-range heterogeneity error*** (*CE_1=FE+GE*) is calculated in the usual way – sum of variances – to be **about 7% - i.e. an expanded uncertainty of < 15% - for this sampling scenario**.

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[75] Judging from Table 14 the fraction < 63 µm or even larger (e.g. < 125 µm) would allow for about the same low FE (and GE) as the fraction < 20 µm – as the sub-sampling of the primary sample shows to be the crucial, error-creating step –, while reducing the effort for its separation considerably, since these fractions can be obtained by dry-sieving instead of wet-sieving – presumably reducing the unknown amount of bias due to incomplete separation of a fraction. As mentioned above there is no strict scientific reason to use a specific grain-size fraction and their definition itself is of course 'purely' arbitrary – varying between different countries and the purpose they are used for – largely for historical reasons. In fact many sediment studies use the fraction < 63 µm, and in case the saved expenditure for separation is invested towards additional samples, this approach could prove to be superior to the use of a fraction 'as fine as possible'. On the other hand, with respect to environmental studies of aquatic systems, the finer the fraction used, the more sure one can be that it represents the most interesting (former) suspended solids of this system, while in coarser fractions increasing amounts of bed-load are present. Moreover it can be advantageous to stay within an established methodology based on a specific grain-size fraction, in order to make the results of different studies comparable and/or use a regulatory based on a specified grain-size on the results – while a sound proof that any regulatory could be applicable would still be hard, if not impossible, to obtain.

All in all, taking the later discussed principal limitations and problems of the sampling target 'sediment' and the more or less arbitrarily chosen regulatory procedures – most of the time based on a loosely defined background or 'effect levels' towards a specific target (e.g. fishery) derived from a few studies of combined chemical and biological monitoring, which can not be transferred unanimously to another sediment body – into consideration, it seems reasonable to draw more attention on the number of samples in order to allow for a more rigorous statistical interpretation of the results. In case one decides to give up the interpretation of single samples – and even the rough estimation of an uncertainty budget leaves almost no other choice unless the differences between samples are huge – there's no other way than increasing the number of samples in order to facilitate a sound and defensible site-characterization.

2.5.3.3 Remaining Errors of Sediment Sampling

The Theory of Sampling distinguishes between ‘correct’ and ‘incorrect’ sampling errors. ‘Correct’ errors (FE and GE) can only be minimized, while (statistically) correct sampling – at least in principle – can eliminate ‘incorrect’ sampling errors.

In contrary to e.g. a stockpile, the chances of eliminating sampling-errors in the case of most environmental sampling-targets are nil. The physical dimensions of the lots are too big and their accessibility is quite limited, so the real composition will always remain unknown, making even the calculation of the error a difficult issue.

As mentioned above (Chapter 2.5.1; p.93) the efforts of reducing sampling errors are usually limited to the reduction of random errors, while the systematic errors remain unknown since the two sampling scenarios which would be able to address these errors (single sampler-multiple protocol and multiple sampler-multiple protocol) are rarely conducted. Additionally **most sampling devices used in environmental sampling (e.g. augers, thief probes and triers) are incorrect according to the Theory of Sampling**, due to the fact that they are liable to cause serious delimitation (DE) and extraction (EE) problems (Lischer, 2001; Myers, 1997).

The here used Van Veen grab sampler is no exception. Although widely used and even recommended by the above-cited US-EPA (2001) manual, already Figure 32 points out that even under idealized conditions biased samples are obtained – while ‘better’ samplers are not available[76].

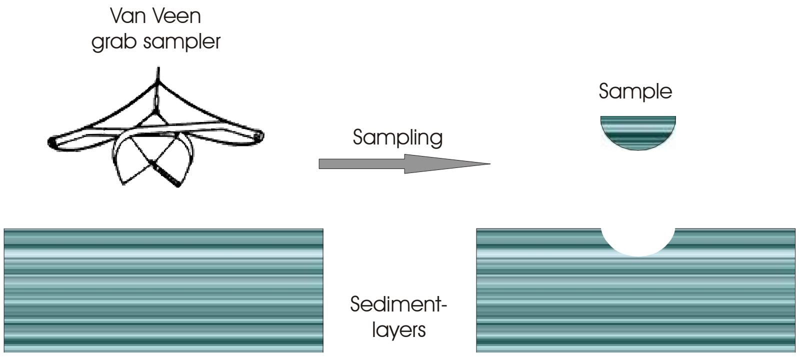

Figure 32 Delimitation error introduced by the (idealized) sampling procedure for sediments (grab sampler drawing from US-EPA (2001)).

In the terminology of the Theory of Sampling an inevitable **Materialization Error** (ME=DE+EE; p. 95f.) – depending e.g. on the vertical heterogeneity of the parameter of interest, the (variability of the) depth of intrusion of the sampling device and the compressibility of the sampling target – is introduced due to the geometry of the sampling-device, over-representing the upper sediment-layers and severely affecting the definition of the sample support (Chapter 2.5.2.1.3.; p.102).

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[76] C.f. US-EPA (2001) which gives a comprehensive overview of devices used for sediment sampling and their shortcomings, mostly based on practical considerations.

At first sight, things get even worse under 'real-life'-conditions. None of the parameters affecting the Materialization Error is constant and the idea of sedimentation taking place layer by layer at a constant rate over a given area may be appropriate in the middle of deep seas, with the lack of a structured ground and the absence of any slope and currents as the limit case, while it is (severely) violated in all other environments – especially in riverine systems. Almost any parameter controlling sedimentation as well as erosion processes is liable to (rapid) changes within time and space, and e.g. a single flooding event can change the system uncontrollable by carrying and resuspending large amounts of sediment. So the sampling target changes as depicted for two dimensions (i.e. a transect) in Figure 33 leaving one with no a priori information about its genetic and temporal origin and one can go as far as to state that **one does not know, what he is sampling!**

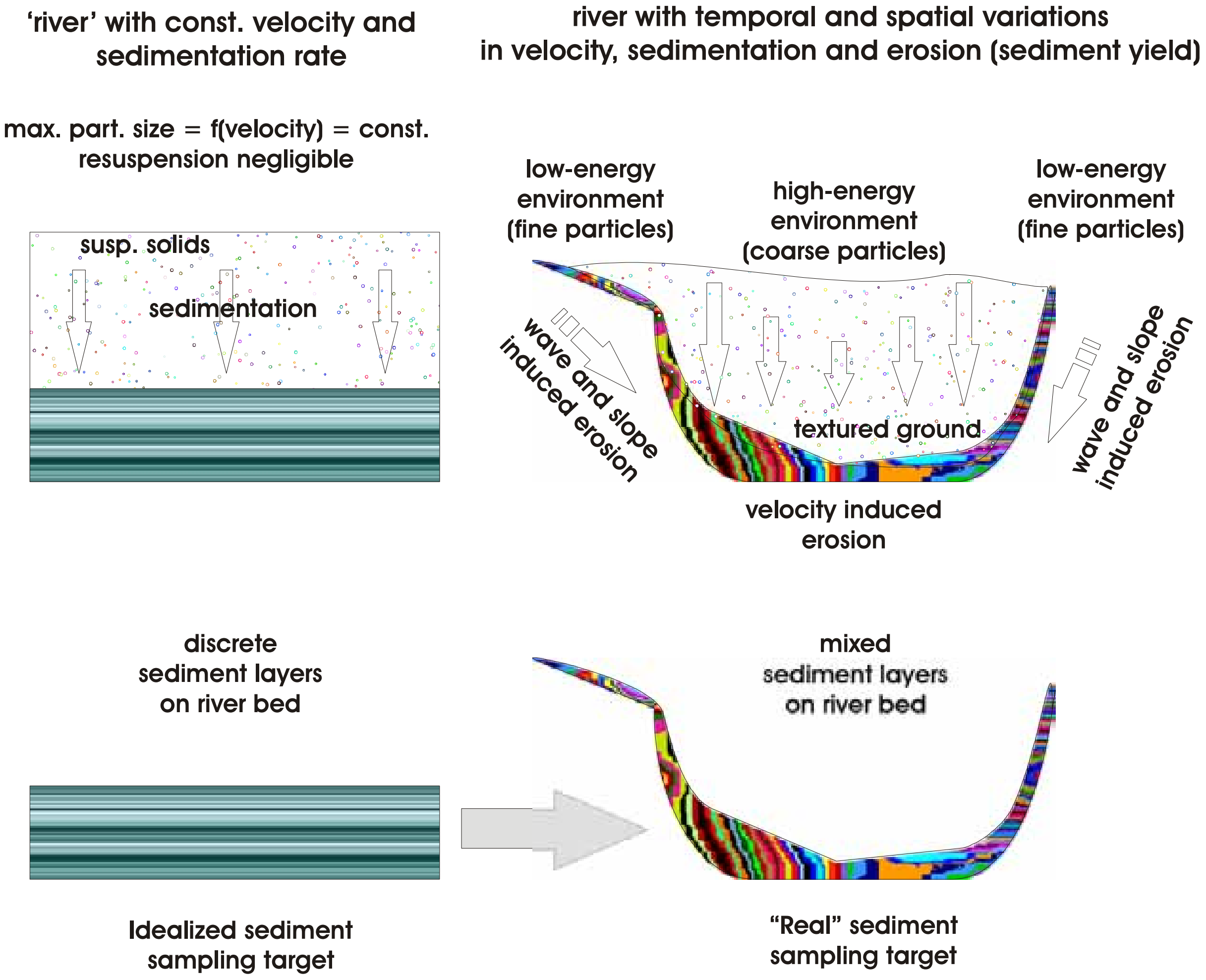

Figure 33 Idealized vs. more realistic sediment sampling target in a riverine system (2-D case). Different colors represent different properties.

Although there are ways to overcome some of the uncertainties bound to the question what our sampling target may be – e.g. sediment 'layer' (sediment sample) ages can be estimated by radioisotopes (^{210}Pb, ^{137}Cs)) – the expenditure and costs prevent them from being used on a routine basis, and one would still have to proof that e.g. the obtained 'average age' of a sample with an unknown

Materialization Error has any meaning and/or the major assumptions when calculating sedimentation rates based on age-dating – deposition occurred at a constant rate without interruption; sediment profile is undisturbed – are fulfilled. Otherwise, one would still compare apples and oranges – albeit of the same age...

2.5.3.4 Crisis? - What crisis?

On the other hand, sediment-studies have been successfully used for geo-chemical prospection, as well as, starting with the early works of Züllig (1956), for the environmental-geo-chemical description of the state of aquatic systems. How come?

Some of the above imponderables that at first sight appear to be weaknesses reflect in fact the strengths of sediments as a sampling target – as long as one is aware of the limitations.

Geo-chemical prospection searched for the '*perfect*' sampling target in which nature had conducted all/most of the comminution and homogenization of the geological formations in a given area; and found (overbank-) sediments to be suitable for this task. Environmental geo-chemistry tried to overcome the serious problems and limitations when describing water-bodies by the use of water-samples due to the difficulties of obtaining meaningful, representative samples.

Instead of using multiple-year time-series of water-samples – indispensable because of the high variability and seasonality of water-bodies – sediments acting as some kind of a buffer – i.e. sink and source of the substances of interest – in the aquatic environment were found to be suitable. Seasonal changes in the aquatic environment are averaged out in the sediment, while principal changes – e.g. new sources – are still reflected in their (chemical) composition.

So in fact, both approaches rely on the idea of the chemical composition of sediments being (markedly) less heterogeneous than the primary sampling target – e.g. soils or water.

Moreover, sediments as an aquatic habitat for many organisms (within the food chain) are a sampling target in themselves, making them one of the most widely used sampling targets in environmental-geochemistry.

- ***Horizontal distribution:***

Both, soils and sediments originate from parent rock through weathering and their natural chemical composition depends primarily on the composition of the parent rock, but unlike soils sediments are not (only) deposited where they are formed[77]. Instead they are (re-) distributed in a waterbody according to their physical properties (size, mass, etc.) and the environmental conditions (carrying capacity, currents, etc.) leading to a variable degree of mixing different sediments/sediment sources. The resulting homogenization is characteristic for a given watershed under fixed environmental conditions. Ignoring the trivial case of uniform sediment sources Figure 34 depicts the two borderline cases of complete mixing or no mixing at all, of two sediment sources having different properties – e.g. (chemical) composition – for two geometries in a riverine system.

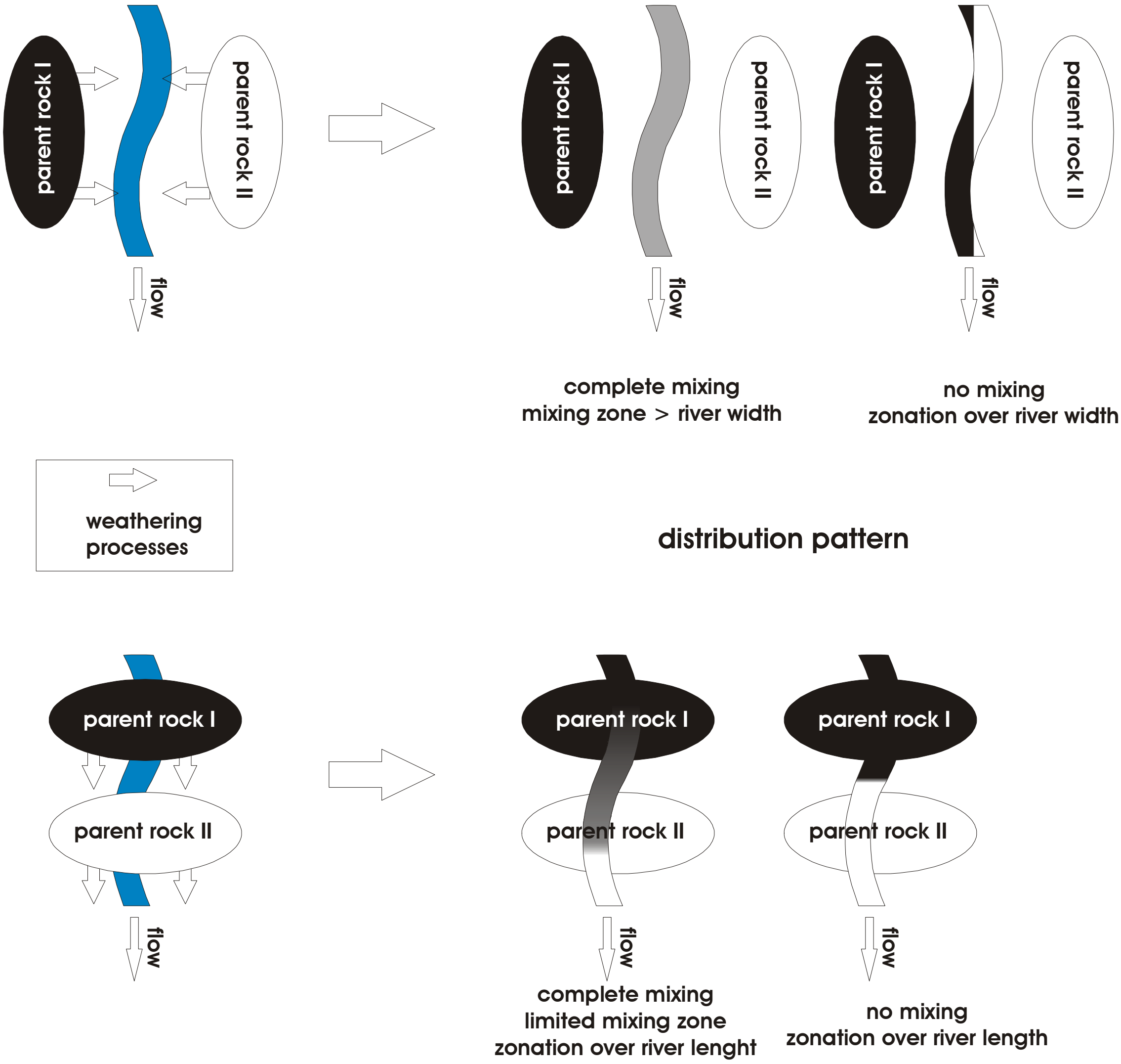

Figure 34 Parent rock as sediment source (color represents different properties) in a riverine system and resulting distribution pattern of sediment properties.

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[77] As with almost all the issues discussed here, this is also a matter of scale, since soils are in no way a 'static' lot, albeit markedly less maneuverable and moved as sediments.

As the distribution pattern for a given property will be somewhere in between these borderline cases the chances of describing the average property of the system with a given number of samples increases as its homogeneity increases. Nevertheless, a reliable description of the zonation could proof to be almost impossible and conclusions towards the parent rock – which would require exact knowledge about the (chemical and physical) fate of a property when the parent rock is transformed into sediment – are almost unfeasible. [78]

This is depicted in Figure 35 for multiple sediment sources and their most common distribution along a river stretch. No matter how complicated – and thus difficult to describe – the real distribution pattern may be (differences between right and left bank, differences between high- and low-energy zones, etc.) as long as one's just interested in the **average property and a rough estimate of its distribution** any probabilistic sampling scheme will result in lower variability than sampling the sources.

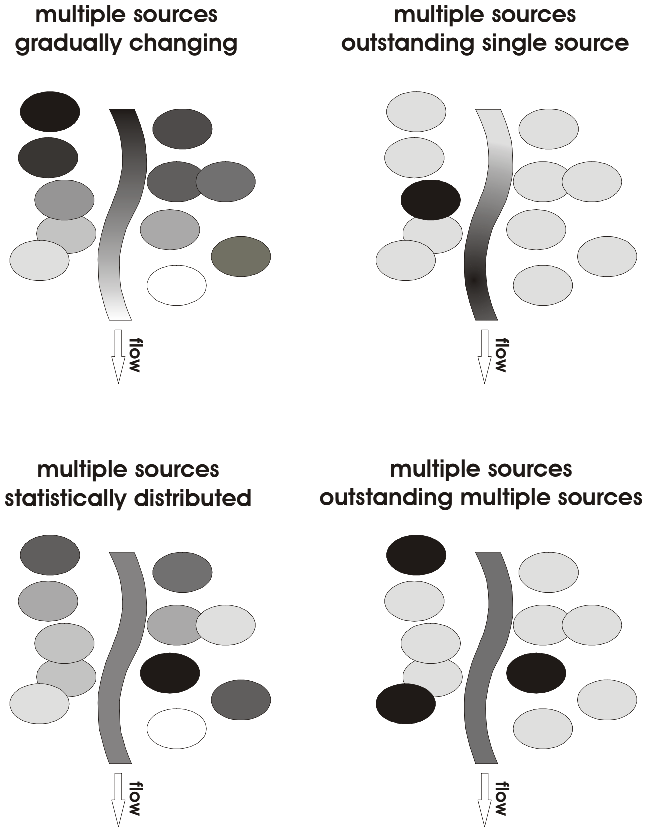

Figure 35 Multiple sediment sources along a river stretch (color represents different properties) and resulting distribution pattern of sediment properties.

This also explains the successful use of sediments in search for COPC's and their sources in the aquatic environment. No matter how 'wrong' the sampling plan may be – i.e. deviation from the ideal case of a completely unbiased probabilistic sampling scheme – the chances of finding elevated

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[78] For these reasons geochemical prospection largely relies on rivulets with a small catchment, since especially the transport-phenomena are difficult to describe quantitatively.

levels are quite good as long as the thinning effect of the homogenization is smaller than the sampling and measurement errors – and thus closely related to the acceptable amount of uncertainty and/or sampling-expenditure affordable.

Moreover the combination of contaminants (or elements of interest) being homogenized and stored within a sediment-body makes it an almost unique sampling target for problem-oriented approaches in environmental and geo-chemical investigations. Unlike in sampling the sources (anthropogenic or geogenic), where the probability for a given number of samples to detect a source is proportional to its physical size, the chances of finding a source in the secondary sampling target sediment is proportional to the sources' output (quantity/concentration) and thus impact on the environment (or its worth towards exploitation) – and by that exactly what one is interested in.

- ***Vertical distribution:***

A simple sediment-model for relative quiescent sedimentation-areas is to look at the sediment body consisting of a less consolidated surface layer (mixed zone) that is biologically active and prone to re-suspension processes by e.g. waves and currents, and a more consolidated sub-surface layer (permanent deposit) not/no longer affected by bioturbation and 'normal' erosion events. In a net depositional environment (particulate import > particulate export) the mixed zone will eventually be buried and become part of the permanent deposit.

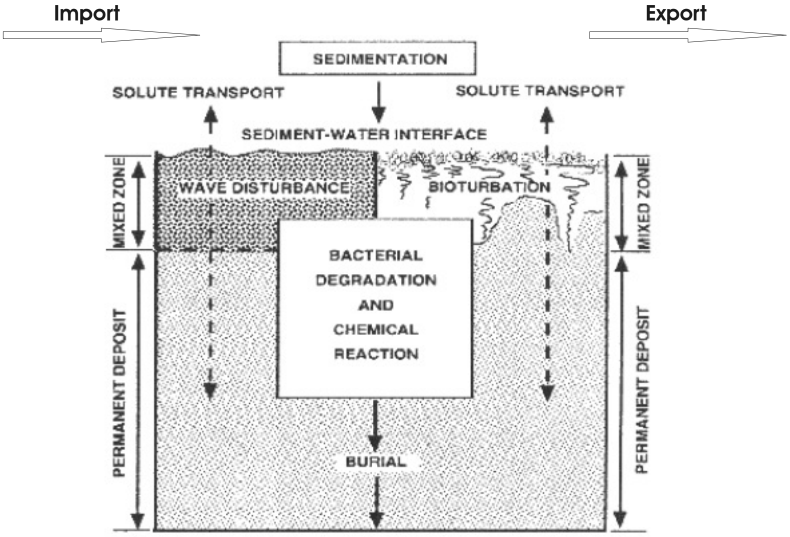

Figure 36 Major chemical fate and transport processes (after Allen, H.E. Metal Contaminated Aquatic Sediments, Copyright CRC Press, Boca Raton, FL 1995; as cited in NAVFAC (2003))

Sediments – usually defined as the fraction < 2 mm – consist of three basic components – inorganic material, organic material and porewater –, the abundance of which as well as their respective composition varies within a sedimentation system vertically and horizontally and the distribution of sediments and their chemical composition is controlled by many factors, including geological, geographical, geochemical, biological and hydrodynamic conditions. Without the change of any of these factors the horizontal and partly the vertical distribution pattern of sediment properties will be solely determined by the physical properties[79] (size, specific weight) of the suspended solids, while changing conditions – natural (e.g. meteorological) or man-made (e.g. a new source of contaminants) – will disturb these patterns. Thus, the idea of vertical sediment layers representing consecutive layer ages – i.e. time since deposition – only holds true in case the sedimentation for a given

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[79] (Early) diagenetic processes are omitted, since their principal changes (increasing inorganic content, decreasing organic content and porewater) are more pronounced in the (undisturbed) permanent deposit – which wasn't our sampling target – while they are markedly masked by (re-) suspension, bioturbation and biological activities in the mixed zone (homogenization, increasing pore space and thus porewater, increased transfer between the aqueous and solid phase, increasing organic content by ingestion and defecation of fine sediments by benthic organisms, etc).

time-period (e.g. a year) equals or exceeds the thickness of the mixing layer, the sedimentation conditions did not change during this time, and no re-suspension occurred.

In other words, even under idealized conditions, the temporal resolution of vertical sediment layers[80] is fixed by the ratio between the sedimentation rate and the thickness of the mixing zone. Although as a rule of thumb, the mixing zone does not extent to depths greater than 10 cm under normal conditions, with the reported low sedimentation rates for the investigated River Volga (several mm up to several cm – see Chapter 1.7.4.3, p. 56 ff.) this would mean in most cases the sample support to represent several years of sedimentation.

Summing up this qualitative picture of the horizontal and vertical distribution that is to say, that the undisputed advantages of sediments as a sampling target come at a cost. The same characteristics that first enabled us to use sediments as a 'perfect' sampling target – namely their higher homogeneity – also delimits their use for detailed interpretations with respect to time and space, once again proofing the basic finding of statistics that an answer is either precise or certain, but never precise and certain.

As long as one's not able to fully explain the origin and fate of the sampled sediments, one's sampling a relatively undefined target representing a little bit of everything and is either forced to increase its knowledge about the specific sample or delimit the addressed questions according to the amount of uncertainty introduced.

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[80] The term 'layer' is here loosely defined as an arbitrary vertical amount of sediment defined by the sampling protocol – i.e. the above 'sample support' (cf. Chapter 2.5.2.1.3; p.102f.) – since a macroscopic layering other than that due to the inevitable physical segregation would require a change in the sediment sources and/or the hydrodynamic environment and thus violate the idealized conditions, changing the system vertically and horizontally .

As much as homogeneity/heterogeneity, elevated concentrations – namely anthropogenic contamination – are a matter of scale. Looking at early classification systems, used to describe and visualize the contamination of sediments – i.e. state a than often disregarded problem – like the I_{geo}-classes[81] (Müller, 1979) it is clear that they accounted for almost any amount of (sampling and measurement) error, relying on the – than – undoubtedly correct assumption that an anthropogenic contamination of sediments with heavy-metals is usually beyond any reasonable methodological uncertainty.

Starting with Igeo-class 0 for 'practically uncontaminated' sediments – representing 1.5 times of the (assumed) background-concentration, and thus accounting for possible variations in the background-levels due to e.g. lithogenic effects, as well as possible shortcomings in determining these levels – this classification reaches up to the unlimited class 6 for 'very strongly contaminated' sediments, while the upper bound of the other classes, in each case represent twice the concentration of the previous one:

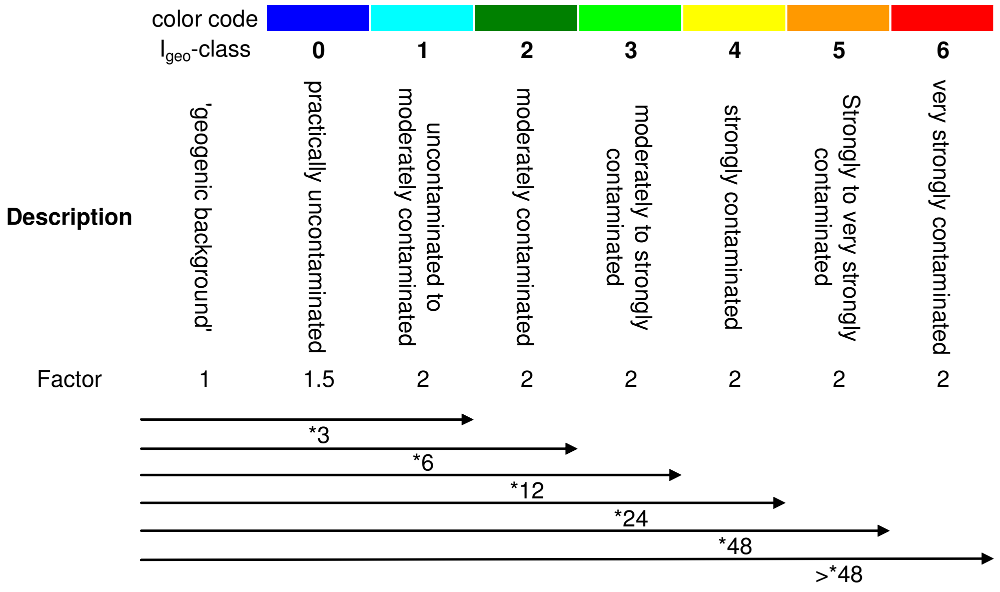

Figure 37 **I_{geo}-classes according to Müller (1979).**

Keeping in mind the high contaminations of sediments in many rivers flowing through industrialized areas up to the early 1990's – and even beyond – and the relatively simple principal distribution patterns (Figure 35), these kinds of classification system represent experience oriented approaches towards a variable, necessarily loosely defined sampling lot. The results are 'bullet-proof' with – as we will see – almost no need to care about uncertainties contributable to the measurement

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[81] $$I_{geo} = \log_2 \frac{C_n}{1.5 * B_n}$$ (the result is rounded up to the nearest whole number)

C_n = the measured concentration of the element in question

B_n = the background level of the element in question or sampling process due to the wide concentration-range of the respective class – resulting in an error of just ± one class even under unfavorable conditions.

Being also tangled in the principal dilemma of a result being either precise or certain these classification-systems opted for certainty, which could easily be obtained, since the basic question was: ‘is there a principal problem in the aquatic environment’. As long as one can assure the almost unquestioned assumption of the sampled uppermost layer(s) of the sediment-body to be the chemically and biologically most active and influential parts, the fate of the sediment up to its sampling site does not matter.

Either there is a contamination, and one can start to search the source; or there is none, no matter why.

‘Unfortunately’ these classification systems – e.g. correcting for grain-size effects from day one on; simply for mineralogical reasons (surface, exchange-capacity, etc.) and thus eliminating en passant errors addressed by the Theory of Sampling for completely other reasons (!) – proofed to be very successful and effective. That eventually led some to the uncritical use of sediments to address much more detailed questions that would require a more rigorous assessment of the underlying uncertainties.

2.5.4 Sampling Error – an approximation

With the exception of the FE and GE – if the material properties are known – the contribution of statistical sampling errors can be estimated only experimentally, analogous to the estimation of the measurement **precision** – i.e. stating random errors, while omitting systematic errors, as mentioned above (Chapter 2.5.1, p.93; Chapter 2.5.3.3, p.110). Although not strictly designed for the calculation of sampling uncertainty, at least a rough estimate is possible by the use of the 64 replicate samples – i.e. 20+% of the samples – taken along transects near the reservoir dams and the transect near Astrakhan.

In principle, there are two basic designs for the experimental estimation of sampling (and measurement) variances:

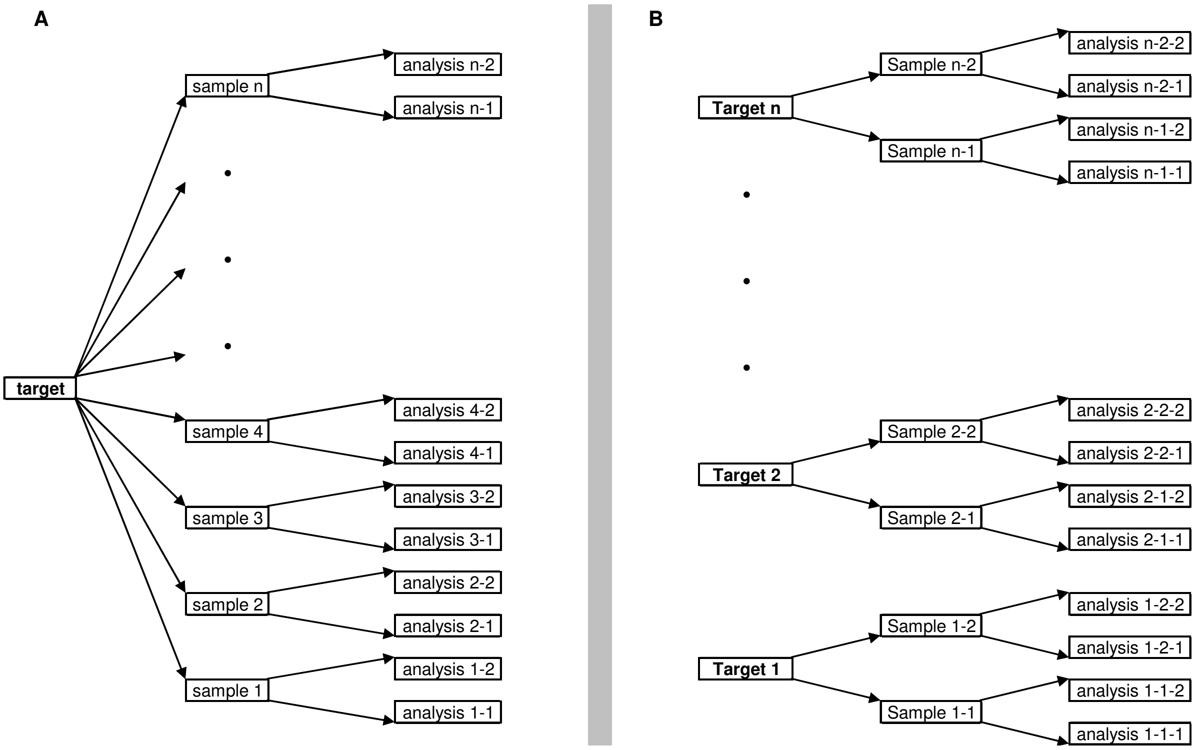

Figure 38 Basic designs for the experimental estimation of sampling and measurement errors (after Thompson (1998)).

The first design (A in Figure 38) relies on repeated sampling of one target – and would have to assure this to be feasible, and the target to be typical for the sampled material as a whole. The second design uses duplicate sampling of a number of distinct targets – and would have to assure them to be similar in composition in case the errors are averaged over all targets.

So in fact, sampling-error is once again a matter of definition, with the sample-support (Chapter 2.5.2.1.3; p. 102f.) as one of the key-issues. First, both designs are just one-dimensional, with the second dimension 'fixed' by the sample support, and secondly it is up to the experimenters decision what a sample is to represent. As can be seen from Figure 39 the sedimentation conditions along the reservoir dams (transects taken at an approximately right angle to the river flow) should vary considerably between a high-energy-environment near the sluices/spillways (little sedimentation, preferably coarse, high-density particles; sample support representing a longer period – i.e. several years; cf. Chapter 1.7.4.3, p.56 ff) and a low-energy-environment in the slack water-areas, and thus account for all the above discussed **sampling errors under various conditions** – defining the average concentration over the river width to be the sampling target.

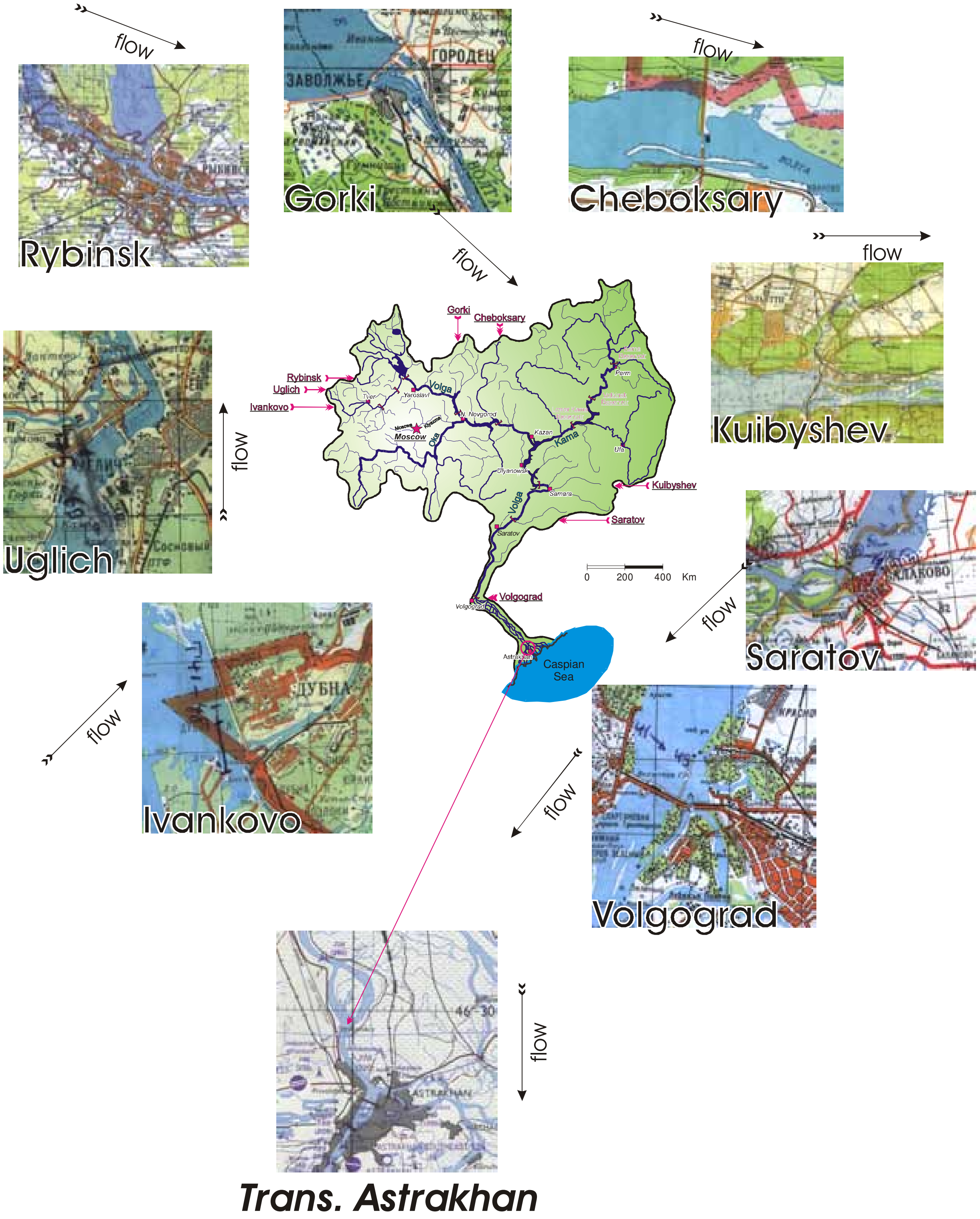

Figure 39 Volga reservoir dams and transect near Astrakhan (below the island at 46° 30'). Map sources: various Russian (street-) maps; Astrakhan: U.S. Defense Mapping Agency - UT Library (2003).

This results in an experimental design somewhere in between model A and B in Figure 38, with a single transect close to design A, while the pooling of the transects would eventually be comparable to model B, and includes **all** uncertainties bound to our sampling process.

Although Thompson (1998), as well as Minkkinen (2003) suggest model B (Figure 38) as the design of choice for the evaluation of sampling-errors – avoiding the reliance on a single sample target '*that might turn out to be atypical of the material as a whole*' (Thompson, 1998) – to achieve 'a more rugged estimate' of sampling precision (Figure 40), the transects were **NOT** pooled initially.

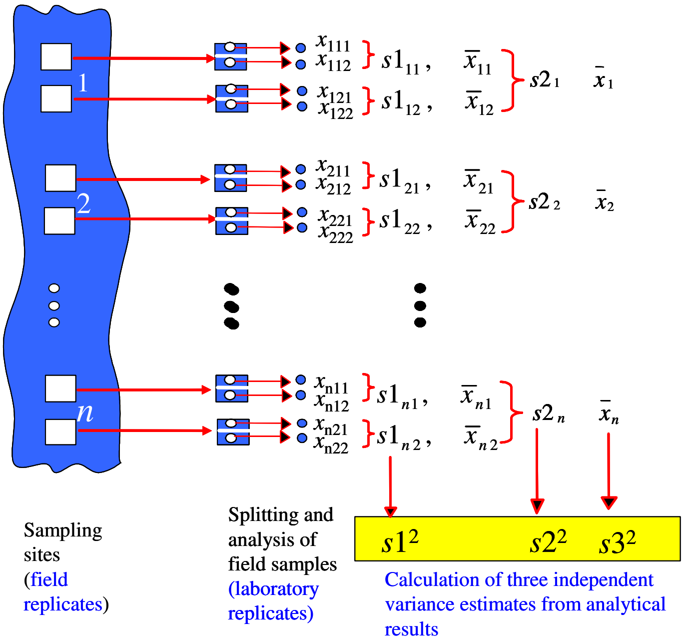

Figure 40 Proposed design for the experimental estimation of sampling variance (Minkkinen, 2003)

Minkkinen (2003) consecutively subtracts the experimentally known 'independent variance estimates' from the total variance. I.e. s1 (the measurement precision) is subtracted from s2 (the variance of the primary sample; experimentally including s1) and they are subtracted from s3 (the between sampling-site variance; experimentally including s2) to obtain $\sigma_T^2 = \sigma_b^2 + \sigma_s^2 + \sigma_L^2$ (σ_b=between-sampling site variance; σ_s=Variance of primary sample; σ_L= within-laboratory variance). Thompson (1998) in contrast suggests the sampling precision to be averaged over a number of targets – i.e. neglecting the σ_b-term in the above calculation.

In fact both sampling designs are almost equivalent, since the σ_b-term can be calculated from different transects, as well as the sampling precision of the transects can be pooled afterwards to achieve an 'average sampling error'. We simply found the first approach (Figure 41) to be more concise – while the final decision, whether to use pooled or non-pooled results is still the experimenters' choice[82].

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[82] Provided a statistically sound experimental design (complete randomization of sampling and analysis, sufficient number of replicates – i.e. as a rule of thumb approx > 10) especially design B would allow for the use of ANOVA

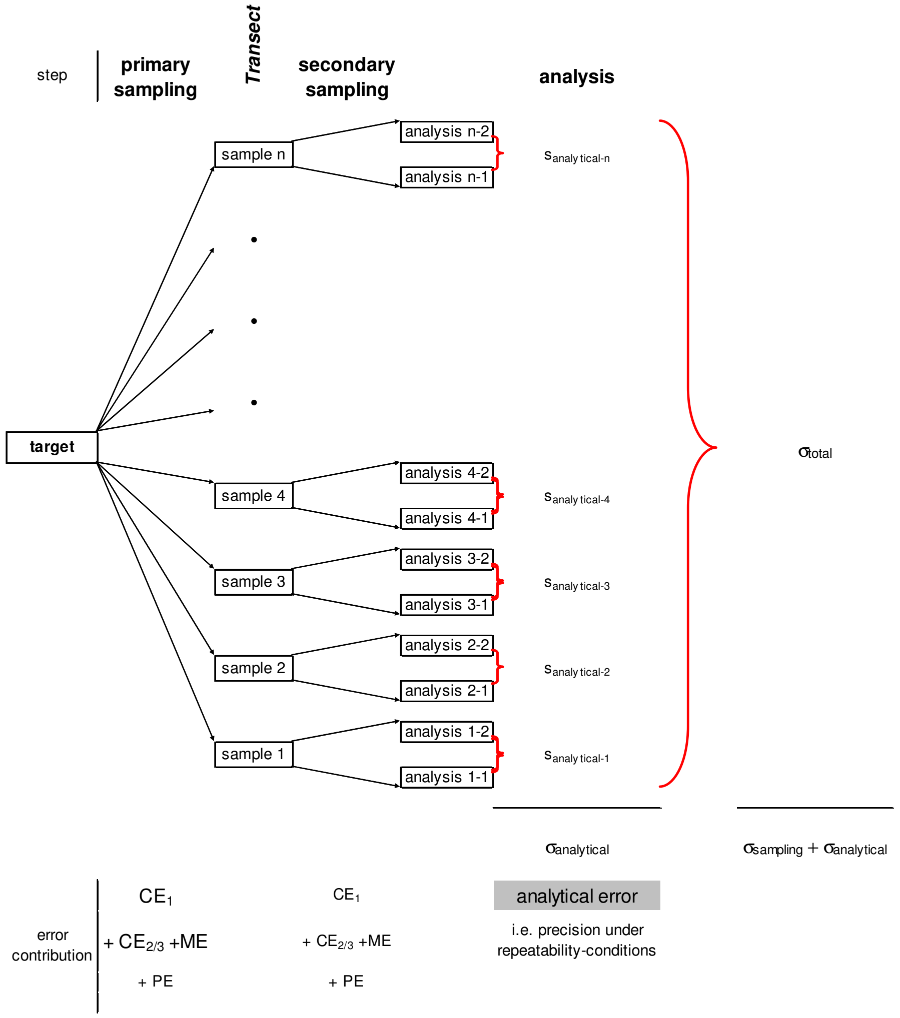


Figure 41 **Replicate sampling and duplicate analysis of a sampling target under repeatability conditions for a single transect.**

The measurement results of the samples taken along a transect (or any other geometry a single sample is later to represent) carry both sampling and analytical errors (uncertainties) – i.e. while a single sample is characterized by the sampling variance ($\sigma_{sampling}$) a single analysis is additionally affected by the measurement-precision ($\sigma^2_{total}=\sigma^2_{sampling}+\sigma^2_{measurement}$).

(analysis of variance) to decide whether the targets are equivalent, or distinct different. Nevertheless, there's a difference between statistical significance and scientific (practical) significance, and provided a large enough data-set almost any difference is statistically significant at a given level; while e.g. the geometry we would like to represent is still our choice and we will never know what effect(s) made a (the major) contribution to our sampling error with any of the above sampling designs – thus not allowing us to decide, whether to pool (error affects sampling, but is not the subject of the investigation – e.g. short-range-heterogeneity) or not to pool (error affects sampling, but is (a) subject of the investigation – e.g.. long-range-heterogeneity).

Since the measurement precision for duplicates (experimentally including all sub-sub-sampling errors) as well as the FE and GE were already known (Chapter: 2.4.1.2, p.85f.; and Chapter: 2.5.3.2, p.108f.) the total variance of a sampled transect, as well as the remaining (sampling) error in case of duplicate analysis are given as:

$$\sigma_{total} = \sqrt{\frac{\sigma^2_{remaining}}{n} + \frac{\sigma^2_{FE+GE}}{n} + \frac{\sigma^2_{analytical}}{2}}; \quad \sigma_{remaining} = \sqrt{n * \sigma^2_{total} - \sigma^2_{FE+GE} - \frac{n}{2}\sigma^2_{analytical}}$$

$n =$ number of samples

Although a closer look at the results would reveal that with a little bit of ‘fine-tuning’ (e.g. outlier-tests) some of the reported ‘sampling’-variances (Figure 42) could be delimited, it would not change much in the calculation of the more impressive and important percentage contribution of the ‘sampling’-variance to the experimental total variance (Figure 43).

σ_{remain} [%]											Element	
	Parameter	Res. Ivankovo	Res. Uglich	Res. Rybinsk	Res. Gorki	Res. Cheboksary	Res. Kuibyshev	Res. Saratov	Res. Volgograd	Trans. Astrakhan	Mean	Median
	n	8	7	4	8	8	6	7	8	8		
	Ag	77	37	62	84	253	52	58	90	25	91	63
	Al	25	19	9	18	18	13	14	7	22	19	21
	As	64	9	29	54	193	30	70	76	28	68	56
	B	9	0	55	139	71	41	131	40	40	67	50
	Ba	24	31	13	37	51	28	13	33	13	30	29
	Ca	24	24	9	29	96	10	8	37	33	31	26
	Cd	39	9	202	36	87	15	40	68	27	65	41
	Co	26	20	22	10	23	7	0	0	22	15	21
	Cr	32	6	12	15	28	11	9	14	21	18	16
	Cu	105	7	66	23	43	22	12	13	21	38	24
	Fe	25	7	0	19	30	7	4	0	10	14	11
	Hg	73	59	68	27	183	82	96	38	99	79	73
	K	37	17	26	38	34	25	11	0	28	26	28
	Li	31	16	11	25	28	41	16	11	29	25	26
	Mg	19	6	15	10	29	0	13	17	29	16	17
	Mn	55	69	71	135	190	156	36	135	34	106	71
	Mo	31	40	22	191	20	19	94	17	21	56	24
	Na	42	16	0	30	84	38	20	19	135	33	32
	Ni	27	5	18	24	35	5	0	13	24	18	19
	P	52	11	26	39	77	31	21	37	21	38	32
	Pb	25	0	10	40	74	15	10	23	24	26	25
	Sc	30	16	10	34	26	7	7	2	22	20	18
	Sr	20	10	0	19	85	10	0	47	17	25	19
	V	24	18	13	12	18	14	22	21	24	20	20
	Y	22	14	5	23	18	0	0	6	22	13	16
	Zn	77	25	14	20	35	21	35	20	25	32	27
	C	21	19	8	83	43	19	2	37	35	31	23
	S	103	61	89	120	151	117	83	102	6	105	104
	LOI	15	0	14	69	34	17	0	10	31	21	17
Reservoir	Mean	40	20	31	48	71	29	28	32	31	40	33
	Median	30	16	14	30	43	19	13	20	24	30	25

25th percentile		13	x≤ 25th percentile
50th percentile		24	25th percentile <x< 75th percentile
75th percentile		40	x≥ 75th percentile

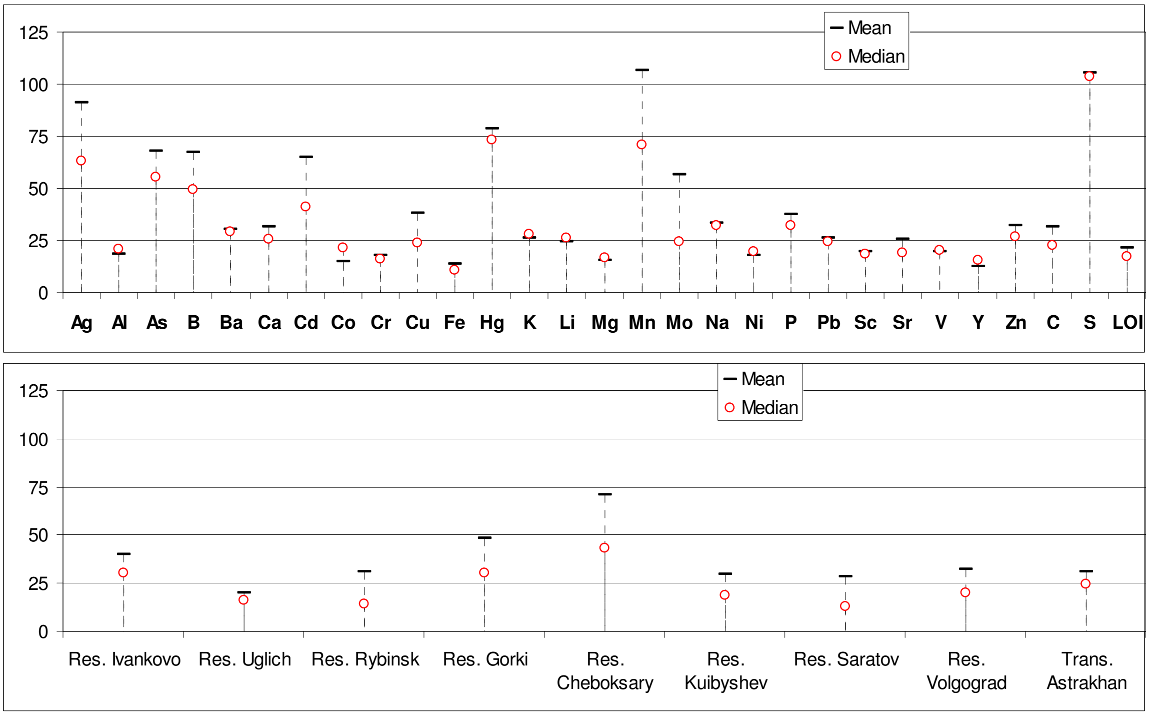
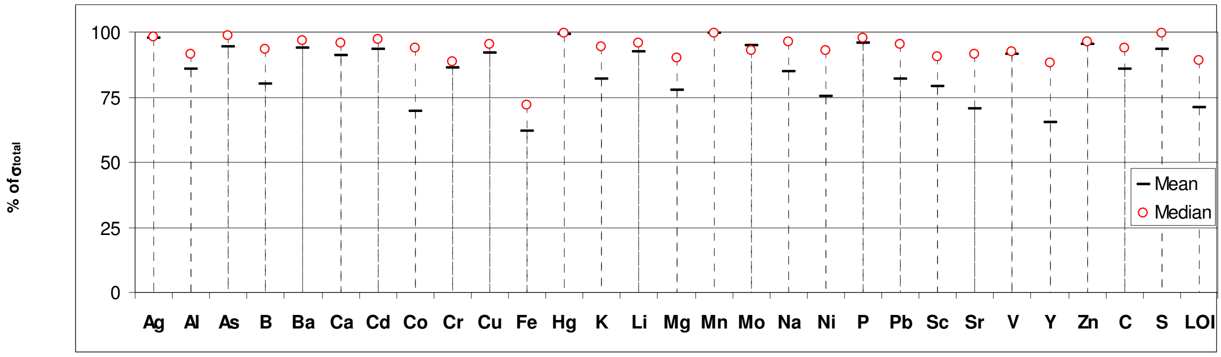


Figure 42 ‘Sampling’-variance as a function of the measured parameter and the sampling-location.

% of σ_{total}

	Parameter	Res. Ivankovo	Res. Uglich	Res. Rybinsk	Res. Gorki	Res. Cheboksary	Res. Kuibyshev	Res. Saratov	Res. Volgograd	Trans. Astrakhan	Element Mean	Element Median
	n	8	7	4	8	8	6	7	8	8		
	Ag	99	96	98	99	100	98	98	99	91	98	98
	Al	95	92	73	92	91	85	87	63	94	86	91
	As	99	68	95	99	100	95	99	99	95	94	99
	B	49	0	96	99	98	93	99	93	93	80	93
	Ba	96	97	87	98	99	97	87	98	88	94	97
	Ca	96	96	78	97	100	82	75	98	98	91	96
	Cd	97	71	100	97	99	85	97	99	95	93	97
	Co	96	94	95	80	95	70	0	0	95	70	94
	Cr	97	61	86	90	97	84	78	89	94	86	89
	Cu	100	70	99	95	99	95	86	87	95	92	95
	Fe	96	69	0	94	97	72	50	0	82	62	72
	Hg	100	99	99	96	100	100	100	98	100	99	100
	K	97	88	94	97	97	94	77	0	95	82	94
	Li	97	91	83	96	97	98	91	81	97	92	96
	Mg	93	62	90	82	97	0	86	92	97	78	90
	Mn	99	99	100	100	100	100	98	100	98	99	100
	Mo	96	98	93	100	92	91	100	89	93	95	93
	Na	98	88	0	96	99	98	92	91	100	85	96
	Ni	97	58	93	96	98	55	0	87	96	75	93
	P	99	83	96	98	100	97	94	98	94	96	97
	Pb	96	0	82	98	100	90	81	95	96	82	95
	Sc	97	90	80	98	96	67	67	23	94	79	90
	Sr	93	79	0	93	100	79	0	99	91	70	91
	V	95	92	86	84	92	88	94	94	95	91	92
	Y	95	88	56	95	93	0	0	63	95	65	88
	Zn	100	96	89	94	98	94	98	94	96	95	96
	C	94	93	72	100	98	93	24	98	98	86	94
	S	99	98	99	100	100	100	99	99	48	94	99
	LOI	89	0	87	99	98	92	0	78	97	71	89
Reservoir	Mean	95	76	80	95	97	82	71	80	93	86	94
	Median	97	88	89	97	98	92	87	93	95	86	94

25th percentile	87	x≤ 25th percentile
50th percentile	95	25th percentile <x< 75th percentile
75th percentile	98	x≥ 75th percentile



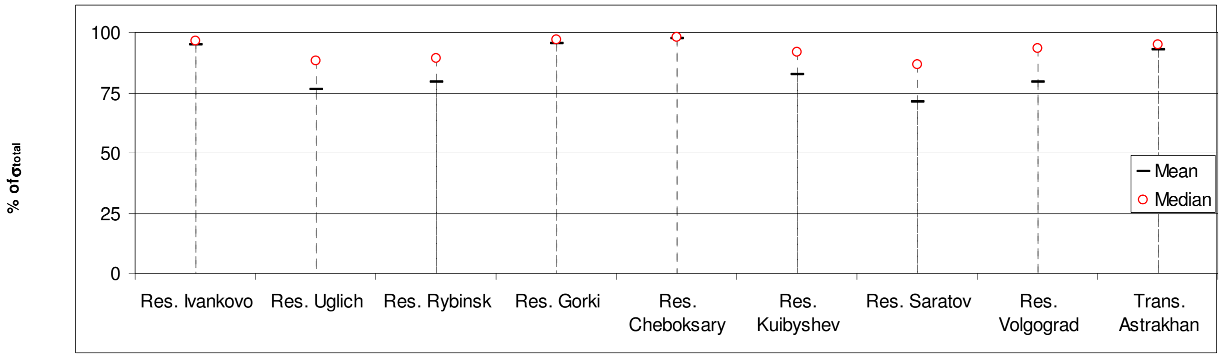


Figure 43 Percentage contribution of 'sampling'-variance to the total variance as a function of the measured parameter and the sampling-location.

To make a long story short, the results are the same as in any study accounting for sampling errors of soils/sediments – cf. Jenkins et al 1996 and footnote[69]. The errors attributable to the sampling account for more than 90% of the total error[83] – and QA-plans that rely on measurement uncertainty alone[84] (‘*first generation data paradigms*’ (Crumbling et al. 2003)) are nothing but a ‘nice’ try.

As already mentioned in footnote[82] a more rugged experimental design would be desirable to allow for a thorough statistical interpretation (cf. Minkkinen, 2003), while the needed three-dimensional design would be almost unfeasible, and it remains questionable whether the extra-information would be of much value for most practical questions. As described in Figure 40 the only way to ascertain the various types of ‘errors’ is to subtract ‘known’ or calculated (combinations of) ‘errors’ from the overall experimental variance. In case of a three-dimensional design, needed to fully describe a three-dimensional lot, this would result in at least the duplicate analysis of 30 samples (samples per target*dimensions: ≥10*3) for a given target (Figure 38, design A), or the duplicate analysis of 60 samples (targets*samples*dimensions: ≥10*2*3) for a single one-dimensional geometry (Figure 38, design B). Even if the measurement uncertainty is known, thus eliminating the need for duplicate analysis, **the costs for just making the sampling error of the transects along a river fully interpretable by (robust) ANOVA[85] - i.e. to address complex questions with a known uncertainty - are enormous: at least ten statistically distributed transects, each consisting of 60 samples would be needed.**

The ‘only’ cost of not doing that, is having to deal with a combination of ‘sampling errors’ accounting for any kind of heterogeneity along a sampling geometry – ranging from ‘natural’ (i.e. geochemical) to ‘home-made’ (i.e. introduced by the sampling itself), with no chance to quantify and explain their respective contribution – and a lot of sampling plans rely on even lower amounts of duplicates, without facing major problems.

E.g. recent U.S.-EPA as well as NAVFAC sampling schemes for sediments (and other compartments) typically demand taking duplicate samples at about 10% of the sampling locations to quan-

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[83] The separately calculated FE/GE is of course also a sampling-error, and should be added to the remaining error, while in fact it would not make that much difference whether the sampling error accounts for 90% or 95% of the total error.

[84] If only they would… one can still find numerous studies relying on a meaningless measurement-precision!

[85] Since ANOVA can be very misleading if outliers are present (while it is quite robust against violations of its other assumptions, like normal distribution within the groups and homogeneity of their variances and covariances) and on the other hand outliers are quite common in geochemical sampling some authors propose the use of so called robust ANOVA (more robust, but less powerful) – cf. Ramsey et al. (1992)

tify ‘sampling precision’. Little, compared to the here used 20+%; much, compared to numerous studies with none, but most obviously enough to address their objectives.

The reasons have been mentioned in footnote[65]: their results have to be ‘bullet’- (or at least ‘court’-) proof, and the basic questions addressed are usually quite ‘simple’ – ‘is there an elevated concentration of ‘xy’ in a given area of a compartment and can it be assigned to a cause?’ Any deviation from ‘simple’ questions – i.e. questions addressed by single samples (e.g. the ‘interpretation’ of a profile) instead of a multitude of statistically treated samples (e.g. the mean concentration of an area) – would require a profound knowledge of possible shortcomings and the need to account for them.

To say it oversubtle: nobody would base any kind of remedial action (‘simple question’) on most sampling schemes used to address academic questions (‘complex questions’).

Going one step further eventually leads to eternal frustration:

Apart from the approx. 6% of cases (combination of measured parameters and transects) where there is *'no'* 'sampling'-error – i.e. the experimental variance can be explained by the error-contribution of the chemical measurement and the short-range-heterogeneity error (CE_1; the only sampling-error that can be calculated based on the properties of the sampled lot) alone – which are statistically sound, taking the ratio of the error-contributions into account[86], **this isn't even half of the truth**:

- The sampling-experiments are conducted under repeatability conditions – anybody familiar with round robins (i.e. experiments under reproducibility-conditions) knows that already this reflects just about half of the truth. Repeatability conditions in chemical analysis– i.e. one material, one method, one analyst and instrument – differ from reproducibility conditions – i.e. one material, one method, different laboratories – by about $\sigma_{\text{reproducibility}}/\sigma_{\text{repeatability}} = 2$! (cf. Boyer et al., 1985) – and nothing changed until than. Sampling being fundamentally different would be a minor miracle…
- The above calculation just addresses the **sampling precision!** As has been discussed in Chapter 2.4.1.1 (p.81ff.) nobody is interested in 'precision', but instead in the performance according to a 'conventionally true' content of a lot – i.e. sampling error as well as analytical error can be expressed in terms of two components, a random and a systematic. When calculating the expanded uncertainty of a chemical measurement – i.e. the analytical performance towards a 'conventionally true' value – one finds precision to be the least important error-contribution that moreover can easily be overcome by repetition.

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[86] In fact, this is a pure 'artifact' of the calculation and cannot be interpreted as the absence of a sampling error. Firstly, CE_1 – which is larger than the chemical measurement error in most cases – is also a sampling error, and secondly all discussed errors are idealized described by a normal distribution function – i.e. by a mean and its variance. 'Fixing' one ore more of these errors to its mean (as done here) unavoidably leads to the over- **AND** under- representation of the error(s) allowed to fluctuate according to their distribution. Provided a large enough number of observations, the net-effect is zero, but it can be utterly 'wrong' – i.e. deviating from the mean, but still within its (multitude of) variance – for a single case. For known distribution functions, their contribution (as well as their statistical presence, or absence) can be calculated: $P \propto \frac{mean_1 - mean_2}{\sqrt{\sigma_1^2 + \sigma_2^2}}$.

Table 15 Precision (RSD [%]) vs. Correctness (expanded uncertainty) – insinuating 'state-of-the-art'-measurements for soils/sediments – cf. Chapter 2.4.1.2, p.85ff.

Calculated (expanded) uncertainty	*Ag*	*Al*	*As*	*B*	*Ba*	*Ca*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	Hg	*K*	*Li*	*Mg*
Mean RSD [%]	9	4	6	14	2	2	5	2	2	2	2	*1.6*	5	3	2
MEAN expanded u CRM (extractable) [%]	34	16	21		12	6	17	8	12	8	8	20	18	18	9
MEAN expanded u CRM ('total') [%]	35	16	24	46	14	8	26	16	14	12	9	20	16	15	9
Factor (RPD->u) extractable	4	4	3		6	4	3	5	5	4	4	13	4	6	4
Factor (RPD->u) 'total'	4	4	4	3	7	5	5	10	6	5	4	13	3	5	4

Calculated (expanded) uncertainty	*Mn*	*Mo*	*Na*	*Ni*	*P*	*Pb*	*Sc*	*Sr*	*V*	*Y*	*Zn*	*C*	*S*	***Median***
Mean RSD [%]	1	5	5	2	2	2	3	3	3	2	2	3	9	
MEAN expanded u CRM (extractable) [%]	6	19	22	9	6	9		9	13		9			
MEAN expanded u CRM ('total') [%]	9	29	17	15	22	15	20	15	16	24	12	10	33	
Factor (RPD->u) extractable	4	4	4	4	4	5		3	4		4			4
Factor (RPD->u) 'total'	6	6	3	6	13	8	7	6	6	15	5	3	4	5

I.e. on our way from measurement 'precision' (random errors) to measurement 'correctness' (random + systematic errors) we're facing a factor of about 4 due to systematic error contributions largely beyond our control (cf. Chapter 2.4.1.2, p.85ff.), and there are no reasons to believe this could be any better in sampling – while there are lots of reasons to fear it being worse. Keeping in mind, that sampling-validation is more or less non-existent in environmental-geochemistry – and so systematic errors simply cannot be addressed to date, one has to accept that: WE – i.e. anybody in this business – are strictly tangled in the middle of nowhere.

'The desire of controlling accuracy without controlling sampling correctness is certainly the worst judgment error that a person can make. It's a direct departure from logic.' (Pitard, 1993)

Consequently, the circle closes in, and we are back at the beginning of this chapter:

'At present, for the sampling of almost anything, there's a protocol regarded as best practice in that field. In contrast, there is an almost total lack of quantitative information about how well these protocols perform. …most of the problems of assessing sampling uncertainty can in principle be addressed by methods similar to those used for analytical uncertainty. In practice there are often considerable difficulties because of the sheer size (and often the financial value) of the sampling target. Moreover, there is an understandable lack of enthusiasm for rousing the sleeping dogs of sampling when there's a fair chance of being severely bitten. Nevertheless, unless analytical chemists can address these problems, we cannot give the customers what they really want.' (Thompson, 1999)

2.5.5 Sampling Error – a practical approach towards ‘unknown’, moving targets

To stay within the ever popular picture of regarding an analysis as some sort of shooting at a target: **We know how confident we can be hitting a target presented to the measurement system** (expanded measurement uncertainty of the sample)**, we even have some basic idea about the movement of the target presented to us** (sampling precision)**, but we do not know if we are shooting at the right target** (sampling bias)**.**

It is like traveling to a place, knowing the correct temperature (measurement) and its fluctuation (precision), but not knowing if it is measured in °C or °F or any arbitrary unit (bias). The best way to answer the question ‘what clothes to pack’ is by throwing dice.

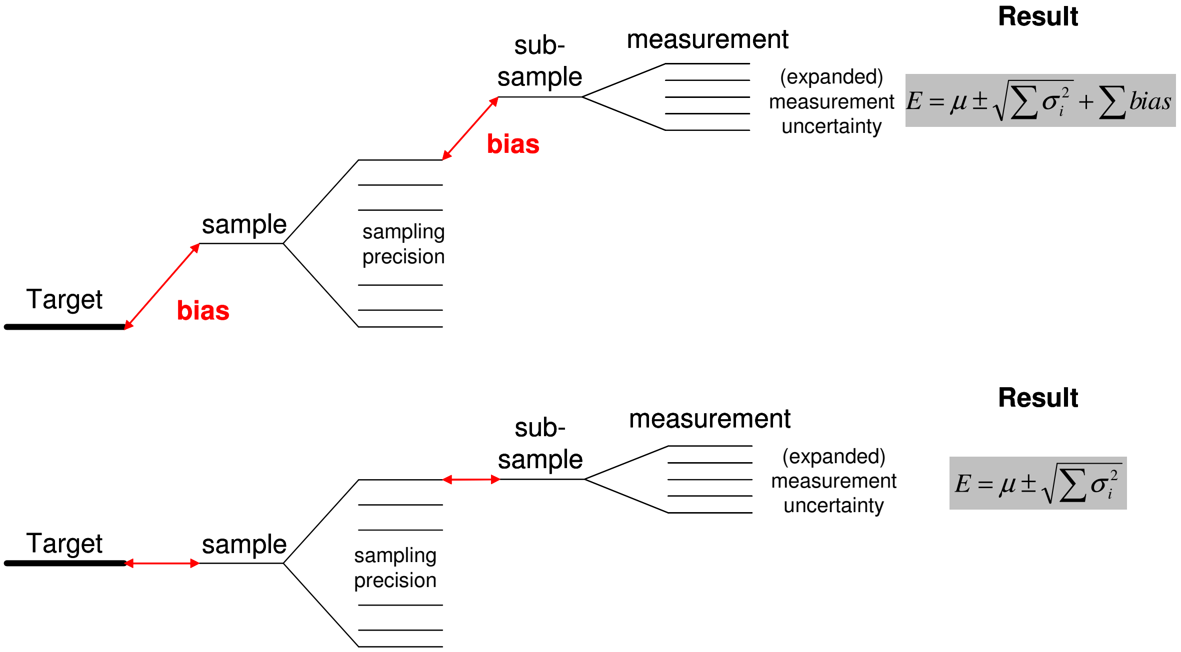

Figure 44 Expected value (E) of a sample average of a biased and an unbiased measurement process (μ=true value of interest; σ=precision of a single step)

However, as soon as one has the additional information about the correct temperature at his place of residence, measured exactly the same way, the chance to pick the right cloths increases drastically – unless one still relies on throwing dice…

Therefore, the idea is, as long as one stays within a single framework affected by a **constant** – albeit unknown – bias, he can address any question based on comparisons of measurements. As soon as one leaves this framework, or attempts any kind of quantification over and above that, the amount of the unknown bias will control the liability and correctness of his results.

2.5.5.1 Expanded measurement uncertainty

Having read up to here, one might think of the expanded chemical measurement uncertainty (discussed in Chapter 2.4.1; p.77ff.) to be the least important – and least uncertain – information within the whole measurement process, while finding the whole idea of shooting quite precisely at unknown, moving targets a bit disturbing – and one can hardly contradict.

The expanded measurement uncertainty – i.e. stating the correctness of the analytical result within a given confidence interval – was the first uncertainty taken into account in QA-plans in environmental-geochemistry. The reason for this at first sight illogical procedure – assuring the correct shooting at a target, instead of assuring the target – is, besides the relative ease of calculating the measurement uncertainty under controlled lab-conditions, simply the fact that only a 'top-down' approach is able address questions concerning unexplained deviations statistically.

It reflects the confidence one can have in the measurement of the sample presented to the measurement-system – nothing more, nothing less. It bears no information about the variance and/or correctness of the sample, and initially does not allow for any conclusions regarding the target. Instead, it allows for the differentiation of samples, raising the need to explain differences greater than the expanded measurement uncertainty and assign them to a cause.

2.5.5.2 Precision

Sampling precision is the first step in making the sample representative for something. While the measurement uncertainty just expresses how correct an a priori undefined and meaningless sample can be measured, sampling precision expresses the variance of the (part of the) lot, the sample is to stand for.

Facing a mean sampling precision of about 40% (Figure 42), and contributions of the *short-range-heterogeneity-error CE_1* (also a sampling error) of about 7% as well as the measurement precision (neglecting Boron) between 1% and 9%, sampling precision is the dominating factor when addressing the variance of a sample, thought to be representative for a given sample support and the geometry used to derive the sampling precision:

$$\sigma_{total} = \sqrt{\sigma^2_{remaining} + \sigma^2_{CE_1} + \sigma^2_{analytical}}$$

$$\sigma_{total} = \sqrt{40^2 + 7^2 + 9^2} = 41.6$$

I.e. as has been shown (Figure 43) the sampling precision accounts for about 90% of the total variance –combining the sampling error ($\sigma_{\text{remaining}}$) and σ_{CE1} would account for about 98%.

Due to the experimental design discussed above, the sampling precision is not interpretable in any way – with the exception of the *short-range-heterogeneity-error CE_1* – since it combines all the errors (heterogeneities) addressed by the Theory of Sampling. Their respective contribution will remain unknown and any discussion whether, or for what reason, there is a difference between the measured parameters and/or the sampled transects is meaningless. Without the knowledge of what kind of error contributes to our variability, and what is controlling this error – the costs of being able to address these questions in full detail have been described (600+ samples in a controlled experiment!) – there is no other chance than 'pooling' the data, to obtain an 'average sampling variability' which will represent the most probable variance contributable to a single sample.

In case the chemical measurement precision is known, already a slightly better designed sampling experiment (≥ 10 transects, each consisting of ≥ 10 samples) would even allow for the use of (robust) ANOVA eventually finding statistically significant – though still not interpretable – differences in sampling precision for the parameters and/or locations measured[87], allowing for a little bit more differentiated picture (e.g. looking at Figure 42 one would expect to find differences between Ni and Mn, or the reservoirs of Rybinsk and Cheboksary).

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[87] Remember: the experimental sampling error (variance) also accounts for the geochemical heterogeneity at this point – while this is usually not an error, but in contrast one of the objectives there's no way to differentiate with such simple experiments – and e.g. this heterogeneity is likely to be different for different elements and locations

2.5.5.3 Bias

As well as measurement precision tells nothing about the correctness of the measurement – unless one relies on (the idea of) 'empirical' methods and assures the absence of bias-components within the individual implementation of the measurement-process, as done here – sampling precision tells nothing about the correctness of sampling. What's more: while in most cases there are generally accepted sampling protocols for a lot, there's not even the slightest chance to assure the individual implementation/conduction of this protocol to be unbiased – at least not with justifiable expenditure (cf. p.93f.).

In both cases, one has to deal with two different kinds of bias. On the one hand the bias between the accepted protocol (measurement or sampling) and its individual implementation, on the other hand the bias between this protocol and 'reality' – i.e. the correct sample or 'true' content. While the latter will always remain unknown – and any attempt to address this question will always be just an approximation; albeit often sufficient – but can be considered 'zero' by redefining the analyte or the target[63], the inability to address, let alone quantify, the first is barely acceptable.

Even though for 'traditional' sampling targets like soils and sediments long-time experience suggests the protocols – and most of their implementations – to be relatively robust against e.g. sampler-related influences and have been successfully used to address basic questions[88], the situation is far from satisfying.

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[88] E.g., at least in Germany it is common practice for a farmer to take soil-samples on his field(s) – according to a more or less standardized protocol provided by an analytical laboratory – and have them analyzed in order to obtain recommendations about e.g. the use of fertilizers. There is no reason to reject this procedure – use of a sampling-protocol with unknown bias by an 'unqualified' person – since it simply works satisfactorily.

The reliance on presumably weak sampling plans and protocols is largely based on these kinds of scenarios, where experience ostensibly shows the adequacy of simplicity, thereby completely overlooking the fact that neither of the involved parties is 'unqualified' or inexperienced – and the farmer acknowledging the measurement-result with a 'yeah, I knew', because of his knowledge of what's 'macroscopically' going on in his yard isn't just a myth. The concentrations of the measured analytes are at least an order of magnitude above any heavy-metal 'we' measure, and the questions addressed are simple 'what-if-then', based on at least one century of experience, instead of measuring some ppm of 'whatsoever' and feeling able to explain HOW this happened – while ,in the worst case, unjustifiably laughing at the farmer who just wants know WHAT happens…

His sampling is definitely not worse than ours, at best we're matching the routine-labs 'correctness', and our confidence in addressing more elaborate questions should account for that – while the need and asking for any kind of sampling-validation will neither come from the farmer nor 'us', but from questions of broader interest and the necessity to address them. Instead already a superficial look at sampling-schemes and protocols of e.g. industries dealing with 'natural material' tells 'us', where 'we' are standing – and 'they' are only asking very simple questions…

2.5.5.3.1 *Bias introduced by sampling and the sampling design*

Bias is generally introduced by:

1. **Sample collection, handling and preparation, sub-sampling, analytical process (van Ee et al., 1990)**
2. **Sampling design – e.g. non-random or discriminatory sampling, misrepresenting the sampled population by violating the rule of equiprobability (Taylor, 1996).**

2.5.5.3.1.1 Traditional approach

The traditional approach towards sampling simply considers the bias addressed by van Ee et al. (1990) to be (approx.) constant and as long as one stays within a specific framework of sampling- and preparation- methods, this unknown bias is thought not to affect the validity of the results or comparisons with other studies using the same framework. It is also thought not to affect the answers to practical questions, which are usually addressed by the comparison of a measurement with a fixed value of more or less ‘unknown’ origin – either a loosely defined ‘geochemical background’ or any other (regulatory) acceptance limit. Since these studies do not have to proof the validity of these (externally) defined limits, they just have to answer whether, and approximately how much above (or below) a given limit the contents of the samples are.

However, already a closer look reveals that the assumption of a (relatively) constant bias NOT to affect the results is more or less regularly violated:

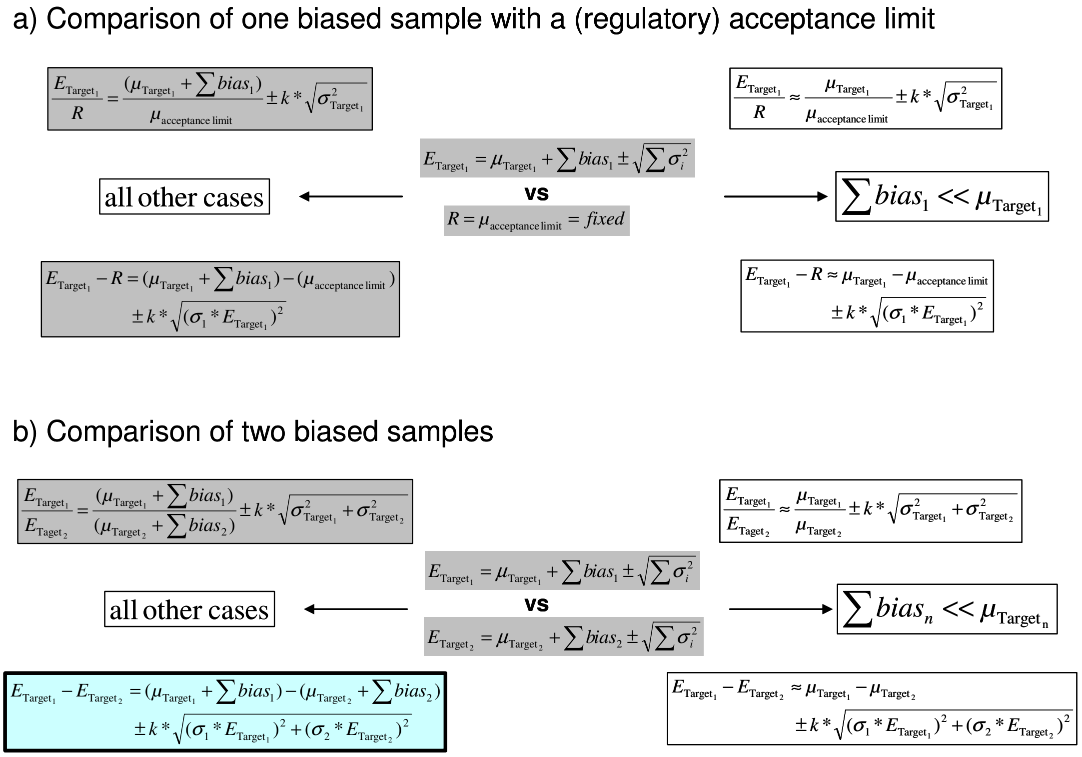

Figure 45 Implications of comparing (division and subtraction) biased samples with an acceptance limit (a), and other biased samples (b).

Apart from the incapable of proof scenario in which the bias would be markedly smaller than the true value of interest (μ), the unknown bias is liable to influence almost any comparison of the sample(s). However, there is **one important exception**: under the assumption of a (relatively) constant bias, subtracting the contents of two samples will lead to an (almost) unbiased result, since as long as the bias is constant any amount is eliminated by this operation!

Moreover, it is exactly this scenario that is used to address most practical questions – be it in the field of remediation: 'is the concentration above an acceptance level, and how much?' or that of agriculture: 'is the concentration of 'xy' sufficient, or how much of it has to be added[89]?

In no way is this approach 'scientific'. No matter how much one will measure and sample, without being able to quantify the bias, he will know almost nothing about the target of his study and/or its content. Already the simplest mathematical operations conducted with biased samples – in order to quantify or even just describe the investigated lot – will result in an enlarged uncertainty (expressed as variance) and an unknown contribution of the bias towards the results (Figure 45).

On the other hand it has been – and still is – exactly this 'unscientific' approach, which enabled 'earth-science' (in its broadest meaning) to address important questions when dealing with systems beyond its control and understanding. E.g., each and every method to estimate the fertility of soils and/or to calculate the amount and kind of fertilizers needed to achieve a better harvesting-result is 'unscientific' and merely based on early agreements – differing from country to country – and 'eons' of experience in what importance these – a priori and scientifically – meaningless sample-contents have for the (less than perfect understood) natural system.

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[89] One might object that these scenarios are equivalent to case a) in Figure 45, where the bias influences the result, but most of the times there is no such distinction between case a) and b), since the acceptance limits are usually defined on the basis of samples taken and treated by the same protocol – and thus most probably with the same amount of bias; hence one eventually ends up in case b).

2.5.5.3.1.2 Statistical approach

The statistical approach towards sampling in contrary relies on the idea of **all** bias components –as already addressed by Gy's Theory of Sampling discussed above (Chapter 2.5.2; p.95ff.) – NOT to be constant[90], but to be accounted for when calculating the sampling precision using an appropriate design – the weaker the sampling, the more variance is envisioned[91].

Since sampling precision is the least detail needed to make a sample meaningful and representative for anything but itself (Chapter 2.5.5.2; p.134) and there is a lack of generally accepted guidelines to address the sampling-bias itself (Chapter 2.5.1; p.93ff.) there is no practical difference whatsoever between the two approaches. The traditional sampling approach still has to account for sampling precision and the implications of the sampling plan[92] towards a **sound description of the sampling lot**, while within the statistical approach these are integral parts, and no artificial distinction between sampling and the sampling plan is made.

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[90] In fact a constant bias is not very likely when looking at Gy's Theory of Sampling, and Pitard (1993) simply states that there is no such thing as constant bias – it may be negligible or small but due to the particulate structure of most sampling lots it will neither be 'zero' nor constant.

[91] This holds true for any reasonable and rational sampling, i.e. statistically sound sampling – otherwise oversimplification would be the solution for all problems: less samples → less variance…

[92] In fact, the sampling plan (design) is usually considered the most important part already in the traditional approach towards sampling as will be discussed later.

2.5.5.3.2 Will sampling-bias have a major effect?

In the above said the importance of soil-samples in addressing agricultural questions has been stressed out and the fact that even under these unfavorable conditions – lot less homogeneous than sediments (cf. Chapter 2.5.3.4; p.113ff.); coarser grain-size (< 2 mm by definition) than sediments (here: < 20 µm by definition) hence e.g. an inherently larger Materialization Error; etc. – revisable results are obtained, gives rise to be optimistic; at least when keeping the questions straightforward. In both cases bias is delimited by the fact that not 'the' soil or 'the' sediment – both of which are fairly undefined – is addressed, but instead a fraction of the lot thought to be of major interest – e.g. the fraction that is considered to be the chemically and biologically (most) active (cf. Chapter 2.5.3.1; p.105ff.).

On the other hand, since the valuation of soils for e.g. agricultural use is not simply based on their chemical properties, but instead also on their physical (mechanical) properties, the coarser grain-sizes (as well as the grain-size-distribution) are of equal interest as the 'fines' – thus traditionally the sampling of the fraction < 2 mm. Moreover, one of the most important questions addressed when chemically analyzing soils is, 'what concentration of 'xy' is available to a plant compared with what it usually needs?' This is best answered by analyzing the 'bulk' soil, since it makes no difference whether there's too little 'xy' because of a small clay ('fines') content of the soil or because of small concentrations within the clay ('fines') fraction. Therefore, the definition of 'soil' as the fraction < 2 mm made – and makes – sense, sediments were defined the same way, and especially in the U.S., sediment-studies are still conducted using 'bulk'-sediment.

Sediments are used to address all kinds of questions; but most of them would require another definition of the sampling target 'sediment'.

Table 16 **Examples of questions addressed by sediment-studies and the preferable fraction to be used.**

question	fraction
general condition of the aquatic system	'chemical active' fraction - i.e. 'fines'
interaction water-sediment	'chemical active' fraction - i.e. 'fines'
chemical sediment quality	depends on definition
sediment quality towards...	depends on target
...e.g. plants	bulk
...e.g. sediment ingesting benthic organisms	'fines'
balancing transport of 'xy' through riverine system	depends on river sediment carrying capacity (including bed-load?)
amount of 'xy' that is stored in the sediment	bulk

As it turns out, the major constraint is grain-size, grain-size distribution – i.e. the particulate nature of the sampling lot – and the chemical properties of the respective grain-sizes, since different fractions of the 'sediment' are able to address different questions, while their inter-comparability is severely delimited – and no scientifically sound borderline can be drawn between them.

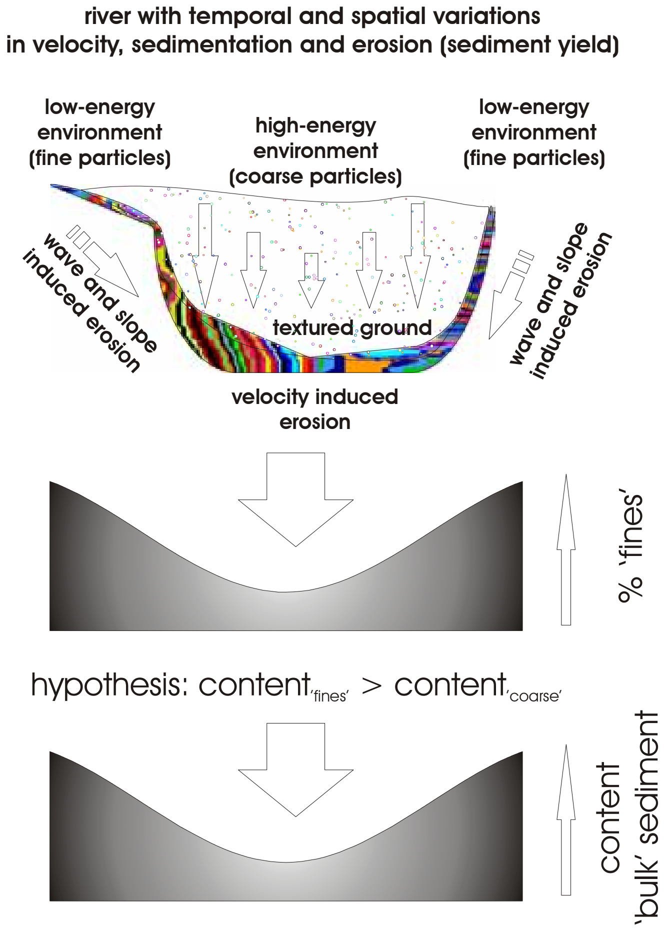

Figure 46 Theoretical grain-size and concentration-distribution of the bulk sediment under idealized conditions.

Unlike for soils, where the grain-size distribution can be considered fairly uniform over a given area[93] – as long as the parent-rock and weathering-conditions are uniform – grain-size-distribution in aquatic environments merely depends on sedimentation-conditions, which are liable to small-scale changes. E.g. within the sampled transects the grain-size distribution changes from almost exclusively 'fines' under low-energy-conditions near the shore to almost no 'fines' under high-energy conditions in the center of the fairway. In case the simple sediment-model of chemically active 'fines' and more or less inert 'coarse' fractions isn't too far from reality, the chemical properties of the 'bulk' sediment will be controlled for the greater part by sedimentation-processes (cf. Figure 46).

That is to say, necessarily we already fail to address our sampling target!
We simply define it – a priori not knowing, how severely these definitions will influence the answers towards the addressed questions.

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[93] One might find some discrepancy between the here stated advantages of soils (grain-size-distribution more homogeneous than for sediments) and the above-mentioned disadvantages of soils (lot LESS homogeneous than sediments cf. Chapter 2.5.3.4; p.113) – while in fact this is only a matter of scale: 'Soil-chemistry' usually tries to describe a (strongly) limited area (e.g. a field), while 'sediment-chemistry' usually tries to describe much larger areas (e.g. the entire catchment area of a river).

When sedimentology started, it relied on the simple – and undoubtedly correct – assumption, that the finer the sediment-fraction, the more chemically active and important for the investigation of sediment-water-interactions it will be. Already than the decision to use the fraction **< 2 µm** was rather based on definitions (< 2 µm ≡ 'clay'; i.e. the fraction 'claystones' (or 'shales' – the majority of sedimentary rocks; in other words large amounts of nowadays earth surface) are composed of) than on proven implications towards the 'aquatic system'. Further changes – at least in Germany – towards the fraction < 20 µm were merely based on practical reasons – e.g. ease of separation (Müller et al., 2001) – to some extent justifiable by the sediment-carrying-capacity of rivers of the humid climate region, where a distinction between 'coarser' bed load and 'finer' suspended load is possible in a narrow grain size interval between 0.032 - 0.016 mm (32 – 16 µm) (Müller and Förstner, 1967; Müller et al., 2001).

Using a fraction more or less readily attributable to the suspended load of a river works perfect, as long as one wants to (not to say: needs to) profit from the homogenization conducted by 'nature' (c.f. Chapter 2.5.3.4; p.113ff.) and attempts towards risky quantifications within the lot – i.e. balancing flows, calculating total amounts and so on – are avoided. As long as a realistic assumption of the sampling-variance for the chosen 'fine' fraction is considered – i.e. accounting for e.g. remaining grain-size-effects – at least the first three questions of Table 16 can be addressed; AND often adequately quantified, even without a complete knowledge of the grain-size-distribution and the chemical properties of the respective fractions.

On the other hand, this systematic bias also cannot be overcome – but considerably restricted. As long as the in most cases correct assumption of 'finer' fractions being chemically more active and having higher (metal) concentrations than 'coarser' fractions holds true, any sample of any fraction will be biased, while the calculation of the sampling variance out of samples derived under different sedimentation conditions should allow for this bias to be considered and kept in check. Any fraction would be able to address the first three questions of Table 16, while the experience within the field of sedimentology shows us that the 'problems' – expressed as variance of a sample – increase with increasing grain-size and Gy's Theory of Sampling tells us exactly the same, even without the need for any assumptions about the chemical properties.

One simply has to choose what question(s) to address with an uncertainty he will know afterwards (or in best case after a pilot-study) at a given expenditure. While the 'bulk' sediment – representing all fractions of the sediment – is of universal applicability and in principle able to address any question attributable to this sampling lot, it is also the most uncertain – or the one connected with the most expenditure. Finer fractions are less uncertain – i.e. their contents are less variable – but also less universally applicable. As mentioned above grain-size effects won't go away, irrevocably how 'fine' the chosen fraction may be – they can only be delimited, with the fraction < 20 µm as a reasonable and practicable compromise, at the cost of not being able to address any question concerning the bulk sediment or implications towards it.

Using an arbitrarily chosen ‘fine’ fraction ads an unknown amount of bias to the study with respect to ‘reality’ – i.e. ‘the sediment’ – while there’s no bias with respect to simple questions addressed (the first three issues of Table 16) within a given framework as long as one accounts for sampling variability and no attempt to address further questions is made.

So as sampling variability accounts for the heterogeneity of the lot – i.e. the chosen fraction – for a given geometry, it also accounts for any systematic bias attributable to a sample within a given framework, while possible bias due to the individual implementation of this framework will remain unknown (cf. Chapter 2.5.5.3, p.135f.) and can only – albeit with some decency – hoped to be noticeably smaller than the sampling-variance.

The crucial point is to find a geometry that will best express this variability – otherwise there will be bias. E.g. looking at the longitudinal-profiles along the Volga River depicted in Chapter 4.2 (p.186ff.) one can find stretches with apparently ‘zero’ variance over hundreds of kilometers, while a single transect shows about 40% of variance. This is simply attributable to the fact, that the samples apart from the transects are taken under more or less the same conditions – since the sampling was conducted in search of fine-grained sediments under low-energy-conditions. Hence the samples over a given stretch of the river under (approx.) comparable sedimentation-conditions, should be (approx.) equally biased, representing one specific stratum of the river[94] – already failing to represent a given grain-size-fraction (also a stratum) over the rivers width.

As with grain size it is again the experimenters decision what geometry the samples are to represent – and trying to describe the variation of parameters along the River Volga, the variance (inhomogeneity) over the rivers width is considered to be appropriate.

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[94] One could argue that under these circumstances, an (approx.) constant bias could be calculated and added/subtracted to the sample – but this could neither be justified statistically (cf. 2.5.4; p.121ff.) nor rationally, since grain-size-distribution is only the most obvious contributor to sample-bias and variability, but not the only one. Variability as calculated here should quantify all ‘errors’ – i.e. an averaged bias – addressed by Gy’s Theory of Sampling, but without being able to quantify or even assess their respective contribution any attempt to interpret this variability would qualify as unjustifiable speculation. On the other hand, a statistically more sound sampling design could reveal differences between distinct stretches of the river according to sampling-variability (c.f. 2.5.5.2, p.134) allowing for a more detailed picture of the river. E.g. it is very likely for the Lower Volga (downstream of Volgograd) to be less variable with respect to grain-size-distribution and thus content of the ‘fines’, but it is beyond any statistically sound proof.

In other words: by redefining the target and accounting for sampling-variance, bias with respect to the ‘new’ target (and a given geometry) is accounted for and will not affect the findings. However, it also reveals the limitations.

E.g., Figure 47 depicts the implications of bias and/or sampling variability on the calculation of enrichment factors – highlighting the most important point: already the consideration of the simplest form of sample- (and sampling-) variance shows the improbability of many ways towards an interpretation, even if sampling bias can (mathematically) be ruled out.

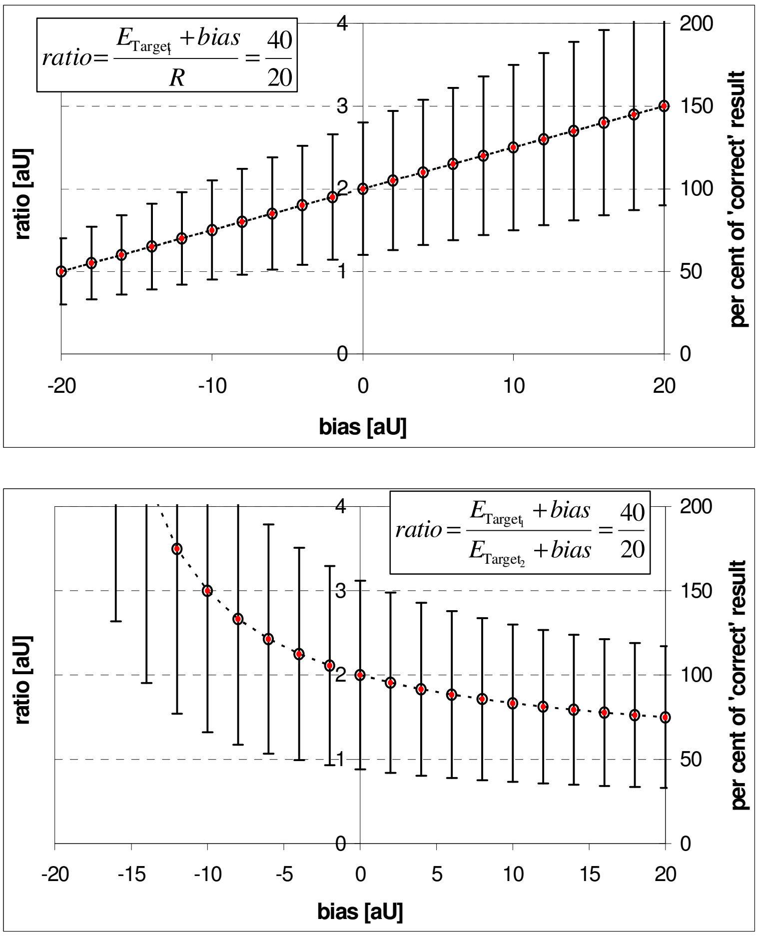

Figure 47 Comparison (division) of a sample with an acceptance limit (R) and a second sample assuming different (but constant) amounts of bias. The error bars indicate the sampling variability (<u>1σ</u>) underlying this study according to the formulas given in Figure 45.

A defensible answer can only be given in case the in-between-sample-variance is larger than the variance (uncertainty) introduced by the complete measurement-process – in case this cannot be assured either the question cannot be answered, or the questions addressed have to be restricted/simplified. There are only two scenarios within which one is able to address and quantify any question:

1. ***The samples are NOT meant to represent anything but themselves.***

Within this scenario one wouldn't have to account for the sampling variability – which is 'only' necessary to make a sample representative for a specified lot (sample support) – and, assuming an accepted rational sampling protocol, the comparison of samples could be conducted relying solely on their (expanded) measurement uncertainty, at the cost of the results being valid simply for the investigated samples and nothing else. In fact, this is a scenario rarely dealt with in environmental geochemistry, while frequently conducted tacitly – e.g. 'interpretation' of a profile without knowing the variability within its 'distinguished' parts. This is not to say that this scenario is worthless – on the contrary if one's interested in small-scale spatial variations it's the scenario of choice – but it's not able to address any questions over and above the investigated samples; albeit often used that way…

2. ***The differences of the parameter(s) of interest of the investigated samples are larger than their combined uncertainties, or these uncertainties can be delimited by 'over-sampling' – i.e. the use of a multitude of samples for describing a single location/characteristic.***

Ignoring the trivial case, where the difference between two samples is deliberately larger than any uncertainty of the measurement process bound to them – e.g. comparing the measurements of a background-site with those of a (highly) polluted area –, the second scenario is more common and can in principle deal with any amount of uncertainty – at the cost of having to use multiple samples; i.e. being spatially (and/or temporally) less precise and more expensive. It's exactly the same scenario frequently used in analytical chemistry, e.g. in Solid Sample Graphite Furnace AAS which is less precise in analyzing a single sample than other techniques based on digested samples, but can compensate this weakness by measuring more samples with less expenditure, resulting in at least comparable correctness of the results[95].

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[95] This example was chosen, since Solid Sample Graphite Furnace AAS (SS-GF-AAS) has to deal with exactly the same problems as we have in the case of sampling. SS-GF-AAS is less precise than e.g. GF-AAS of digested samples using the same detection-system, since it is operated with much smaller amounts of the sample (several milligrams) and is thus affected by its small-scale-heterogeneities. In order to characterize the sample with the same amount of un-

The same setting is used when addressing questions in ‘the real world’, i.e. questions beyond the analyzed sample that have to be answered in a defensible way, be it for e.g. remediation, site-description or in water-chemistry – not to speak of industrial quality control or receiving inspection of natural materials – ‘**over-sampling’**. The effect of ‘over-sampling’ is best clarified looking at the percentage contribution of the geochemical variability – i.e. the variability not explained by the measurement process – towards the mean of all analyzed samples (Table 17).

Somewhere in between these two scenarios are the above mentioned early classification-systems in sedimentology: A priori they are not trying to address academic questions, but to simply give a rough and sound estimate of the actual state of the sediment (aquatic system) – merely differentiating between a ‘good’ or a ‘bad’ condition. Comparing two samples based on e.g. their respective I_{geo}-classification (c.f. Figure 37); ignoring differences of ± 1 class is valid and justifiable, while it would be already a ludicrous attempt to differentiate between two samples with a measured difference of say 100% (cf. Figure 47). Estimating roughly the combined amount of uncertainty bound to a single sediment sample[96] and comparing it with these classification systems, reveals why they were (and still are) useful: they simply allow for 100% sample-uncertainty within a net-uncertainty of the result of ± 1 class – by that way assuring a robust albeit not very precise answer.

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certainty as GF-AAS, it simply uses a multitude of repetitions and averages the results – which at least in some cases proves to be more (cost-)efficient.

Here we’re dealing with the small-scale-variability of the sampling lot and ‘simply’ would have to analyze more samples in order to achieve the same amount of uncertainty we would face when analyzing a larger part of the lot (i.e. having a different ‘sample support’ c.f. Chapter 2.5.2.1.3; p.102) – while the above mentioned US-EPA ‘TRIAD-approach’ (cf. footnote[64]) goes even one step further, questioning the necessity for ‘definite’ analytical techniques in analyzing samples far from being representative…

[96] $U_{sampe} = k * \sqrt{u^2_{measurement} + u^2_{sampling}} = 2 * \sqrt{20\%^2 + 40\%^2} \approx 90\%$

2.5.6 A way out of laughableness – a realistic uncertainty budget

As already mentioned (Chapter 2.5.3, p.104) varying sampling objectives require different kinds of samples and sampling efforts and the most important question is, how many samples are necessary to obtain a result with a given (un-)certainty – i.e. what kind of sampling (scheme) will be sufficient?

Unfortunately, no completely formalized sampling strategy is available – nor is there any chance for such strategies to be developed because of the a priori unknown variability (spatial, temporal, etc.) of most natural sampling targets and in most cases only an a posteriori evaluation is feasible. While the Theory of Sampling considers any sampling problem to be solvable without any error (see footnote[68]) financial constraints usually prohibit this – and for most practical issues 'representative' sampling is neither achievable, nor necessary as long as a realistic uncertainty budget is (can be) calculated and fits our needs[97]. I.e. the measurement process as a whole – with sampling and the adjacent sampling plan as the main sources of uncertainty, as discussed above – has to be 'fit-for-purpose', but not to be 'correct' as depicted for a simple example in Figure 48.

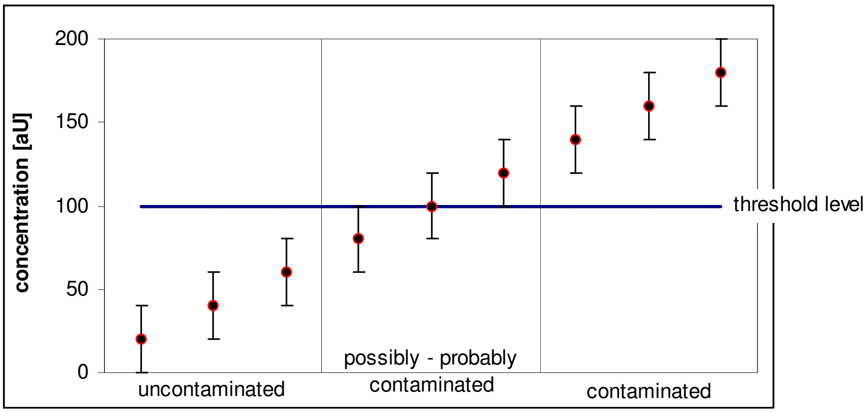

Figure 48 **Probabilistic classification of samples (or population means) referring to an (external) threshold level (error bars indicate uncertainty of the measurement process).**

While the (absolute) uncertainty is identical for all 9 samples (or population means) solely the three cases close to the threshold level wouldn't be 'fit-for-purpose' and would require additional sampling – although the measurements are as 'correct' as the others.

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[97] This of course only holds true for the commonly used qualitative 'definitions' of represantativness, while in fact this chapter is merely an (extended) discussion of the quantitative definition given by the Theory of Sampling (c.f. Chapter 2.5.2.1.1, p.98) based on the same principles.

Ramsey (2002) summarizes three basic types of criteria suggested to assure a measurement process to be 'fit-for-purpose' (FFP):

- **Relative precision of a measurement method** – typically, the relative analytical precision should be better than 10% (at a 95% confidence level). This is considered the most crude and insufficient type of FFP-criterion ('first generation data paradigms' (Crumbling et al., 2003)) as has been discussed above and e.g. led to the US-EPA TRIAD-approach (e.g. Crumbling, 2001).
- **Uncertainty of the measurement process** – typically, the uncertainty of the measurement process (including sampling!) '*should not contribute more than 20% of the total variance of the analyte across all the samples in a particular survey*' (Ramsey, 2002) – a rule of thumb based on practical assumptions and thus already a:
- **Balance between uncertainty and financial loss** – i.e. a balancing the costs arising from (additional) measurements (sampling) and the costs that may arise due to (wrong) decisions based on uncertain assumptions. In fact, one of the main impetuses that eventually led to the US-EPA TRIAD-approach, but an issue beyond the scope of this study[98].

Reliable (i.e. scientifically sound and defensible) answers can only be based on the latter two FFP-criterions. However the amount of **acceptable variance** introduced by the measurement process is of course fully 'arbitrary' as with any statistical acceptance and significance level, it is 'our' decision what amount of uncertainty (confidence interval, confidence level and so on) we are ready, willing and able to accept[99]. At best, the acceptable variance simply depends upon the consequences of making the wrong decisions; **apparently, the only reason for studies (not only) in the field of environmental geo-chemistry conducted without the slightest estimation, let alone understanding, of uncertainty: nobody cares, since there will be no consequences…**

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[98] On the one hand, simply an a posteriori calculation of the uncertainty of the measurement process is feasible, with no apparent chance to conduct an additional sampling in case of emerging limitations. On the other hand, the costs of any (potentially) wrong decision/explanation cannot be calculated, since any action taken (based on this study) is unlikely for several reasons. Hence, all calculations here are just used to discover and state the limitations of this study and to describe the Volga-sediments as reliable as possible within the given framework.

However with e.g. the Sampling Cost Advisor (SCA) an easy to use EXCEL-based '*software tool designed to facilitate the cost-effective and defensible evaluation of environmental sampling plans*' is available (http://www.hanford.gov/dqo/SCA.html) – great as it may be, these kind of tools are merely for designing sound sampling plans before conducting a study, rather than to reveal and overcome limitations and weaknesses of an already conducted sampling based on (statistically) less sound assumptions and/or practical limitations.

[99] E.g., in pharmacological studies or industrial processes involving big money (e.g. refining REE's) a confidence level of 95% is unacceptable – since already the confidence level is a compromise between analytical costs and possible costs of wrong decisions, which could be lethal (or costly) – while for most problems in case of routine analysis in the field of environment geochemistry no one would need to achieve a 99+% confidence level.

2.5.6.1 Basic sampling schemes and objectives

In many cases, the basic sampling objectives can be defined in terms of one of two basic conceptual sampling models (cf. p.:104):

1. **Sampling to estimate the average properties of a characteristic in a given area (e.g. average concentration of an analyte). →<u>Chapter 2.5.6.2; p.153ff.</u>**
2. **'Hot Spot' sampling (e.g. areas having high levels of contamination – i.e. above some level considered 'hot'). →<u>Chapter 2.5.6.3; p.156ff.</u>**

While the first conceptual model considers the characteristics of interest (e.g. pollutants) to be distributed over the entire site, the 'hot spot'-scenario is often associated with point sources of 'non-mobile' contaminants (spills, leaks, towns, etc.) and is used to find these localized areas of contamination. Not only are the underlying assumptions – whether based on prior knowledge or professional judgment – of the two models completely different, but also the implications of a particular sampling plan towards the results and the uncertainty (or representativeness) of the measurement process. 'Hot spot' sampling is trying to answer the question whether there are any red balls ('contaminated') in jar full of green balls ('uncontaminated') whereas the other conceptual model tries to describe the average weight (color) of the balls.

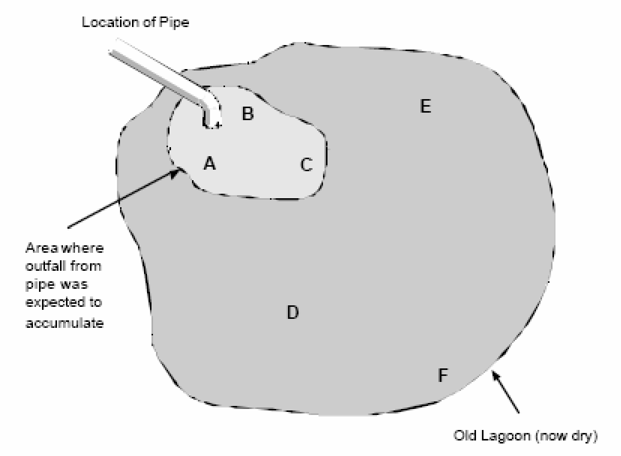

Figure 49 Site map for 'Old Lagoon' (EPA QA/G-5S see footnote[100])

E.g.: depicted in Figure 49 is the (hypothetical) site map of a dry lagoon formerly fed by a pipe. If the objective were to address whether the pipe has released a particular contaminant, the randomly located sites A, B, and C would be representative – in case the contaminants can be considered as relatively nonmobile. However if the objective is to estimate the average concentration level of the entire lagoon these data would be insufficient and not representative – and what is more: even when adding additional (random) samples (D, E and F) the results would be biased unless one corrects for the different areas represented by the samples.

In other words: The choice of an appropriate sampling model depends on characteristics of the site in question and upon the contaminants of interest at that site – an often overlooked fact, that severely influences the results since the wrong conceptual model will lead to 'wrong' results (i.e. results with an unknown bias).

In principle, there are two main categories of sampling designs[100]:

- **Judgmental sampling** – based on expert knowledge or professional judgment.

  Although judgment is indispensable in any survey and often comes – or at least should come – into play even within probabilistic sampling (defining the kind and size of sampling units; delineating homogeneous of heterogeneous areas; classifying sites into strata in order to reduce the sampling error) – with no apparent limitation of the judgment/knowledge to be used – '*this kind of knowledge is not allowed to influence the final selection of the particular locations of samples that are to be in the sample*' (Deming, 1950). It can be very efficient in small-scale surveys of well-known sites, but any assessment of uncertainty in the decisions is prohibited and no quantitative conclusions can be drawn, making it inapplicable under most circumstances.

- **Statistical (or probabilistic; probability-based) sampling** – based on known, proven (and revisable) statistical assumptions.

  Random selection of sampling units, so each member of the sampled population (compartment) has a known probability to be selected. **Only these kinds of design allow for statistical inferences about the sampled population to be made and lead to reproducible results within known uncertainty limits**.

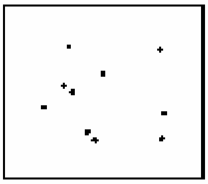

Figure 50
Simple Random Sampling
(EPA QA/G-5S see footnote[100])

The most simple, yet most fundamental probability-based sampling scheme is Simple Random Sampling, where the sampling points (or units) are selected using random numbers – e.g. using pairs of random coordinates – which provides statistically unbiased estimates of the populations mean, proportions and variability **and most statistical procedures for data analysis explicitly (or implicitly) assume the data to be an outcome of this kind of sampling design**. On the other hand Simple Random Sampling is not very (cost-) effective since it ignores any prior information about the sampling site – except for the expected variability of a given characteristic; needed to estimate the minimum sample size – and by random chance the sample points may not be uniformly dispersed, only to be overcome by a large number of samples – making it **the benchmark for other sampling designs but rarely the design of choice**[101].

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[100] For a comprehensive overview on sampling designs for environmental measurement data see e.g.: EPA QA/G-5S (Guidance on Choosing a Sampling Design for Environmental Data Collection; US-EPA (2002). http://www.epa.gov/quality/qs-docs/g5s-final.pdf

[101] This chapter by far oversimplifies sampling designs, as well as it omits sampling designs not feasible in our case (like Stratified, Ranked Set or Adaptive Cluster Sampling –all of which would need professional judgment, i.e. a

One way to overcome the weaknesses of Simple Random Sampling i.e. to assure the uniform coverage of an area (or time) plus being able to estimate trends, identify spatial (temporal) correlations or looking for 'hot spots' are systematic sampling designs as e.g. Grid Sampling, where the samples are taken at regularly spaced intervals, so that they are located according to a regular pattern.

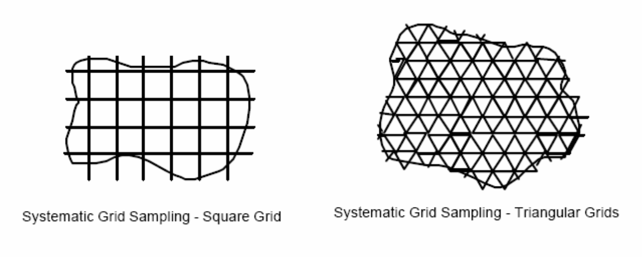

Figure 51 Grid Sampling
(EPA QA/G-5S see footnote[100])

From a statistical point of view, solely these two sampling designs – omitting any kind of judgment[102] – are capable to describe any site as unbiased and accurate as necessary; but with respect to expenditure and (cost-) effectiveness, they can result in an utter disaster when addressing most practical questions in the field of environmental geochemistry.

However, as already mentioned (Chapter 2.1, p.72) the here used sampling scheme turned out NOT to be fully probability based, mostly for practical constraints during the sampling campaigns:
Most samples (>70%) were taken near the right bank of the Volga at irregular intervals, so the sampling can be neither fully qualified as 'Simple Random Sampling', nor as 'Grid Sampling'. Planned as a Grid Design – usually considered the design of choice for pilot/exploratory studies of a site for which little or no prior information is available – the here used sampling design shows some characteristics of a Simple Random Sampling at stretches where the regular interval couldn't be kept (in other words, where we had to decide whether to take a sample at the 'wrong place' or no sample at all…), while calculating the sampling variability out of the 8 river transects should account for that, and arising limitations will be discussed in the results-section.

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degree of knowledge about the sampled site not available to date in the case of the River Volga) and is discussed in more detail e.g. in the above mentioned EPA QA/G-5S.

[102] Apart from the assumptions ('judgment' vs. 'educated guess') needed to calculate the necessary number of samples. E.g., the expected standard deviation can be estimated – as a last resort! – by dividing the expected range of the population by six: $\hat{\sigma} = \frac{Expected\ Maximum - Expected\ Minimum}{6}$ (by that assuming an rectangular distribution (factor 6), I.e. a conservative approach. However optimistic approaches (factor 3, i.e. a triangular distribution) are also used, but are far from being reasonable; e.g. the same assumption is used by the GUM for calibrated glassware if no further information on the stated error is available…).

2.5.6.1.1 *A cautionary word about composite samples*

Although an extensive literature about sampling designs and their known strengths as well as their shortcomings exists and (statistically) sound procedures to overcome the limitations are well documented[103], a lot of sampling schemes are simply limited by the budget and/or are conducted within a 'golden opportunity'-scenario – with no apparent chance for implementing a desirable probability based sampling scheme in extenso, let alone allow for more sophisticated multi-stage sampling schemes. This study is no exception, and one common answer towards budget-constraints – if the necessary number of samples to describe a site with a given confidence level is calculated at all – as well as other constraints is **Composite sampling**; albeit often simply used as an excuse for improper sampling[104] at the same time making things even worse.

In contrary to the here used grab samples – i.e. individual samples collected from a single location at a specific time – composite samples are physically combined and homogenized samples made of a series of discrete, equal specimens (aliquots) taken at one location and several depths (a vertical composite) or several locations and one depth (a spatial composite). The composting averages the individual samples thus reducing the intrinsic variability of the sampled lot and **can** produce an estimated mean as precise as the one based on the same number of samples used to make the composite sample – but at reduced analytical costs.

Even without considering an in-depth discussion about additionally introduced delimitation errors (e.g. how to assure the same location/depth?) and the far from being trivial task of forming a 'good' – i.e. homogeneous – composite[105] these samples are **only** meant to be representative of the mean composition of a vertical profile (vertical composite) or an area (spatial composite).

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[103] These procedures come at a cost: the need for (statistically sound) prior information. No matter how 'clever' the sampling design may be there's no way to avoid multiple-stage sampling schemes for comparatively unknown sites. I do not want to overstress the several times mentioned fundamental law of a result being either precise or certain, but there is no easy way out. At least no cheap one, since excessive (Simple) Random Sampling can solve any sampling problem… except that of the budget ;-)) and 'clever' sampling – i.e. the use of **statistically sound** prior information to it's fullest content – is unfeasible on 'terra incognita'.

[104] The use of too little samples to achieve a rational significance level for the results is often masked by (stating) the use of composite samples; implicating the (often necessarily unproved) assumption that they are as representative for the site as would be the corresponding number of individual samples used to form the composites. In order to prove their equivalence one would have to know the heterogeneity of the site, while in fact, this information is wiped out by the composting…

[105] In general composite sampling works best for relatively homogeneous media – while again homogeneity is a relative concept as has been discussed. E.g. liquids tend to be more homogeneous than solids and are typically good candidates for composting, especially since the thorough mixing needed to achieve a 'good' composite is usually quite easy to conduct. On the other hand composting solids is another story – some of the problems have been discussed in the above sections dealing with Gy's Theory Of Sampling – and already technical difficulties can generate large, unpre-

Composite sampling yields a reduced amount of information on population variability, as well as it loses information on individual samples, spatial (or temporal) patterns, and information on possible associations (e.g. correlations on concentrations of two constituents)[106]**!**

What composting in fact does, is to increase the sample support (cf. Chapter 2.5.2.1.3, p.102 ff.) and in case the long-range heterogeneity of the site is unknown, eventually multiple strata are mixed – thereby seriously delimiting the understanding of the heterogeneity of the site.

In other words, Composite Sampling is usually only appropriate in case no risk-assessment is conducted and the homogeneity of the characteristic of interest (e.g. a contamination) is well known. Any interpretation over and above the population mean is usually prohibited (for important exceptions like Multi-Increment-Sampling see: e.g., US-EPA QA/G-5S) and its application towards the description of practically unknown sites is very limited.

To give an extreme example: composting all the 270 samples taken on the River Volga, the measured values should be exactly the same as the arithmetic mean of the individual samples, while loosing any further information and even the ability to state any measure of confidence towards the result!

In addition, already composting the samples of the respective river-transects would have prevented the faintest understanding of the rivers heterogeneity – ending at worst in the discussion of longitudinal profiles (i.e. one dimension of heterogeneity) without knowing the transversal heterogeneity (i.e. the second dimension of heterogeneity) – cf. Figure 29.

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dictable uncertainties within the measurement process especially if conducted ‘on the fly’ during field sampling; e.g. homogenizing humid, clayey samples, composting samples with dissimilar properties (e.g. sand and clay), and so on.

[106] Nevertheless also composite samples are frequently used to calculate correlations – one of the most popular and absurd ways of ‘interpreting’ environmental data – and in case the sample support is redefined according to the geometry the composite is to represent, the results are as ‘meaningful’ (i.e. usually meaningless) as they are using individual samples. Once again it’s a matter of scale, since already a grab sample only represents averaged characteristics – defined by the sample support (cf.: Figure 31 and accompanying discussion). I.e. in both cases, the sample support (and the number of individual samples used to form the composite) influences the results of a correlation analysis, which in contrary to other (statistical) interpretations and parameters (e.g. mean, (tests for) proportions, etc.) is based on a ‘one-on-one’ comparison of samples and thus much more susceptible to arbitrarily biased results.

2.5.6.2 Sampling to estimate the average properties of a characteristic

The uncertainty of a single sample (i.e. the uncertainty of the measurement process), as discussed above, is given by the analytical uncertainty and the sampling uncertainty:

$$\sigma^2_{measurement} = \sigma^2_{analytical} + \sigma^2_{sampling}$$

the variance of multiple samples additionally contains the geochemical variability (or population variability to be statistically more sound) – i.e. the variability we're interested in (!):

$$\sigma^2_{total} = \sigma^2_{geochemical} + \frac{\sigma^2_{measurement}}{n}$$

where n is the number of independent samples.

Given a probabilistic sampling design – and assuming a Gaussian data distribution –, the contribution of this variability can be calculated the same way, as has been done with the sampling error (c.f. chapter 2.5.4, p.121ff.).

Table 17 Percentage contribution of the geochemical variability
(parameters with a noticeable number of samples below the respective LOQ (cf. Table 13) are shaded grey – while using the distinct higher analytical uncertainty for the calculation would not change the results markedly. Because of too little samples within the transects being measured for carbonate no sound sampling uncertainty can be calculated for this parameter.).

	total variability					variability introduced by the measurement process and resulting sample uncertainty					percentage contribution to the total variance of the mean		
	$\sigma^2_{total} = \sigma^2_{geochemical} + (\sigma^2_{measurement})/n$					$\sigma^2_{measurement} = \sigma^2_{analytical} + \sigma^2_{sampling}$					$\frac{\sqrt{\sigma^2_{total} - \left(\frac{\sigma^2_{measurement}}{n}\right)}}{\sigma_{total}} * 100$		
Parameter	n	Mean	Median	σ	σ [%]	LOD	LOQ	analytical uncertainty [%] for x>LOQ	mean sampling uncertainty [%]	mean sample uncertainty [%] for x>LOQ	geochemical variability	sampling uncertainty	analytical uncertainty
Ag	266	0.39	0.28	0.47	**121**	0.06	0.27	**18**	**91**	**93**	**99.89**	neglectable	
Al [%]	266	3.50	3.47	0.59	**17**			**52**	**19**	**55**	**97.97**		
As	269	8	8	4	**48**			**19**	**68**	**71**	**99.60**		
B	264	24	25	9	**35**	9	39	**23**	**67**	**71**	**99.23**		
Ba	266	238	238	74	**31**			**7**	**30**	**31**	**99.81**		
Ca [%]	266	1.67	1.36	1.28	**77**			**11**	**31**	**33**	**99.97**		
Cd	269	0.75	0.64	0.78	**104**			**20**	**65**	**68**	**99.92**		
Co	266	18	18	3	**18**			**8**	**15**	**17**	**99.83**		
Cr	270	76	75	23	**30**			**17**	**18**	**25**	**99.87**		
Cu	270	44	38	23	**52**			**8**	**38**	**39**	**99.90**		
Fe [%]	270	4.51	4.52	0.92	**20**			**9**	**14**	**17**	**99.88**		
Hg	270	0.27	0.13	0.47	**176**	0.03	0.10	**19**	**79**	**81**	**99.96**		
K [%]	266	0.73	0.70	0.20	**27**			**8**	**26**	**27**	**99.81**		
Li	268	38	39	8	**20**			**8**	**25**	**26**	**99.68**		
Mg [%]	266	1.20	1.19	0.39	**32**			**13**	**16**	**21**	**99.92**		
Mn [%]	270	0.16	0.12	0.12	**75**			**8**	**106**	**106**	**99.63**		
Mo	266	1.9	1.7	0.9	**46**			**15**	**56**	**58**	**99.70**		
Na [%]	266	0.10	0.10	0.03	**32**			**9**	**33**	**34**	**99.79**		
Ni	267	51	52	15	**29**			**15**	**18**	**23**	**99.88**		
P_2O_5 [%]	269	0.40	0.36	0.31	**77**			**7**	**38**	**39**	**99.95**		
Pb	270	24	20	16	**67**			**11**	**26**	**28**	**99.97**		
Sc	266	8	7	2	**25**			**10**	**20**	**22**	**99.85**		
Sr	266	91	89	55	**60**			**8**	**25**	**26**	**99.96**		
V	266	66	65	17	**26**			**8**	**20**	**22**	**99.87**		
Y	266	16	16	2	**15**			**12**	**13**	**18**	**99.74**		
Zn	270	171	128	121	**71**			**9**	**32**	**33**	**99.96**		
C_{total} [%]	263	3.87	3.42	2.08	**54**			**5**	**31**	**31**	**99.94**		
S_{total} [%]	263	0.18	0.15	0.12	**69**	0.1	0.36	**33**	**105**	**110**	**99.51**		
CO_3 [%]	174	3.6	2.5	3.9	**108**		5	**2% absolute**					
moisture content$^{105°}$ [%]	260	4.5	4.7	0.7	**16**			**5**	**14**	**15**	**99.84**		
loss on ignition$^{550°}$ [%]	260	9.9	9.3	3.5	**35**			**5**	**21**	**22**	**99.93**		
Mean					52			13	39	42			
25th percentile		x≤ 25th percentile			27			8	19	23			
50th percentile		25th percentile<x<75th percentile			35			10	28	31			
75th percentile		x≥ 75th percentile			70			16	52	57			

Since this geochemical (or population) variability accounts at least for 97+% of the total variability an in-depth interpretation of the data is possible at all, only limited by the amount of 'artificial' uncertainty – i.e. variability introduced by the measurement process – one's willing to accept.

Using Equation 4 (Confidence interval for Student's t-distribution, p.81) the number of samples (n) with a known standard deviation (σ) needed to achieve a certain confidence interval (L [%]) at a given confidence level (usually that of 95%; expressed by the K-value, the equivalent to – and calculated the same way as – Student's t-factor) can be calculated according to ISO 5667-1[107]:

$$\sqrt{n} = \frac{2K\sigma}{L}$$

In fact, this formula is based on Equation 4 – and Student's t-distribution – simply adding a factor of two in order to get rid of the ±-sign. Hence, the Confidence interval (L) according to ISO describes the (two-sided) interval **within** which the true mean of a population is believed to lie in at a given confidence level, while Equation 4 would describe the single-sided solution – i.e. the range on **either side** of a sample mean:

$$\sqrt{n} = \frac{t_{df,\alpha/2}\sigma}{\pm L/2}$$

Since the latter is more common in the literature – and has been used throughout the rest of this work –, the ISO-definition has solely been used for information purposes in Table 18.

The table depicts the number of samples needed to achieve different confidence intervals for the sample mean, based on the uncertainty introduced by the measurement process – i.e. variability NOT to be explained by natural and/or man-made fluctuations in the aquatic system. It also highlights the effort needed to assure the 'mythical' confidence interval of ±10% often postulated for individual samples in the literature…. At least for three parameters (Ag, Mn and S_{total}) this confidence interval cannot be achieved by this study, even when taking all samples into account – a consequence of their high sampling variability.

This table is the basic key to any further interpretation. It allows calculating the maximum number of distinguishable group-means of samples with a specific confidence interval[108] – i.e. the maxi-

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[107] Water quality; Sampling; Part 1: Guidance on the design of sampling programmes; (ISO 5667-1 : 1980); German version EN 25667-1 : 1993

[108] Tacitly assuming a Gaussian data distribution, which is usually violated so the numbers will represent merely the lower bound of needed samples as will be discussed in the results-section. Hence the US-EPA usually recommends an iterative determination of the number of samples presented by R.O. Gilbert ("*Statistical Methods for Environmental Pollution Monitoring*", pp 30-34, Van Nostrand Reinhold, 1987) while in this case (number of samples >10; distribution functions at least roughly of the t-type) no significant differences were encountered using the two models, and the here presented – more intuitive – solution was kept.

mum number of geo-chemically different stretches along the Volga to be found within this study (dividing the total number of samples by the number of samples needed to achieve a certain confidence interval).

Table 18 **Number of samples needed to achieve different confidence intervals (according to ISO 5667-1) and minimum confidence interval achievable using all samples, at a 95% confidence level for the population mean (for shaded parameters and (the missing) carbonate see Table 17).**

			confidence interval [%]				
Parameter	n	**mean sample uncertainty [%] for x>LOQ**	**10**	**20**	**50**	**100**	**confidence interval [%] achievable using all samples**
		i.e. uncertainty expressed as RSD	±5	±10	±25	±50	**!!! two-sided confidence interval !!!**
Ag	266	**93**	1375	344	**55**	**14**	**23**
Al [%]	266	**55**	483	**121**	**19**	**5**	**13**
As	269	**71**	797	**199**	**32**	**8**	**17**
B	264	**71**	804	**201**	**32**	**8**	**17**
Ba	266	**31**	**152**	**38**	**6**	**2**	**8**
Ca [%]	266	**33**	**174**	**43**	**7**	**2**	**8**
Cd	269	**68**	742	**186**	**30**	**7**	**17**
Co	266	**17**	**47**	**12**	**2**	**1**	**4**
Cr	270	**25**	**96**	**24**	**4**	**1**	**6**
Cu	270	**39**	**242**	**61**	**10**	**2**	**9**
Fe [%]	270	**17**	**45**	**11**	**2**	**1**	**4**
Hg	270	**81**	1054	**264**	**42**	**11**	**20**
K [%]	266	**27**	**119**	**30**	**5**	**1**	**7**
Li	268	**26**	**109**	**27**	**4**	**1**	**6**
Mg [%]	266	**21**	**70**	**17**	**3**	**1**	**5**
Mn [%]	270	**106**	1807	452	**72**	**18**	**26**
Mo	266	**58**	536	**134**	**21**	**5**	**14**
Na [%]	266	**34**	**186**	**47**	**7**	**2**	**8**
Ni	267	**23**	**88**	**22**	**4**	**1**	**6**
P_2O_5 [%]	269	**39**	**240**	**60**	**10**	**2**	**9**
Pb	270	**28**	**128**	**32**	**5**	**1**	**7**
Sc	266	**22**	**80**	**20**	**3**	**1**	**5**
Sr	266	**26**	**110**	**27**	**4**	**1**	**6**
V	266	**22**	**75**	**19**	**3**	**1**	**5**
Y	266	**18**	**52**	**13**	**2**	**1**	**4**
Zn	270	**33**	**176**	**44**	**7**	**2**	**8**
C_{total} [%]	263	**31**	**158**	**39**	**6**	**2**	**8**
S_{total} [%]	263	**110**	1941	485	**78**	**19**	**27**
moisture content$^{105°}$ [%]	260	**15**	**35**	**9**	**1**	**1**	**4**
loss on ignition$^{550°}$ [%]	260	**22**	**75**	**19**	**3**	**1**	**5**

Table 18 also highlights the improbability of many approaches towards the interpretation of longitudinal river profiles, as well as cores – already under idealized conditions. Even in case of the Volga – an as we will see relatively homogeneous river – a single sample is almost meaningless, and any attempt towards an in-depth interpretation of the results (i.e. anything going beyond the above discussed early classification systems) on a sample-to-sample basis will lead to erroneous results of unknown uncertainty.

However a defensible interpretation is possible – even though sample uncertainties of up to 110% surely aren't that promising at first sight – albeit less detailed than one might be used to, once again corroborating the most important and simple finding of science/philosophy:

Any answer to a question is either precise or certain.

2.5.6.3 'Hot Spot'-sampling / Threshold Comparison Method

The objectives of 'Hot Spot'-sampling are fundamentally different than the above discussed sampling scheme with a focus on estimating the average properties of a characteristic – and the question whether a characteristic of interest (exceeding a limit) is expected to be distributed over the entire site or localized in 'hot spots' has to be answered in advance[109].

Since the primary objective of 'Hot-Spot'-sampling is to pinpoint[110] localized areas of characteristics exceeding a limit – e.g. a contamination – this conceptual model that has to account for the geometry of a stratum – i.e. the 'hot spot' – and the area sampled. The probability of finding a hot spot depends on its size and shape, the pattern of the sampling-grid, and the relationship between the size of the hot spots and the grid spacing[111]. While in principle this also holds true for the above mentioned conceptual model, there's one big difference: as the size of the stratum of interest – e.g. the hot spot – decreases, its important with respect to the average property of a characteristic decreases also – i.e. the uncertainty of the result decreases (even if the hot spot is missed!) – whereas in the case of decided 'Hot Spot'-sampling the chance of a false negative answer – i.e. missing the hot spot – increases. In other words: when it comes to 'Hot Spot' sampling, sampling-density plays the key-role, while for the above conceptual models site-variability is the key-issue; making 'Hot Spot'-sampling the task with the by far highest expenditure – and the only one with a need to classify individual samples (cf. footnote[111]).

The easiest – yet most impressive – way to calculate how many samples are needed to detect a hot spot is by using a square sampling grid to search for a circular hot spot of radius r. The probability of locating it is 100% when the distance between the grid points equals the radius; this probability

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[109] This choice has to be made for practical reasons. Although any probabilistic sampling-scheme can be used to pinpoint hot spots, this approach is far from being rational. It is either not very (cost-) effective or the outcomes are pure artifacts, since for a given hot spot-definition or site-variability the probability of finding a hot spot is simply determined by the sampling-density.

[110] Due to the systematic search needed for 'Hot Spot'-sampling – i.e. usually a grid-sampling design – the hot spot (if present) is also delineated within the grid-geometry and spacing, and kriging-techniques can be used in search of its most probable geometry – or better: be used for an optimized second sampling stage. Since multiple stage sampling-schemes are beyond the scope of this report – and unfortunately are rarely conducted – this point is left out.

[111] A thorough calculation would of course reveal that it also depends on the definition of what has to be considered as 'hot', while this problem is usually eliminated by assuming the complete absence of classification errors. Taking the uncertainty budget of the measurement process and the often encountered (heavily) skewed and flat distribution functions of natural compartments into consideration, overlooking this assumption can cause major problems. And all of a sudden we're back at the 'old school' classification-systems with an error margin of ± 100%… (cf. p.119)

decreases as the grid spacing increases and the number of samples required can be approximated by the following equation (Gilbert, 1987):

$$n = \frac{A}{G^2}$$

n = number of samples
A = area to be sampled (square of the units for G)
G = grid spacing

Considering the River Volga as a simple geometrical body – which it is not – with an area of at least 20000 km² (i.e. the sum of the reservoirs surface) with 270 equally distributed samples a circular hot spot with a radius of about 9 km (G^2=A/n=8.6), i.e. a diameter of about 18 km – could have been detected. Systematically searching for hot spots with a radius of 1 km would simply need no less than 20000 samples…

Obviously it takes a great many samples to find small hot spots on a large site, and while the other conceptual model profits from the decreasing size of a hot spot (or stratum) since its weight towards an average characteristic decreases, 'Hot Spot'-sampling becomes increasingly uncertain (or costly). I.e. a hot spot is an utterly subjective construction depending on its sharpness ('what is 'hot'?') and the dimension of the sampling grid ('what size and geometry are 'we' searching for?').

According to Gilbert (1987) the sampling design for hot spot sampling depends on four factors – some of them making things even worse (1 and 2); some of them allowing for slightly less samples than discussed above (3 and 4):

1. The size of the hot spot (length (L) of the long axis of an ellipse (where L is equal to one-half of the length of the long axis – i.e. the radius in case of a circular hot spot; and the semi-major axis if the hot spot is elliptical))
2. The shape (S) of the hot spot (ratio of the long axis of the ellipse to the short axis of the ellipse (e.g. S=1=circular shape; 0<S<1 for elliptical hot spots)
3. The acceptable risk (α=1-β)) of failing to detect a hot spot that is present; and
4. The grid pattern (grid spacing (G), and geometry (square, rectangular, or triangular)).

Especially the (unknown) size and shape of the hot spot, as well as its (unknown) orientation towards the sampling grid, is what makes 'Hot Spot'-sampling one of the most difficult and costly sampling tasks in environmental geology – especially if there is only little prior information available[112]. All of this is discussed in much more detail in Gilbert (1987) and computer programs (e.g. ELIPGRID PC (Davidson, 1995 – provided free of charge by the US-EPA) for calculating the optimal grid spacing for a hot spot of prespecified size and shape with a specified confidence of finding the hot spot – are available. They destroy any illusion one might have had, about finding hot spots simply as a 'by-product' of sampling and 'good judgment', as still found in the literature…

Closely related to the 'Hot Spot'-scenario, and highlighting the problem of classification errors (i.e. the question: 'what is hot? Cf. footnote[111]), is the widely used **Threshold Comparison Method.** This method – explicitly ***not*** **recommended** by e.g. NAVFAC (1999) – uses some sort of threshold level to decide whether a chemical at the investigated site is a COPC. If one or more site measurements exceed e.g. the 95th percentile of a background distribution, the chemical of interest is declared to be a COPC. However, supposed the site and background distributions are identical, and thus the chemical definitely not a COPC, the probability of one or more of n site measurements to exceed the 95th percentile is equal to $1\text{-}(0{,}95)^n$. No matter which threshold level will be used (background mean, two times the background mean, nth percentile, and so on) it will always correspond to some percentile of the background distribution and the same formula, $1\text{-}(\text{threshold percentile})^n$ can be used for computing the probability of making a false positive decision error.

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[112] E.g., an elliptical hot spot – the most probable geometry in a riverine system – of almost 'any' size (in terms of its semi-major axis) can go by unnoticed within a square grid, provided its shape-factor is close to zero and so on.
In fact, 'Hot Spot'-sampling is rarely conducted without the use of prior information (judgment) due to these reasons. E.g. the chances of a hot spot (of anthropogenic origin) being present in a riverine system deliberately increase near towns and/or industrial facilities, whereas the area to be sampled decreases. On the other hand, any search for anomalies (i.e. hot spots of geogenic or anthropogenic origin) is either limited to the detection of rather large areas affected by this anomaly (loose systematic grid covering the entire investigated site) or heavily biased (dense systematic grid covering the 'most interesting' parts of the investigated site).
Depending on the quality of the judgment this can cause serious decision errors, as e.g. envisioned in the case of the Oka-sediments: near the industrial town of Dzerzhinsk – 'famous' for its massive problems with respect to industrial effluents – no significant enrichment of inorganic COPC's could be detected, while our Russian partners later reported the effluents NOT to be entering the Oka, but the River Volga downstream the city of N. Novgorod – at a place we sampled by chance; with a single sample… Without additional information – hardly available – there's no way to prove, or disprove this theory, and within a traditional (single-stage) sampling design this site of potential concern would go by unnoticed – e.g. averaged out, when describing the site and/or eliminated by an outlier-test. This points out the (at least potential) superiority of multi-stage sampling schemes (e.g. 'Ranked Set Sampling' or 'Adaptive Cluster Sampling' – where an initial probability based sampling scheme is used to pinpoint areas of interest for additional sampling, thus scrutinizing a 'questionable' result rather than 'interpreting' it without sufficient evidence) as e.g. favored by the US-EPA TRIAD-approach.

In other words, the probability of obtaining a false positive result depends on the used (and perhaps unknown) percentile of the background distribution and the number of samples – thereby increasing with a more extensive sampling!

Table 19 Probability that one or more of n site measurements will exceed a threshold percentile if site and background distributions are identical.

Number of samples n	**Threshold percentile**		
	50th	**95th**	**99th**
	$1-(0.50)^n$	$1-(0.95)^n$	$1-(0.99)^n$
1	0.50	0.05	0.01
5	**0.97**	0.23	0.05
10	> **0.99**	0.40	0.10
20	> **0.99**	0.64	0.18
50	> **0.99**	**0.92**	0.39
100	> **0.99**	**0.99**	0.63
200	> **0.99**	> **0.99**	0.87
270	> **0.99**	> **0.99**	**0.93**

'The danger of using this type of decision rule is clear: the probability of making a false positive decision error can be unacceptably large when many site measurements are compared to a background threshold value' (NAVFAC, 1999).

To make a long story short: Already due to the sampling-density (varying over the rivers length), and the several times stated lack of prior information, this study is in no way capable of pinpointing hot spots below about 20 km diameter with a certainty that would be fit-for-purpose.

Instead of that, it will be valuable as prior information within a multi-stage sampling scheme – highlighting areas of interest, where additional sampling would be desirable and ingenious/convenient (c.f. footnote[112]).

2.6 Summary

- Results and decisions with ‘absolute certainty’ would require the knowledge of the ‘true condition’ of the population in question. The ‘true condition’ can only be known when faultlessly testing **all** possible population units (census) – which is usually already prevented by expenditure and money considerations. Testing a few samples from a population, will lead to estimates of the ‘true condition’ that will be wrong to some degree because they use incomplete information. **Estimates are no factual statements; they are educated guesses**.
- Estimation ‘errors’ are NOT mistakes, but deviations from the truth that will introduce uncertainty into the process of interpretation and/or decision-making. While these ‘errors’ and uncertainties are inevitable, they can and have to be managed in order to get the job done and prove it. If unmanaged, the ‘errors’ in estimates can lead to interpretation- and decisions-errors which ARE mistakes, that are not defensible scientifically, technically or legally.

- The currently prevalent and widely accepted concept to the expression of estimation errors is that of ‘**uncertainty**’ as defined in the ISO *Guide to the expression of Uncertainty of Measurement* (GUM, 1993) (cf. Chapter 2.4.1, p. 77ff.).
- ‘Uncertainty’ is not to be mixed up with the ‘error’ of the measurement[113] – that is the difference between the result and the ‘true value’ – which would be a single value, and cannot be known. ‘Uncertainty’ takes the form of a range, and according to the GUM should be reported as an ‘expanded uncertainty’ (U), which is obtained by multiplying the calculated ‘standard uncertainty’ (u) by a ‘coverage factor’ (k). The reported result is a confidence interval, in which the ‘true value’ is believed to lie in with a certain level of confidence (usually that of 95%):
- Primary used to characterize the reliability of the (e.g. chemical) measurement of a characteristic in the laboratory, **the concept can and has to be applied to the entire measurement process**.
- Controlling for analytical correctness alone (‘*first generation data paradigms*’ (Crumbling et al., 2003)) simply is not enough. It will lead to defensible and reliable results of the **sample** presented to the measurement system, while the objective is usually the composition of the **‘target’**, i.e. the larger body of material the sample was taken from. These two things are not identical.

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[113] Although these two expressions are often used synonymously (cf. footnote[68]).

- The (chemical) measurement is only one part of a measurement process that leads to results that will characterize and/or represent the ‘**target**’ in any way (cf. Figure 27, p.91) and the results of this process can never be more reliable/accurate than its least accurate sub-process.
- Uncertainty of the measurement process – like the uncertainty of any other multiple-stage process – is additive:
    - analytical uncertainty
    - + sampling- and sub-sampling uncertainty
    - + natural heterogeneity of the site
    - = total uncertainty of the measurement process
- If any of these steps fails to be ‘fit-for-purpose’ – i.e. its uncertainty is unknown or larger than the demanded accuracy to address a question regarding the target of the measurement process – the results are meaningless.

- Analytical uncertainty is well understood, simple and scientifically sound to calculate (Chapter **2.4**, p.77 ff.).
- Sampling and sub-sampling uncertainties as well as natural heterogeneity are not.
    - The one phenomenon that causes ALL non-systematic sampling errors is heterogeneity (cf. Figure 28 Continuous Selection Error).
    - Frequently at least one dimension of the natural heterogeneity is the objective of the study (cf. Figure 30). While the heterogeneity of the investigated dimension does not contribute to the sampling- and sub-sampling uncertainty, it is influenced by the heterogeneity of every single of the other dimensions of the lot (cf. Chapter 2.5.2.1.2, p. 100 ff.).
    - No generally accepted guidelines to its expression exist to date (cf. Chapter 2.5.1, p.93f.), even though starting with Pierre Gy’s works in the 1950’s a complete Theory of Sampling exists.

- Numerous studies taking sampling-uncertainties into account – mostly using an ‘in-between-samples’-variance as an estimator – find about >90% of the total uncertainty of the measurement process arising from sampling considerations (cf. Crumbling, 2003).
- ‘Perfect’ (chemical) analysis + non-representative sample(s) → ‘bad’ data.

- **Gy’s Theory of Sampling** seems to be the only comprehensive sampling theory for particulate matter and implicitly addresses (almost) every source of uncertainty[114] as well as it gives guidance for:
    - **Designing sampling equipment and procedures** – most sampling devices used in environmental sampling (e.g. augers, thief probes and triers) are incorrect according to the Theory of Sampling, because they are liable to cause serious delimitation (DE) and extraction (EE) problems (cf. Chapter 2.5.3.3, p. 110ff.).
    - **Auditing and monitoring of sampling protocols** – the validation of sampling procedures and protocols in environmental-geochemistry is more or less non-existent and largely based on ‘acceptance’ rather than ‘verification’ (cf. Chapter 2.5.1, p. 93f.).
    - **Designing sampling experiments** – an extensive literature and knowledge exists, but at least practical and/or financial constraints often lead to deviations from the desirable rigorous probability based sampling schemes (cf. Chapter 2.5.6.1, p. 148 ff.).
    - **Designing cost effective fit-for-purpose sampling protocols** – which is beyond the scope of this work.
- Most approaches towards a quantification of sampling-uncertainties in the field of environmental-geochemistry only deal with (some sort of) sampling-precision (i.e. repeatability); disregarding reproducibility, let alone sampling bias. At the same time the experiences in the field of (chemical) analysis shows the repeatability to be the least important element of an uncertainty budget.
- In view of the fact that it is virtually impossible to sample the same target twice – unless it is completely homogenous and stable within time and space – any estimate of the sampling precision, necessarily based on multiple spatial or temporal samples, will be affected by the (natural) spatial and/or temporal heterogeneity of the sampled site.
- **However, it has to be mentioned that some experts on sampling deny the validity of the whole concept: If the sampling is carried out according to an accepted protocol it cannot be biased (i.e. the equivalent to ‘empirical’ analytical methods – cf. Chapter 2.5.1, p. 93f.).**
- On the other hand, the absence of sampling-uncertainties can only be rationalized in case the tiny sample is the target of the investigation. Once the sample is meant to represent a larger compartment, the concept of ‘error-free’ sampling proofs to be unsustainable.

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[114] There may be limitations of this theory for volatile and semi-volatile measurands (cf. footnote[67]).

- There is no such thing as a ‘representative sample’ unless the heterogeneity of the sampled lot is fully known and understood, or zero – a condition that would make sampling superfluous. The character of natural heterogeneity (of non-zero-dimensional lots) prohibits that.
- As soon as conclusions from a group of samples are drawn towards the sampled lot, both the ‘error-free’, traditional approach and the statistical calculation of the sampling-uncertainty are equivalent:
    - Currently, sampling-bias can not be addressed for the sampling-protocols used in environmental-geochemistry (cf. Chapter 2.5.3.3, p. 110ff.) – except for the Fundamental Error and the Grouping and Segregation Error in case the properties of the sampled lot are known (cf. Chapter 2.5.3.2, p.108f.)
    - Without rigidly designed sampling experiments (cf. Chapter 2.5.4, p. 121ff.) the resulting sampling-uncertainty (i.e. sampling-precision) will in either case be an apodictic fact. It is the sum of all uncertainties bound to the sampling process – determined by the sample support (cf. Chapter 2.5.2.1.3, p. 102) and the sampling-geometry to be represented.
    - Sampling theory instead demands the independent analysis of heterogeneity of the sampled lot as a fundamental step in advance of any sampling operation, providing information going far beyond the sole purpose of sampling – since only the hypothesis of considering a lot as homogenous allows solving all sampling problems; by oversimplifying them.
- **In other words: the key towards justifiable decisions and/or conclusions from sampling data lies in the sampling-design and the consideration of possible shortcomings.**
    - The sampling-design is basically a function of the sampling-scheme (i.e. the geometry) and the number of samples (cf. Chapter 2.5.6.1, p. 148ff.).
    - The sampling-design to be implemented depends on the sampling objectives as well as on the consequences of misinterpretation and/or making a wrong decision (cf. Chapter 2.5.6.1, p. 148ff.).

DILEMA:

- *“Lacking distribution information, it is impossible to devise an optimal sampling strategy.”*

(Jenkins, et al. 1996)

Q: Where to obtain the natural and/or manmade distribution information from, in order to select the correct sampling design and number of samples needed to assure representativeness[115], etc.?
A: From sampling data!

- **BUT: with discreet sampling, an average is a random variable as well as the standard deviation is an artifact of the sample collection process**
  (Part of 'Ramsey's "Rules"' as promoted by the US-DOE in their DQO-training. Highly recommended and available online: http://www.hanford.gov/dqo/training/contents3-day.html).
- **In other words: a single stage sampling-design can never be proven to be statistically correct in terms of Gy's Theory of Sampling, and the calculated sampling-uncertainty (i.e. repeatability (!)) will almost certainly represent the lower bound of the 'true' uncertainty since the dispersion of a characteristic can only be underestimated, not over-estimated by a sampling-scheme.**
- It is up to the investigators judgment whether the assumed or experimentally achieved distribution information (to calculate the sample size needed) can be considered reasonable (cf. Chapter 2.5.6.2, p. 153ff. and footnote[102]) and which distribution information to use in order to calculate the sampling-uncertainty (cf. Chapter 2.5.5.3.2, p. 139ff.).

- What 'we' have to deal with is[116]:
  - **An <u>expanded</u> measurement uncertainty** – well below 40% for most elements (based on a measurement precision ≤ 9% (neglecting Boron) c.f. Figure 25, p. 86 – representing everything that might randomly **and** systematically 'go wrong' in the laboratory – thereby considering (potential) measurement bias.
  - **An <u>expanded</u> sampling uncertainty[117]** – of about 80% (cf. Figure 42, p. 126). Representing everything that might randomly 'go wrong' in the field – i.e. making the sample representative for a specific area or geometry – here a river-transect (cf. Chapter 2.5.4, p.121ff.) – without knowing the systematic error (i.e. **sampling precision**).

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[115] As defined in Chapter 2.5.2.1.1 (p. 98) - i.e. a sample (or a multitude thereof) that answers questions about a population with a specified confidence.

[116] This in fact means about everybody in the field of environmental-geochemistry, since these problems are far from being 'exclusive' to our institute – however the amount of uncertainty may vary.

[117] Calculated in the usual way: Expanded sampling uncertainty = k * sampling uncertainty (k=2).

    - **A sampling bias** – unknown, but at least partially accounted for in the calculation of the sampling precision (cf. Chapter 2.5.5.3.2, p.139ff.).
- **This leads to an expanded uncertainty of the measurement process[118] for a single sample of about 90%. As mentioned above, most probably a lower bound.**

- There are several rules of thumb to calculate the sample size needed to estimate the distribution information:
    - "*For practical purposes it will be assumed here that a 'too small number' is less than 30, and a 'large number' is at least 50.*" (Gy, 1998)
    - "*In practice, there appears to be no simple rule for determining how large n should be… if the distribution is highly skewed, an n of 50 or more may be required.*" (Gilbert, 1987)
    - "*Samples of less than 10 are usually too small to rely on sample estimates even in 'nice' parametric cases… In many practical contexts, the number 30 is used as a 'minimum' sample size… Although it is always dangerous to set 'rules of thumb' for sample sizes, I would suggest that in most cases it would be wise to take n ≥ 50.*" (Chernick 1999)
- These rules of thumb are as precise (or imprecise) as any statistical calculation of the sample size needed, since the basic parameters (distribution function and its dispersion) are unknown a priori and thus a matter of the experimenters judgment or based on an preliminary (necessarily imperfect) sampling-step.
- Comparing these rules of thumb (largely based on natural compartments; since e.g. industrial processes are usually way less variable and uncertain) with Table 18 (p. 155) shows no less than the assumptions (cf. Chapter 2.5.4, p. 121ff.) to be within reasonable limits:
    - With the exception of Silver and total Sulfur we are able to describe the measured characteristics of the Volga as a whole within a confidence interval[119] of ± 10 %.
    - 'De-trending' the data (cf. Chapter 4.5, p.232ff.) leads to sample sizes, as recommended by the above given rules of thumb.
    - Even without 'de-trending' the data (i.e. data-set still affected by the dispersion of the data of the whole river course) 50 samples would have been enough to describe 19 out of 30 measured characteristics within a confidence interval[119] of ± 10 %.

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[118] $U_{measurement-process} = k * (u_{measurement} + u_{sampling}) = 2 * \sqrt{20^2 + 40^2}$

[119] At a 95% confidence level.

- Therefore, what at first sight might be unsettling for people basing their findings on just a handful of samples – namely the impossibility to do that reliably – is simply the consequence of (natural) heterogeneity and unsuited approaches towards its description.

- **The only way that will lead to justifiable interpretations and/or decisions within the framework of a less than perfect single-stage sampling scheme is simplification. Consequently, the results and conclusions presented are necessarily less detailed than one might be accustomed to from studies ignoring any form of uncertainty. In exchange for that, they are reasonable and revisable.**
- **However, the results are solely revisable on the scale of the sampling unit (i.e. the sample support; Chapter 2.5.2.1.3, p.102ff.) and sampling plan (i.e. respective sampling density; cf. Figure 94). Any interpretation over and above is invalid.**

3 State of knowledge/confusion

Numerous articles concerning the environmental situation in the Volga-basin as a whole, and (heavy) metals in its sediments in particular, tend to fall in the category ‘hard to believe’.

They reach from claiming an at least severe situation, without stating any strict evidence (e.g. EEA, 2003), to reporting the total contents of heavy metals in the reservoirs (e.g. in t/reservoir (!)) without mentioning, how these figures were derived, and/or what they could mean (Avakian, 1994).

The EEA-paper is a typical example for many (semi-)official reports, and the ‘western’ view on the environmental situation in the FSU and Russia as a whole – in this specific case based finally on the Russian State of the Environment Report[120].

“*Some of the major rivers in the Russian Federation (e.g. the Volga, Obj, Yenisej, Northern Dvina and Federation the Don) and their tributaries are highly polluted. The main reservoirs are also highly polluted, especially the Volga cascade. The main sources of pollution are wastewaters discharged by industrial and agricultural enterprises, communal services, and surface runoff. The most common surface water contaminants include oil, phenol, easily oxidised organic substances, metal compounds, nitrates, and nitrites*.” (EEA, 2003)

While there may be some knowledge on the situation, one can be sure it is not fully published. The information is often considered commercially valuable/usable which prohibits its public availability. What is left is some sort of ‘it’s got to be bad’-attitude, putting together figures, facts and fiction that may indicate a problematic situation and extrapolating regional environmental problems to the whole FSU and especially the Volga-basin, as one of the economic key-regions.

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[120] The (semi-)official Russian reports to a number of UN (UNEP, UNECE, etc.) projects all seem to be based on the datasets of the ‘*Federal Service of Russia for Hydrometeorology and Environmental Monitoring*’ (Roshydromet or RosGidromet) (http://www.meteo.ru/fund/hydro.html#pollution) – as part of the ‘*State Service for Monitoring of the State of Environment*’ (GSN); the former OGSNK (‘*Unified System of Observation and Supervision*’). The same holds true for the Russian ‘State of the Environment’ (SoE) reports – as well as for a lot of papers and reports citing either of these sources. I.e. a lot of information is based on one single data-source of fairly unknown, but questionable quality (e.g. Zhulidov, 2003) at least with respect to the parameters mentioned in the EEA – and many other reports.

These data sets are not available free of charge, and individual measurements are not reported. Only summaries are given, often, as in the above EEA-paper actually without any values for the measurants.

Speaking about the Volga, three approaches are widely used to legitimate the claim of a demanding situation:

1. **Water-withdrawal and waste-water-input:** there are e.g. 30.7 km^3 water-withdrawal from, and 23.3 km^3 waster-water input (11.0 km^3 of which are characterized as 'non- or under- treated')[121] to the Volga.
2. **Adverse ecological effects of dams:** because of slowing down the Volga-flow, its capability to self-purification should decrease; and the bacterial pollution should increase.
3. **Extrapolation of known ecological problems:** a (presumably) single event (e.g. in the city of Volgograd) or a catastrophic situation (e.g. city of Dzerzhinsk on the Oka, close to its confluence with the Volga) is used to deduce the situation in the whole basin.

Considering the existing difficulties and uncertainties in describing/quantifying diffuse and point-sources of contaminants entering surface waters even under much more favorable conditions with respect to the availability of data in Western Europe (Böhm et al., 2001) these approaches are speculative to say the least. Especially the amount of contaminants entering through Non-point sources is quite difficult and uncertain to quantify – while their share of the total input is approx. 75% with respect to heavy metals in West European Rivers (Böhm et al., 2001). No matter the wastewater input, one would have to balance the amount of pollutants entering the Volga and take account of their fate and transport to draw any conclusions. Furthermore one would need quite precise regional data, because the sediment trapping of the dams can be advantageous for the downstream situation with respect to chemical contaminants; increasing the capability to self-purification, instead of decreasing it. Since most of these data are either not available or not existent, it is not very likely to obtain realistic estimates with/for any of the above approaches.

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[121] These data were taken from the Avakian (1994)-paper (i.e. Rosgipovodkhoz Institute data for 1990 – as do numerous of early (i.e. pre-1998 papers). As mentioned several times before one can find almost any number to suit his needs… There are profound differences in time – due to changes in the economic situation and changes in the regulatories (since the definition of 'under-treated' waste-water depends on the official requirements for the quality of effluents) – the above mentioned data representing the upper bound – but since no source reports at least an average composition of these discharges it doesn't matter anyhow...

On the other hand, the Avakian-paper (Avakian et al., 1994) is typical for many Russian papers. Instead of reporting the measurements – and sometimes ,as in this case, not even the methodology – ‘total’ contents for a specified compound ((rarely) sediment, water, or pollutant disposal) are given. With respect to sediments, in this case the upper 10cm layers of the Volga reservoir sediments (with the exception of the Ivankovo reservoir) were analyzed – unknown methodology, unknown sampling, unknown samples size – and the results reported in t/reservoir.

There is no information about how this was done, no information about the amount of sediments believed to be in the reservoirs, not to speak of the assumed density or dry-weight (water-content) thereof[122]. Consequently, there is absolutely no chance to calculate the concentrations, to make these findings comparable.

Even when taking the ‘information’ serious, they are of very little use. Nobody is, or should be interested in the total amount of a substance in bottom sediments or any other substrate, when talking about possible risks, benefits or the state of the (aquatic) environment. It is the concentration that matters – or seawater would be valuable, because of the large amounts of e.g. gold in it…

Moreover, the results in this specific case are at least questionable. Beside other inconsistencies, the reported amount of several heavy metals in sediments for some reservoirs does not seem reasonable.

Table 20 Examples for total content of heavy metals in Volga reservoirs (unknown methodology and number of samples; Avakian et al., 1994)

	Total content [1000t]			
Reservoir	Fe	Pb	Cu	Zn
Rybinsk	94.200	45.000	1.800	46.900
Gorkij	369.900	0.243	0.747	14.500

While the element **ratios** in the Gorkij reservoir seem reasonable – with an apparent enrichment in Zn – in comparison to ratios derived from geochemical ‘background’ levels, the ratios in the Rybinsk reservoir are beyond imagination (Fe/Pb/Zn ≈ 2/1/1). Additionally, although the reported pollutant disposal [t/year] into the Volga basin for the years 1988-1990 follows the expected order Zn>Cu>Pb (for point-sources), the Gorkij reservoir is the only reservoir where the amount of Pb – and thus its concentration – is reported to be smaller than that of Cu, and it is not very likely, that

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[122] Ershova et al. (1996) report values for the Kuibyshev reservoir, which confirm the assumed heterogeneity of sediments at least in this reservoir. Moisture content in bedload deposits: 15-85%; density of bed-load deposits: 2.41-2.64 g/cm^3; bulk mass of the matrix: 1.45-1.9 g/cm^3.

So, the idea of balancing (any of the Volga reservoirs) for just one of these parameters has to be called courageous – the idea of being able to do so, presumptuous.

the geogenic amount of Pb is larger than that of Cu. For the most part, this does not improve the confidence at least in this report.

It is also this time-period and methodology, which gave rise to claims about the pollution of the Caspian Sea, and the Volga as the main cause thereof (e.g. Finlayson et al., 1992; Oradovskij et al., 1997). Excerpts of the than (presumably) existing extended data-sets on water-quality have been used to establish the idea of an increasingly polluted river, mostly based on the interpretation of year-to-year fluctuations, instead of longer time-periods.

The most comprehensive **available** data-set with respect to water-quality seems to be the one provided by the *Global Environment Monitoring System* (GEMS/Water) – triennial aggregated datasets for the years 1979-1999 are available on their web-site (http://www.gemswater.org/) – and have been published by Kimstach et al. (1998). This data set – once again of course provided '*by the national water quality agencies*'; which would mean Roshydromet – contains only very sparse information on heavy-metals (except for Fe) and, as mentioned above, its quality is questionable already with respect to the measurements and the methodology (Zhulidov, 2003). Even more interesting than the reported figures are the ones not reported. Apart from the fact, that most of the time there are less than 20 measurements used to describe a 3years-period (!) only Fe, Zn and (rarely) Pb are reported, almost forcing one to speculate about possible reasons and/or the database for the above-mentioned claims about an increasingly polluted river….

Earlier data sets on water-quality have been published (e.g. Zenin et al. (1978) – time period approx. 1968-1973), but contain no data about heavy metals (except for Fe).

With respect to heavy metals in sediments, it has only been in recent years that studies based on actual, well-documented measurements were conducted or published. What these reports have in common, is the absence of claims about a catastrophic situation and 'some' doubt about the (official) 'facts and figures' used to describe the situation on the Volga. On the other hand, with respect to sediment-quality all these studies were just regional, not regarding the situation on the Volga as a whole[123].

They also depend on some amount of speculation, and this report will make no exception, but at least they have some foundation and are not based on 'common sense' or unknown and/or undocumented data sets.

Starting with the works of Lychagin et al. (1995) and Winkels et al. (1998) at least the idea of the Volga being a major source of pollution with respect to the Caspian Sea became shaky.

Winkels et al. (1998) determined priority pollutants (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, as well as PCB's and PAH's) in 6 dated cores (^{137}Cs, ^{134}Cs), taken in sedimentation zones of the main branch of the Volga delta. The present-day and historical levels of pollutants since the late 1930s were found to be low and hardly changing during the last five decades.

These findings corroborated the work of Lychagin et al. (1995) with samples of soils and sediments evenly spread over the Volga delta, whose heavy-metal contamination was considered negligible.

Table 21 Average contents and standard deviations of sediment-core-samples from the Volga delta (Winkels et al., 1998)

n=52	[mg/kg]								
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**CF [%]**	**OC [%]**
	4.1 ± 1.0	<0.5 ± -	62 ± 14	26 ± 8	<0.1 ± -	52 ± 11	9 ± 5	65 ± 16	31.8 ± 10.9	1.3 ± 0.7

CF= Clay Fraction content (<2µm)
OC= Organic Content

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[123] The first claim may be wrong, while the second is surely wrong, since only a small part of the Russian literature was/could be reviewed for numerous reasons – language being the most important.

The ecological situation in the Volga basin has been described in several published monographs – all in Russian (Shubin 1986, Naidenko et al. 1993, Komarov et al. 1993, Komarov et al. 1996, Naidenko et al. 2003). From these reports only those of Naidenko et al. are (partly) available to us. The 1993-report is based approx. on the same assumptions and data as the Avakian-paper, while – with respect to sediments – the 2003-report is/should be based on the same data-set as this work, since they were derived from the 'Volga-Rhine-project' - the framework in which this report was conducted, and in which our institute was responsible for the sediment-sampling (in cooperation with the Najdenko-group) and measurement.

The already mentioned monographs of Behning (1928) (in German) and Mordukhai-Boltovskoi (1979) (in English) are predominantly based on (micro-) biological observations, and contain no data on heavy metals.

Summing up these two reports no evidence, neither temporal nor spatial, for a major contamination with respect to heavy metals could be established – and was further confirmed by additional works of these two groups (e.g.: Lychagin (1999); using partially the data of the above publications).

These studies, as well as their own measurements led the *Caspian Environment Programme* (CEP) – a regional program developed for and by the five Caspian Littoral States, funded among others by UNDP, UNEP, the World Bank and the European Union/TACIS – to revise their earlier reports (based on the CEP national reports[124]) with respect to contamination on the Caspian Sea, almost completely:

Table 22 (Heavy) metal content of transect-samples from the Volga avantdelta (CEP, 2002) (data compiled from: Konoplev (2001) and de Mora and Sheikholeslami (2002) – total content (HF-HClO$_4$-HNO$_3$-digestion, fraction <5mm).

n=22-24	Min (μg g^{-1})	Ø (μg g^{-1})	Max (μg g^{-1})
Ag	0.005	0.018	0.032
Al	2557	-	38290
As	0.42	3.2	6.71
Ba	69.7	273	669
Cd	0.022	0.06	0.099
Co	1.33	-	7.62
Cr	2.08	35.4	69.3
Cu	2.54	9.2	21.9
Fe	1600	5873	9680
Hg	0.009	0.03	0.068
Li	3	-	35.3
Mn	90	-	455
Ni	5.42	16	34.2
Pb	0.69	4.6	8.03
Sb	0.3	-	0.3
Se	0.1	<0.1	0.1
Sn	10	<10	10
Sr	356	-	6240
V	7.25	-	84.5
Zn	2.77	19.6	52.9

"*Pollution is an often-quoted threat to the biodiversity of the Caspian. The sources of pollution are industry, agriculture, accidental discharges, and sewage. The main flow of pollution comes from the Volga, according to conventional wisdom, but the levels of contaminants … detected in the river sediments indicate a relatively clean river. …*

For instance, it is often said that 80% (or 85%) of the hydrocarbons (or total pollution) entering the Caspian Sea come from the Volga River. Most reports on Caspian pollution report this figure, and it is repeated in PC CRTC (CRTC/PC Caspian Centre for Pollution Control; R.O.) *reports (e.g., 91% of yearly flow comes from the Volga, 79% of the yearly BOD, 95% of the hydrocarbons, 84% of the cadmium, etc.). These figures are based on estimates made from discharge questionnaires, but do not take account of the effects of dams and wetlands in sequestering many of these materials from the Caspian Sea. There is at present inadequate mass balance data to provide a quantitative estimate of existing pollution loads from the Volga or other Caspian rivers. Indeed, pollution levels in Volga sediments and deltaic sediments do not confirm the large load purported to come from the Volga. …*

Measurements of contaminants in rivers are more difficult to come by. For the Volga River, original data was not released to the CEP; rather, only reports and aggregated data were available. The general literature supports the notion that contamination in the Volga River is significant, and be-

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[124] At this point, the circle closes in. The 'State Committee of the Russian Federation for Environmental Protection and Hydrometeorology' prepared the CEP national report of the Russian Federation 1998. For the underlying data sets, see footnote[120].

cause of the river's vast reservoirs and wetlands, a large percentage of these contaminants must be sequestered prior to reaching the Caspian Sea. The sediment data from the ASTP ('At-Sea Training Programme'; R.O.) *cruise (analyzed by the Russian Laboratory Typhoon) supports the idea that the Volga may not be as contaminated as has been reported, at least in its lower reaches*." (CEP, 2002)

No consistent data for the Volga reservoirs is said to be available, and so the speculation whether *'the Volga reservoirs can now be regarded as storage tanks of pollutants'* (CEP, 1998) remains. In fact all the above reports (still) use this idea as an explanation for the unexpected good sediment quality in the Volga delta, considering, that it's only influenced by two major point-sources of pollutants – Volgograd (approx. 500km upstream, and therefore only of minor influence) and Astrakhan (as well, as the agricultural activities in the delta-region). On the other hand this gives rise to fears, that these presumed contaminated sediments in the Volga reservoirs could be considered a 'chemical time bomb' for the downstream parts of the Volga, and a real threat to the Caspian Sea, once they are released.

Although not explicitly mentioned in the CEP-report, data for the Volga reservoirs has been published, mainly for those on the upper Volga (Ivankovo, Uglich, and Rybinsk). A big drawback is owed to the fact, that most of these studies are not comparable to 'western' studies with respect to methodology and interpretation.

E.g. Kosov et al. (2001) report data for heavy metals (Pb, Cu, Cd, Zn, Cr and Hg) in Upper Volga sediments (from the Upper Volga lakes downstream up to the Ivankovo reservoir). They sampled 16 stations in two years (resulting in 25 samples); the bulk sediment was dried, digested with 5M HNO_3 and measured by the use of AAS-techniques.

The sample with the lowest concentration within the upper Volga lakes was defined as background-sample, and an Index of Accumulation (IA)[125] was calculated, to characterize the excess of a given element – the anthropogenic impact. The reported IA's are impressively high – as long, as one is not looking at the underlying data:

Table 23 Heavy metal contents in Upper Volga bulk sediments up to Ivankovo reservoir (Kosov et al., 2001)

n=25	[mg/kg]					
	Pb	**Cu**	**Cd**	**Zn**	**Cr**	**Hg**
assumed 'background'	1.05	1.09	0.13	11.1	3.94	-
Mean	9.5	5.4	0.21	42.9	4.8	0.001
Max. reported value	14.1	14.53	1.99	93.9	6	0.0019

Except for Cd the assumed 'background' values are beyond discussion for fine grained sediments (and according to their IA-calculations even change between 1998 and 1999 (!)) – while in case of bulk sediment (i.e. 'quartz' with an unknown amount of fines and organic debris) the Cd-background would be much too high, with respect to the other elements. No matter what the sediment may be like, the 'background'-values just do not fit any reasonable assumption for the Upper Volga, and the reported maxima are far from being frightening.

So what in fact is reported, are low concentrations of heavy metals and unjustifiable low background-values with questionable elemental-ratios[126].

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[125]
$$\mathrm{IA} = \frac{C_i - C_b}{C_\mathrm{b}} \times 100\%$$
$$C_i = \text{Concentration of the measurand } i$$
$$C_b = \text{Background concentration of this measurand}$$

[126] In fact this paper is only cited, because it is the only one (to my knowledge) dealing explicitly with the geochemistry of sediments upstream the Ivankovo reservoir.

The Water Problems Institute, Russian Academy of Science (IWP RAS) in 1983-1998, has sampled the sediments of the **Ivankovo reservoir**. Results of this work were published by Brekhovskikh et al. (2001) and characterized according to the overall Contamination Index (CI)[127], which is not yet another index as one might think, but the standard procedure used in Russia to characterize the contamination of soils[128], applied to sediments. Once again, the reported CI's are impressive (up to 150), but many questions remain. Not only is the digestion-method for the sediments not mentioned, but also the sample size, sampling procedure, pre-treatment, and so on.

No matter what one might think about the CI, some results using it seem unreasonable – e.g. a reported change in CI (with respect to Mn, Zn, Cu, Pb, Cd, Ni, and Cr) from 150 to 9 between 1989 and 1998 for the Ivankovo reservoir would rather reveal an error in the methodology, than support the claim that "*such drastic changes in heavy metals concentration in the reservoir bottom sediments are caused, primarily, by decreased input of industrial wastewaters due to the production decline in the 1990s*" (Brekhovskikh et al., 2001).

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[127]

$$\boxed{\begin{array}{l} CI = \sum K_i n \quad ; \quad K_i = \dfrac{C_i}{C_b} \\ C_i = \text{Concentration of the } i\text{th element} \\ C_b = \text{Concentration of this element in the background area} \\ n = \text{number of integrable elements} \end{array}}$$

Presumably wrong! See[128]

[128] According to a manual by the Russian NGO's ECOLOGIA and ECOLINE the Index of Pollution (Z_c) used to evaluate the level of danger due to pollution in soils is calculated according to:

$$Z_c = \sum_{i=1}^{n} K_i - (n-1) \quad ; \quad K_i = \frac{C_i}{C_b}$$

Khotuleva ed. (1999)

This formula seems much more reasonable than the one reported by Brekhovskikh et al. (2001) - see[127] -, since it is independent of the number of measurants per sample.

A CI between 0 and 10 is considered as indicating a minimum level of contamination, 11-15 as a medium level of contamination, and over 15 as a high level of contamination by Brekhovskikh et al. (2001) – and even if one's not multiplying by *n*, as implied by their formula, the measurement of 11 elements at their background-level would characterize a sample as medium contaminated (!).

Khotuleva ed. (1999) report the "*Reference evaluation scale for the level of danger due to pollution in soils by total index*" as follows: <16 (allowable), 16-32 (moderately dangerous), 32-128 (dangerous) and >128 (extremely dangerous), claiming these values were "*developed on the basis of health studies of populations living in areas with varying levels of pollution in the soil.*"

If one is willing to trust the underlying measurements, at least heavy metal contents for the Upper Volga Lakes (used as ‘background’ – spatial reach not mentioned) and the Ivankovo reservoir are reported:

Table 24 Average metal(oid)-content of sediments in the Ivankovo reservoir and the Upper Volga lakes (number of samples unknown) (Brekhovskikh et al., 2001)

[mg/kg]

		Ag	As	Cd	Cu	Co	Cr	Mo	Mn	Ni	Pb	Sr	Ti	V	Zn
Ivankovo Reservoir	1989	-	-	35.5	198.3	-	175.5	-	1840.8	64.4	42	-	-	-	2099.4
	1990	-	-	4.89	60.8	-	130.7	-	847.0	34.8	18.5	-	-	-	377.0
	1997	-	4.2	0.7	143.7	4.9	8.6	-	424.0	7.2	10.5	-	-	-	177.8
	1998	-	-	0.7	32.3	9.7	-	-	316.6	11.2	12.8	-	-	-	155.5
Upper Volga Lakes	sand	-	-	-	30	2.4	11	1.4	354	1.8	14	22	1013	30	-
	loam	0.04	-	-	33	10.6	40	0.6	692	8.5	15	27	1656	102	36

Besides other peculiarities in Table 24 (e.g. Cr-concentration in the Ivankovo Reservoir 1997 and the assumed background-level) a change in heavy-metal concentrations like the one reported for Cd in the Ivankovo Reservoir between 1989 and 1990 is only reasonable for an individual sample location, due to e.g. sediment transport, but they would be beyond imagination if they would have been derived from a representative sampling scheme, since such a large variation is at least very unusual for a fluvial environment, unless some sort of ‘event’ (e.g. dredging, flood) would change the composition of the sediment significantly. No such event is reported in the article, but instead the changes are explained by the decreased input of wastewater as mentioned above.

All in all, without the methodology mentioned – and at least a questionable representativeness – the results are of not much use, irrespective whether the reported decline in heavy-metal concentrations may be realistic or not.

Based on altogether 451 samples taken between 1990 and 1992 Gapeeva et al. (1997) report the average total bulk concentrations (HF-$HClO_4$-HNO_3-digestion) of heavy-metals (Cu, Pb, Cd, Ni, Co, Cr, Fe, Mn, Zn) and Li in the sediments of the Upper Volga Reservoirs (**Ivankovo**, **Uglich**, (The Volzhskii Pool[129] of) **Rybinsk** and **Gorkii**) as well as their spatial distribution.

Table 25 Average concentration (total content) of heavy metals and Li in bulk sediments of the Upper Volga reservoirs (Gapeeva et al., 1997)

	n=	175	149	52	75
	Reservoir	Ivankovo	Uglich	Rybinsk	Gorkii
[mg/kg]	**Cd**	**5.3** ± 2.4	**2.0** ± 0.7	**1.9** ± 0.7	**3.2** ± 0.8
	Co	**-**	**46.6** ± 17.9	**20.3** ± 6.8	**26.3** ± 8.9
	Cr	**119.3** ± 55.2	**94.1** ± 27.3	**120.1** ± 24.0	**129.9** ± 25.8
	Cu	**80.6** ± 108.4	**39.2** ± 26.7	**22.7** ± 11.7	**31.4** ± 9.2
	Ni	**34.4** ± 11.8	**48.4** ± 17.4	**34.9** ± 11.2	**48.6** ± 15.6
	Pb	**19.6** ± 12.0	**29.3** ± 8.5	**13.4** ± 8.4	**42.5** ± 11.2
	Zn	**415.7** ± 371.9	**239.8** ± 141.6	**119.5** ± 65.9	**140.1** ± 62.6
	Li	**14.4** ± 6.2	**15.1** ± 5.6	**21.3** ± 7.5	**29.6** ± 10.9
[g/kg]	**Fe**	**7.15** ± 3.11	**8.9** ± 3.6	**6.5** ± 2.5	**8.9** ± 3.0
	Mn	**0.79** ± 0.4	**1.5** ± 1.0	**1** ± 0.4	**0.8** ± 0.3

From the uniformity of the normalized heavy metal values (normalization with respect to Li), they considered the Reservoirs to be **not** polluted by heavy-metals – except for a considerable anthropogenic pollution with Cu and Zn in the Ivankovo Reservoir and the upper parts of the Uglich Reservoir.

Unfortunately it is not mentioned, what measure of spread is reported ((2*) standard deviation?). The bulk sediment was digested, and unsurprising the location of the samples with the highest concentration of heavy metals coincided with the "*zones of accumulation of silty deposits*."

No such complete and consistent data seems to exist for the Reservoirs downstream and except for some sparse hints for the Reservoirs of **Cheboksary** and **Volgograd**, only aggregated data for the **Kuibyshev** Reservoir have been reported.

E.g. an unknown number of samples from 13 stations within the Kuibyshev reservoir sampled in 1991 and 1992 were measured by AES, injecting the powdered (presumably bulk) sediment in an arc discharge by an air current – which should result in some sort 'total content' of the samples. The concentrations of heavy metals were considered as 'insignificant', not exceeding background levels (Ershova et al., 1996):

Pb: 10-48.5 – Zn: 60-285 – Cr: 88-170 – Cu: 13-80 – Ni: 44-180 – Co: 12-78 – As: <20-30

Fe: 5.3-29.1*10^3 – Mn: 0.5-8.5*10^3 [mg/kg]

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[129] I.e. the southern part of the Reservoir under the influence of the Volga River inflow.

3.1 Reasons for this study

Due to different methodologies especially with respect to sampling/sampling-preparation (sampling schemes sometimes unknown, measured fraction bulk sediment (< 5 mm; < 2 mm)) and digestion/measurement-techniques (ranging from 5M HNO_3 up to techniques resulting in 'total content' of the samples), the reported results (raw-data up to normalized data) are hardly comparable – and the question whether Volga-sediments are (heavily) contaminated or not remains open.

Except for the cited works of Winkels et al. and parts of the works of Lychagin et al. – conducted in the Volga-delta – none of these studies accounts or the grain-size distribution and/or its effect on the heavy-metal content of the sediment. While the aforementioned authors normalize their results according to a Dutch procedure to a uniform soil type with 25% of clay (i.e. fraction < 2 µm) and 10% of organic matter, in order to make them comparable, other studies don't – even in case parameters generally used for normalization were measured.

Simplified, sediment – as a result of weathering – can be divided into two fractions: an 'inert' fraction, with little or no ion exchange and sorption capacity which is therefore (almost) not involved in any (ionic) water-sediment-exchange, and an 'active' fraction. Mineralogically the 'inert' fraction is identical with the 'coarse' (or sand) fraction (i.e. approx. > 63 µm), mostly consisting of quartz, feldspar (if freshly weathered), and occasionally mica and other silicate minerals, while the 'active' fraction corresponds to the 'fines', containing variable amounts of so-called 'clay minerals' (phyllosilicates of the illite-, kaolinite-, chlorite-, and smectite families) with a large surface and corresponding ion exchange and sorption capacity (Müller et al., 2001). It is almost exclusively this 'active', 'fine' fraction, which is affected by changes in (trace-) element contents due to natural and/or man-made changes in the aquatic environment – the processes we are interested in. Inevitably, a strong dependence between the metals under investigation, as well as other trace elements, and the grain-size distribution of sediment-samples is observed, since the 'coarse' fraction mainly acts as a thinner[130]. This already led Förstner and Wittman (1979) to the conclusion: *"One can even go as far as to state that without a correction for grain-size effects, a mutual comparison of metal data in fluviatile deposits would be impossible."*

No strict border-line can be drawn between 'coarse' and 'fine' fractions – as well as between ''inert' and 'active' – leaving little more than a rule of thumb for monitoring and assessment of trace-

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[130] Things get a bit more complicated, with respect to the organic fraction of the sediment, which can act as an 'inert' thinner, or take an 'active' part in ion-exchange and accumulation, depending on its nature. Without knowledge about the kind of organic substances in the 'fine' fraction, no statement is possible, which in turn makes normalization with respect to the organic content quite uncertain.

elements: ‘the finer, the better’, with the fraction < 20 µm presumably a good compromise between expenditure of separation and remaining grain-size-effects (Müller et al., 2001).

So an additional variable susceptible for large errors – especially in a fluviatile environment with its usually large variations with respect to sedimentation conditions – is introduced to the sampling scheme: grain size. If measuring bulk sediment, one would have to assure additionally, the grain-size distribution of the samples to be representative for the sampled sediments – or follow the assumption, that the heavy-metal content of the ‘fines’ only depends on their nature (background-concentration, ion-exchange-capacity) and the environmental conditions (e.g. natural and man-made offer of ions for exchange), but not – or to a much lesser content – on sedimentation-conditions, and use them. Although this will not eliminate grain-size-effects completely, as they will remain no matter how ‘fine’ the fraction might be, they are considerably delimited compared to the coarser fractions – and so are the requirements of the sampling-scheme.

In order to overcome these problems, there are numerous ways to normalize the results of studies based on bulk sediment, e.g. with respect to Li, Al, Fe, TOC, the grain-size itself. Besides the fact that none of these ‘normalizers’ is of general applicability (NAVFAC, 2003) and the underlying assumptions would have to be checked at background samples (Louma, 1990), an additional amount of uncertainty will be introduced to the data-set (division of two measurements and thus propagation of error). The only advantage of measuring bulk sediment, besides its ease of ‘separation’, namely to know what amount of (trace-) metals are stored in a specific sample at a specific place with a specific grain-size distribution would only be useful for balancing the element load and, to a limited extend, the element fluxes in the sediments along the river; tasks with a complexity and expenditure far beyond the scope of this study, as well as any known study on the River Volga. For any other purpose, especially for monitoring and assessment of (trace-) elements, the use of ‘finer’ fractions – like the < 20 µm fraction used here – is not only equivalent, but superior with respect to methodological uncertainties (e.g.: no necessity for representative sampling with respect to grain-size distribution, less expenditure for homogenization and preparation (grinding) of the samples) as well as being more sensitive to potential natural and/or man-made changes, since only the ‘active’ parts of the sediment are considered.

It seems reasonable to assume that the advantages of using a smaller grain-size fraction, like the fraction < 20 µm used within this study, outweighs the disadvantages of producing yet another data set which is not comparable to the existing data-sets on the River Volga. Moreover it is the only consistent data-set with respect to sediments regarding the whole course of the River Volga, including all major Reservoirs and the Delta-Region, whose results are not only comparable to the Oka-Elbe-project (Rivers Oka, Moscwa and Klyazma) but also to comparatively well-investigated 'German' Rivers like the Rhine or the Elbe and the there established concentration-limits, since it uses the same methodology of monitoring

4 Results and discussion

4.1 Statistical overview – the 'traditional' approach

Table 26 gives an overview of some basic statistic parameters of all 270 samples taken in the River Volga itself – ignoring the tributaries and cores.

Table 26 **Basic descriptive summary statistics for the investigated Volga sediments**

	Count	Valid N	Missing Values	Maximum	Mean	Standard Error of Mean	Std Deviation (s)	RSD [%]	25th Percentile	Median	75th Percentile	95th Percentile	No. of Extremes [a)]	
													Low	High
Ag	270	266	4	5.32	0.39	0.03	0.47	121	0.18	0.28	0.44	0.83	0	13
Al [%]	270	266	4	5.12	3.50	0.04	0.59	17	3.13	3.47	3.84	4.59	1	2
As	270	269	1	40	8	0.24	4.01	48	6	8	10	15	0	10
Ba	270	266	4	611	238	4.51	74	31	180	238	290	349	0	3
Ca [%]	270	266	4	14.0	1.7	0.08	1.3	77	1.11	1.36	1.79	3.38	0	21
Cd	270	270	0	9.60	0.50	0.05	0.81	163	0.19	0.36	0.56	0.96	0	11
Co	270	266	4	27	18	0.20	3.27	18	16	18	20	23	5	3
Cr	270	270	0	284	76	1.37	23	30	65	75	86	103	2	6
Cu	270	270	0	174	44	1.40	23	52	34	38	47	98	0	19
Fe [%]	270	270	0	8.57	4.51	0.06	0.92	20	3.93	4.52	5.07	5.77	4	5
Hg	270	270	0	5.19	0.27	0.03	0.47	176	0.08	0.13	0.23	1.06	0	33
K [%]	270	266	4	1.40	0.73	0.01	0.20	27	0.58	0.70	0.84	1.10	0	8
Li	270	268	2	62	38	0.47	7.65	20	33	39	43	49	0	5
Mg [%]	270	266	4	4.98	1.20	0.02	0.39	32	0.99	1.19	1.35	1.71	3	5
Mn [%]	270	270	0	0.83	0.16	0.01	0.12	75	0.09	0.12	0.19	0.44	0	23
Mo	270	266	4	9.6	1.9	0.05	0.86	46	1.5	1.7	1.9	3.2	0	17
Na [%]	270	266	4	0.25	0.10	0.002	0.03	32	0.08	0.10	0.11	0.15	19	14
Ni	270	267	3	91	51	0.92	15	29	41	52	61	77	0	0
Pb	270	270	0	143	24	0.97	16	67	16	20	25	57	0	19
Sc	270	266	4	11.8	7.7	0.12	1.9	25	6.3	7.3	9.1	11.1	1	0
Sr	270	266	4	592	91	3.38	55	60	50	89	117	166	0	4
V	270	266	4	113	66	1.06	17	26	55	65	76	102	0	3
Y	270	266	4	23	16	0.15	2.5	15	14	16	18	21	0	1
Zn	270	270	0	752	171	7.35	121	71	101	128	180	451	0	31
C_{total} [%]	270	263	7	12.61	3.87	0.13	2.08	54	2.06	3.42	5.16	7.50	0	3
S_{total} [%]	270	263	7	0.98	0.18	0.01	0.12	69	0.10	0.15	0.23	0.42	0	14
P_2O_5 [%]	270	270	0	4.57	0.40	0.02	0.30	76	0.26	0.37	0.46	0.61	0	5
P [%]	270	270	0	1.98	0.17	0.01	0.13	76	0.11	0.16	0.20	0.26	0	5
CO_3 [%]	*270*	***174***	***96***	*38.0*	*3.6*	*0.3*	*3.9*	*108*	*2.5*	*2.5*	*2.5*	*9.3*	.	.
105°	270	260	10	7.4	4.5	0.05	0.7	16	4.2	4.7	4.9	5.5	14	5
LOI $^{550°}$	270	260	10	23.4	9.9	0.22	3.5	35	7.3	9.3	12.2	16.5	0	4

[a)] Number of cases outside the range (Q1 - 1.5*IQR, Q3 + 1.5*IQR).

IQR = interquartile range = Q3 (75th percentile) - Q1 (25th percentile)

Legend for Table 26:

Count (n): number of samples considered.

Valid N: number of samples actually used to calculate the statistics.

Missing values: number of samples with non-detects or missing values.

Maximum: largest extreme of the dataset.

Mean (**$\bar{x}$**): arithmetic mean of the dataset.

Standard error of mean: measure of how much the value of the mean may vary from sample to sample taken from the same distribution:
($s/\sqrt{n}$).

Std. deviation[131] (s): measure of dispersion around the mean given only a sample of values $x_1,\ldots,x_n$ from some larger population. In a normal distribution, 68% of cases fall within one SD of the mean and 95% of cases fall within 2 SD:

$$s=\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i-\bar{x})^2}$$

RSD [%]: relative standard deviation. It is identical with the coefficient of variation (CV [%]). Often more convenient than the standard deviation itself:
(RSD=100*s/$\bar{x}$)

nth percentile: divides cases according to values below which certain percentages of cases fall. The 25th, 50th and 75th percentiles are also called quartiles. While the 50th percentile is the median – a more robust measure of the central tendency for skewed distributions and distributions affected by outliers – the 25th and 75th percentile are used to calculate the interquartile range (Q3-Q1) and the 95th percentile is frequently used to establish a threshold of acceptance.

No. of extremes: observations that lie at an ‘abnormal’ distance from other values in the sample of a population as defined by the interquartile range (see footnote[132]).

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[131] Note that s is **not** an unbiased estimator for the standard deviation σ, it tends to underestimate the population standard deviation, as in fact does the whole process of sampling a population and the discussion whether to use n or n-1 in the denominator of the formula is rather academic – at least for that large samples of a population.

Already this table 'spoils' most expectations one might have had about a catastrophic situation with respect to inorganic pollutants on the River Volga. Neither the measures of central tendency (mean and median), nor the number of 'extremes[132]', or even the (necessarily arbitrary) maxima for most COPC's, support this still popular view (cf. Chapter 3, p.168ff.).

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[132] These are observations that lie at an 'abnormal' distance from other values in the sample of a population, which in a sense leaves it up to the analyst to decide what will be considered abnormal. The here used 'definition' of an outlier as the multitude of the interquartile range – i.e. the middle 50% of the data – is commonly used in Exploratory Data Analysis (EDA), but only considered a rough approach. It is essentially based on the widely used box-plots – a simple, yet powerful tool for conveying location and variation information in data sets. The sometimes used differentiation between 'outliers' (cases with values between 1.5 and 3 times the interquartile range) and 'extreme' values (cases with values more than 3 times the interquartile range) has been omitted.

4.2 Graphical overview – the ‘traditional’ approach

The basic idea of exploratory data analysis (EDA) is to let the data speak for itself and as with the above statistical overview, already some undemanding and basic graphical presentations are sufficient to answer the most important question concerning the River Volga’s contamination with inorganic COPC’s.

In no way is it possible to construct a demanding situation for the Volga as a whole.

For convenience, three types of charts, each providing a slightly different viewpoint are used:

Scatter Plot: plots two groups of numbers as one series of xy coordinates. In this case, the concentrations of a given characteristic for a specific sample vs. the Volga flow where the sample was taken. It is the most basic and unbiased way to represent the data, making no assumptions whatsoever. Despite the discussion about the uncertainty bound to the measurement process as a whole, only the analytical uncertainty has been assigned to the individual samples, since all other contributions towards the net-uncertainty are already the result of an in-depth interpretation[133].

Bubble chart: a variation of a Scatter plot in which the data points are replaced with bubbles. The concentration of a given characteristic is represented by the area or width of a bubble and is plotted vs. the GPS-data (easting and northing) of the point the sample was taken from. It provides a quick overview about where to expect ‘unusual’ concentrations compared to the ‘geogenic background’.

Box Plot (box-and-whisker-plot): a summary plot based on the median, quartiles, and extreme values. The box represents the interquartile range that contains the middle 50% of values. The whiskers extend from the box to the highest and lowest values, excluding outliers (see footnote[132]). Box plots are used to compare different groups of data, and prior to an in-depth interpretation of the data set, the man-made subdivision of the Volga discussed in Chapter 1.7.4.3 (p.56ff.) has been used to define these groups. Although NOT recommended as to state any real subdivision of the River Volga these plots provide information about individual reservoirs and have been kept in case one would not like to follow the later approach towards an assumedly more sound subdivision of the Volga.

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[133] However, in no way is this trying to encourage anybody to disrespect these other contributions!

The figures of the respective parameters (Figure 53 to Figure 80) follow the basic scheme described below considering as example zinc:

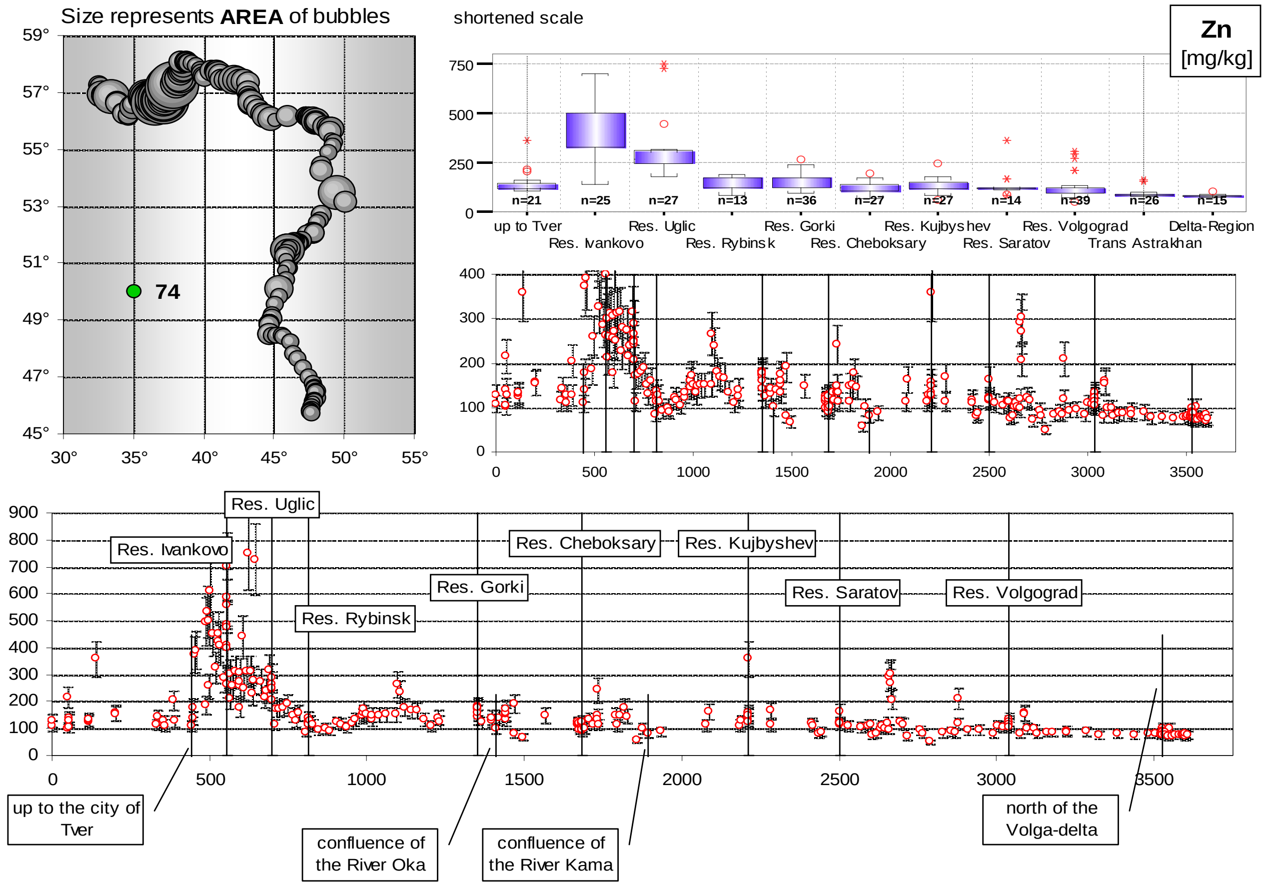


Figure 52 Basic scheme for Figure 53 to Figure 80.

<u>Upper left: Bubble chart</u>. Concentration of a characteristic is represented by the area or width of a bubble and plotted vs. the River course (axis: easting and northing). Green bubble represents the 'geochemical background' – where applicable the values reported by Ronov and Migdisov (1996) for clay rocks of the Russian plate; otherwise (Ag, As and Hg) the shale-values reported by Turekian and Wedepohl (1961) – cf. Table 27 (page 207).

<u>Upper right: Box plot</u>. Comparison of groups defined by the man-made subdivision of the Volga, namely the reservoirs. The scale may be shortened in order to present more details, while ignoring extreme values.

<u>Bottom margin: Scatter plot</u>. Concentration of a characteristic is plotted vs. the Volga flow [km]. The expanded uncertainty of the analytical measurement (**NOT** the measurement process) is assigned to the data-points. A second scatter plot with a shortened scale may be included in case extreme values dominated the initial scale and caused details to get lost.

Continuous horizontal lines represent the reservoir dams, while the smaller ones represent (from left to right) the artificial transect near the city of Tver, the confluence of the River Oka, the confluence of the River Kama and the fictitious transect north of the Volga delta-region (cf. Figure 39).

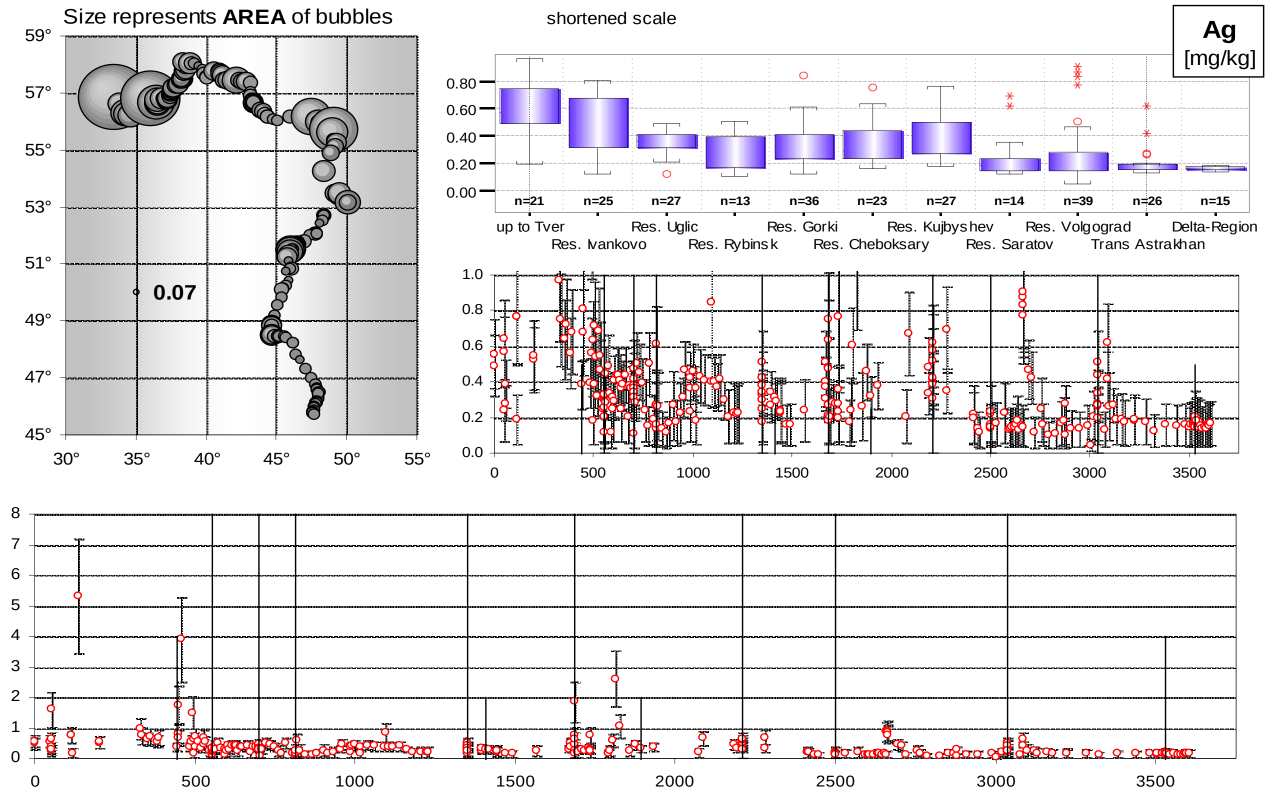
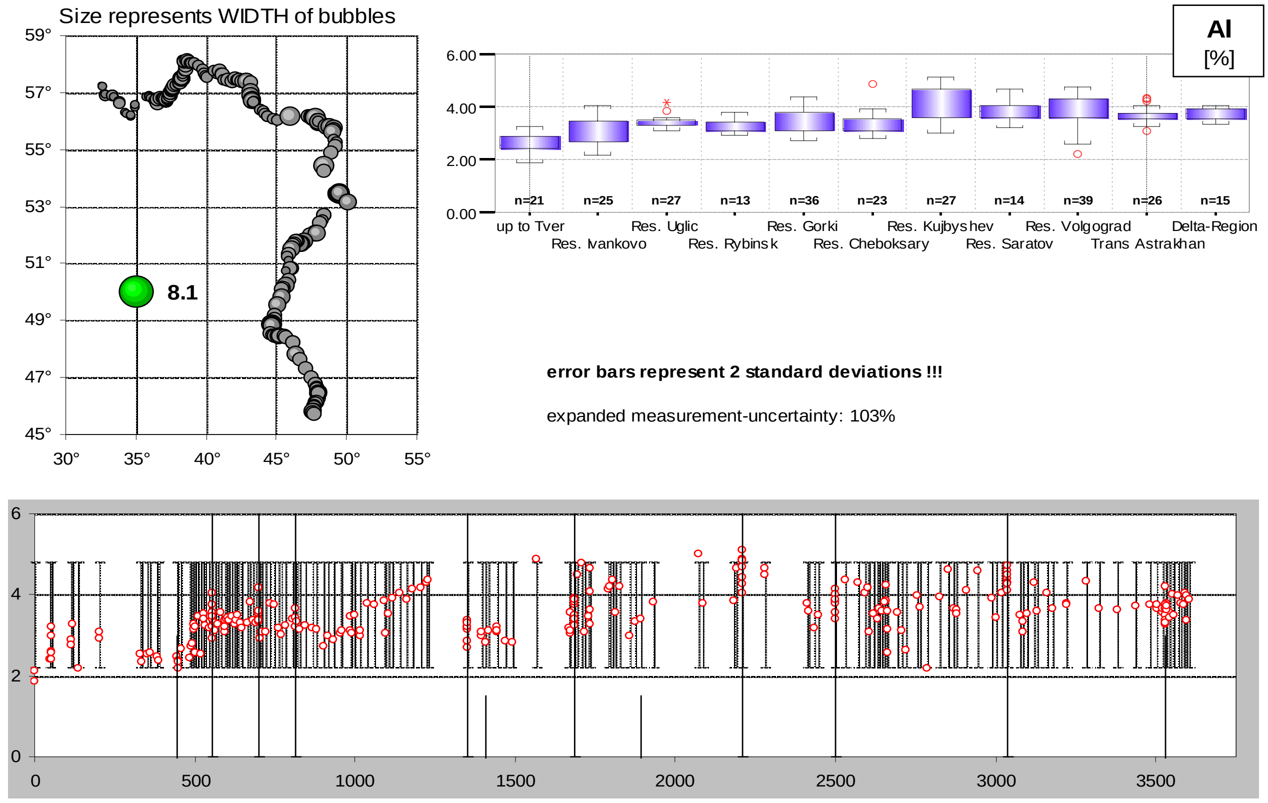


Figure 53 Silver-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)



error bars represent 2 standard deviations !!!

expanded measurement-uncertainty: 103%

Figure 54 Aluminum-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

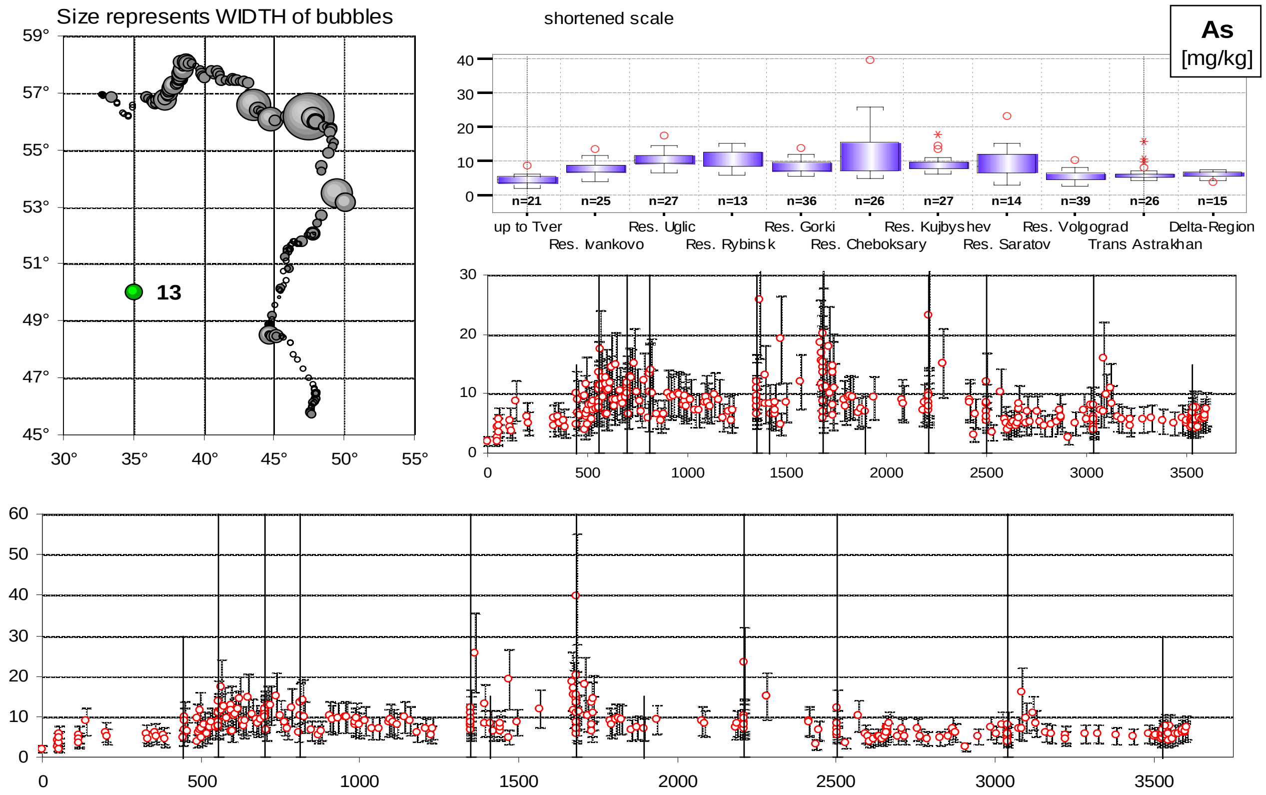


Figure 55 Arsenic-contents of the Volga-River sediments – fraction < 20µm (Legend see p. 187)

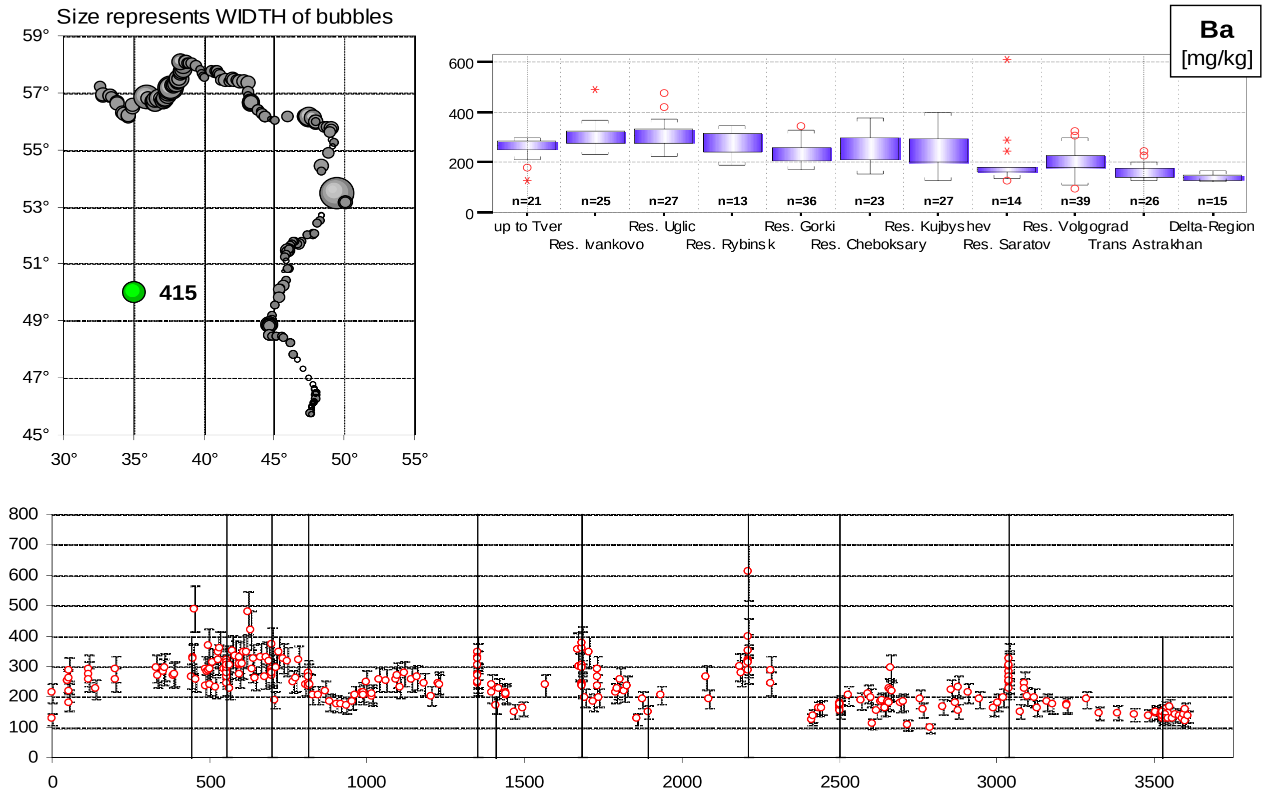


Figure 56 Barium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

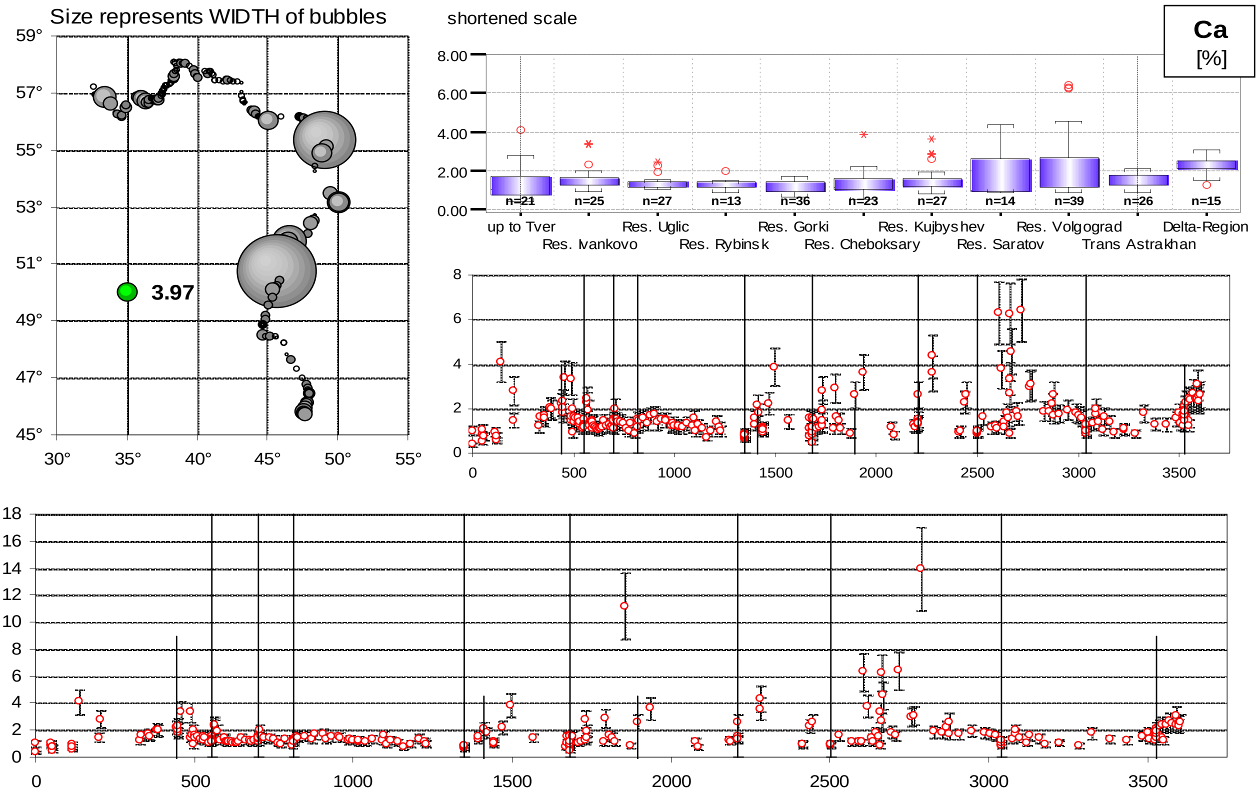


Figure 57 Calcium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

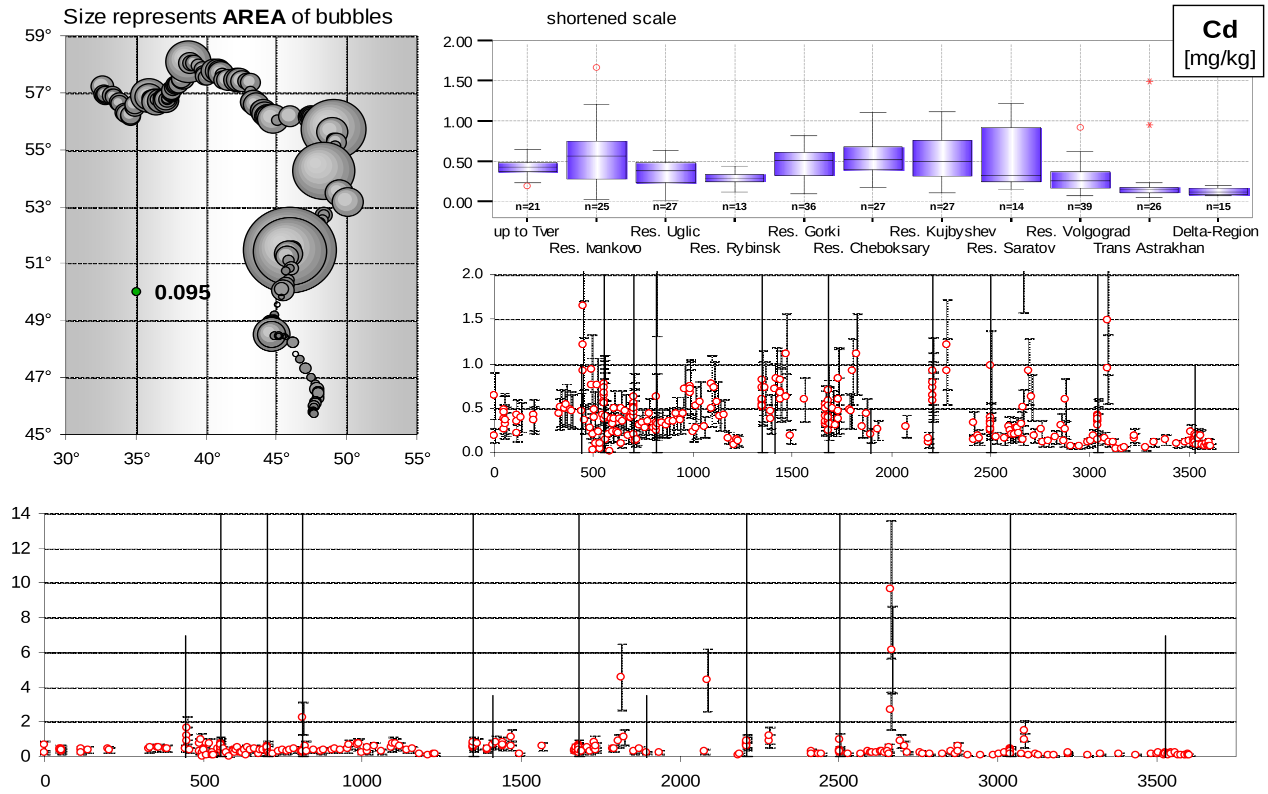


Figure 58 Cadmium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

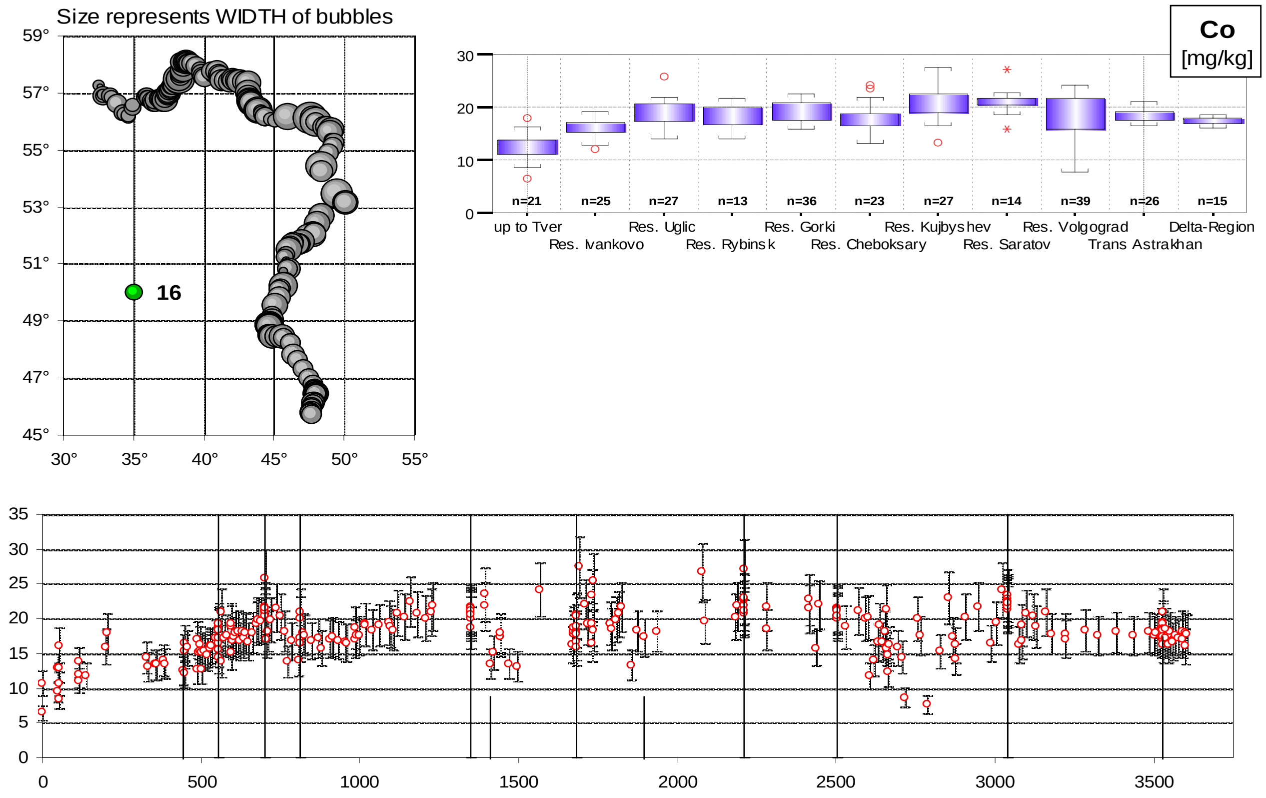


Figure 59 Cobalt-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

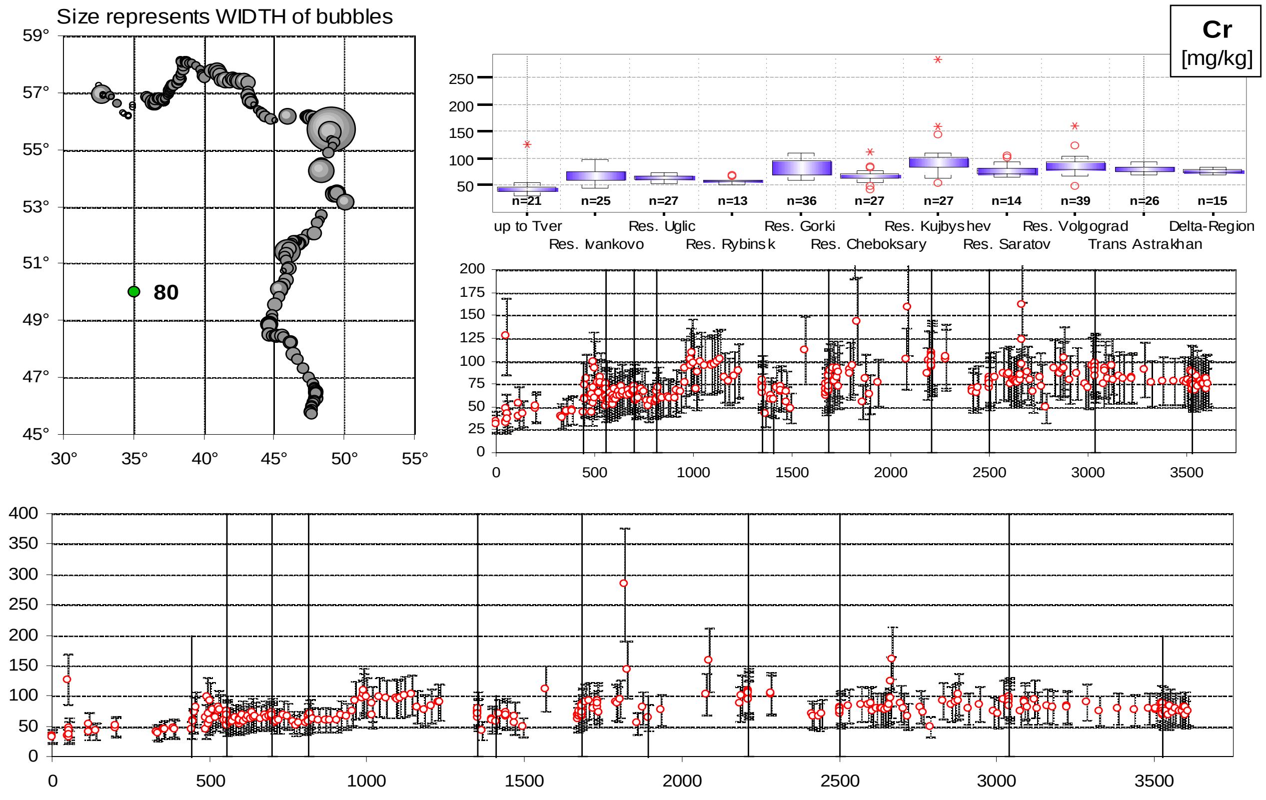


Figure 60 Chromium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

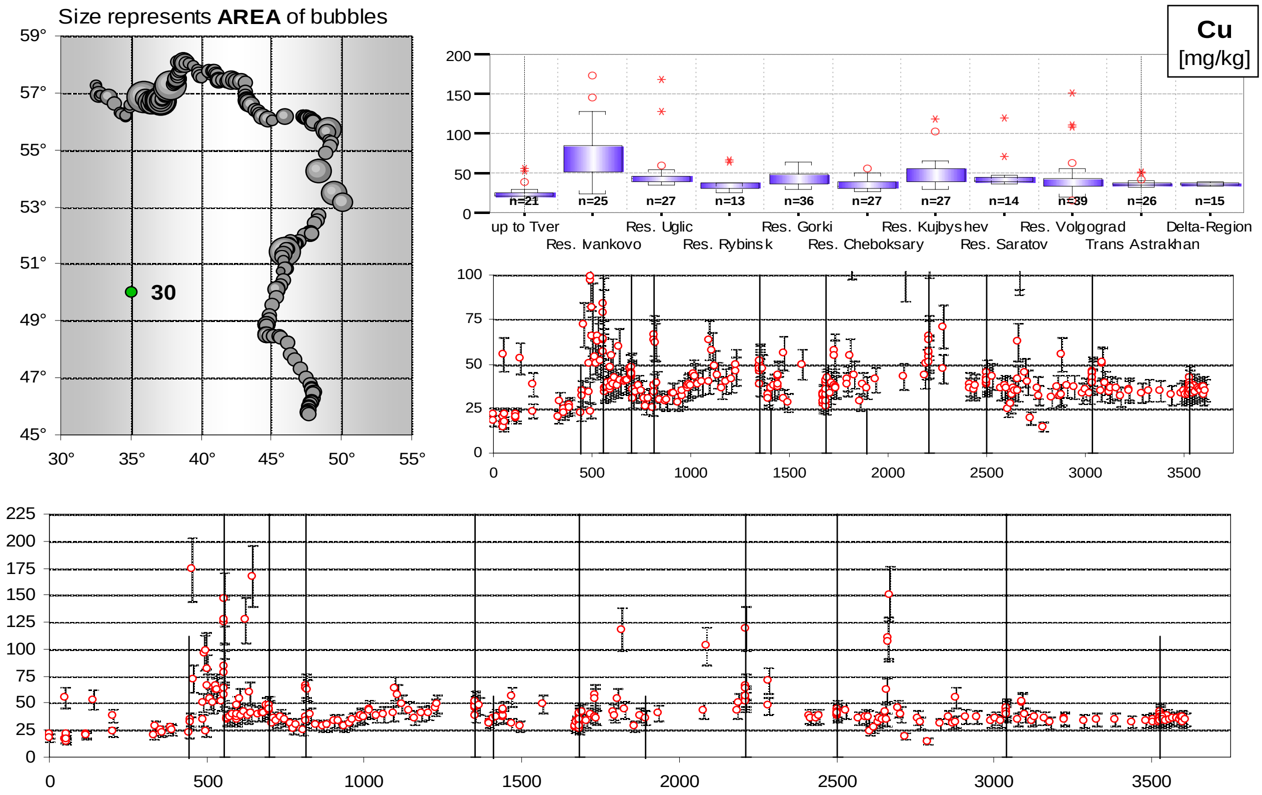


Figure 61 Cupper-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

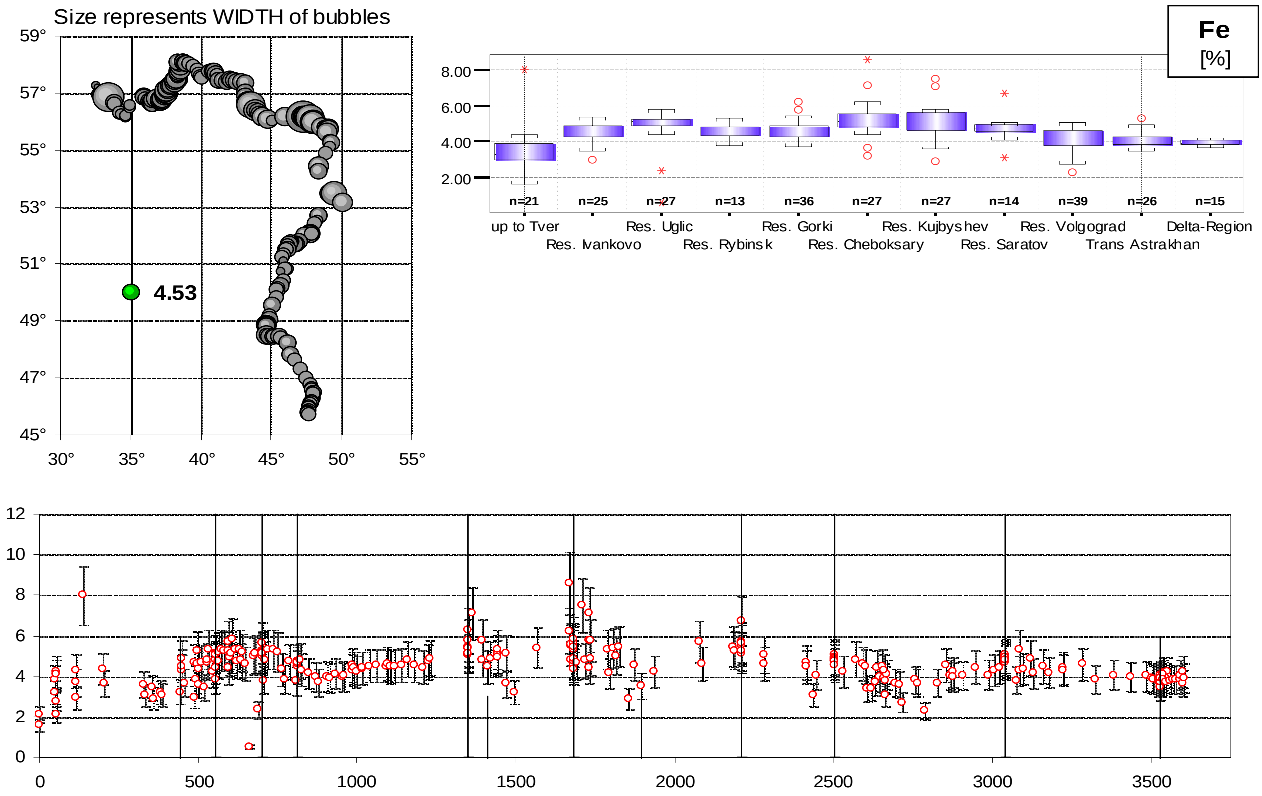


Figure 62 Iron-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

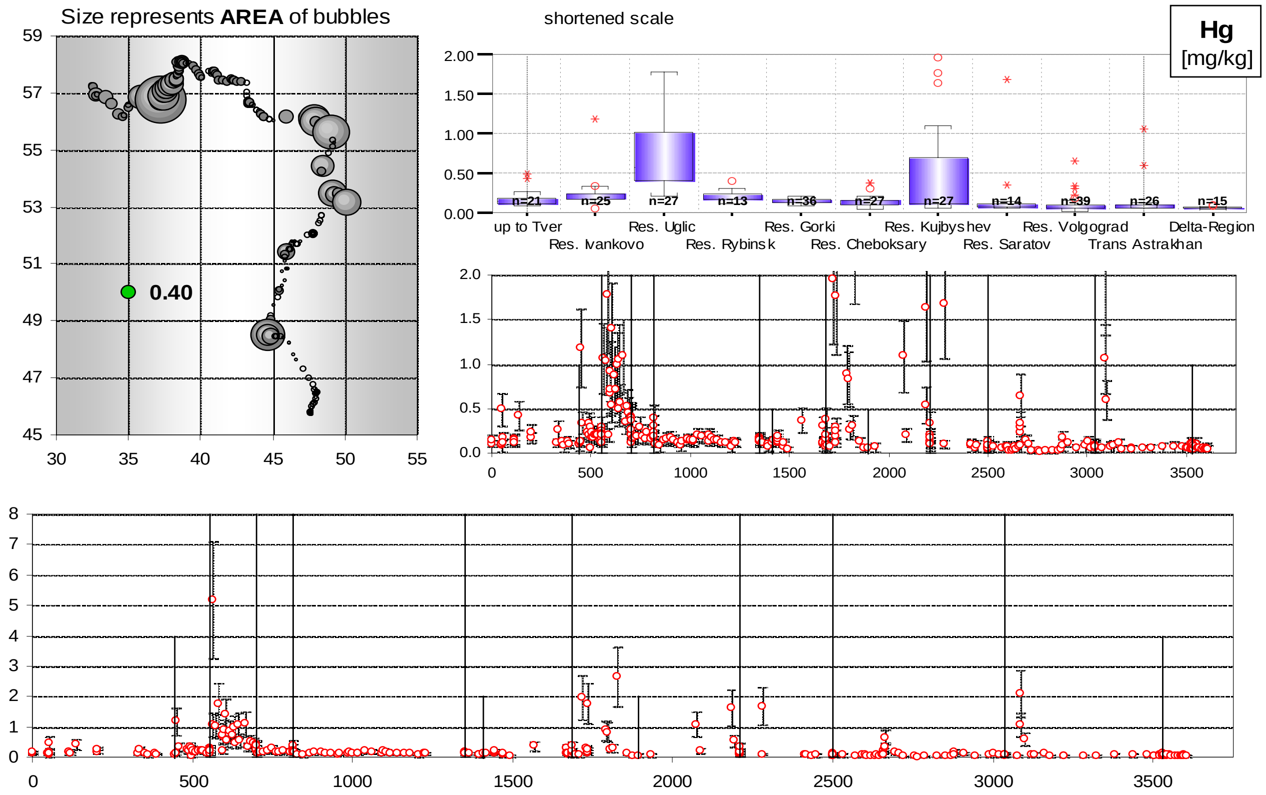


Figure 63 Mercury-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

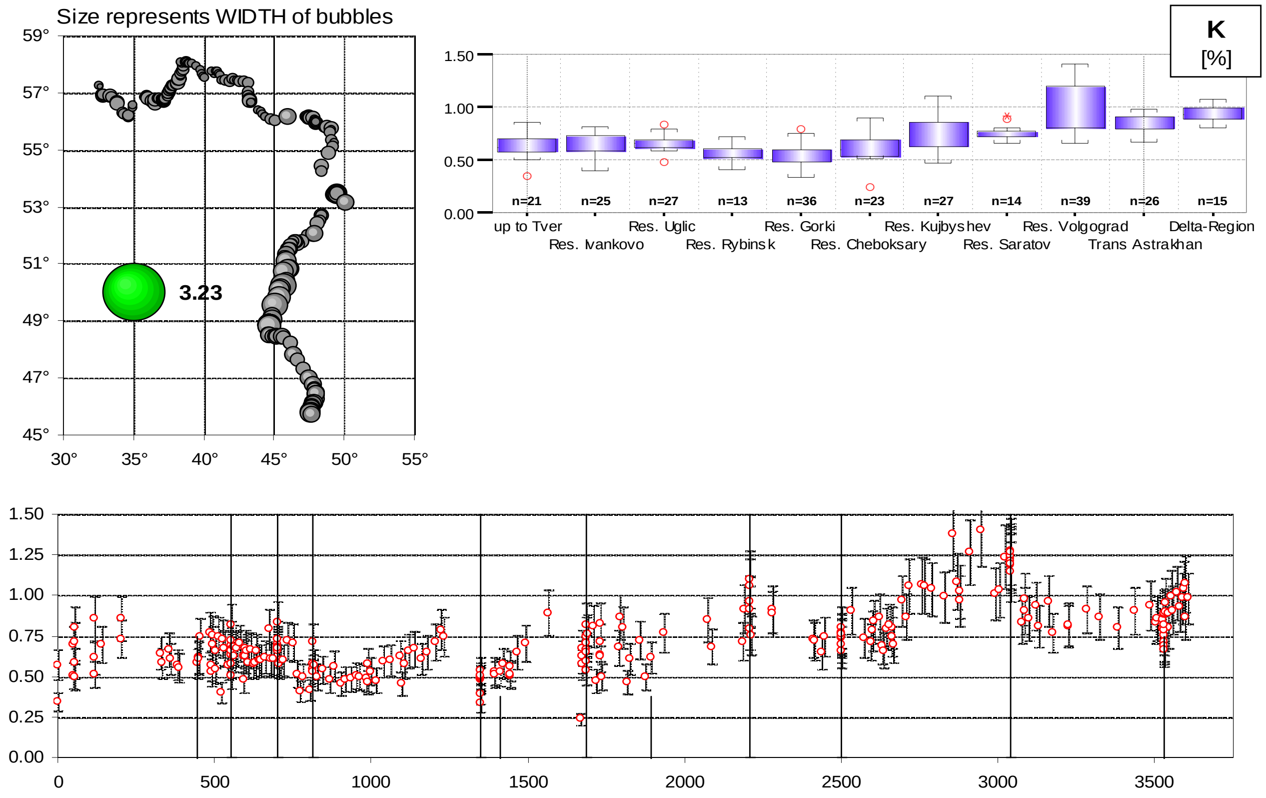


Figure 64 Potassium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

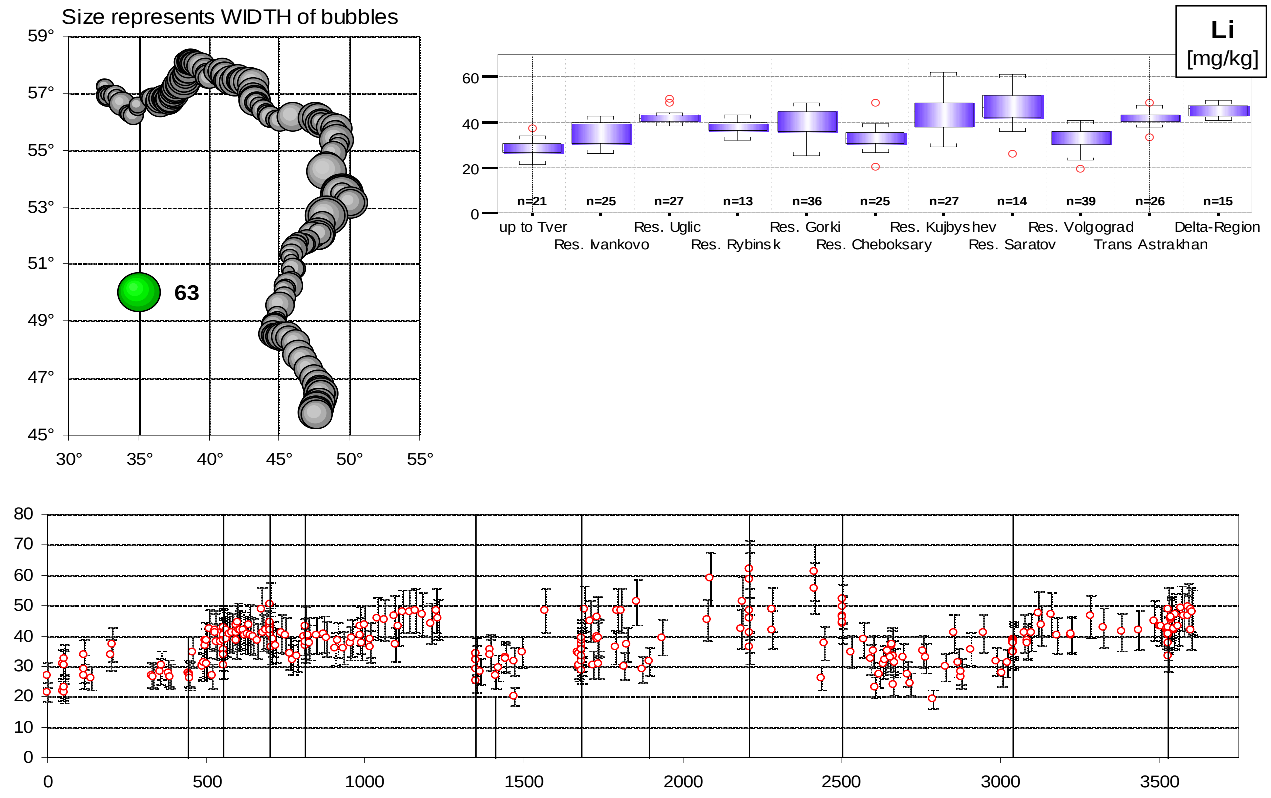


Figure 65 Lithium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

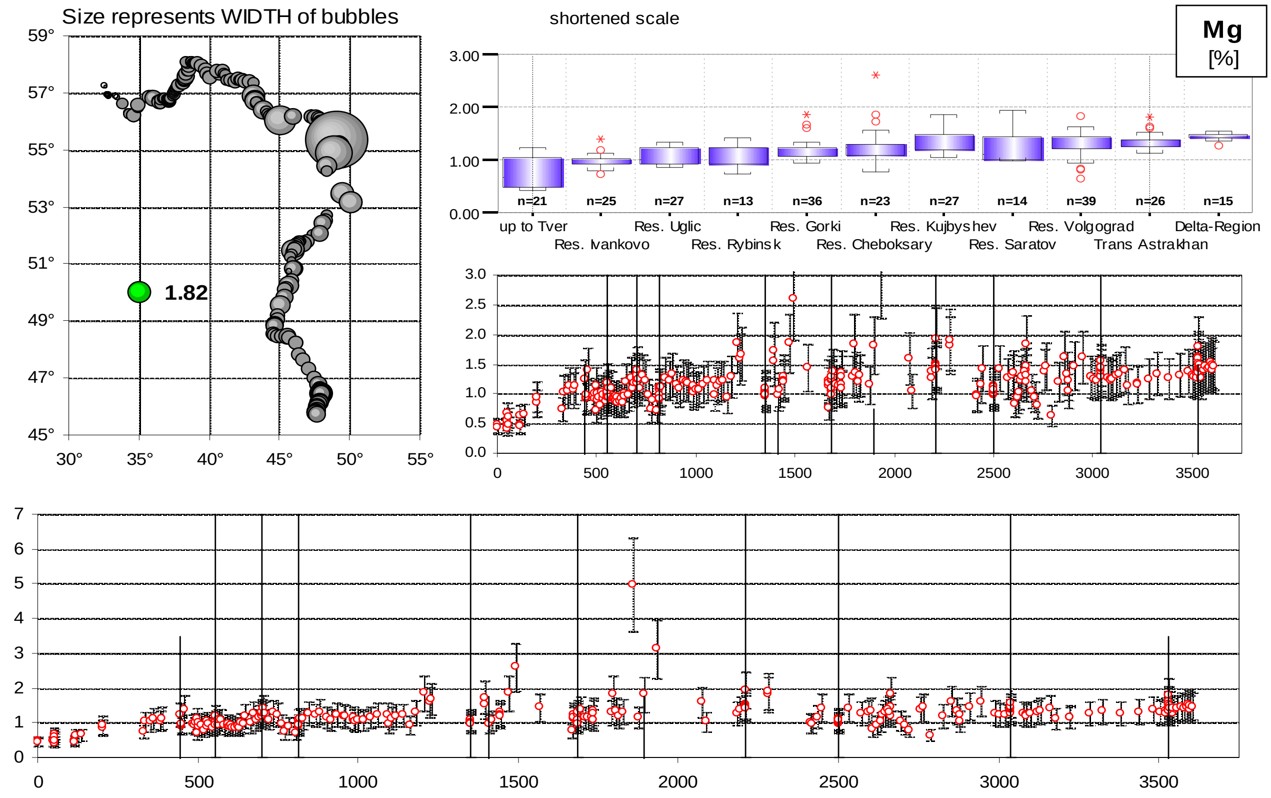


Figure 66 Magnesium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

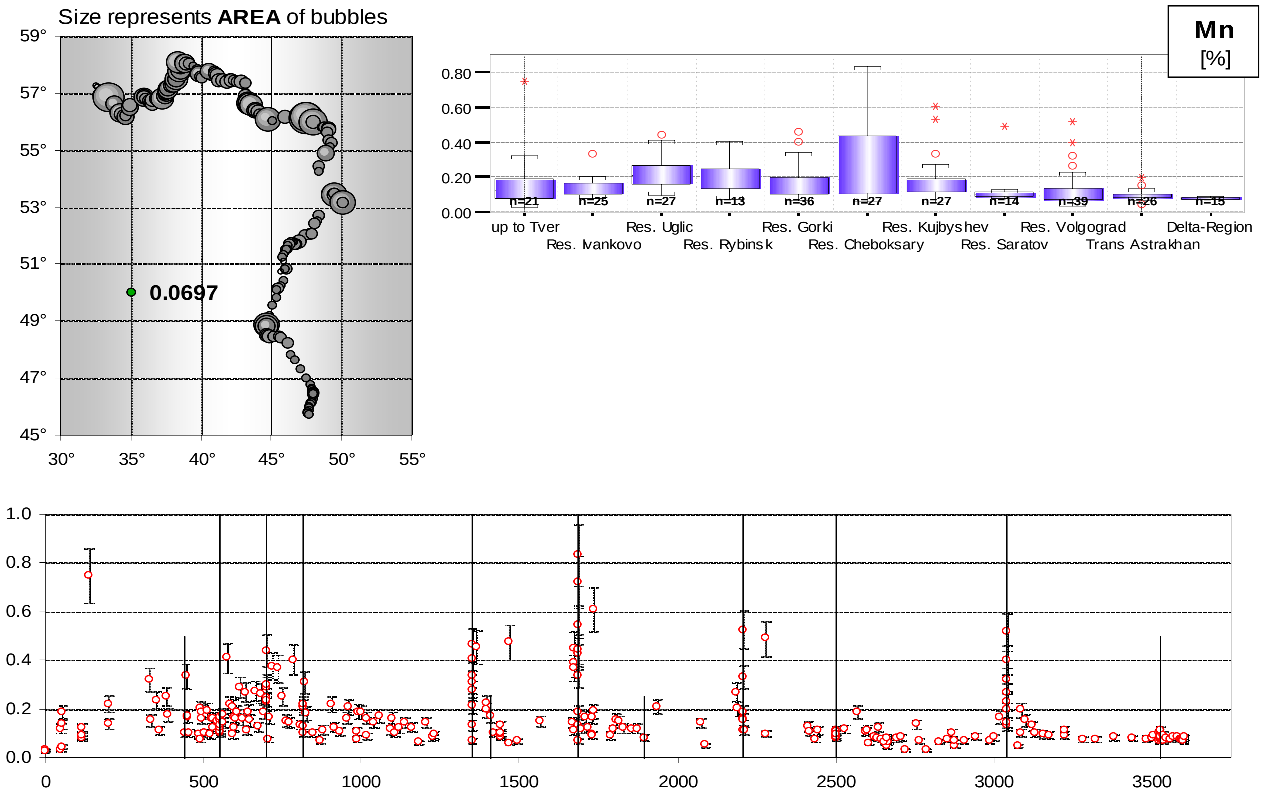


Figure 67 Manganese-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

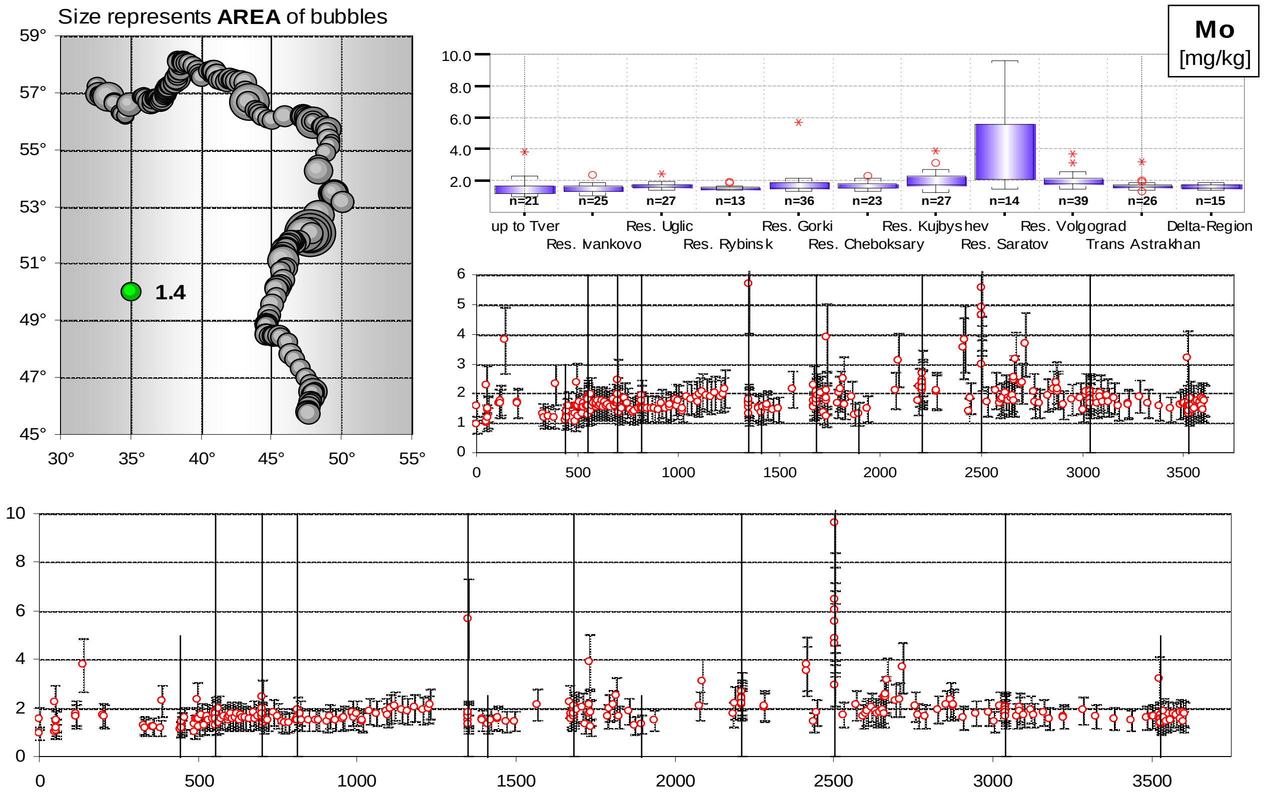


Figure 68 Molybdenum-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

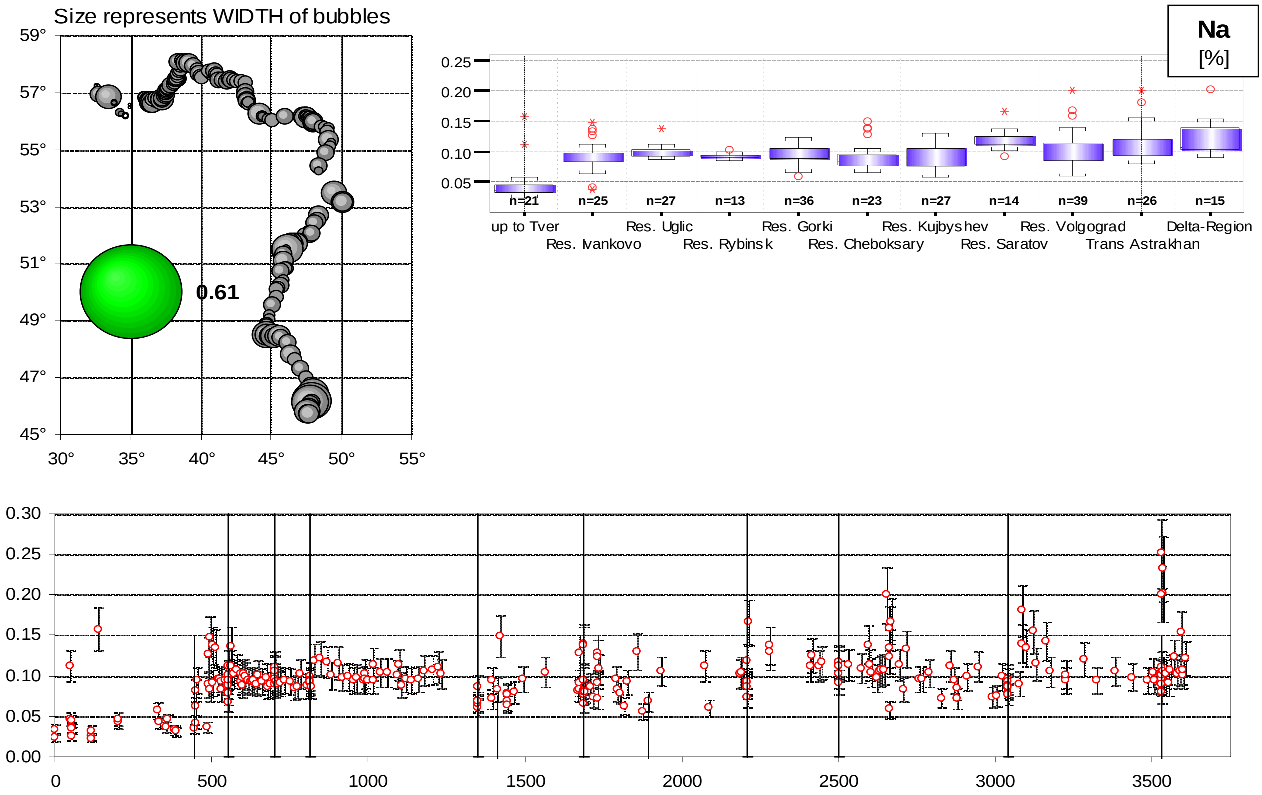


Figure 69 Sodium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

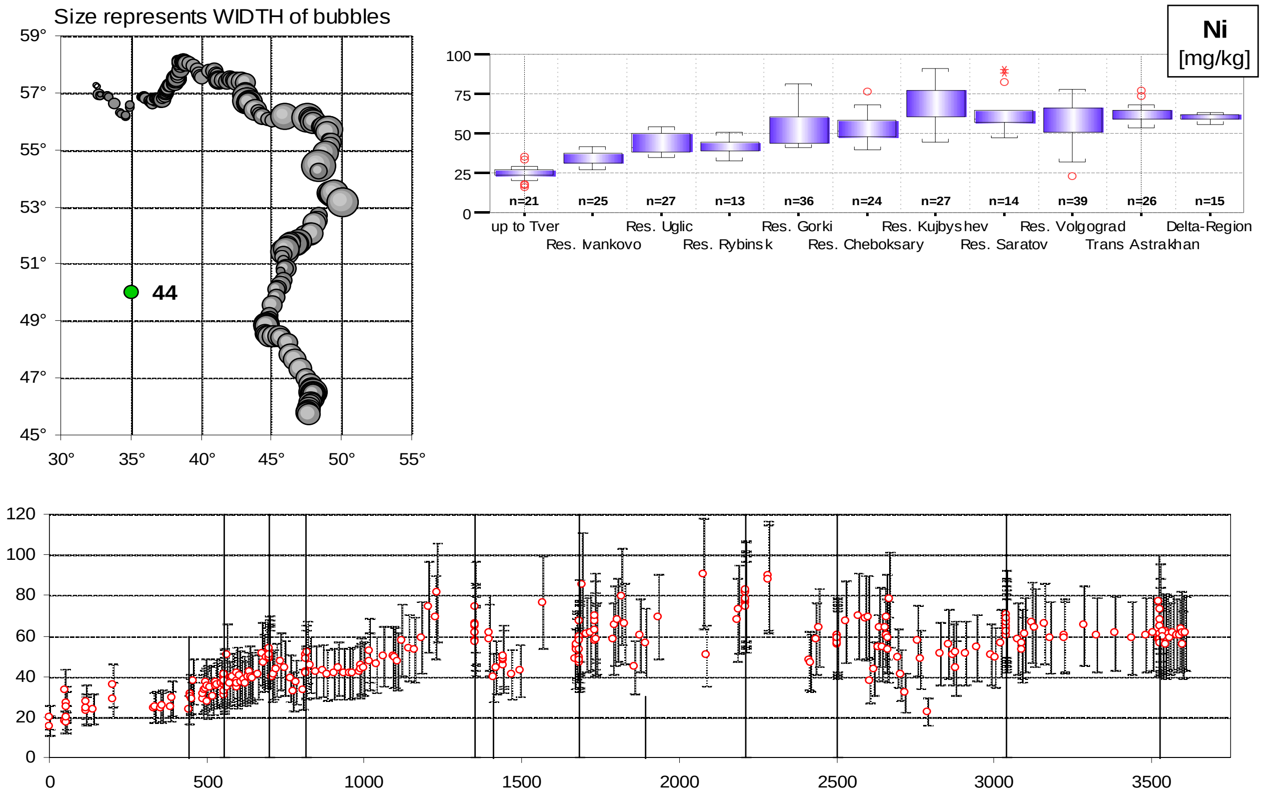


Figure 70 Nickel-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

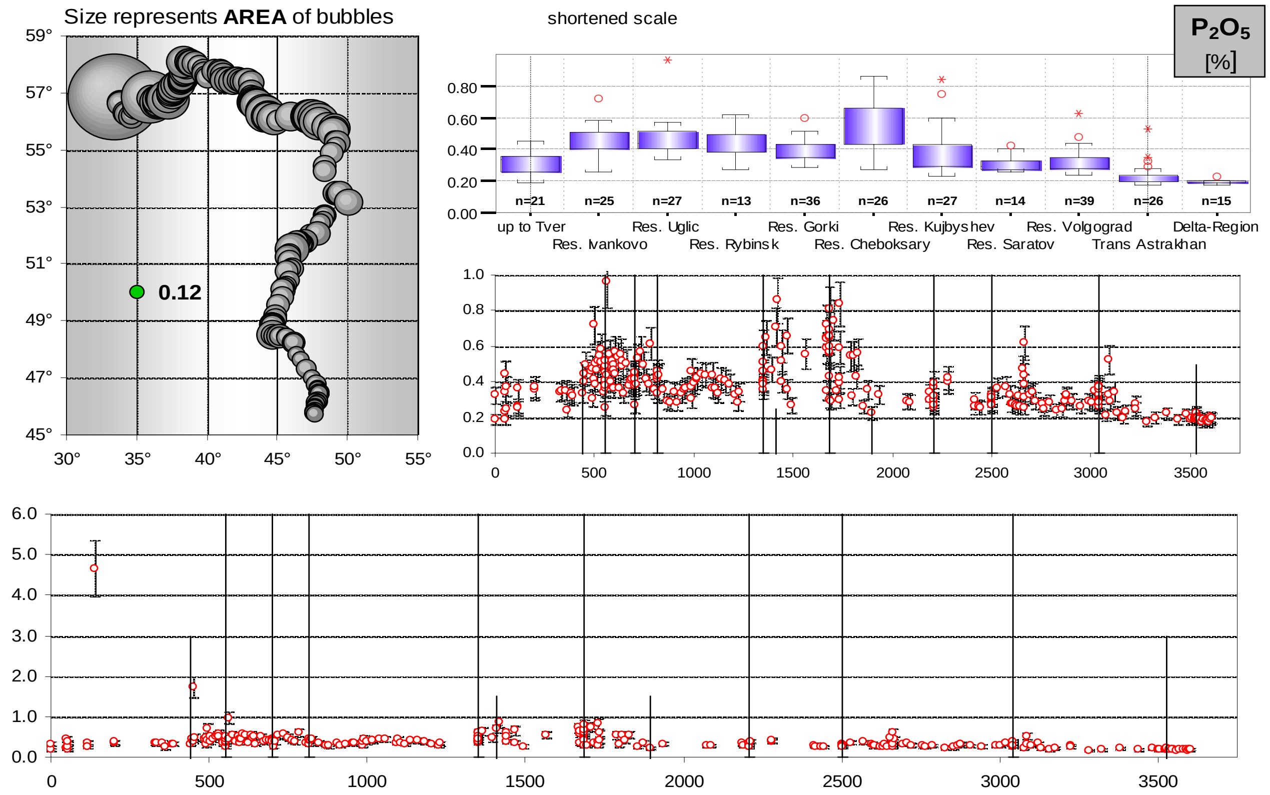


Figure 71 **Phosphorus-contents (expressed as P_2O_5) of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)**

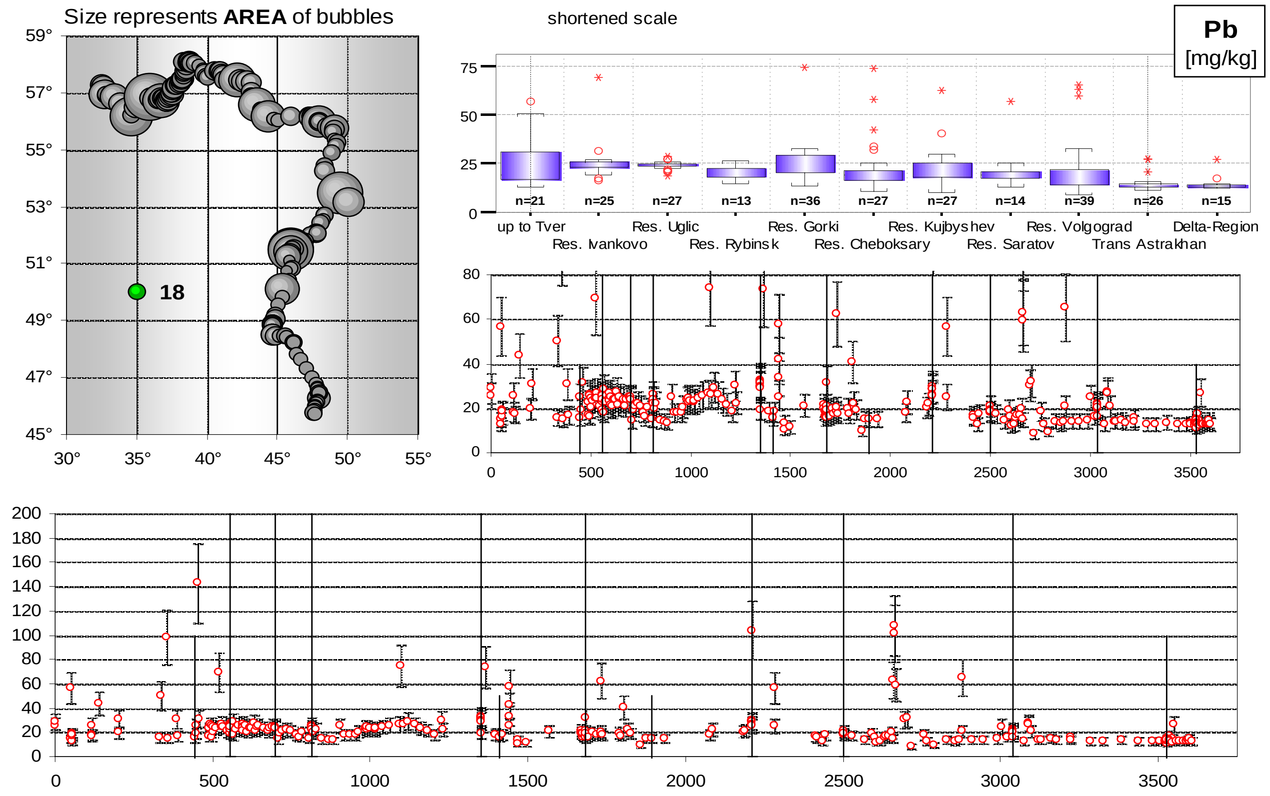


Figure 72 **Lead-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)**

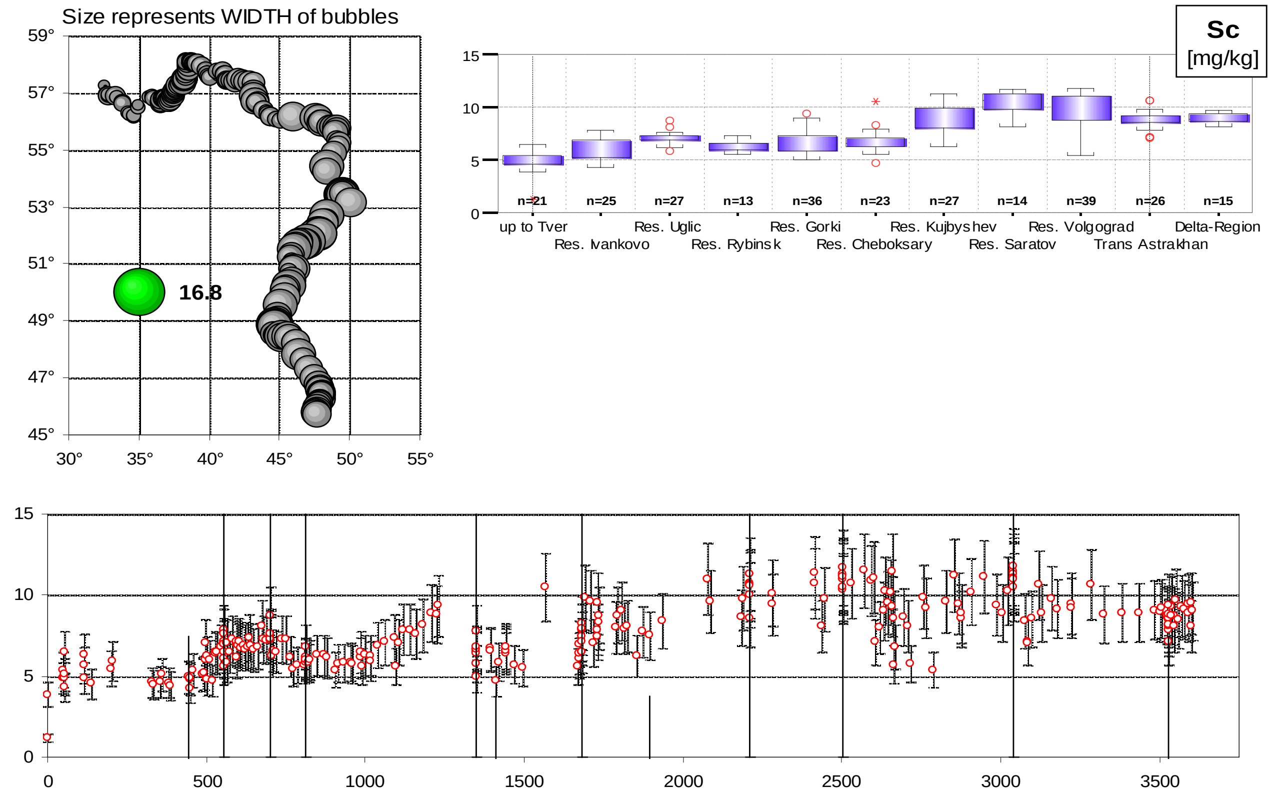


Figure 73 Scandium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

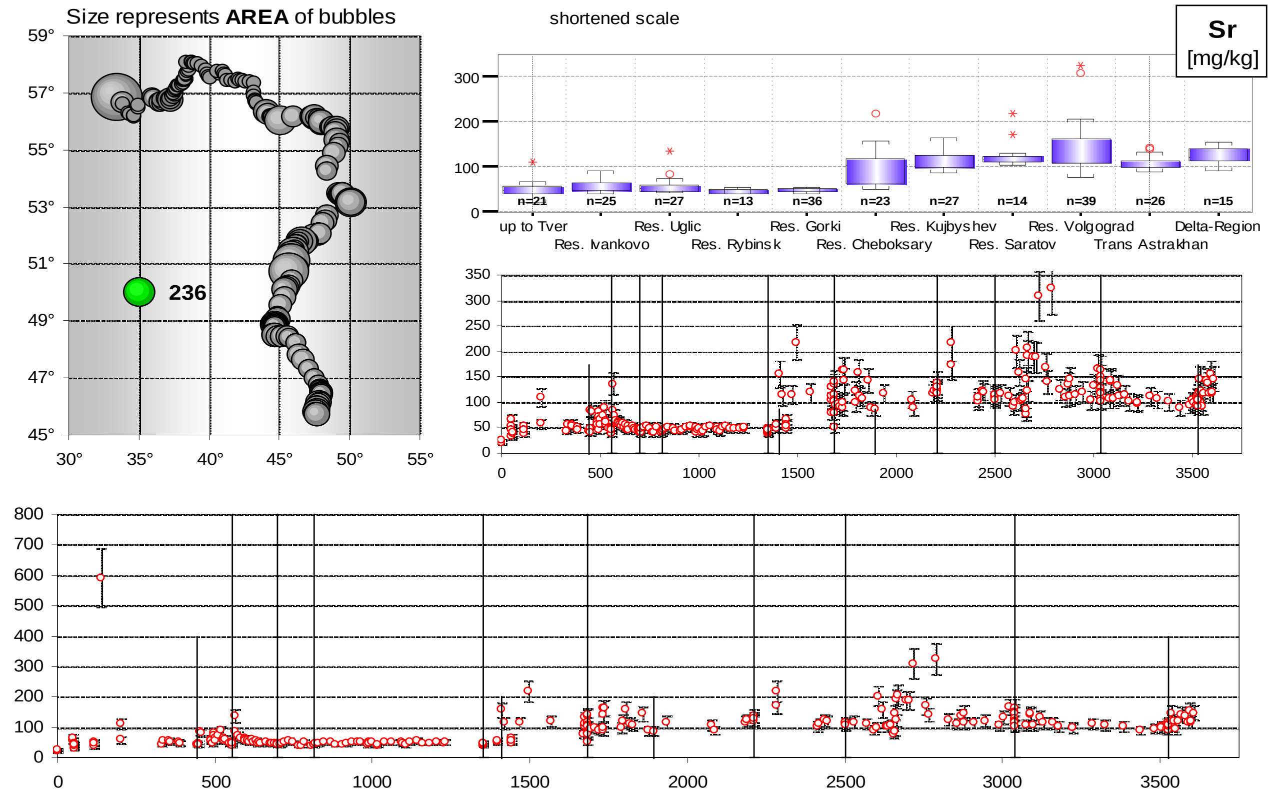


Figure 74 Strontium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

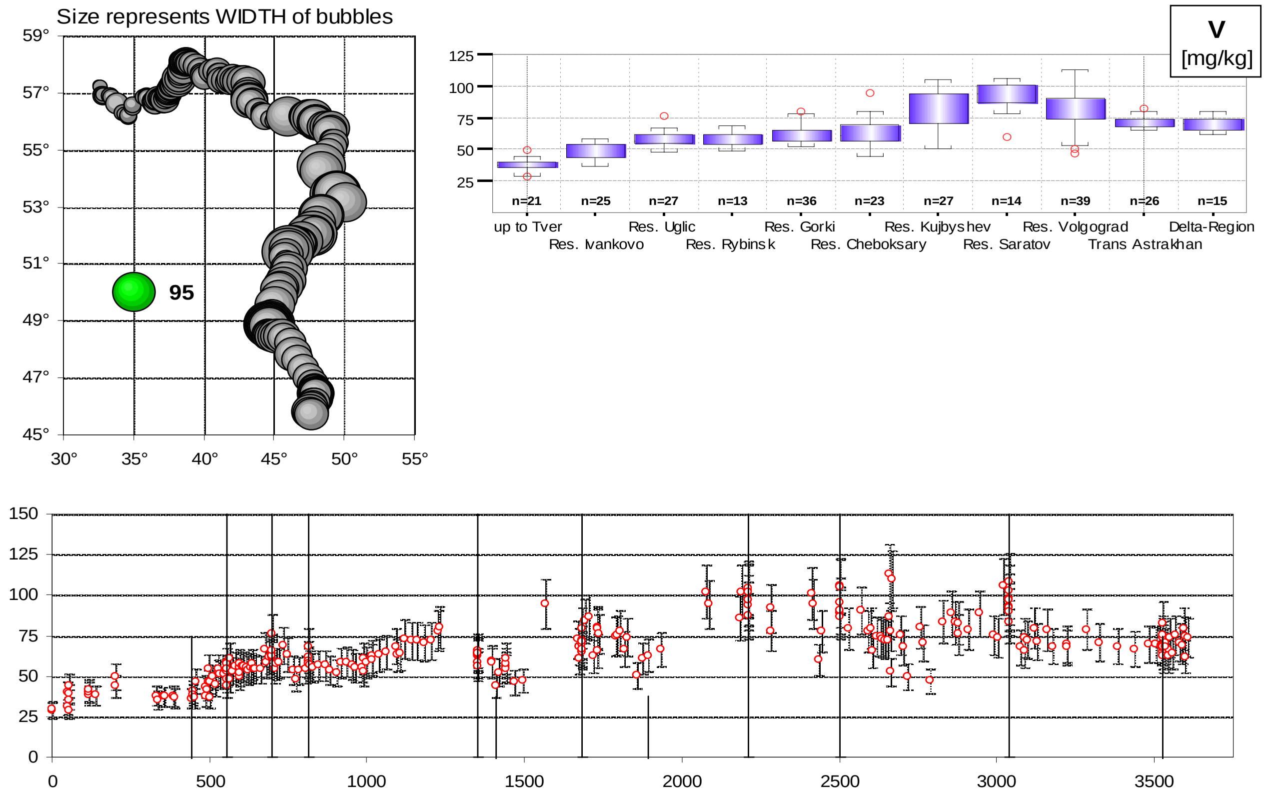


Figure 75 Vanadium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

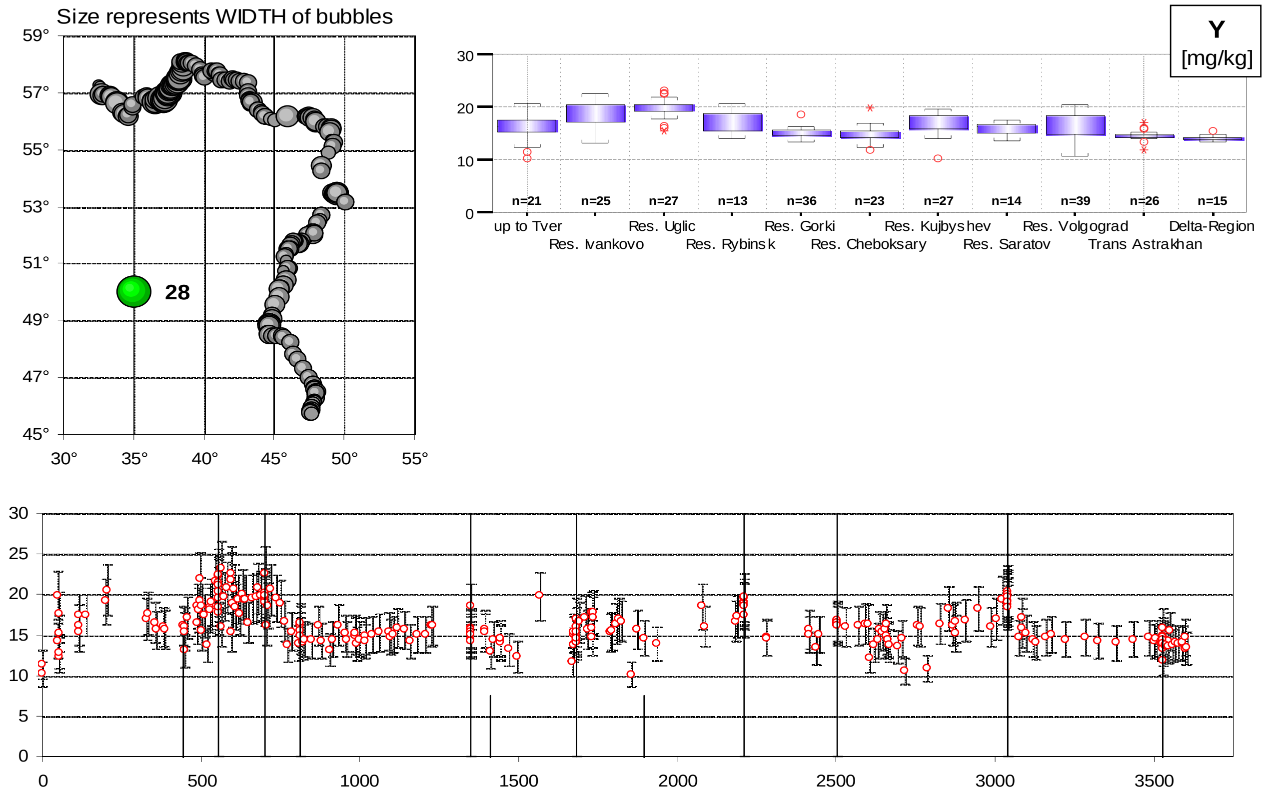


Figure 76 Yttrium-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

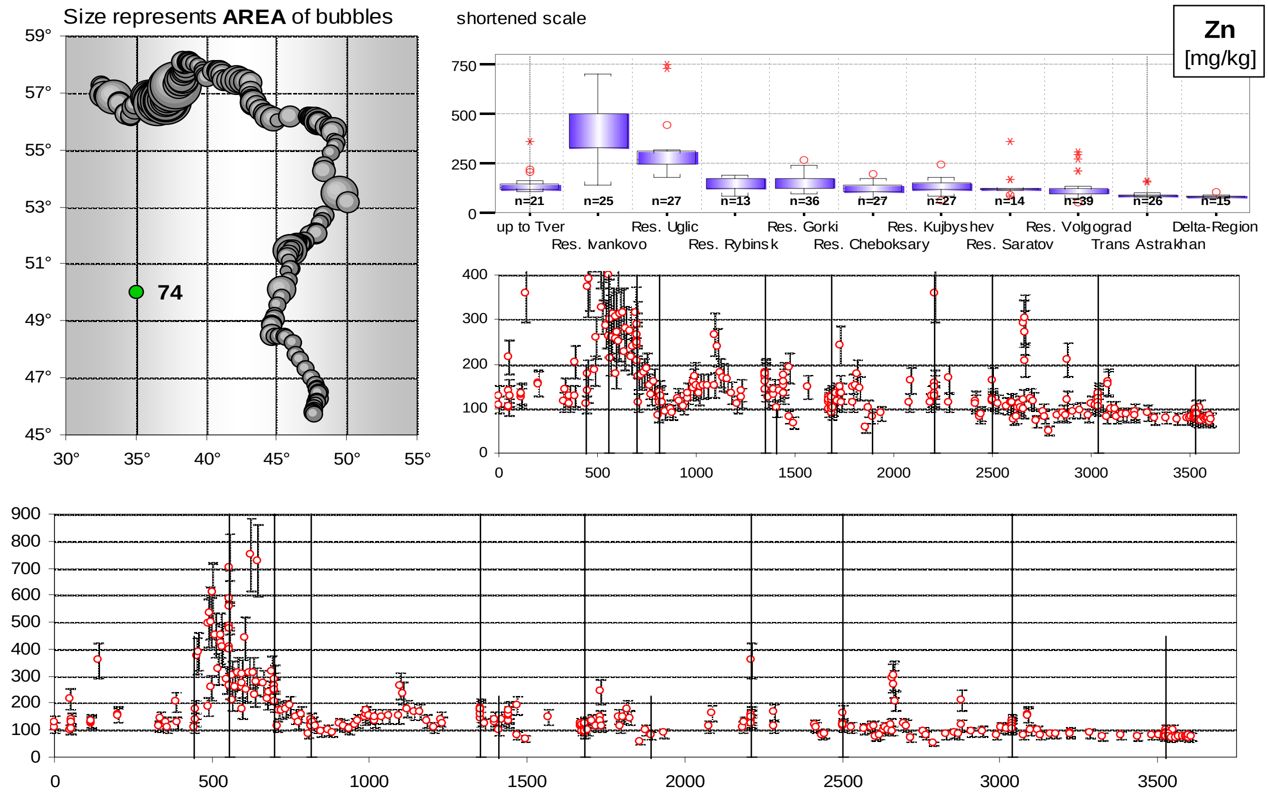


Figure 77 Zinc-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

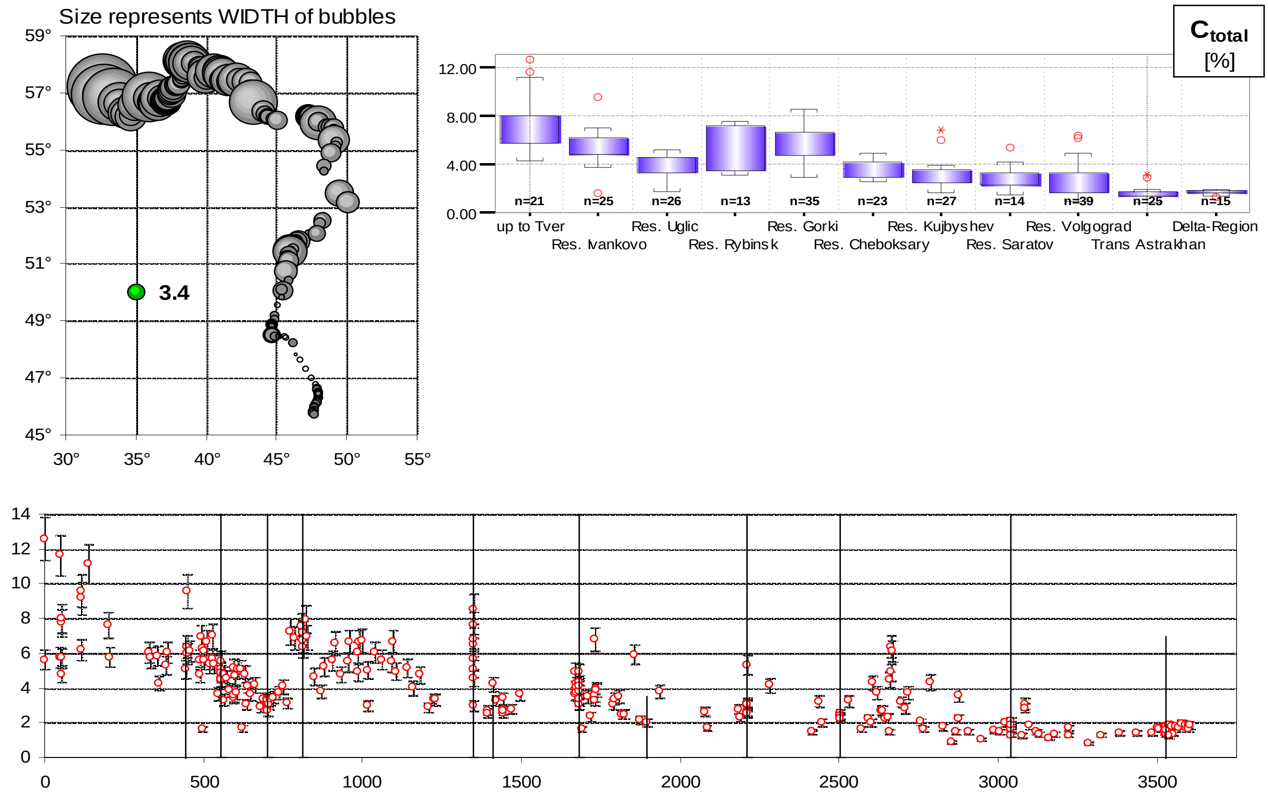


Figure 78 C$_{total}$-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

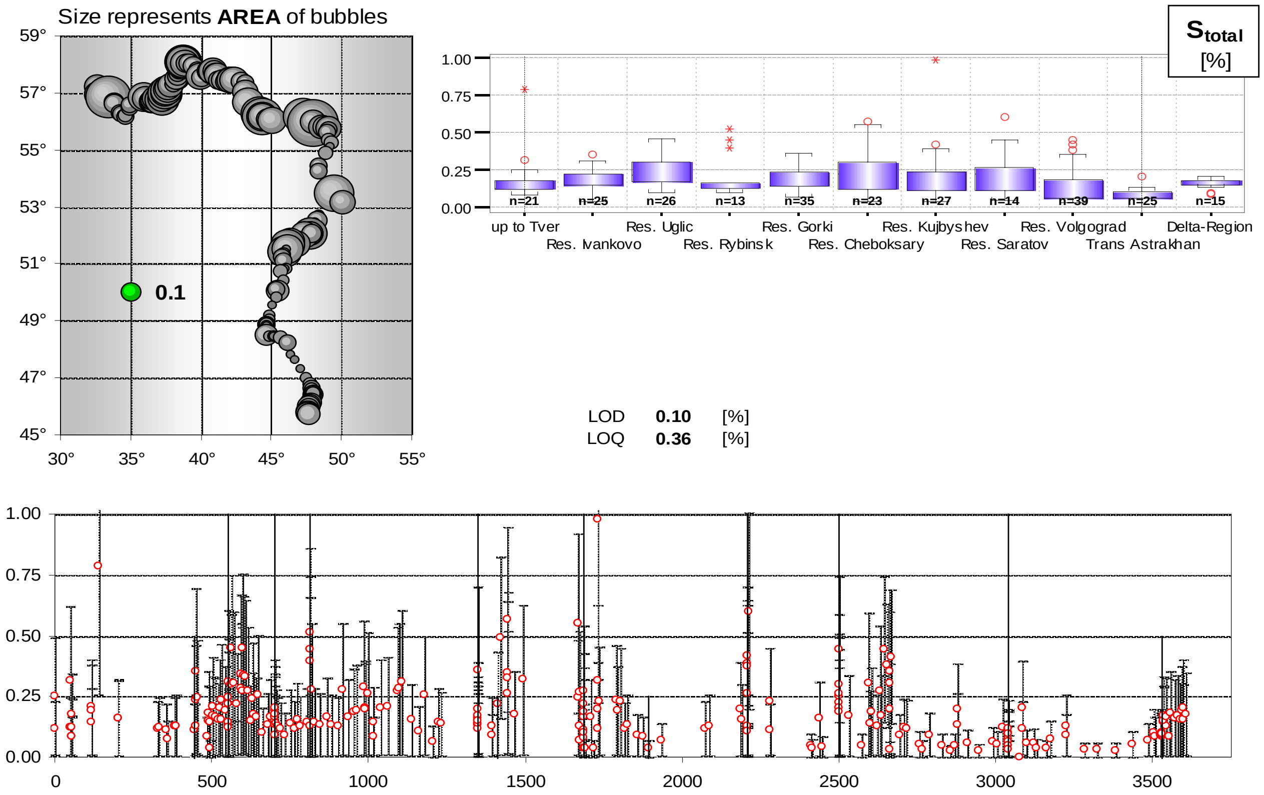


Figure 79 S_{total}-contents of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

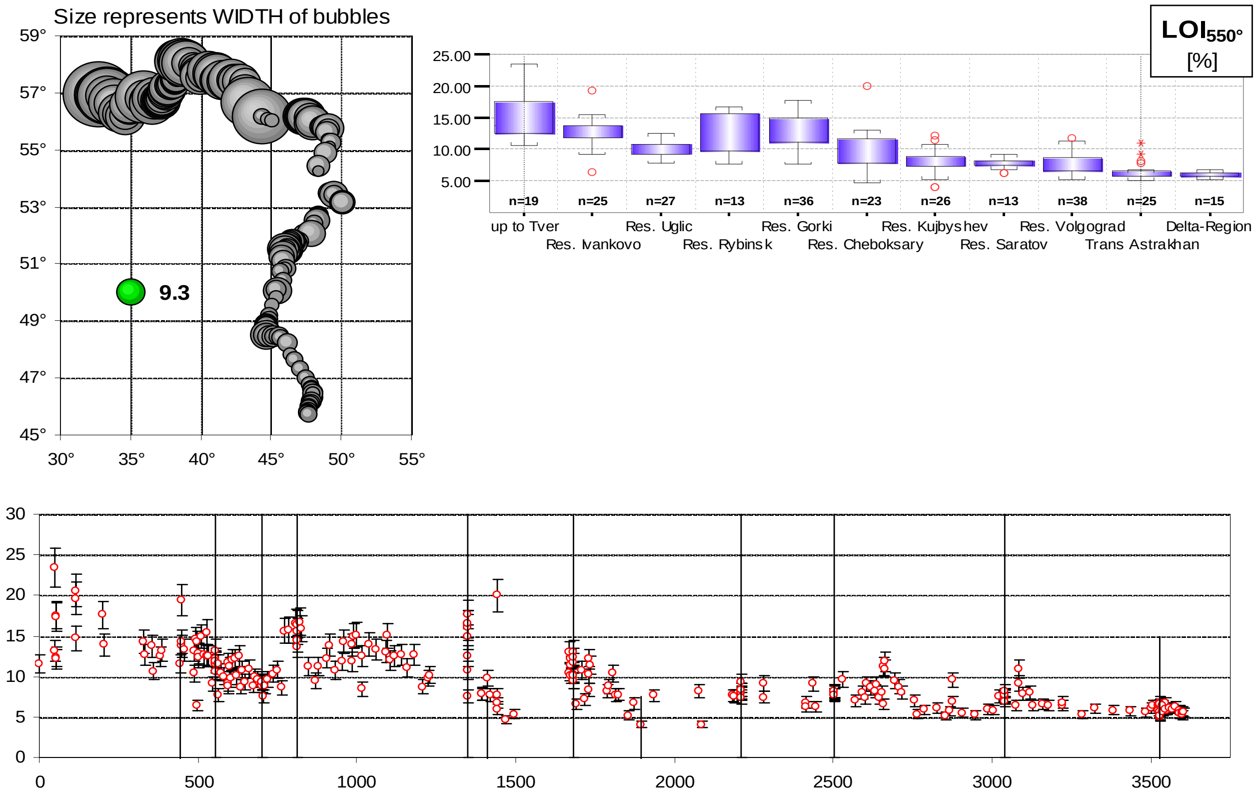


Figure 80 Loss on ignition of the Volga-River sediments – fraction < 20 µm (Legend see p. 187)

4.3 Classification of Volga sediments

In principle, there are three main approaches for assessing sediment quality:

- **chemical-specific sediment quality guidelines**
- **biological guidelines or community assessments**
- **toxicity tests**

However, already the US-EPA '*Sediment Classification Methods Compendium*' (US-EPA, 1992) lists 12 different approaches for the classification of sediments within the scope of the above main approaches as well as combinations thereof. Nevertheless, down to the present day also **risk estimations** are for the most part based on chemical analysis of (a fraction of) the bulk sediment, i.e. on numerical Sediment Quality Guidelines (SQG)[134].

This may be inappropriate, mainly since not every substance released to the aquatic environment will or can be monitored, as well as aquatic organisms are rarely affected by a contaminant as a single substance, but instead as **diverse mixture of contaminants**.

Statistically speaking, that is what makes any numeric approach based on chemical measurements prone to be affected by type 2 or false negative errors – i.e. assuming the sediment as uncontaminated, when in fact it is contaminated. On the other hand it is not the total amount of a given contaminant that will affect aquatic organisms, but its bioavailability. Statistically speaking, that will make approaches based on chemical measurements prone to be affected by type 1 or false positive errors – i.e. assuming the sediment as contaminated, when in fact it is uncontaminated. In other words with respect to implications towards aquatic organisms – and human health – additional data from other assessment tools (toxicity tests, tissue residues of e.g. freshwater fish, benthic community structure and function, biomarker studies, etc.) would be necessary.

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[134] However, it has to be mentioned, that within the European Community in 2000 the EU Water Framework Directive (WFD) was finally adopted. With respect to sediment and water quality objectives this integrated approach towards river basin management in Europe largely relies on biological quality elements:
'Ecological status is determined by biological quality elements, supported by hydromorphological and physico-chemical quality elements. The point of reference is given by "undisturbed" conditions showing no or only "very minor" human impacts' (WFD-Guidance document no. 10)
(see: http://europa.eu.int/comm/environment/water/water-framework/index_en.html - for a quick overview - and http://forum.europa.eu.int/Public/irc/env/wfd/library - for the complete documents relevant for the implementation of the WFD).

‘*An important initial step in addressing the contaminated sediments problem is the identification of scientifically sound methods that can be used to assess whether and to what extent sediments are “contaminated” or have the potential for posing a threat to the environment. …*
Unfortunately, there simply is no single method that will measure all contaminated sediment impacts at all times and to all biological organisms. This is the result of a number of factors, including environmental heterogeneity and associated sampling problems, variability in the laboratory exposures, analytical variability, differing sensitivities of different organisms to different types of contaminants, the confounding effects caused by the presence of unmeasured contaminants, the synergistic and antagonistic effects of contaminants, and the physical properties of sediments’ (US-EPA, 1992).
In other words, a comprehensive **risk assessment** based on a single method is virtually impossible and scientifically sound processes towards any sort of risk assessment are far beyond the scope of this work (cf. e.g. the above-mentioned EU-WFD[134]).

Consequentially early classification systems avoided any form of risk assessment in its narrower sense – although they were/are often misleadingly interpreted that way. Positioned within a **geochemical framework**, their reference center was a ‘system’ – i.e. (a part of) the investigated ‘environment’ – unaffected by man, no matter whether this starting point might have been favorable for organisms or not. Regardless of what the concentration of a certain ‘contaminant[135]’ in a given system or compartment might be, in case it is of natural origin there is no way to change/decrease it and represents the **chemical reference condition** of the investigated system. So despite its still less than satisfying definition (cf. Matschullat et. al., 2000) this ‘geogenic’ (or: natural) background became the starting point for these classification-systems[136] – and unsurprisingly will be the reference condition for each and every classification system.

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[135] In contrast to many organic contaminants that are solely released by man, (heavy) metals – and metalloids – are no xenobiotic substances. I.e. ‘contamination’ refers to a concentration above ‘natural background’, not the mere detection of a substance.

[136] It is beyond the scope of this work, to give yet another definition of the ‘geochemical background’, since this would be a task in its own.

4.3.1 Geochemical approach – comparison method

70-80% of all sediments and sedimentary rocks of the geological past are derived from suspended material and after induration represent fissile or laminated '*siltstones*' and '*claystones*' (named '*shales*') or simply '*mudstones*', if no preferential structure is to be observed (Pettijohn 1957). Therefore, the mean geochemical composition of these pre-civilizational silt- and clay-sized sediments and sedimentary rocks often serves as the 'geogenic background' in environmental studies, in order to estimate the 'anthropogenic[137]' input. E.g. the oftentimes so-called '*shale standard*', calculated by Turekian and Wedepohl (1961) which is closest to the above definition, but also average crustal abundances of elements, known e.g. as '*Clarke-values*'(Clarke, 1924), can and have been used as an estimate of background-concentrations.

However, this global background cannot be applied unrestrictedly in local studies, since e.g. rivers dewatering present or former mining areas – i.e. areas with a geochemical anomaly! – will show characteristic enrichments of (heavy) metals and/or metalloids that are (or have been) mined[138].

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[137] In many eastern European countries, the term '*technogenic*' is used instead.

[138] To be frank, even nobody ever showed these 'background'-values – originally compiled 'just' to describe the abundance of elements in major units of the earth's crust – to be reasonably applicable to sediments at all.

There are two principal methods used to determine the chemical composition of the Earth's upper crust:

- weighed averages of the composition of rocks exposed at the surface (e.g. the above 'Clarke-values')
- composition of fine-grained clastic sedimentary rocks or glacial deposits (originally proposed and employed by Goldschmidt (1933)).

The latter approach relies on the already discussed idea to use an 'ideal' sampling target, in which nature has conducted (most of) the homogenization. Sedimentary rocks are the product of litification, i.e. the process by which unconsolidated sediments become sedimentary rock. Sediments typically are derived from preexisting rocks by weathering, transported and redeposited, and then buried and compacted by overlying sediments. Cementation causes the sediments to harden, or lithify, into rock. In other words, sedimentary rocks are chemically altered sediments, which in turn are chemically altered rocks – oftentimes sedimentary rocks…

Weathering of rocks produces three fractions: sand (consisting of the most resistant minerals), clay (which ultimately forms the '*shales*') and a solution. These products are transported to varying degrees – according to their physical properties – and elements will be fractionated during these processes according to their solubility – and weathering resistance of their form of binding – so that none of these three fractions will be representative of their source region or rock. Especially the most soluble elements, i.e. alkali and alkaline-earth elements (as well as boron, rhenium, molybdenum, gold and uranium) (cf. Taylor and McLennan, 1985), will thus be depleted in the two solid products of weathering, while the mechanically and chemically most stable minerals (e.g. quartz, zircon) will be enriched in the sand-fraction, and the rare earth elements (as well as some Group 3 elements, namely Sc and Y but also Th, which behave similar to the REE) will be concentrated in the clay-fraction. The same fractionation should hold true for a comparison between sedimentary rocks (or any other given source rock) and sediments – and given the fact that these are 'just' rules of thumb, albeit oftentimes quantifiable on the basis of experience from numerous studies (and thus regularly used to correct elemental concentrations (cf. Taylor and McLennan, 1985) who reduced REE-concentrations by empirically justi-

Furthermore although these tables are usually cited as they are, at least the authors were aware of their shortcomings: ‘Any compilation is necessarily subject to great uncertainties in the reliability of the analytical work, the sampling, and the interpretations, both of the original investigator and the compiler. Hence the accompanying table should be accepted not so much as a doctrine but as a motion on the floor to be debated, and amended or rejected’[139] (Turekian and Wedepohl, 1961).

With respect to the Russian platform – as well as sedimentary rocks in general – another valuable source of information, associated with the name of Aleksandr P. Vinogradov, is available. Based on altogether ‘*over 35.000 specimens of the major lithologic types… in the Russian platform either exposed on the surface or found in boreholes, which are more or less evenly distributed over the region*’ (Ronov and Migdisov, 1996) the mean composition of ‘*clay rocks*’ (which should equal the above mentioned ‘*shales*’) as well as the sedimentary cover of the Russian plate (and platform) as a whole (i.e. including ‘*silt-sand rocks*’ and ‘*carbonate rocks*’) were calculated. Up to date this seems to be the largest data-set for any of the Ancient Platforms and – in case one would like to follow the idea that the upper crust and/or sedimentary rock composition can be reasonably compared with the composition of sediments (see footnote[138]) – should be closest to the here sampled Volga-sediments.

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fied 20% when calculating the upper crustal composition from ‘*shales*’, or the usage of ‘known’ elemental ratios to derive an unknown ‘original’ concentration .of an element and so on, within the whole ‘business’ of estimating the overall composition of the upper crust – an incredibly difficult one, since the deepest borehole – once again by the Russians in the Kola Peninsula – has only reached about 12 km, while the average thickness of the continental crust is estimated to be about 35 km, thus a lot of speculation but also knowledge about natural processes is needed for any reasonable estimate) – this gives at least an impression about the inherent uncertainty of any measure of central tendency, not to speak of ‘our’ desire to know anything about distribution functions…

With respect to a river basin (or a sedimentary basin in general) which is an open system with spatiotemporal variable input ((freshly) weathered material, erosion, etc.) and output (e.g. ‘loss’ of dissolved and suspended metals through transport processes) one would have to balance at least these processes in order to allow for reliable estimates of elemental concentrations of the sediment. Having in mind that already (‘simply’) balancing the sediment transport of riverine systems is (usually) affected by high uncertainties (cf. Chapter 1.7.4.3) makes this approach fairly impractical – at least up to date.

[139] It would also be important to mention their short discussion on sedimentary rocks in the cited article, pointing out that things are not that easy and logical as described here – and the addicted reader might e.g. have wondered about the omitted 20-30% of sediments and sedimentary rocks at the beginning of this paragraph. But as already mentioned this is not going to be an in-depth discussion of ‘background’-concepts, since its actual ‘true’ value is fairly irrelevant for the later interpretation.

Additionally in a more recent work Rudnick and Gao (2003) compiled the available sources dealing with the composition of the upper crust – as well as proposing (yet another) estimate thereof – and their results have also been included in Table 27 (page 207). Although there are some inconsistencies within their compilation[140], the span of reported values (labeled as Min and Max in Table 27) give at least a rough idea of what amount of uncertainty one would have to expect when having to answer the question: ‘what is the geochemical background for a given element ?’.

As has been discussed this is not a matter of scale – ‘the Earth’ vs. ‘the Volga’ – but instead a matter of ‘our’ less than appropriate understanding (and sometimes even the lacking awareness) of natural heterogeneity. No matter how ‘bullet-proof’ a mean might be, it means about nothing – at least for the questions addressed in this work. Without having as a minimum a faint idea about the distribution function this mean was derived from it is simply the most probable value to be observed, at the same time as already the question ‘how probable ?’ cannot be answered, let alone the question up to what extent positive (or negative) deviations can be considered as ‘normal’.

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[140] E.g.: There are two tables allegedly reporting their recommended values of the elemental composition of the upper crust, while in fact there are markable differences (table 2, column 12 and table 3 within the article – the results reported here are derived from table 3 within their article). Their reported standard deviation (**s**) – called ‘*standard deviation of the mean*’, which could be a standard deviation of the ‘distribution’ (at best 9 independent sources, i.e. values!) or the standard error of the mean (i.e. s/sqrt(n)) – doesn’t always match the ones we calculated from their information on how the value for each element was derived (the **s** reported in Table 27 are also derived from table 3 in their article).. Additionally the values of Wedepohl (1995) are largely ignored, stating that his work is ‘*largely derived from the Canadian Shield composites of Shaw et al. (1967, 1976)*’ and so his suggestions were simply replaced…

Table 27 Mean composition of fine-grained clastic sedimentary rocks and the upper crust from various sources in comparison to the Volga sediments investigated here.

	Volga sediments			Turekian / Wedepohl		Ronov / Vinogradov			Rudnick and Gao (2003)					
[mg/kg] unless noted	**Mean**	**Standard Error of Mean**	**[%]**	**(1961) Shales**	**(1995) upper crust**	**Clay Rocks**	**Russian plate**	**Russian platform**	**Mean of means**	**s**	**[%]**	**Min**	**Max**	**Variance [% of Mean of means]**
Ag	0.39	0.03	7	0.07	0.07	-	-	-	0.053	0.003	5	0.050	0.055	9
Al [%]	3.50	0.04	1	8.00	7.96	8.10	4.44	4.11	8.15	0.397	5	7.50	8.80	16
As	8	0.24	3	13	1.7	-	-	-	5	0.5	10	1.5	5.1	75
Ba	238	4.51	2	580	584	415	347	355	628	83	13	550	1070	83
Ca [%]	1.7	0.08	5	2.2	3.9	4.0	11.6	12.1	2.6	0.14	6	2.3	3.7	54
Cd	0.50	0.05	10	0.30	0.10	0.095	0.130	0.140	0.09	0.01	15	0.075	0.102	30
Co	18	0.20	1	19	24	16	9	9	17	0.6	3	12	18	35
Cr	76	1.37	2	90	126	80	46	54	92	17	19	35	112	84
Cu	44	1.40	3	45	25	30	22	18	28	4	14	14	32	64
Fe [%]	4.51	0.06	1	4.72	4.32	4.53	2.79	2.66	3.92	0.41	10	3.18	5.64	63
Hg	0.27	0.03	11	0.40	0.04	-	-	-	0.05	0.04	76	0.0123	0.096	167
K [%]	0.73	0.01	2	2.66	2.14	3.23	1.83	1.69	2.32	0.19	8	2.29	3.43	49
Li	38	0.47	1	66	18	63	32	34	24	5	19	20	22	8
Mg [%]	1.20	0.02	2	1.5	2.2	1.8	2.6	2.4	1.5	0.21	14	1.3	2.8	100
Mn [%]	0.16	0.01	5	0.085	0.072	0.070	0.054	0.046	0.077	0.008	13	0.054	0.093	50
Mo	1.9	0.05	3	2.6	1.1	1.4	0.8	1.1	1.1	0.3	28	0.8	1.5	65
Na [%]	0.10	0.002	2	0.96	2.36	0.61	1.00	1.41	2.43	0.171	8	1.59	2.91	54
Ni	51	0.92	2	68	56	44	27	29	47	11	24	19	60	87
Pb	24	0.97	4	20	14.8	18	12	11	17	0.5	3	17	18	6
Sc	7.7	0.12	2	13.0	16.0	16.8	9.8	9.5	14.0	0.9	6	7.0	15.0	57
Sr	91	3.38	4	300	333	236	349	495	320	46	14	266	380	36
V	66	1.06	2	130	98	95	58	65	97	11	11	53	107	56
Y	16	0.15	1	26	24	28	17	18	21	2	11	17	24	31
Zn	171	7.35	4	95	65	74	46	48	67	6	9	52	70	27
S_{total} [%]	0.18	0.01	4	0.24	0.07	0.35	0.20	0.26				0.03	0.06	
P_2O_5 [%]	0.40	0.02	5	0.16	0.17	0.12	0.11	0.07	0.15			0.12	0.31	127
P [%]	0.17	0.01	5	0.07	0.08	0.05	0.05	0.03	0.07			0.05	0.13	127

Volga sediments: this study
Turekian / Wedepohl: 1961: Turekian and Wedepohl (1961) 1995: Wedepohl (1995)
Ronov / Vinogradov: Ronov and Migdisov (1996)
Rudnick and Gao: Rudnick and Gao (2003)

Furthermore, a few cautionary words with respect to Table 27 are necessary:

With the exception of the Volga-sediments the reported values are '**total contents**', while the here used aqua regia-digestion is merely an extraction leaving particularly the silicate components (e.g. clay minerals) intact – this should result in too low results for several elements (e.g. Aluminum).

To a certain extent, this table compares oranges with apples. Although fine-grained clastic sedimentary rocks can be used to approximate the composition of the upper crust (see footnote[138]) the reported '*shales*' and '*clay rocks*' represent only a part of the sedimentary cover beside '*sandstones*' and '*carbonates*'. Their – with respect to heavy metals usually lower – values, also reported by Turekian and Wedepohl (1961) as well as Ronov and Migdisov (1996) have been ommited in this table. The reason for this inadequacy is the fact, that exactly these '*shale*'-values are frequently used to approximate the 'geogenic background' of sediments, rather than the composition of the sedimentary cover as a whole.

The '*standard deviation of the mean*' (**s**) reported by Rudnick and Gao (2003) is NOT the standard deviation of a geogenic distribution function, but the standard deviation calculated from the mean of the compiled means (i.e. mean of means). It is neither fully comparable with the standard deviation of the Volga sediments (see Table 26) nor the standard error of the mean (s/sqrt(n)). Even though it is a clue with respect to heterogeneity and/or uncertainty of the composition of the upper crust, the minima and maxima of the data-sets used to calculate this number provide a better – although also incomplete – estimate.

To illustrate the sometimes large variability of **mean(!) background values** used to approximate the composition of sediments, the maxima and minima derived from Table 27 have been graphically compared to the mean composition of the investigated Volga sediments (Figure 81). In order to be able to depict the elements in a single figure the values have been normalized to the respective minimum background value (i.e.: value/minimum).

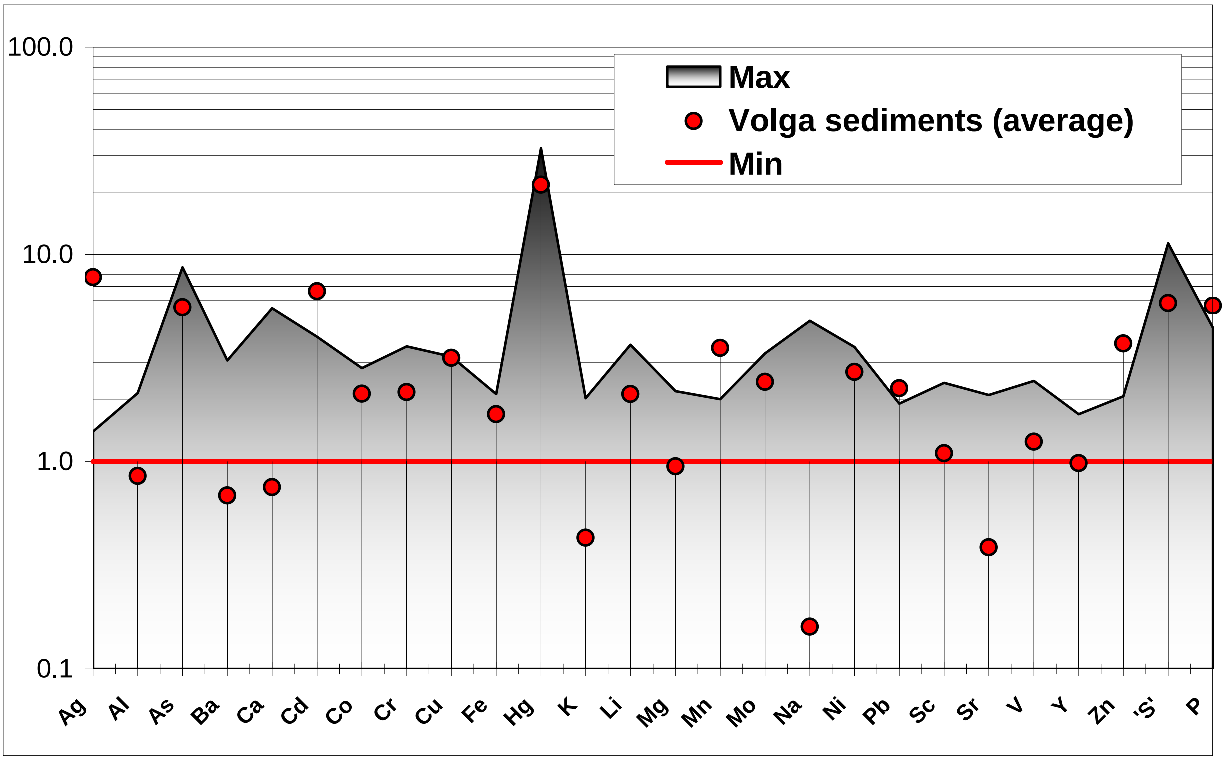

Figure 81 Comparison of the mean composition of the investigated Volga sediments with the respective maximum and minimum of a hypothetic 'geogenic background' as derived from Table 27 (values normalized to the respective minimum; logarithmic scale!).

With the exception of (Arsenic,) Sulfur and Mercury – whereas for the latter the value of Turekian and Wedepohl (1961) of 0.4 mg/kg for '*shales*' is considered to be too high every now and then – the proposed 'geogenic backgrounds' for the investigated elements are at least within the same order of magnitude.

Negative deviations of the Volga sediments are largely restricted to alkali and alkaline-earth elements, which seems reasonable for an aquatic environment (cf. footnote[138]) – while the slightly too low value for Aluminum can be flawlessly explained by the used aqua regia digestion and its known limitations (cf. Chapter 2.2).

Positive deviations of the Volga sediments could (and usually would) be explained by some sort of human impact (Cadmium, Copper, Lead, Zink and Phosphorous) – while reasons for the elevated Silver and Manganese concentrations would be less obvious. Although there is some evidence that Silver in sediments can be used as a marker of human impact and activities (Müller, 2001) and at least for practical reasons no one would care about Manganese – non-toxic at almost any concentration, and besides Iron known as about the only element doing 'all' the chemistry in the sediment, thereby affected by large variations depending on e.g. the Redox-conditions – these two elements do not fit particularly well.

On the other hand, as already mentioned (cf. footnote**[138]**), nobody ever showed any of these 'geogenic backgrounds' – originally calculated for completely other reasons! – to be applicable to sediments at all.

4.3.1.1 How reliable can a ‘geogenic background’ be?

Although far from being representative or reasonably transferable to other cases, a single example might highlight the shakiness of the whole concept. In 1990, the *Canada Centre for Mineral and Energy Technology* (CANMET) – a branch of *Natural Resources Canada* (NRCan) –prepared a set of four stream sediment samples to be used as certified reference material (Lynch, 1990). These references are interesting for two reasons. First, they “*were chosen to represent typical stream sediments from various geochemical environments in Canada*”, so an independent comparison with the ‘geochemical backgrounds’ of Table 27 (page 207) is possible. Secondly ‘total’ as well as ‘aqua regia extraction’ values are reported, allowing to asses what amount of error is introduced by comparing values derived from these two methodologies – one of the weaknesses of Table 27.

Starting with the last point, Table 28 and the accompanying Figure 82 show a comparison of the certified “total” and “partial extraction”-contents of the Canadian stream sediments STSD-1 through STSD-4. With the exception of Chromium and Vanadium it is reasonable, to consider the two approaches as roughly equivalent for the investigated elements (especially if one would take measurement uncertainties into account) – which in fact was done (tacitly) by CANMET for Silver, Cadmium and Mercury, while as already mentioned e.g. Aluminum should differ considerably (and most probably for that reason have not been reported/conducted).

Table 28 Contents of CANMET certified reference material intended to *‘represent typical stream sediments from various geochemical environments in Canada’* – “total” vs. “extraction” and resulting ratio thereof.

	"total content"				"partial extraction"				"total" / "extraction"			
[mg/kg] unless noted	**STSD-1**	**STSD-2**	**STSD-3**	**STSD-4**	**STSD-1**	**STSD-2**	**STSD-3**	**STSD-4**				
Ag	< 0.5	0.50	< 0.5	< 0.5	0.3	0.5	0.4	0.3	1.0	1.0	1.0	1.0
As	23	42	28	15	17	32	22	11	1.4	1.3	1.3	1.4
Cd	-	-	-	-	0.8	0.8	1	0.6	1.0	1.0	1.0	1.0
Co	17	19	16	13	14	17	14	11	1.2	1.1	1.1	1.2
Cr	67	116	80	93	28	50	34	30	**2.4**	**2.3**	**2.4**	**3.1**
Cu	36	47	39	65	36	43	38	66	1.0	1.1	1.0	1.0
Fe [%]	4.70	5.20	4.40	4.10	3.5	4.1	3.4	2.6	1.3	1.3	1.3	1.6
Hg	-	-	-	-	0.11	0.046	0.09	0.93	1.0	1.0	1.0	1.0
Mn [%]	0.40	0.11	0.27	0.15	0.37	0.07	0.26	0.12	1.1	1.5	1.0	1.3
Mo	< 5	13	6	< 5	2	13	7	2	1.0	1.0	0.9	1.0
Ni	24	53	30	30	18	47	25	23	1.3	1.1	1.2	1.3
Pb	35	66	40	16	34	66	39	13	1.0	1.0	1.0	1.2
V	98	101	134	106	47	58	61	51	**2.1**	**1.7**	**2.2**	**2.1**
Zn	178	246	204	107	165	216	192	82	1.1	1.1	1.1	1.3

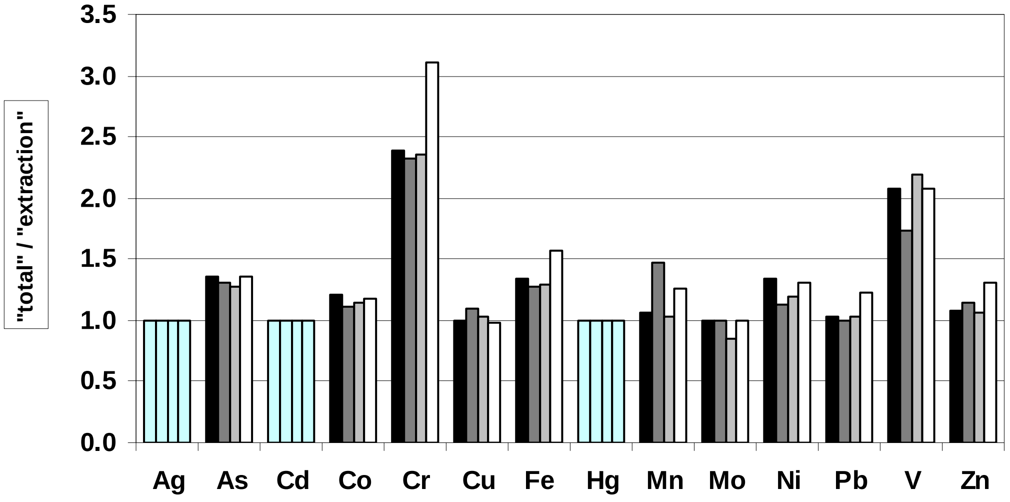

Figure 82 Ratio of the 'total' and 'extractable' content of the above-mentioned CANMET CRM's.

The outcome is in fact little surprising, since the success of an extraction procedure like the here used aqua regia-extraction depends on the binding form of a given element – and in that way on the fate and transport of the element towards the aquatic system and sediment body, as well as its principal chemical properties and the environmental conditions. Actually, as already mentioned this is a designated result of the extraction-procedure in order to interpret the results as 'maximum endangerment' caused by a given element. Nonetheless, although the two approaches – "total" vs. "extraction" – are fundamentally different the retrieved results with respect to a good number of elements usually considered as COPC's (As, Cd, Cu, Hg, Ni, Pb, Zn) are about the same, while there may be substantial differences for elements known to be present in the sediment in a more or less insoluble form (e.g. $FeCr_2O_4$, alumosilicates, etc.).

In other words: depending on the element, its – usually unknown – physicochemical environment within the investigated sediment, as well as the binding form in which it originally entered the aquatic system, the extractable portion will vary. As will the success of a comparison with 'total' concentrations of any given frame of reference.

While these findings are far from being breathtaking, a comparison of the CANMET-CRM's STSD-1 through STSD-4 with the mean composition of the Volga-sediments is quite interesting (as is a comparison with miscellaneous 'background'-values of Table 27[141]).

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[141] In fact, these Canadian CRM's have been chosen for two reasons. Talking about the composition of the upper crust, as well as different rock types, there is usually no differentiation made between the different platforms of the world and at least two independent studies of the Canadian Shield are available which are frequently used to calculate crustal abundances (cf. Rudnick and Gao, 2003)). So actually, there is a lot of Canadian Shield included in Table 27. Secondly CANMET claims these stream sediment standards to represent "*typical stream sediments from various geo-*

Judging from Table 29, most problems encountered when comparing the Volga-sediments with common ‘geochemical’ backgrounds (cf. Figure 81) diminish. Especially the (at first sight unreasonably) elevated concentrations of Silver, but also those of Cadmium, Copper, Lead, Zink and Phosphorous are at least within the range of these Canadian stream sediments. The remnants of the apparent problems are Sodium[142], Potassium and Strontium as astonishingly depleted elements (but cf. footnote[138]) as well as a handful of other elements either explainable by the ‘weaknesses’ of the aqua regia-extraction (e.g. Aluminum) and/or at least roughly matching one of the Canadian stream sediments (e.g. Mo).

Table 29 Comparison of the above-mentioned CANMET CRM’s (‘total’ and ‘extractable content) and the average content of the here sampled Volga-sediments (extractable content)

	"partial extraction"							**"total" content**						
[mg/kg] unless noted	**STSD-1**	**STSD-2**	**STSD-3**	**STSD-4**	**STSD Mean**	**Volga Mean / STSD Mean**	**Volga Mean**	**Volga Mean / STSD Mean**	**STSD Mean**	**STSD-1**	**STSD-2**	**STSD-3**	**STSD-4**	**[mg/kg]** unless noted
Ag	0.3	0.5	0.4	0.3	0.38	1.0	0.39							**Ag**
Al [%]							3.50	0.5	6.36	4.76	8.52	5.77	6.40	**Al [%]**
As	17	32	22	11	21	**0.4**	8	**0.3**	27	23	42	28	15	**As**
Ba							238	**0.2**	1165	630	540	1490	2000	**Ba**
Ca [%]							1.7	0.6	2.7	2.6	2.9	2.4	2.9	**Ca [%]**
Cd	0.8	0.8	1	0.6	0.80	0.6	0.50							**Cd**
Co	14	17	14	11	14	1.3	18	1.1	16	17	19	16	13	**Co**
Cr	28	50	34	30	36	**2.1**	76	0.9	89	67	116	80	93	**Cr**
Cu	36	43	38	66	46	1.0	44	0.9	47	36	47	39	65	**Cu**
Fe [%]	3.5	4.1	3.4	2.6	3.40	1.3	4.51	1.0	4.60	4.70	5.20	4.40	4.10	**Fe [%]**
Hg	0.11	0.05	0.09	0.93	0.29	0.9	0.27							**Hg**
K [%]							0.73	0.5	1.39	1.00	1.74	1.49	1.33	**K [%]**
Li							38	1.4	28	11	65	23	14	**Li**
Mg [%]							1.20	0.8	1.45	1.33	1.87	1.33	1.27	**Mg [%]**
Mn [%]	0.374	0.072	0.263	0.12	0.21	0.8	0.16	0.7	0.23	0.40	0.11	0.27	0.15	**Mn [%]**
Mo	2	13	7	2	6.0	**0.3**	1.9							**Mo**
Na [%]							0.10	**0.1**	1.16	1.09	1.03	0.90	1.63	**Na [%]**
Ni	18	47	25	23	28	**1.8**	51	1.5	34	24	53	30	30	**Ni**
Pb	34	66	39	13	38	0.6	24	0.6	39	35	66	40	16	**Pb**
Sc							7.7	0.5	14.3	14.0	16.0	13.0	14.0	**Sc**
Sr							91	**0.3**	288	170	400	230	350	**Sr**
V	47	58	61	51	54	1.2	66	0.6	110	98	101	134	106	**V**
Y							16	**0.5**	35	42	37	36	24	**Y**
Zn	165	216	192	82	164	1.0	171	0.9	184	178	246	204	107	**Zn**
P_2O_5 [%]							0.40	1.2	0.33	0.40	0.30	0.40	0.20	**P_2O_5 [%]**
P [%]							0.17	1.2	0.14	0.17	0.13	0.17	0.09	**P [%]**

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chemical environments in Canada” which in turn should make them ‘representative’ for any ‘average’ stream sediment…

[142] While Taylor and McLennan (1985) report e.g. Sodium contents of the River Congo particulates to be as low as 0.22%, representing ‘just’ a factor of two compared with the Volga-sediments instead of about ten as in Table 29. That is to say, it is supposable to find matching values for virtually any parameter in other allegedly ‘undisturbed’ riverine systems – little surprising, when taking the later discussed factors controlling the sediment-composition into account.

Of course, one should not overrate these comparisons. After having read Chapter 2.5 (esp. Chapter 2.5.2.1 p.98 ff.) no one would assume these Canadian stream sediments as ‘truly’ representative in a strict meaning[143], as little as comparing only two sources (CANMET and this study) can by any means lead to ‘representative’ findings. Nevertheless, the Canadian stream sediments fit the possible geochemical backgrounds as of Table 27, just as well – or bad – as the Volga sediments, while the only element for which the mean composition of the Volga-sediments clearly exceeds that of the Canadian sediments – namely Chromium – is still within the given methodological uncertainty[144].

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[143] Although these CRM’s are intended to ‘*represent typical stream sediments from various geochemical environments in Canada’* (Lynch 1990) there is no strict evidence for this claim:

“*STSD-1: This sample is a single lot from Lavant Creek (31F) in Ontario.*

STSD-2: This sample is a mixture of a lot from Hirok Stream (104P) and a composite lot from 93A and 93B; both lots are from British Columbia. Composites were produced by mixing unused portions of regional survey samples collected in the corresponding NTS sheets.

STSD-3: This sample is made from the same lots as STSD-2 with the addition of a lot from Lavant Creek (31F) in Ontario.

STSD-4: This sample is made from a mixture of a lot which is a composite sample from 31F in Ontario and a lot from the same composite from British Columbia used for STSD-2.”

(http://www.nrcan.gc.ca/mms/canmet-mtb/mmsl-lmsm/ccrmp/certificates/stsd-1.htm

No matter how reasoned the initial sampling step and/or the composting might have been, this will not qualify as representative to any reasonable degree.

[144] The mean concentration of Chromium within the Volga sediments is well above that within the Canadian stream sediments when comparing the extraction results, while fully comparable when using the ‘total’ content of the Canadian stream sediments. Although not backed up by hands-on experience this could be due to a higher proportion of aqua regia-soluble Chromium in the Volga sediments – not overly likely, but unproven and hence within the methodological uncertainty.

Additionally, there are also more general objections making the simple approach of defining a general sedimental background questionable.

Despite the generally assumed equivalence of the Canadian Shield and the Russian Plate – as well as amongst the other ancient platforms (cf. footnote[141]) – this uniformity refers to their **mean crustal composition** and no conclusions towards individual geological units are intended.

The geological material is prepared for transport by weathering processes, which are the rate-limiting step within the sedimentary system of a river as well as they will control the initial composition of the products. Already a simplistic examination of the processes controlling the weathering of rocks leaves little confidence in the idea of a universally applicable background.

Roughly speaking weathering is controlled by:

- **Rock characteristics:**
- **Rock type (mineral stability)**
- **Rock structure (surface area)**
- **Slope (high slope can lead to increased mechanical weathering; but may e.g. delimit the intrusion of water, i.e. chemical weathering.)**
- **Climate (high rainfall and high temperature favor chemical weathering)**
- **Time (a longer exposure means more weathering)**

Notwithstanding an in-depth discussion of these processes and their less than satisfying quantifiability – a comprehensive overview is e.g. provided by Hay (1998) – as well as their implications towards the products (soil or sediment), at least these four factors would have to be (approx.) identical in order to achieve identical weathering-products. Moreover, there seems to be little agreement, about what value to accept as some sort of ‘global geochemical background’ for sedimentary rocks – or the crustal composition (cf. Table 27 and Figure 81) – let alone for sediments.

That is to say, nothing is known quantitatively about the influences of the above factors towards the chemical composition of the weathering products – and thus initial sedimentary composition.[145] Nothing is known quantitatively about how severely alterations in these factors will affect the (composition of the) weathering products. Nothing is known quantitatively about the further fate of the eroded weathering products within the sedimentary system – additionally dependent on the environmental conditions within the riverine system. In addition, already the mean composition of the parent rock is quite uncertain and what’s more, is affected by an unknown variability.

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[145] This is already a simplification: ‘*Except in desert regions, it is the soil that ultimately is eroded to become the suspended load in rivers*’ (Hay (1998). In other words, things are way more complex, since at least one additional compartment as well as its chemistry would have to be considered.

For those reasons, a scientifically sound 'geochemical background' for sediments is quite unlikely to be definable by this approach, and e.g. the *U.S. Department of Energy* rejected the idea of a background completely – finally yet importantly for purely practical reasons – by simply stating that '*surface water and sediment are transient media in which concentrations and activities can change rapidly. …Currently, a comparison of concentrations and activities in upstream versus downstream samples is to be used to determine if a unit or area is releasing contaminants to the environment*' (DOE 2000). For the same reasons the *U.S. EPA* concluded earlier: '*It is not feasible to establish a single universal background concentration for soils or sediments; it is more useful to discuss the* ***range*** *of background concentrations for a contaminant.*' (US-EPA, 1995) – and later studies under the auspices of the U.S. EPA in the field of sediments almost exclusively rely on the idea of regional backgrounds (ranges or upper control levels) derived from an appropriate '*background site*'[146].

Even if some of the inconsistencies e.g. the U.S. EPA has to deal with, are introduced by their methodology – sediment, as well as soil is defined as the material <2 mm, and the arising problems of analyzing those coarse fractions have been discussed earlier (e.g. Chapter 2.5.3.1) – the principal problems remain the same[147]:

- **'background' concentrations can not be approximated in a scientifically sound way from other compartments like the parent material or e.g. sedimentary rocks.**
- **'background' concentrations take the form of a range not a single number.**
- **'background' concentrations are site-specific and controlled by a large number of variables, usually not (fully) accounted for within a study (e.g. the above mentioned four factors controlling the weathering, as well as the factors controlling the further fate of the weathering products (pH/Eh, salinity, cation exchange capacity, organic carbon, particle size and distribution). Purely 'technical' issues like sampling design, number of samples, investigated fraction, analytical method, also controls them.**

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[146] '*To minimize confusion, the term "background concentration" is defined in this document as* ***the concentration of inorganics found in soils or sediments surrounding a waste site, but which are not influenced by site activities or releases****. A "background site" should be a site that is geologically similar and has similar biological, physical, and chemical characteristics (e.g. particle size, percent organic carbon, pH) as the contaminated site (…) but also should be upstream, upgradient, or upwind of the site*' (U.S. EPA 1995). I.e. in fact the same approach as used by the above cited U.S. Department of Energy.

[147] Note that this is NOT to say their methodology is 'wrong'. Simply the tasks and philosophies are different, with the 'U.S.'-approach notedly geared towards risk-assessment with respect to aquatic organisms, where the 'whole' sediment can be more meaningful than just a fraction of it (cf. Chapter 2.5.5.3.2, p.139ff.).

4.3.2 I_{geo}- and LAWA-classification

The basics of these two classification systems are identical. The starting point for evaluating the anthropogenic impact towards a water-body is the above discussed ‘geogenic background’ and the subsequent classes are in general derived by doubling the upper bound of the previous one.

The earlier of these two systems, the **geo-accumulation index** (i.e. **I_{geo}-classes** according to Müller (1979)), is based on the ‘*argillaceous*[148] *rock standard*’ as order of magnitude for natural impact levels. Admittedly, it is affirmed that these global standard can, and has to be, modified in case the regional conditions make it necessary. Therefore, whereas usually the ‘*shale*’-values of Turekian and Wedepohl (1961) are used to calculate the subsequent classes, here the ‘*clay-rock*’-values provided by Ronov and Migdisov (1996) are used, since they should best reflect the regional geology.

Starting with Igeo-class 0 for ‘practically uncontaminated’ sediments – representing 1.5 times of the (assumed) background-concentration, and thus accounting for possible variations in the background-levels due to e.g. lithogenic effects, as well as possible shortcomings in determining these levels – this classification reaches up to the unlimited class 6 for ‘very strongly contaminated’ sediments, while the upper bound of the other classes, in each case represent twice the concentration of the previous one:

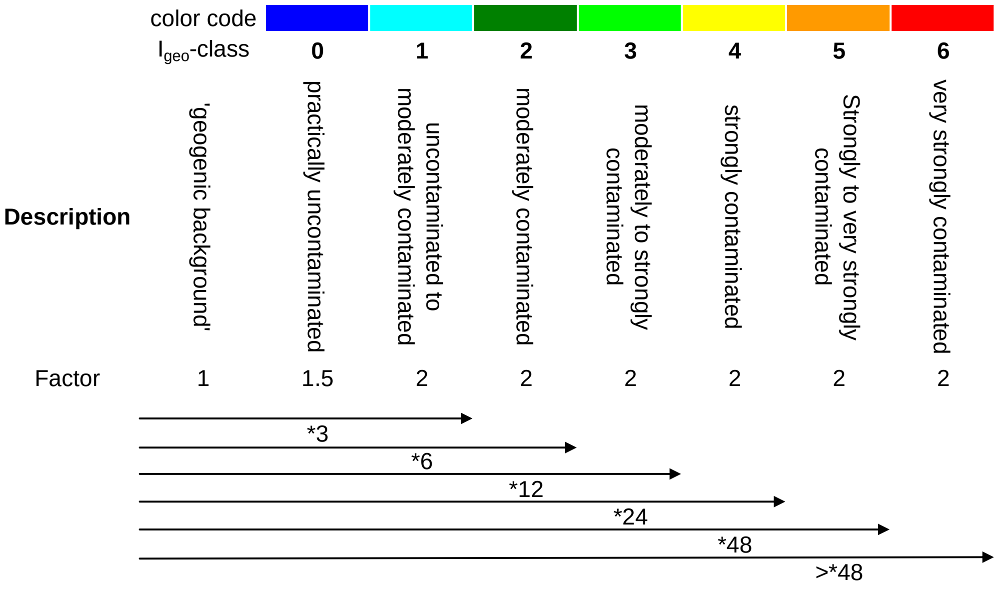

Figure 83 **Definition and calculation of the I_{geo}-classes (after Müller, 1979)**

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[148] “*Describing rocks or sediments containing particles that are silt- or clay-sized, less than 0.625 mm in size. Most have a high clay-mineral content, and many contain a sufficient percentage of organic material to be considered a source rock for hydrocarbon*” (Schlumberger Oilfield Glossary. Available online: http://www.glossary.oilfield.slb.com/default.cfm).

By that, this index is ‘simply’ a scale for the relation of trace elements in current loads and the original geogenic state. In addition, the I_{geo}-classes and their respective color codes, when assigned to the individual samples or stretches of a river, allow for a quick and sufficiently accurate – taking the above-discussed methodological uncertainties of sediment-studies into account – quantitative impression of the long-term quality situation of a water-body.

Many of the basic ideas have been tacitly adopted by the ‘**chemical quality classification for suspended solids and sediments**’ for seven inorganic COPC’s worked out by the **LAWA**[149] (current version: LAWA, 1998).

Besides minor cosmetic modifications, like renumbering the respective classes, a different ‘*geogenic background*’ is assumed and assigned to their first class – without applying any safety margin. The subsequent classes are usually calculated by doubling the value, while for Cr, Ni, and Zn the first three classes have been modified (cf. Table 30) for no apparent reason, except to allow for a more subtle differentiation.

Moreover, the major difference to the aforementioned I_{geo}-classification system is that the LAWA-classification is a **valuing system** and their class II (‘*moderately contaminated*’) is defined as a ‘*quality target*’.[150] In addition, the comparative value explicitly **must not be a single measurement**, but the Median of a series, since the endangering potential of sediments towards a given subject of protection is characterized by the average load – rather than a maximum as holds true for water measurements. However, it is frequently ‘misused’ for the classification of single samples, as has been done here.

Scientifically speaking the convincing simplicity and applicability of the I_{geo}-classes is lost for no apparent reason. Consequentially the LAWA-classification is not undisputed, and even (semi-) official reports in Germany oftentimes prefer using the I_{geo}-classification for its adoptability to regional

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[149] The ‘Länderarbeitsgemeinschaft Wasser’ (**LAWA**) is the German Working Group of the Federal States on water issues (http://www.lawa.de/lawaroot/LAWA/index-en.html).

[150] There are also different definitions of the subsequent classes for different ‘subjects of protection’ – e.g. aquatic communities – but usually the ‘most severe subject of protection’ is used, and thus is reported in Table 30. However it is admitted by the German ‘Umweltbundesamt’ (the Federal Environmental Agency of Germany (**UBA**)), that because of the still missing commonly accepted evaluation-criteria with respect to the toxicity towards e.g. ‘aquatic communities’ no quality targets for suspended solids and sediments could have been worked out (http://www.umweltbundesamt.de/wasser/themen/ow_s2_1.htm#T2.1.2 (in German)). In other words: the LAWA-classes are as artificial and arbitrary as any other… and the idea of giving up the, of course also questionable, but at least simple and sound I_{geo}-classes, for an unneeded – and following the above discussion about methodological uncertainties oftentimes even unfeasible (!) – differentiation is simply hilarious.

geologic conditions[151] as well as its more sound definition and thus ease of use and initial interpretability (cf. e.g. the latest Environmental Atlas of the city of Berlin)[152].

However, since this study has been conducted within a Russian-German-cooperation framework and Russian criteria for sediments are missing, as well as there will never be a single 'correct' classification-system, both German systems were used. The subsequent classes are shown in Table 30.

While the I_{geo}-classes have been adapted to Russian geological conditions – i.e. if possible they were calculated from the 'geogenic background' of Russian '*clay rocks*' as reported by Ronov and Migdisov (1996) rather than the '*shales*' reported by Turekian and Wedepohl (1961) used by default – the LAWA-classification has been used 'as is'.
This holds true with the exception of Ag, As and Hg where no 'Russian' data are available and thus the default definition of the I_{geo}-classes has been used. Although in principle also applicable to the omitted elements of Table 30 this is rarely done, and for elements with a natural occurrence of more than 2.1% already mathematically makes no sense, since there would be class-limits of more than 100%.

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[151] Nevertheless, the LAWA itself encourages the use of regional backgrounds, instead of their 'general' background values – while by doing so one would leave the German regulatory framework and would rather use the 'original' I_{geo}-classes...

[152] Available online (in English): http://www.stadtentwicklung.berlin.de/umwelt/umweltatlas/edua_index.shtml

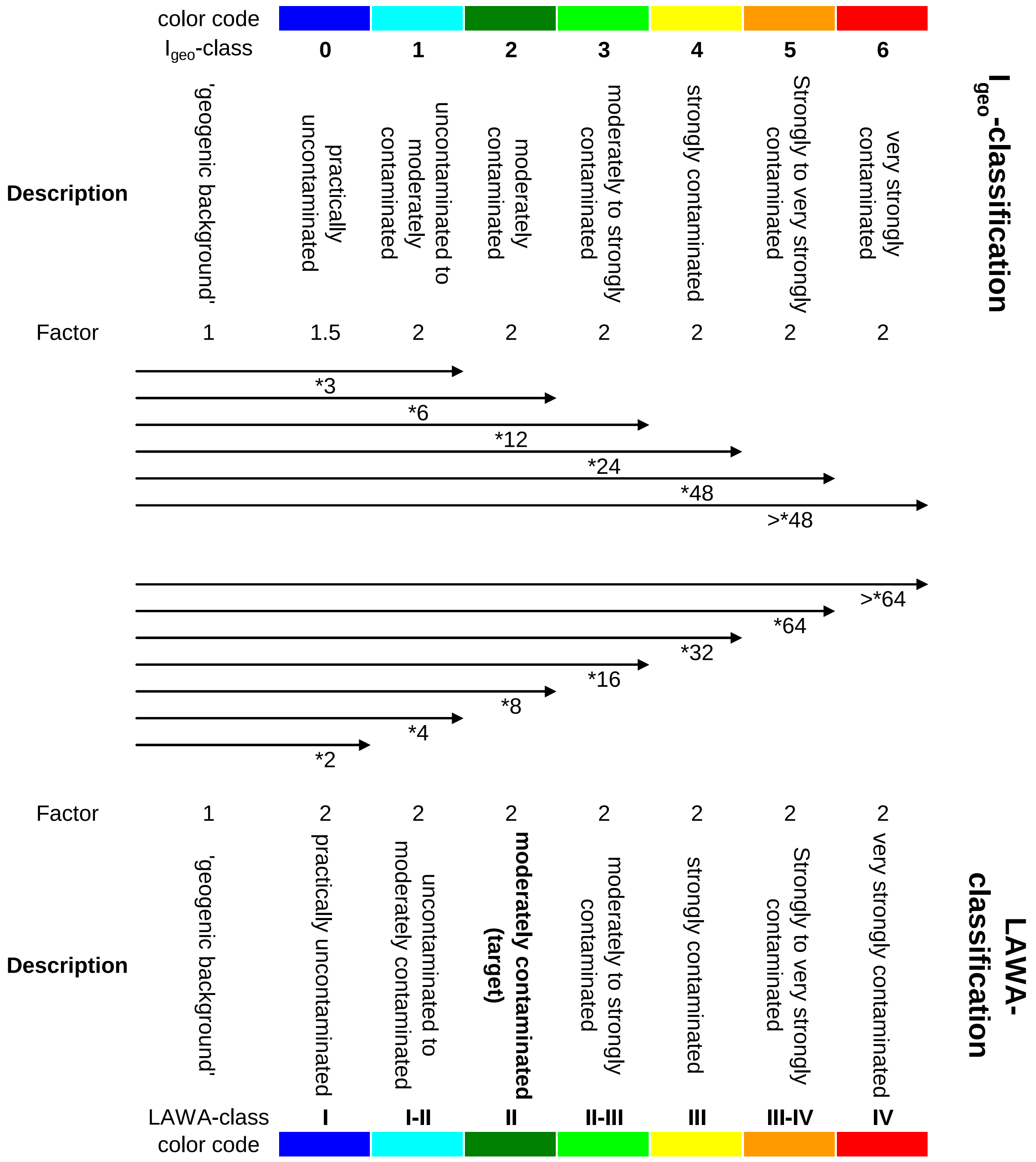

Figure 84 Initial definition and calculation of the I_{geo}-classes (Müller (1979) and LAWA-classes (LAWA (1998); for deviations within the LAWA-classification see Table 30, p. 220).

Table 30 I_{geo}- and LAWA-classification system – and basis for the calculation of the I_{geo}-classes.

	Turekian / Wedepohl 'Shales'	Ronov / Vinogradov 'Clay Rocks'	I_{geo}-classification 0	1	2	3	4	5	6	LAWA-classification I	I-II	II	II-III	III	III-IV	IV
			🟦	🟦	🟩	🟩	🟨	🟧	🟥	🟦	🟦	🟩	🟩	🟨	🟧	🟥
Ag	**0.07**	-	0.11	0.21	0.42	0.84	1.68	3.36	> 3.36							
Al [%]	8	**8.1**														
As	**13**	-	19.5	39	78	156	312	624	> 624							
Ba	580	**415**	623	1245	2490	4980	9960	19920	> 19920							
Ca [%]	2.2	**4**														
Cd	0.3	**0.095**	0.14	0.29	0.57	1.14	2.28	4.56	> 4.56	0.3	0.6	1.2	2.4	4.8	9.6	> 9.6
Co	19	**16**	24	48	96	192	384	768	> 768							
Cr	90	**80**	120	240	480	960	1920	3840	> 3840	**80**	**90**	**100**	200	400	800	> 800
Cu	45	**30**	45	90	180	360	720	1440	> 1440	20	40	60	120	240	480	> 480
Fe [%]	4.72	**4.53**														
Hg	**0.4**	-	0.6	1.2	2.4	4.8	9.6	19.2	> 19.2	0.2	0.4	0.8	1.6	3.2	6.4	> 6.4
K [%]	2.66	**3.23**														
Li	66	**63**	95	189	378	756	1512	3024	> 3024							
Mg [%]	1.5	**1.8**														
Mn [%]	0.085	**0.07**														
Mo	2.6	**1.4**	2.1	4.2	8.4	16.8	33.6	67.2	> 67.2							
Na [%]	0.96	**0.61**														
Ni	68	**44**	66	132	264	528	1056	2112	> 2112	**30**	**40**	**50**	100	200	400	> 400
Pb	20	**18**	27	54	108	216	432	864	> 864	25	50	100	200	400	800	> 800
Sc	13	**16.8**	25.2	50.4	100.8	201.6	403.2	806.4	> 806							
Sr	300	**236**	354	708	1416	2832	5664	11328	> 11328							
V	130	**95**	142.5	285	570	1140	2280	4560	> 4560							
Y	26	**28**	42	84	168	336	672	1344	> 1344							
Zn	95	**74**	111	222	444	888	1776	3552	> 3552	**100**	**150**	**200**	400	800	1600	> 1600
P [%]	0.07	**0.05**	0.075	0.15	0.3	0.6	1.2	2.4	> 2.4							
	Turekian and Wedepohl (1961)	Ronov and Migdisov (1996)														
		Description	practically uncontaminated	uncontaminated to moderately contaminated	moderately contaminated	moderately to strongly contaminated	strongly contaminated	strongly to very strongly contaminated	very strongly contaminated	uncontaminated	unpolluted to moderately contaminated	**moderately contaminated (target)**	moderately to strongly contaminated	strongly contaminated	strongly to very strongly contaminated	very strongly contaminated

Applying these two classification-systems to the here sampled Volga-sediments, as well as comparing the results with major German rivers, reveals an at least far from being alarming situation for the Volga-sediments with respect to the 7 heavy-metals monitored by default in Germany (cf. Figure 85). Even though one has to admit that the results reported for major German rivers (Figure 85a) are derived preferably from stations with known pollutant load – although not necessarily loaded with heavy-metals – and are thus presumably skewed towards higher classes, the situation in Volga-sediments has to be described at least as 'not worse' than in Germany. Starting from reports about a demanding situation on the River Volga and a severe load with respect to heavy-metals (cf. Chapter 3) one would have expected a situation much worse than for German rivers, where the '*Umweltbundesamt*' (UBA; the Federal Environmental Agency of Germany) reports the heavy-metal load to be declining since about 1988 (!).[153] While this decline in Germany is acclaimed mostly as a result of continuous control of point-sources and increasingly improved waste water treatment, one has to admit that the situation for the River Volga – for what reason soever – is at least 'satisfying' with no apparent need for actions to be taken..

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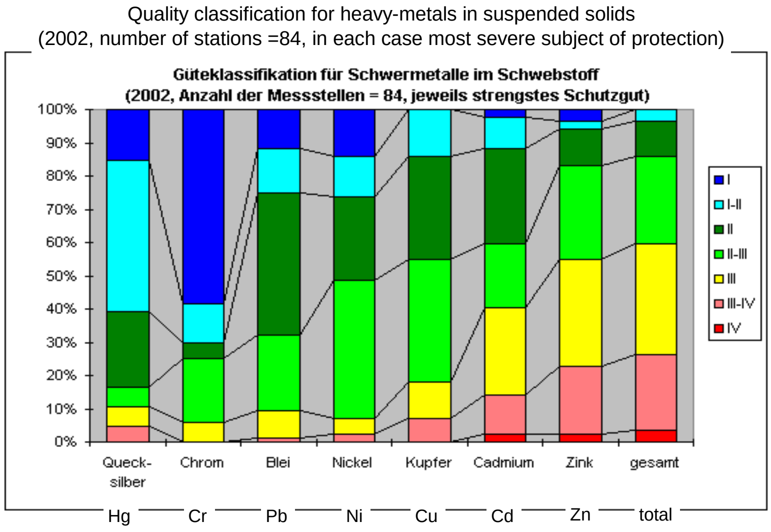
[153] Most of the data are available online (in German): http://osiris.uba.de:8081/gisu/dienste/Blondzik/atlantis/start.html

a) Quality classification for major German rivers (Danube, Elbe, Odra, Rhine, Weser)



Source: Umweltbundesamt, data as of LAWA.
Available online: http://www.umweltbundesamt.de/wasser/themen/ow_s4_4.htm

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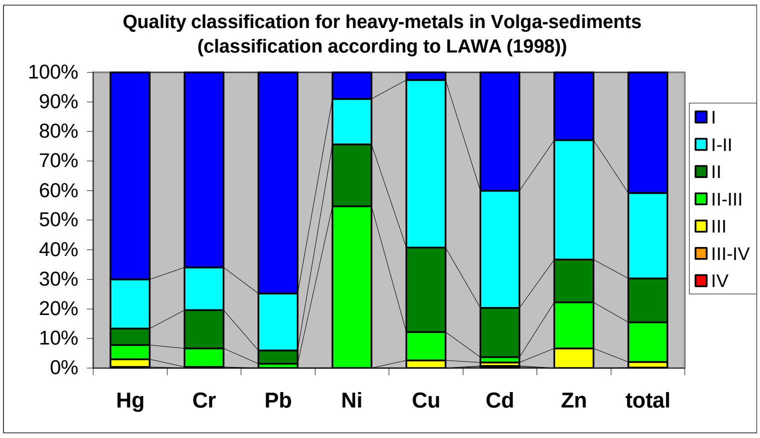
b) Quality classification for the River Volga-sediments (LAWA-classification)



c) Quality classification for the River Volga-sediments (I_{geo}-classes)

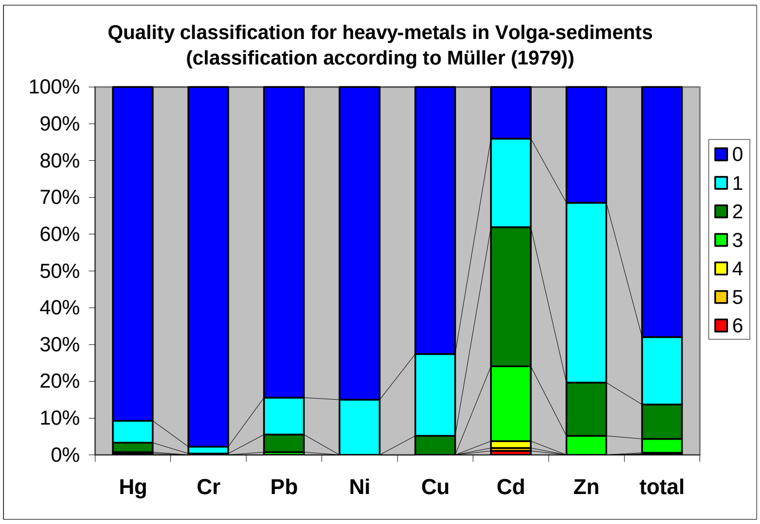


Figure 85 Classification of Volga-sediments (Igeo-classes (c) and LAWA-classes (b)) and comparison with the classification of major German rivers (a).

However, Figure 85 also reveals differences in the assessment of the data. The I_{geo}-classification (Figure 85c) would suggest a spacious, albeit not severe, contamination of Volga-sediments with

Cd and Zn, whereas the LAWA-classification (Figure 85b) would suggest a spacious contamination with respect to Ni, Cu, Cd and Zn. This is owed to the different assumptions about the 'geogenic background' as well as the ostensibly inconsistent LAWA-classification for Ni.[154] Without being able to testify which 'geogenic background' may be closer to reality, this is simply a methodological uncertainty one has to accept.

A similar inconsistency – even though within the same classification system – is observed when classifying the remaining elements of Table 30, as depicted in Figure 86.

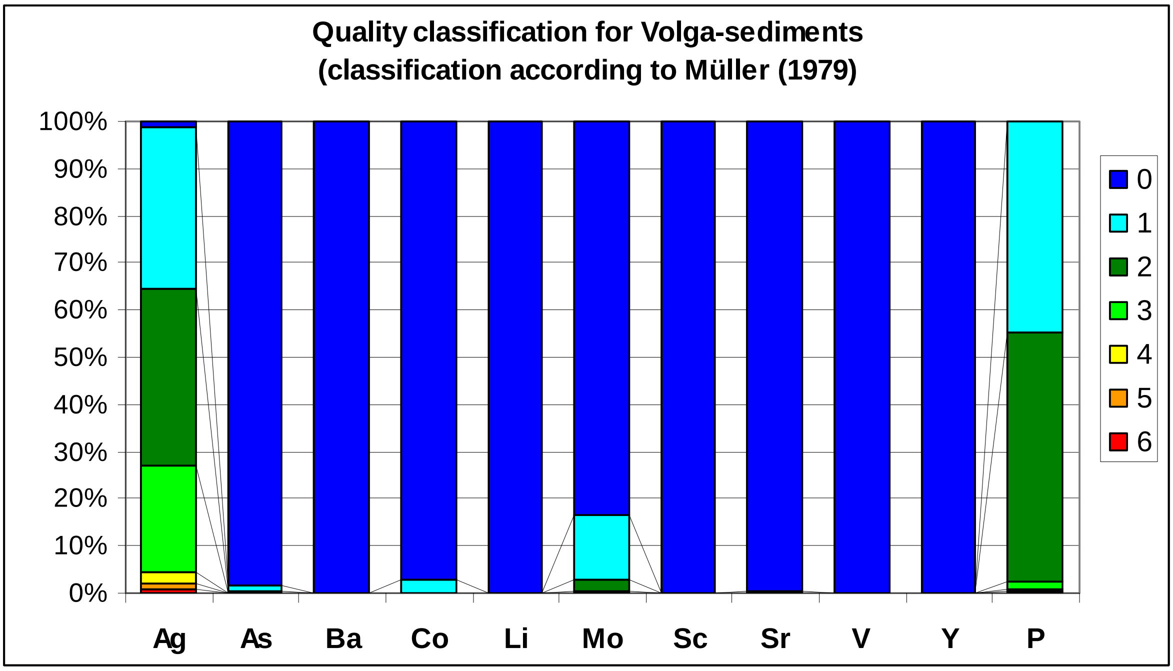


Figure 86 I_{geo}-classification of the remaining (heavy) metals, arsenic and phosphorus in Volga-sediments.

While the elements generally considered as of 'geogenic' origin, i.e. usually not, or only very little redistributed by man (Ba, Co, Li, Mo, Sc, Sr, V, Y) are classified the way one would have expected, the classification with respect to Ag as well as Phosphorous is puzzling.

Why should just Ag and Phosphorus be the only elements with virtually not a single sample in I_{geo}-class '0', i.e. not a single sample to be 'practically uncontaminated', while notorious contaminants (cf. Figure 85) behave clearly different? One could of course hypothesize, about e.g. Ag redistributed by man along with Cd and Zn (cf. Müller (2001)), and/or assume the extensive use of phosphate-fertilizers throughout the whole catchment area, and thus necessarily elevated concentrations in run-off and sediments, but one will not be able to prove any of these ideas on the here available data-basis and methodology.

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[154] Already the expanded **measurement** uncertainty has been calculated to be about ± 30% (cf. Figure 25, p.86) and thereby ± 1 class for the first three LAWA-classes. The same holds true for Cr. So this classification may be appropriate, when dealing with median-values of a sufficient amount of samples, but surely fails for the classification of primary samples.

4.3.3 Geochemical vs. statistical approach

Irrespective of the above described problems, all kinds of ‘global geochemical backgrounds’ – however weak their justification might have been – have been used to classify sediments without facing major problems. How come?

There are two fundamentally different approaches to find (areas with) ‘abnormal’ concentrations for a measurand. The first is to compare the measured concentrations with an ‘external standard’ – that may be an assumed ‘background-level’, a threshold level or a governmental regulatory. The second is trying to derive these areas from the data set itself. Both approaches have some shortcomings.

Any comparison with an external standard would have to prove that the ‘external standard’ can be applied reasonably to the sampled medium. With the exception of using a governmental regulatory as an ‘external standard’ – this simply states how things should be, regardless of any inconsistencies – that is not a simple task as we saw.

Even in this study, where we are fortunately not dependent on worldwide data sets with all their stated limitations (e.g. the above mentioned ‘shales’-values by Turekian and Wedepohl), but instead are able to use values derived from a breathtaking number of samples in the region itself (the values provided by Ronov and Migdisov (1996)), it is almost impossible. Too little is known quantitatively about the connection between a parent rock and/or a mixture of them and the resulting weathering products – and vice versa.

The first approach is far from being rational, but it can never be (all) wrong. It is comparing an actual measurement with a fixed value; i.e. a normalization of the data-set with a fixed value. In other words: it does NOTHING! No matter, what that value might mean or represent, the data-set remains unchanged – and one could also use any arbitrary figure to do that... or the original data-set.

At least, this procedure adds no extra ‘noise’ to the data. Other approaches are normalizing one measurand with another one from the same data-set, e.g. with Li for grain-size effects, or Sc, Ti, Al, and so on as ‘conservative elements’, for enrichment. No matter how correct the underlying assumptions may be, the result is usually only more noise (the division of two values with an expanded uncertainty of lets say 30% – a very conservative assumption, representing the best case – would lead to a result with an expanded uncertainty of approx. 42%).

The only shortcoming of the second approach, to derive the ‘abnormal’ concentrations from the data set itself, is its complete dependency on the data set and the way it was obtained. This can be a big problem – depending on the data set and its underlying limitations (e.g. if the sampling-plan is not representative for the covered region, or one is preferably sampling hot-spots). However, since the original-data set is the only thing one will ever have, and as long, as one is aware of the problems and limitations bound to it, it is the most rational approach.

4.3.3.1 Z-score-classification

Some ways to derive the most likely, unmodified (i.e. naturally occurring) values and/or their distribution function – especially for ‘background’-calculations – are presented elsewhere (Matschullat et. al., 2000). Another very simple, but effective way is provided by z-scores. It is just another way to normalize values and make them comparable to each other, especially when they got different magnitudes.[155]

A z-score is calculated by: $z = \frac{x_i - \bar{x}}{\sigma}$;

where x_i is the measured value, $\bar{x}$ is the mean and σ the standard-deviation of the data set.

It is important to note that unlike the above-mentioned normalizations, this procedure adds no further ‘noise’ to the data set, nor alters it in any way**[156]**.

The values are just transformed to a scale, where they represent their original deviation from the mean – expressed as multiples of the standard deviation, which is the z-value.

The data set is centralized (x_i-$\bar{x}$) and normalized (division by σ) with itself, resulting in a distribution of the data with a mean of zero and a σ of 1, but not changing anything or making any assumptions.

One mathematical definition of the ‘normal range’ of a (normal-) distribution is that of the mean $\pm 2\sigma$.[157] That is, because when dealing with normally distributed data – and a sufficient amount of them, which holds true with 270 values – more than 95% of the data would fall in this range. This kind of classification can be, and is, used in proficiency testing (PT) schemes. Although there are of course some major differences between PT and our work, the basic problem is quite the same: there is a vast quantity of data and the task is to find out, what’s ‘normal’.

In PT-schemes the material given to the participants is ‘exactly’ the same – the difference derives from the laboratories, whereas in our case the laboratory is ‘exactly’ the same – the difference derives from the samples. However, the basic question remains the same.

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[155] In fact a z-transformation is one of the prerequisites e.g. for correlation (-analysis) when dealing with values on different scales.

[156] One might argue that this assumption is not fully correct, since both the mean and the standard deviation are affected by a specific amount of uncertainty – depending on the uncertainty of the primary measurements and the number thereof. Apart from the more or less philosophical question, whether it is admissible to simply **define** these two variables as error-free for the use as ‘normalizers’ (no matter how large the uncertainty of the measurements may be, their numerical value will not change; albeit their uncertainty will), even when taking their uncertainty into account, the additional noise is negligible – at least in this case of 270 measurements.

[157] In fact, as already discussed there is no such thing as a ‘normal range’, but everyone can define it, to fit his needs. There are various definitions; none of them is scientifically sound, but derived from practical considerations.

A classification of Z-scores as suggested by the International Organization for Standardization – Committee on Reference Materials (ISO/REMCO N 280[158]) is:

$|z| < 2$ satisfactory
$2 < |z| < 3$ questionable
$|z| > 3$ unsatisfactory

Assigned to the problem here, ‘satisfactory’ would be ‘normal’ and ‘unsatisfactory’ would be ‘abnormal’ (naturally, i.e. an anomaly; or manmade, i.e. a pollution).

Since this approach uses the overall mean and standard deviation (σ) of a data set to classify single measurements, one should be aware of the inherent limitations, when applying it to this kind of problem:

- In order to receive a significant result, 2σ has to be noticeably greater than the ‘expanded uncertainty’ of the measurement.
- The mean of the data set has to be a meaningful measure to describe/approximate the central tendency of the undisturbed data set, and the standard deviation has to be a meaningful measure of its spread.[159] E.g. if one is sampling (preferably) ‘hot-spots’ this approach makes no sense, since the mean describes the ‘hot-spots’ rather than the riverine system.

In our case, 2σ is always greater than the respective ‘expanded uncertainty’ and the differences between the mean and the median are too small, to influence the results.[160]

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[158] Thompson M, Wood R, International Harmonised Protocol for the Proficiency Testing of (Chemical) Analytical Laboratories, J AOAC Int, 76: (926-940 (**1993**)

[159] This limitation tacitly includes the requirement of the data set to be (approx.) normally-distributed, with the absence of (strongly) skewed distributions and e.g. the absence of multi-modal distributions.

[160] In case there are larger differences, the MAD-value (median average deviation) may be used. Since no apparent differences between the two approaches were observed when applied to the Volga-data, the more common z-scores were used.

There are several ways conceivable to define the subsequent classes. The first would be to use the above three definitions (satisfactory ('normal'), questionable and unsatisfactory ('abnormal')) and thus three classes. Nevertheless, in order to allow for a comparison with the above two classification-systems we also choose a six-stepped approach:

Class 0:	$z \leq 0$	i.e. values ≤ mean	values below the mean
Class 1:	$z \leq 1$	i.e. values ≤ mean + 1s	satisfactory, i.e. 'normal'
Class 2:	$z \leq 2$	i.e. values ≤ mean + 2s	satisfactory, i.e. 'normal'
Class 3:	$z \leq 3$	i.e. values ≤ mean + 3s	'questionable'
Class 4:	$z \leq 4$	i.e. values ≤ mean + 4s	**unsatisfactory, i.e. 'abnormal'**
Class 5:	$z \leq 5$	i.e. values ≤ mean + 5s	**unsatisfactory, i.e. 'abnormal'**
Class 6:	$z \leq 6$	i.e. values ≥ mean + 6s	**unsatisfactory, i.e. 'abnormal'**

In fact only three of the class-limits have a distinct meaning:

Up to class 2 the samples are considered as '**normal**';[161]

The samples in class 3 are considered '**questionable**' – with no apparent chance for a decision;

From class 4 on the samples are considered '**abnormal**'.

Since the chances to classify a data set are limited, this approach has of course many similarities with other approaches, like the above-mentioned I_{geo}-classes and LAWA-classification, but also with classifications based on percentiles that are used every now and than. While the I_{geo}- and LAWA-classes are (primarily) based on the multiplication of an assumed background, and thus an external benchmark, and classifications based on percentiles are purely geometrically defined, the z-score approach is 'floating'. The class-limits and widths vary depending on the data set they were calculated from and for.

This may be a strength, but also a severe weakness as discussed above (cf. Chapter 4.3.3). There are several ways conceivable to overcome this weakness, e.g. outlier testing or one of the above mentioned ways to calculate the most likely, unmodified (i.e. naturally occurring) values and/or their distribution function (Matschullat et. al., 2000). But this ostensible weakness could also be used as is sometimes in PT-schemes to define the allowable amount of deviation from a 'known' measure of central tendency: in case a most probable background value is known, or agreed on, one could define how much spread will be allowed for, e.g. from the distribution functions of presumably 'geogenic' elements. E.g. looking at Table 26 (p.183) the huge differences in the RSD's of the elements is eye-catching and in case one would have some knowledge about what amount of fluctuation can be considered as 'normal' (for a given element) the z-scores would allow for the most ob-

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[161] Samples in class 0 may be 'depleted', which is of minor interest when searching for 'enrichment'.

jective distinction between ‘normal’ and ‘abnormal’ by simply applying this external benchmark to the data-set. Unfortunately, this knowledge is missing up to date.

On the other hand, a sure strength of the z-scores-approach is the possibility to classify all elements – even those where the I_{geo}-classes are not unanimously applicable (namely those with abundances ≥ 2.1%). Moreover, it allows for a quick overview of the distribution function of the element – since for a perfect Gaussian normal distribution class 0 should compromise exactly 50% of the data, up to class 1 ~84.2 % of the samples should occur, ~97.7% up to class 2 and so on.

Judging from Figure 87 the z-score approach is simply an intermediary between the LAWA-classification and the I_{geo}-classification. On the one hand, this classification relies on the skewness of a distribution in order to differentiate; on the other hand, this skewness will affect the standard deviation and thus the class-width. In other words, the more skewed a distribution function will be – i.e. the larger the standard deviation will get – the gentler this classification-system will deal with elevated concentrations. Some elements show notedly skewed distribution functions – with notedly more than 50% of the samples in Class 0, and thus necessarily a long right tail, as well as an enlarged standard deviation.

Especially Hg, Pb, Cu, Cd and Zn, but also Ag, Mo, Ca, Mn and S_{total} are definitely not normally distributed. But being intermediary – albeit not by purpose – the classifications with respect to the aforementioned 7 inorganic COPC’s (Hg, Cr, Pb, Ni, Cu, Cd and Zn) is always at least roughly backed up by one of the other classification-systems as can be seen from Table 31 and Figure 87.[162] Thereby eliminating the disturbing idea of a Ni-contamination of Volga-sediments (suggested by the LAWA-classification due to their inconstant class-limits) as well as the idea of spacious elevated Cd-contents (suggested by the Igeo-classification due to the use of the very low ‘background concentrations of this element suggested by Ronov and Migdisov (1996)).

Table 31 Number of samples per class of the three used classification-systems for seven inorganic COPC’s

	LAWA								z-scores								I_{geo}						
class	**Hg**	**Cr**	**Pb**	**Ni**	**Cu**	**Cd**	**Zn**	**class**	**Hg**	**Cr**	**Pb**	**Ni**	**Cu**	**Cd**	**Zn**	**class**	**Hg**	**Cr**	**Pb**	**Ni**	**Cu**	**Cd**	**Zn**
I	189	178	202	24	7	108	62	**0**	214	146	178	133	193	187	192	**0**	245	264	228	227	196	38	85
I-II	45	39	52	41	153	107	109	**1**	35	100	73	99	58	75	46	**1**	16	5	27	40	60	65	132
II	15	35	12	56	77	45	39	**2**	12	18	4	31	5	2	16	**2**	7	1	13	0	14	102	39
II-III	13	17	4	146	26	5	42	**3**	2	2	8	7	5	2	9	**3**	1	0	2	0	0	55	14
III	7	1	0	0	7	3	18	**4**	5	3	2	0	5	0	4	**4**	1	0	0	0	0	5	0
III-IV	1	0	0	0	0	1	0	**5**	0	0	2	0	2	1	3	**5**	0	0	0	0	0	2	0
IV	0	0	0	0	0	1	0	**6**	2	1	3	0	2	3	0	**6**	0	0	0	0	0	3	0
No. of samples above Class II	**21**	**18**	**4**	**146**	**33**	**10**	**60**		**9**	**6**	**15**	**7**	**14**	**6**	**16**		**2**	**0**	**2**	**0**	**0**	**65**	**14**
[%] of samples above Class II	**8**	**7**	**1**	**54**	**12**	**4**	**22**		**3**	**2**	**6**	**3**	**5**	**2**	**6**		**1**	**0**	**1**	**0**	**0**	**24**	**5**

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[162] It is however important to note that the regular definition of the I_{geo}-classes with respect to Cd would be exactly the same as the LAWA-classification and in fact the I_{geo}-classes and z-score-classification would be pretty much similar.

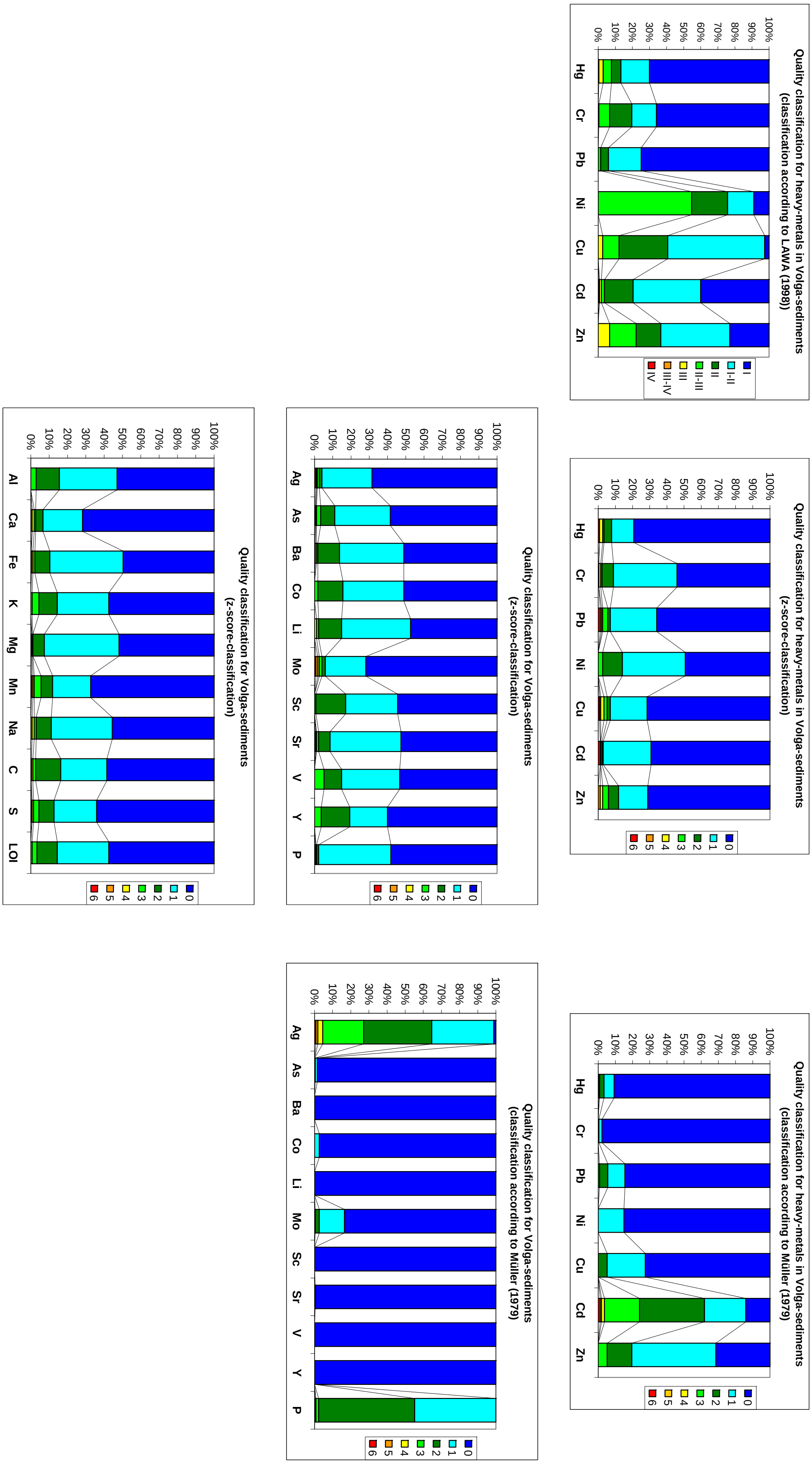

Figure 87 Comparison of the two geochemical classification-systems used and the mathematical one via z-scores.

Furthermore the aforementioned and little comprehensible spacious contamination with Ag and phosphorus suggested by the I_{geo}-classification, is not backed up by the z-scores.

Ignoring the LAWA-classification for its incomprehensible classification of Cr, Ni and Zn – artificially creating sub-categories – these problems could also be solved by the I_{geo}-classes by the use of another background-value for the affected elements. E.g. taking the Ag-contents of the aforementioned Canadian Stream sediments as ‘geogenic background’ (cf. Table 28 and accompanying discussion) would change its I_{geo}-classification drastically to look pretty much like that of Molybdenum (cf. Figure 87).

As already mentioned one could also ‘play around’ with the data set, in order to create lower means and standard-deviations and thus more samples with an ‘abnormal’ content, but in case of the Volga-sediments little changed when applying outlier-tests, or use calculated distribution-functions (cf. Matschullat et. al., 2000). Of course there were changes especially for the heavier skewed distribution functions, but the changes in classes-limits was each and every time well below the expanded measurement uncertainty of the respective element, making any of these efforts of no value. There may be cases – especially within heavily polluted catchments – where the z-scores in this simple form may fail; the Volga River surely is not one of them.

However, it has to be stated clearly and precisely: as soon, as one is able to define background-estimates with a certain amount of evidence, there is no classification system more objective and convincingly simple as the I_{geo}-classification. It uses a, than founded, external benchmark, and is unaffected by any peculiarities of the distribution function of an element or shortcomings in the sampling scheme – both of which affect the z-scores since it is completely data-set dependant (‘garbage in – garbage out).

4.4 Statistical considerations

There are at least two comprehensive guides for the statistical treatment of environmental data.

The '**Handbook for Statistical Analysis of Environmental Background Data**' (NAVFAC, 1999) '*…provides step-by-step instructions for conducting graphical and statistical data analyses and test of hypotheses to identify contaminants of potential concern (COPC) at Navy installations' and is rather practice-oriented in order to allow a sound (legally and scientifically) site-description as well as corroborate potential decisions towards remedial-actions*."

The '***Guidance for Data Quality Assessment – Practical Methods for Data Analysis***' (US-EPA, 2000), from an earlier version of which large parts of the above NAVFAC-guide are derived, is more general and '… *focuses primarily on using DQA in environmental decision making; however, the tools presented for preliminary data review and verifying statistical assumptions are useful whenever environmental data are used, regardless of whether the data are used for decision making.*'

Over and above, the '***NIST/SEMATECH e-Handbook of Statistical Methods***'[163] covering most statistical methods applicable (not only) to environmental data, with the first chapter about Exploratory Data Analysis (EDA), '*…an approach to data analysis that postpones the usual assumptions about what kind of model the data follow with the more direct approach of allowing the data itself to reveal its underlying structure and model.*'

At first sight, the easiest way to deal with the data would be to use either the NAVFAC- or the U.S. EPA-guide in order to end up with sound results based on accepted principles. Actually, this approach is almost unfeasible within the scope of a study dealing with that little sample for such a vast area as the Volga catchment.

The major limitations of – not only – this study, the sampling and the sampling scheme have been discussed in depth (see Chapter **2.5**; p. 91ff.). These limitations necessitate simplification in the questions addressed.

However, one can find numerous studies – scientific as well as regulatory ones – that comply even less with any reasonable DQO's, but presenting an allegedly elaborate statistical analysis. It is simply a matter of straightforwardness and (scientific) decency to identify and acknowledge the inherent limitations.

For all that, the idea of Exploratory Data Analysis showed a way to obtain few, but sound results.

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[163] NIST/SEMATECH e-Handbook of Statistical Methods, http://www.itl.nist.gov/div898/handbook/, 2005.

4.5 An approach – too simple to be wrong

The basic idea of the approach finally used to subdivide the Volga, arose from the **Runs-test**, a non-parametric test for randomness. One way to conduct this test is to code values above the median as positive and values below the median as negative. The number of runs, i.e. subsequence of consecutive numbers of the same sign, immediately preceded and followed by numbers of the opposite sign, are counted and compared with that expected under the null hypothesis, which is such that all orderings of signs are equally probable.

Searching for the exact opposite, namely patterns within the data set, a very simple, graphical form of this test seems to work effective. What is more, one of the major limitations of the initial data set speaking against a more rugged statistical analysis – its underlying non-random sampling-scheme – turned out to be helpful for this approach.

The sampling points are essentially sequential – with the exception of the transects – and thus already reasonably ordered. Averaging the respective transects to create a single data point at a time, resulted in a fully sequential – albeit NOT equally spaced[164] – data set of altogether 217 data points. Coding these data points as described above – values above the median are coded positive (+1) and values below the median are coded negative (-1) – already allows for a distinction between different elements and their fundamental behavior within the rivers course, namely:

- Parameters with a predominance of **positive** median-deviations in the **Upper Volga** AND a predominance of **negative** median-deviations in the **Lower Volga** (e.g. zinc).
- Parameters with a predominance of **negative** median-deviations in the **Upper Volga** AND a predominance of **positive** median-deviations in the **Lower Volga** (e.g. nickel).

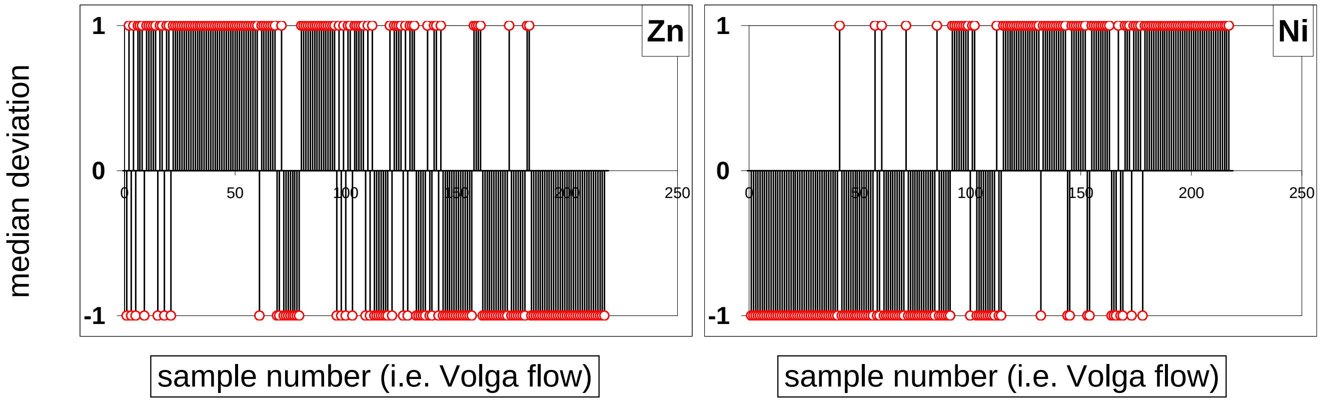

Figure 88 **Median-deviation plot of zinc and nickel.**

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[164] One of the reasons that prohibit the use of e.g. techniques for the interpretation of 'time-series'.

The differences between the two groups of parameters are even more evident, when adding up the Median-deviations and plotting the sum up to the respective sampling point – similar to the calculation of a moving-average, but without dividing the sum.

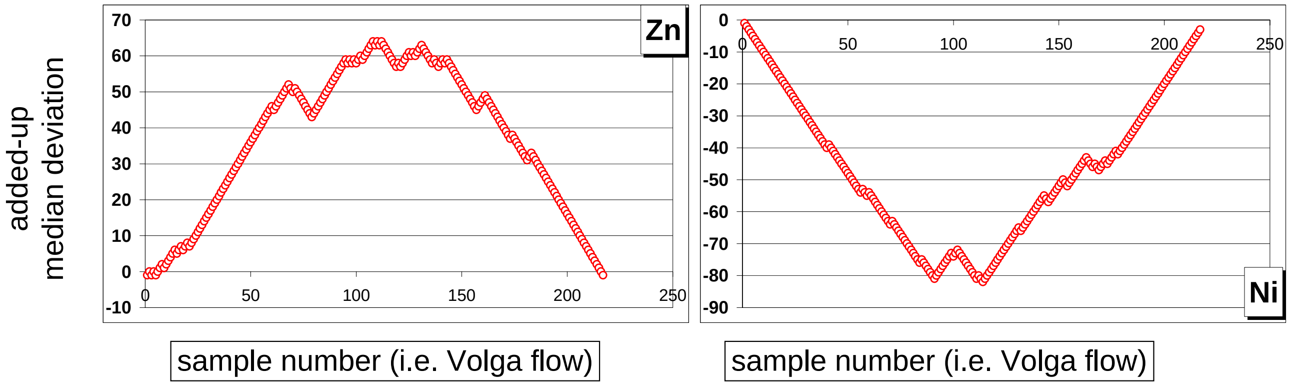

Figure 89 **Added-up median-deviation plot of zinc and nickel.**

At first sight, this simple method is sufficient not only to classify the measured parameters, but also to subdivide the rivers course into sections. E.g., it is apparent that zinc and nickel have different – not to say, opposed – distribution patterns in the Volga sediments, as well as that there is a difference between the Upper Volga (low sample numbers) and the Lower Volga (high sample numbers). However, median-deviations are in fact very crude approaches. They are sort of ‘digitizing’ the measurements of the Volga sediments, and analog-to-digital conversions always result in a loss of information.

What is more, when considering the measurement uncertainty they loose lots of their initial charm. When talking about more or less normally distributed data, the median is a robust measure of central tendency. The prerequisites needed to make the median-deviations robust are less often achieved. A given measurement ± its expanded uncertainty must be distinguishable from the median, otherwise it cannot be classified. That can be a serious restriction, depending on the amount of uncertainty and the distribution of the data. Parameters with a high associated uncertainty and/or a tight distribution function – i.e. many measurements close to the median[165] – are highly affected by this issue. The most eye-catching outcome encountered in the data set of the Volga sediments is depicted in Figure 90.

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[165] Mathematically speaking, particularly distribution functions with a tendency towards a positive kurtosis and skewness close to zero.

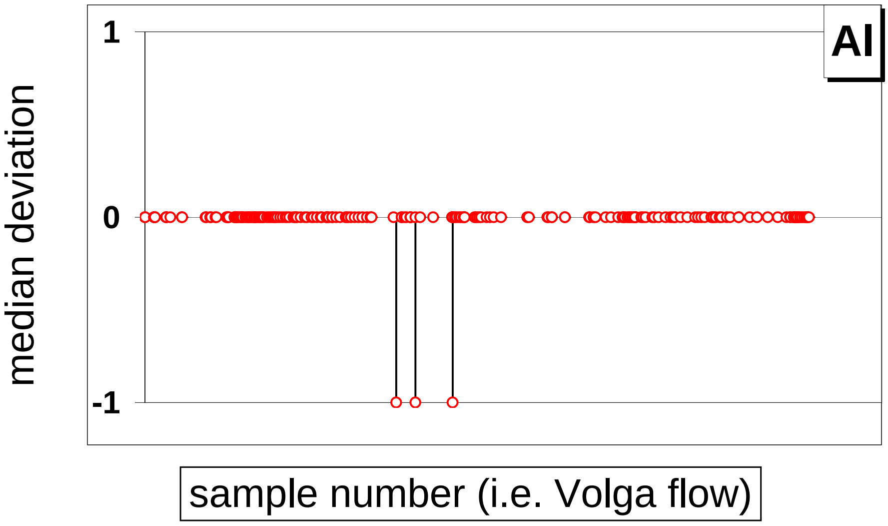


Figure 90 **Median-deviation plot of aluminum considering the expanded measurement uncertainty for this parameter. Measurements indistinguishable from the median are labeled as ‘0’.**

4.5.1 Added up z-scores

Z-scores (see Chapter **4.3.3.1**; p.225 ff.) have all the wanted characteristics of the median-deviations (they are either positive or negative; or exactly zero) **and** they contain the full information of the measurement (the respective value and algebraic sign). Plotting the z-scores vs. the respective sample or the Volga flow leads to exactly the same diagrams as when plotting the measurements itself. Summing up the z-scores the same way as the median-deviations, leads to plots of the same nature as for the added-up median-deviations (Figure 92 and Figure 93) – without introducing any distortion as in case of the median-deviations. The added up z-scores maintain all the details of the measurement process, like jump discontinuities in case of extreme values, while the median-deviations tend to exaggerate small differences near the median and understate the distinct peculiarity of the extremes.

The calculation of the respective added-up z-score ($A_{z-score}$) its variance ($s^2_{A_{z-score}}$) and the z-score itself (z_i) is presented in the box below:

$$\boxed{\begin{aligned} A_{z-score} &= z_1 + z_2 + \ldots + z_i \\ s^2_{A_{z-score}} &= s^2_{z_1} + s^2_{z_2} + \ldots + s^2_{z_i} \\ &---\\ z_i &= \frac{x_i - \bar{x}}{\sigma} \\ x_i &= \text{measured value} \\ \bar{x} &= \text{mean of the data set} \\ \sigma &= \text{standard deviation of the data set} \end{aligned}}$$

Similar to the calculation of an average, where a large enough number of measurements can outweigh any amount of uncertainty, the adding up of single measurements reduces the overall importance of the respective samples. However, unlike for the calculation of an average, the uncertainty will not get lost, no matter how many samples will be added up. On the contrary, while the relative uncertainty (expressed as variance (s^2) or standard deviation (s)) may decrease the absolute uncertainty increases. That is what makes the respective error bars – while mathematically correct – questionable (cf. Figure 92 and Figure 93). Depending on the starting point of the adding up, the error bars will vary for a given point and it would be most reliable to assume the maximum absolute value of uncertainty for every sample.

On the other hand, the error bars depicted in Figure 92 and Figure 93 – solely representing the measurement – provides a rough estimate about how detailed an interpretation can be performed.

They do NOT account for the uncertainty of the measurement process as a whole– i.e. especially the sampling uncertainty.

Although the sampling uncertainty has been calculated as a statistical error (cf. Chapter 2.5.4; p.121ff.) there is no evidence for the **absence of bias** in the sampling scheme. Since the calculated sampling uncertainty is the result of making the sample representative for the target (the Volga sediment), it is simply a product of the initial assumptions. However, when subdividing the Volga – i.e. the Volga-samples to be precise – they do not have to represent anything but themselves and the error attributable to a measurement in order to make it representative for the sample is the **expanded measurement uncertainty**.

- In case single samples are biased – i.e. representing a different population – they can only be identified in case of extreme values.
- In case a group of samples is biased, they will deviate from the rest of the samples and can be identified in the plots.
- Assigning the **expanded uncertainty of the measurement process** at this stage is possible, but not necessary.
- If assigned, one would compare groups of samples representative for the target – i.e. the Volga-sediment.
- If not assigned, one compares groups of measurements representative for the samples.
- In both cases, one would use the same inflection points for subdivision.

4.5.1.1 Interpretation of the added-up z-scores

The outcomes of plotting the added-up z-scores vs. the respective sample are consecutive data points with a varying slope. This change in slope is used to subdivide the data into groups of data points with similar values, since any change in the slope indicates a (major) change in the underlying measurements:

- A constant positive (negative) **slope** is the result of adding up measurements of more or less the same positive (negative) deviation from the overall mean. However, it does **NOT** indicate a trend! A slope close to zero is the result of adding up measurements close to the overall mean.
- In case the **slope changes**, the underlying data set has changed, indicating a new, distinguishable group of data points.
- The **steepness of the slope** represents the deviation (positive or negative) of the respective group of values from the mean of the data set.
- **(Local) maxima and minima** indicate a basic change in the behavior of the respective parameter. Predominant positive (negative) z-scores are displaced by predominant negative (positive) z-scores. The steeper the slope on either side of the maximum (minimum), the more pronounced is this change.
- **Jump discontinuities** indicate one or more extreme values compared to the rest of the data set. They only occurred as positive extremes.

Plotting the added-up z-scores vs. the sample number (i.e. the Volga flow), results in roughly two groups of parameters. An **upside-down "U"** – i.e. ⋂ – can more or less describe the diagrams of **Group 1** parameters (Figure 92), while a "**U**" can more or less describe the diagrams of **Group 2** parameters (Figure 93).

As abovementioned (Chapter 4.5.1), the z-scores are just a transformation of the original data set. That is to say, they contain the full, unaltered information of the original data set, but also its limitations – especially those arising from the measurement process, namely the expanded measurement uncertainty and the bias introduced by the sampling scheme.

On the one hand, that is what makes them superior to the median-deviations; on the other hand, one could also use the original data. The first consideration is the reason to use the added-up z-scores instead of the added-up median deviations for subdividing the data set and not to discuss differences in the results of the two approaches. The rationale to use added-up z-scores, instead of adding-up the original data set is justified by the fact, that the resulting diagrams are much more user-friendly in case of the added-up z-scores. Of course, both of them contain the same information, but this information is much more readily identifiable in the added-up z-score plots as can be seen from the example below (Figure 91).

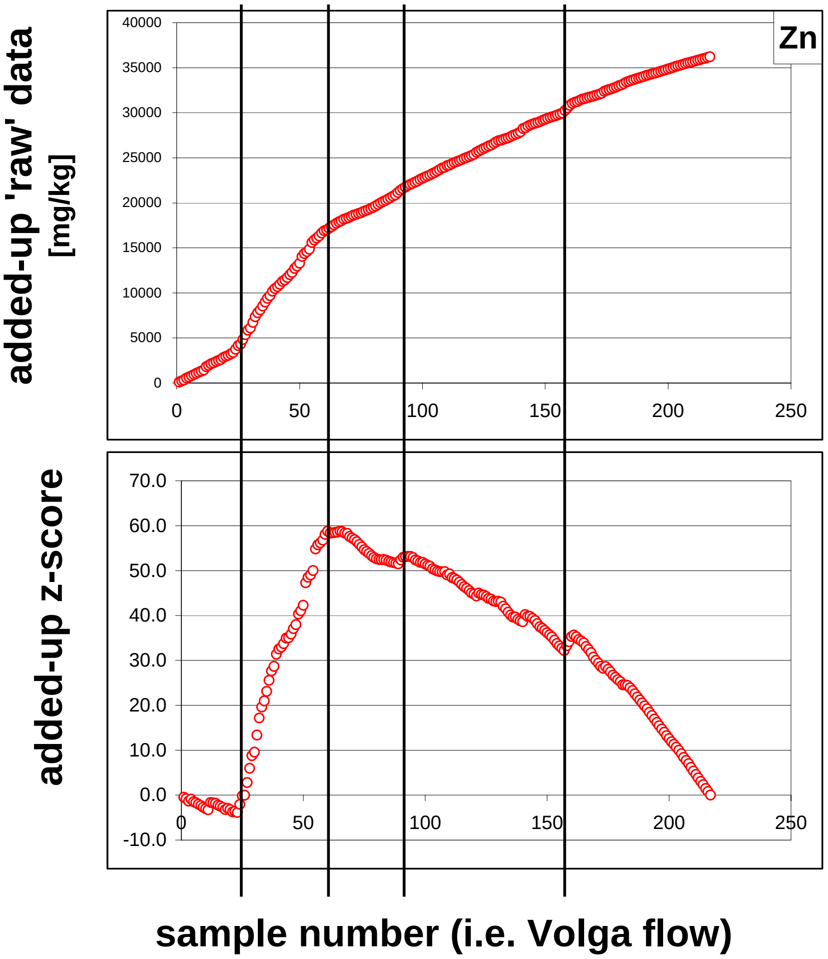


Figure 91 Comparison of the added-up z-score plot for zinc, with the plot resulting from adding up the original (untransformed) zinc data.

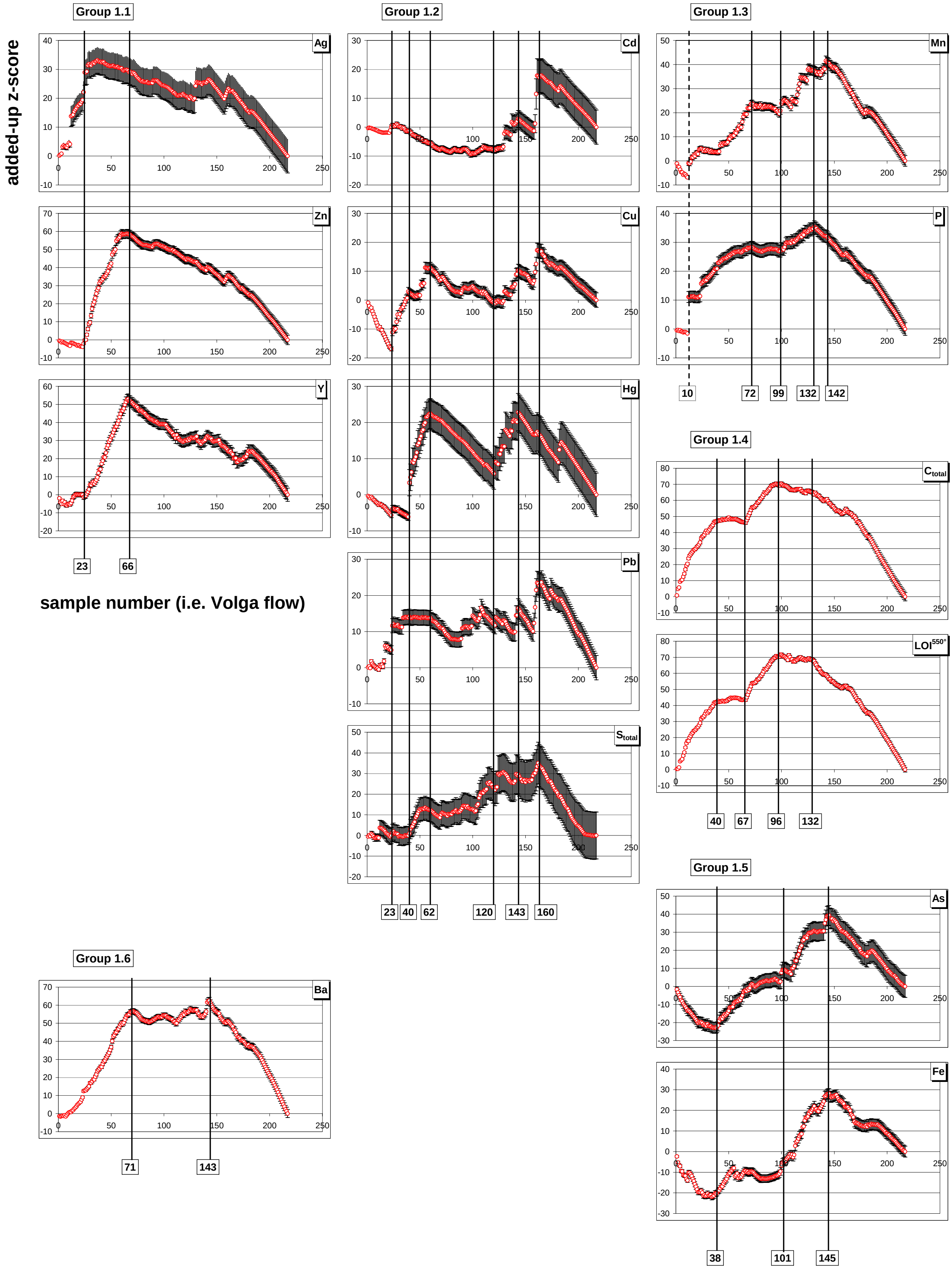


Figure 92 Added-up z-score plots for Group 1 parameters and provisional subdivision. Error bars indicate expanded measurement uncertainty (cf. Chapter 4.5.1). Numbers represent sample number (cf. Table 32, p.241).

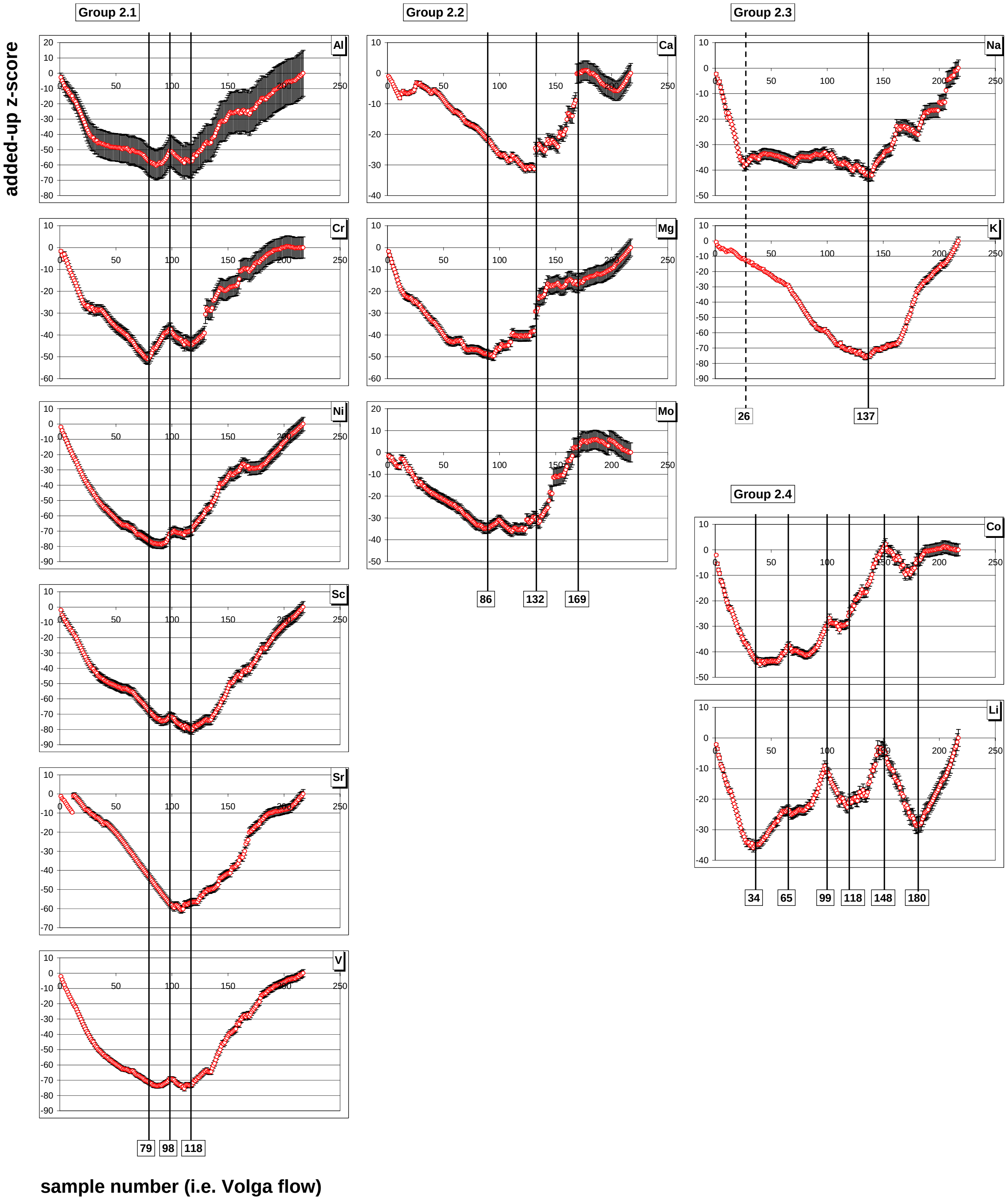


Figure 93 Added-up z-score plots for Group 2 parameters and provisional subdivision. Error bars indicate expanded measurement uncertainty (cf. Chapter 4.5.1). Numbers represent sample number (cf. Table 32, p.241).

4.5.2 Outcomes of the interpretation

Comparing the provisional classification of the measured parameters as well as the respective subdivision of the Volga (Figure 92 and Figure 93) with some characteristic landmarks (Table 32) gives rise to the assumption that:

- The measured parameters can roughly be subdivided into two major groups with fundamentally different distribution patterns.
- Oftentimes the subdivision is almost in accordance with the intuitional approach of subdividing the Volga according to the man-made chain of reservoirs and the major industrial centers on the Volga (cf. Chapter 1.8.1).

Most jump-discontinuities in the added-up z-score plots – especially those of presumably anthropogenically redistributed elements (Zn, Cd, Cu, Hg, Pb and Cr) – can be explained by the proximity of a city to the respective sample, and the city of Saratov is the most prominent example. However, this is rather a result of the sampling scheme. In fact, Saratov is simply the ‘best’ sampled major city on the Volga – while e.g. the city of Volgograd is ‘covered’ by just two samples downstream the city limit...

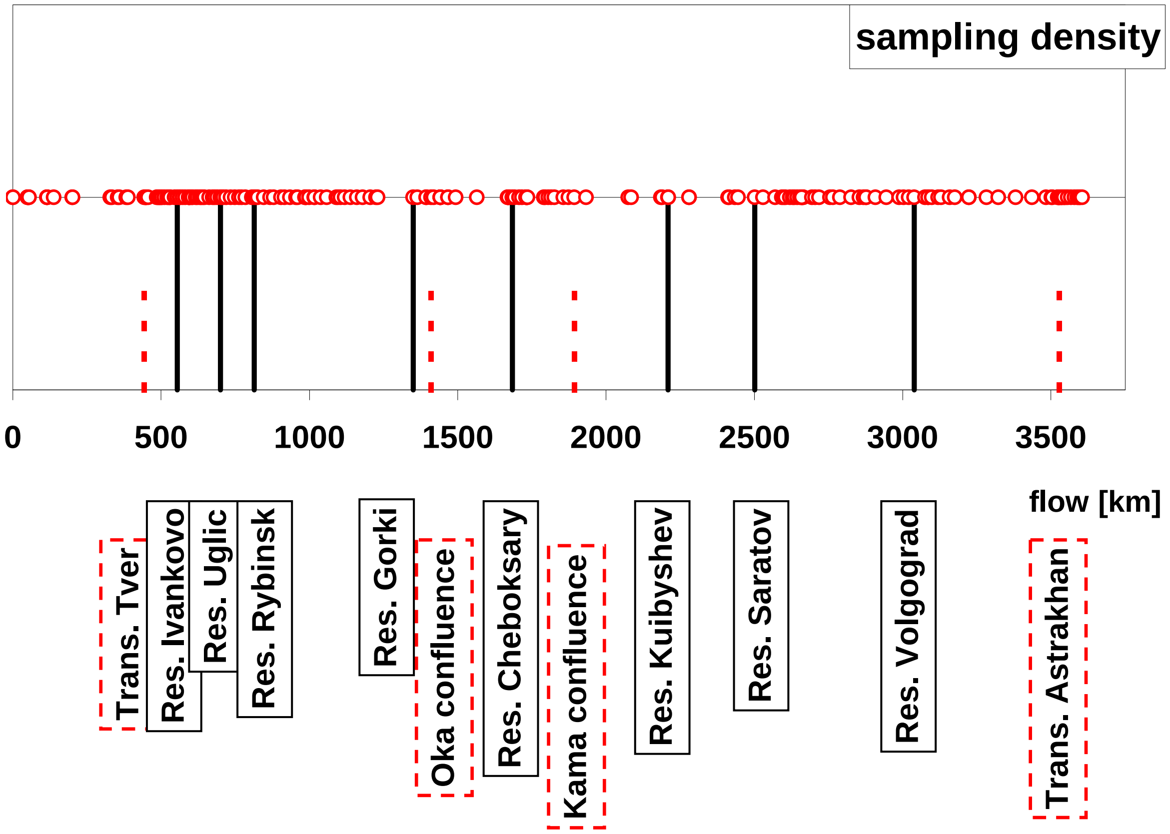
Table 32 **Characteristic landmarks on the River Volga and their respective sample No.**

Sample No.	Description
21	Transect before the city of Tver
25	First sample after the city of Tver
39	Ivankovo Dam
60	Uglic Dam
70	Rybinsk Dam
99	Gorki Dam
118	Cheboksary Dam
140	Kuibyshev Dam
148	Saratov Dam
157-160	Samples in the city of Saratov
180	Volgograd Dam
203	Transect before the city of Astrakhan

However, at least for the parameters of Group 1.2 (Cd, Cu, Hg, Pb and S_{total}) the subdivision especially in the Middle Volga is less obvious and the respective diagrams are puzzling at first sight. Therefore, with respect to parameters usually assumed COPC’s, the added-up z-score plots for Cr, Ni and Zn are relatively smooth and readily interpretable, while those for Cd, Cu, Hg and Pb are not.

4.5.2.1 Limitations

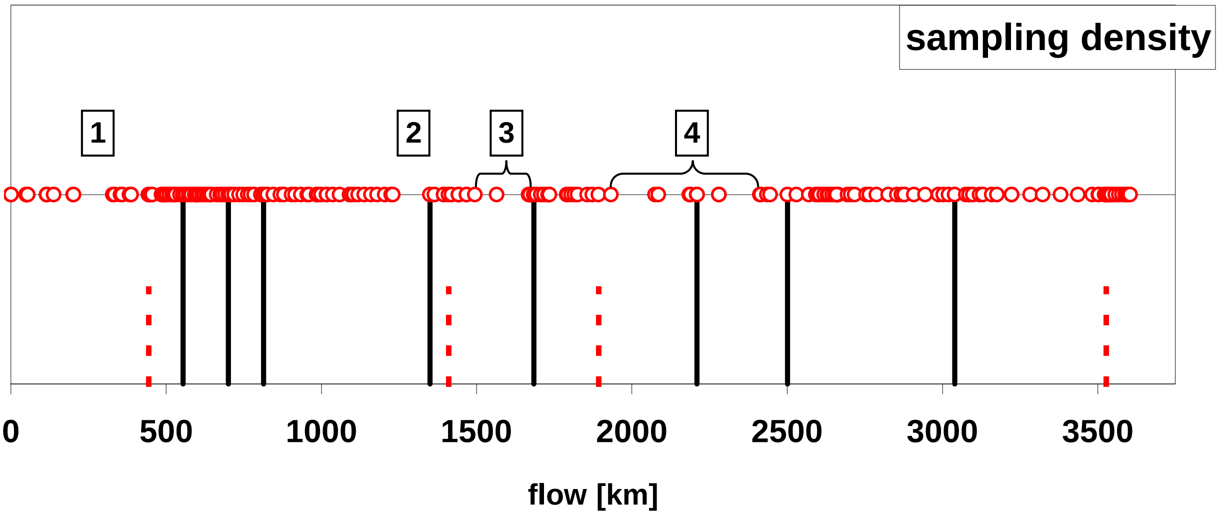
It has been stated oftentimes, that in no way this study is appropriate to identify, let alone quantify the degree of pollution of Volga sediments with respect to point sources, and exploratory data analysis can not ‘repair’ the underlying major weakness bound to the data set – the inappropriate sampling scheme. In fact, most problems emerge in ‘less than perfect’ sampled stretches of the river (cf. Figure 94).



from	up to	No. of samples	km	km/sample
Source	Trans. Tver	21	443	21
Trans. Tver	Res. Ivankovo	18	112	6
Res. Ivankovo	Res. Uglic	21	145	**7**
Res. Uglic	Res. Rybinsk	10	114	11
Res. Rybinsk	Res. Gorki	29	536	18
Res. Gorki	Res. Cheboksary	19	334	18
Res. Cheboksary	Res. Kuibyshev	22	525	24
Res. Kuibyshev	Res. Saratov	8	292	**37**
Res. Saratov	Res. Volgograd	32	538	17
Res. Volgograd	Trans. Astrakhan	23	489	21
Trans. Astrakhan	Caspian Sea	14	77	**6**
Source	Caspian Sea	217	3605	17

Figure 94 **Sampling density within this study for various stretches of the Volga**

Alternatively, giving up the man-made and natural subdivision, the least sufficiently sampled stretches on the Volga are as follow:



Region		from	up to	Δ	km/sample
1	**km**	**138**	**329**	191	
	sample-No.	12	15	3	**64**
2	**km**	**1230**	**1350**	120	
	sample-No.	98	99	1	**120**
3	**km**	**1494**	**1672**	178	
	sample-No.	111	117	6	**30**
4	**km**	**1933**	**2415**	482	
	sample-No.	135	144	9	**54**

Figure 95 Sampling density – least sufficiently sampled Volga-stretches.

First, it is important to realize the difference between diagrams of the added-up z-scores vs. the sample number and diagrams of the added-up z-scores vs. the river flow:

Added-up z-score vs. sample number: the samples are treated effectively as equidistant and sampling density has no effect on the slope or any of the other simple rules for interpretation (cf. Chapter 4.5.1.1)

Added up z-score vs. river flow: sampling density has an distinctive effect on the slope and overall appearance of the diagrams, since denser sampled stretches will have a tendency to dominate. Cf. Figure 96 were e.g. the denser sampled stretch below the transect near the city of Astrakhan simulates a change, while in fact there is none – the measurements are about constant.

Despite the fact that only the plots of the added-up z-scores vs. the sample number are sufficient to subdivide the rivers course unbiased, the plots of the added-up z-scores vs. the rivers flow give a more realistic picture with respect to sampling shortcomings.

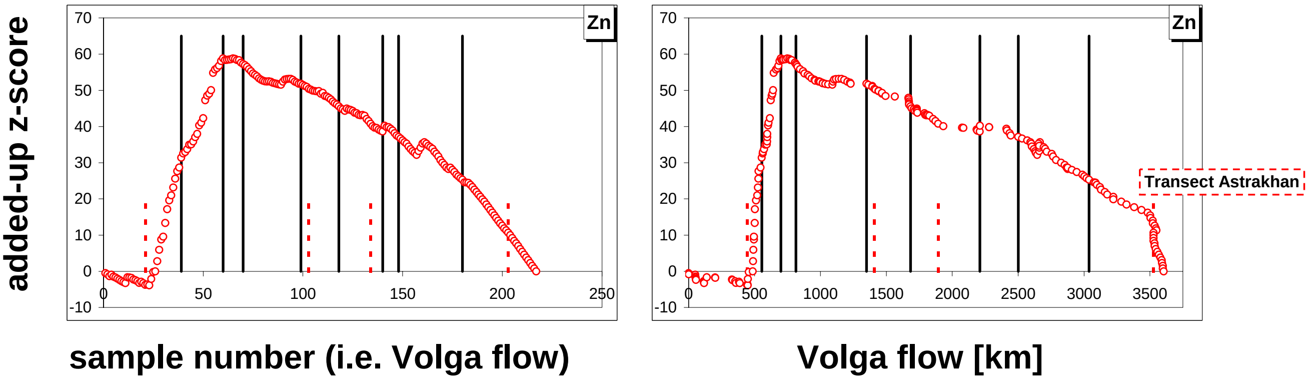


Figure 96 **Comparison of plotting the added-up z-scores vs. the sample number and the flow [km] respectively (for explanation of the dashed and straight vertical lines see Figure 94)**

Over and above, it is NOT solely the number of samples (or sampling-density), but also the amount of variance (e.g. expressed as standard deviation), that has to be taken into account. The less variance, the less samples are needed for a flawless (or statistically sound) description of a given river stretch. E.g., the stretch from Volgograd to Astrakhan is in fact ‘oversampled’ with respect to the measured parameters because of their low variance downstream the Volgograd Reservoir, although the sampling-density does not differ markedly from ‘insufficiently’ sampled stretches. That is also, what makes the z-score plots of Cr, Ni, and Zn relatively smooth and readily interpretable, while those for Cd, Cu, Hg, and Pb are not; the sampling-density is identical, but the variance differs.

4.6 Subdivision of the Volga

The allegedly objective approach of the added-up z-scores is obviously subjective – as is any other statistical or non-statistical approach. Apart from the fact, that there is no such thing as ‘statistical significance’ a prioiri – but classifications representing arbitrary conventions that are only informally based on general research experience – there is also a big difference between ‘statistical’ and ‘practical’ significance.

‘Statistical’ significance refers to the result of a hypothesis test, and by that on the true value of the population parameter tested (e.g. μ), how much that value deviates from the value hypothesized under the null hypothesis (e.g. μ_0), and the sample size. As a result, using large sample sizes and/or large differences for hypothesis testing (μ-μ_0) will lead to a high likelihood of detecting differences with a given statistical confidence (i.e. a steep power curve of the statistical test, cf. Figure 97). Figure 97 also depicts one of the most severe issues that are inconsistent with any rigorous statistical analysis of – not only – the here used data set, the impossibility to assure the absence of bias. Any data set NOT derived from a random sampling scheme in its strictest meaning, is biased, and this **unknown** bias will affect any statistical test – parametric and non-parametric – to an **unknown** extent.

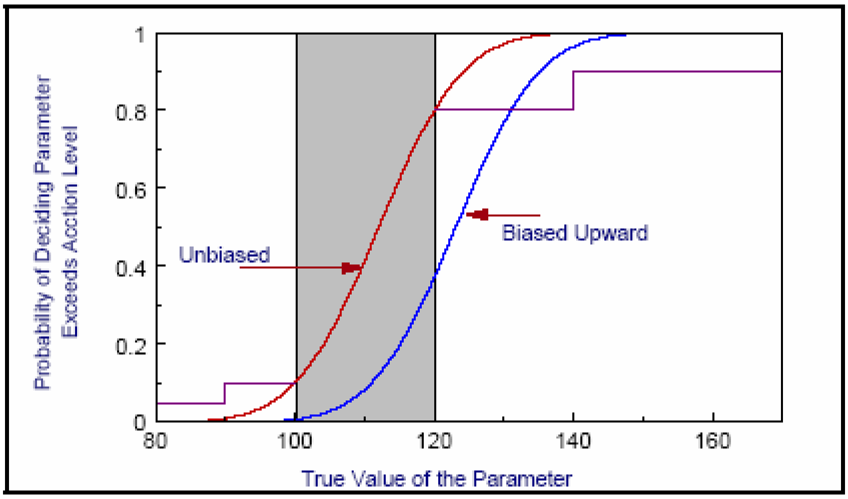


Figure 97 Illustration of biased vs. unbiased power curves (US-EPA, 2000)

Moreover, even in case one could rule out bias, statistically significant differences may be insignificant from a practical standpoint. How large the difference between the parameter and the null value is of real importance, is still the experimenters choice. E.g., one could subdivide the Volga according to the man-made reservoirs, use e.g. the Shapiro-Wilks test to check the assumption of normality for either reservoir, and conduct an analysis of variance between groups (ANOVA) to find out whether the groups differ[166]. This procedure is statistically sound, but at least in case of the Volga sediments oftentimes leads to inconsistent results, where e.g. already group-differences well below the expanded measurement uncertainty of a parameter are statistically significant.

- While the **expanded measurement uncertainty** of the respective parameter represents the least difference between samples or groups necessary to make them distinguishable from each other, the **expanded uncertainty of the measurement process** (i.e. including all the uncertainties of the sampling and sample preparation) determines the number of samples needed to achieve a given confidence interval of a group-mean.
- The **expanded measurement uncertainty** for this study has been discussed in Chapter **2.4.1.2** (p. 85ff.) and the **expanded uncertainty of the measurement process** has been discussed in Chapter **2.5.4**(p. 121ff.).
- The most important outcomes with respect to the average property of a given parameter have been discussed in Chapter **2.5.6.2** (p. 153ff.) and are once more depicted in Table 33. Despite the fact that the mean **uncertainty of the measurement process** is in the range from about 20% up to about 100% (i.e. the expanded uncertainty is in the range from about 40% up to about 200%) it is still the geochemical variability that controls the overall variability, taking all samples into account.

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[166] One could of course also use non-parametric statistics - as has been done here, and the runs-test eventually led to the simple graphical way of interpretation – but the underlying problem remains.

Table 33 Percentage contribution of the geochemical variability to the variance of the overall mean – prior to subdividing the Volga (see Chapter 2.5.6.2 (p. 153ff.) and Table 17)

	total variability					variability introduced by the measurement process and resulting sample uncertainty					percentage contribution to the total variance of the mean		
	$\sigma^2_{total} = \sigma^2_{geochemical} + (\sigma^2_{measurement})/n$					$\sigma^2_{measurement} = \sigma^2_{analytical} + \sigma^2_{sampling}$					$\frac{\sqrt{\sigma^2_{total} - \left(\frac{\sigma^2_{measurement}}{n}\right)}}{\sigma_{total}} * 100$		
Parameter	n	Mean	Median	σ	σ [%]	LOD	LOQ	analytical uncertainty [%] for x>LOQ	mean sampling uncertainty [%]	mean sample uncertainty [%] for x>LOQ	geochemical variability	sampling uncertainty	analytical uncertainty
Ag	266	0.39	0.28	0.47	**121**	0.06	0.27	**18**	**91**	**93**	**99.89**	neglectable	
Al [%]	266	3.50	3.47	0.59	**17**			**52**	**19**	**55**	**97.97**		
As	269	8	8	4	**48**			**19**	**68**	**71**	**99.60**		
B	264	24	25	9	**35**	9	39	**23**	**67**	**71**	**99.23**		
Ba	266	238	238	74	**31**			**7**	**30**	**31**	**99.81**		
Ca [%]	266	1.67	1.36	1.28	**77**			**11**	**31**	**33**	**99.97**		
Cd	269	0.75	0.64	0.78	**104**			**20**	**65**	**68**	**99.92**		
Co	266	18	18	3	**18**			**8**	**15**	**17**	**99.83**		
Cr	270	76	75	23	**30**			**17**	**18**	**25**	**99.87**		
Cu	270	44	38	23	**52**			**8**	**38**	**39**	**99.90**		
Fe [%]	270	4.51	4.52	0.92	**20**			**9**	**14**	**17**	**99.88**		
Hg	270	0.27	0.13	0.47	**176**	0.03	0.10	**19**	**79**	**81**	**99.96**		
K [%]	266	0.73	0.70	0.20	**27**			**8**	**26**	**27**	**99.81**		
Li	268	38	39	8	**20**			**8**	**25**	**26**	**99.68**		
Mg [%]	266	1.20	1.19	0.39	**32**			**13**	**16**	**21**	**99.92**		
Mn [%]	270	0.16	0.12	0.12	**75**			**8**	**106**	**106**	**99.63**		
Mo	266	1.9	1.7	0.9	**46**			**15**	**56**	**58**	**99.70**		
Na [%]	266	0.10	0.10	0.03	**32**			**9**	**33**	**34**	**99.79**		
Ni	267	51	52	15	**29**			**15**	**18**	**23**	**99.88**		
P_2O_5 [%]	269	0.40	0.36	0.31	**77**			**7**	**38**	**39**	**99.95**		
Pb	270	24	20	16	**67**			**11**	**26**	**28**	**99.97**		
Sc	266	8	7	2	**25**			**10**	**20**	**22**	**99.85**		
Sr	266	91	89	55	**60**			**8**	**25**	**26**	**99.96**		
V	266	66	65	17	**26**			**8**	**20**	**22**	**99.87**		
Y	266	16	16	2	**15**			**12**	**13**	**18**	**99.74**		
Zn	270	171	128	121	**71**			**9**	**32**	**33**	**99.96**		
C_{total} [%]	263	3.87	3.42	2.08	**54**			**5**	**31**	**31**	**99.94**		
S_{total} [%]	263	0.18	0.15	0.12	**69**	0.1	0.36	**33**	**105**	**110**	**99.51**		
CO_3 [%]	174	3.6	2.5	3.9	**108**		5	**2% absolute**					
moisture content$^{105°}$ [%]	260	4.5	4.7	0.7	**16**			**5**	**14**	**15**	**99.84**		
loss on ignition$^{550°}$ [%]	260	9.9	9.3	3.5	**35**			**5**	**21**	**22**	**99.93**		
Mean					52			13	39	42			
25th percentile		x≤ 25th percentile			27			8	19	23			
50th percentile		25th percentile<x<75th percentile			35			10	28	31			
75th percentile		x≥ 75th percentile			70			16	52	57			

However, the idea to subdivide the Volga sediments longitudinally, is to reduce the geochemical variability within the obtained data subsets – in other words, to perform some sort of ‘clustering’; i.e. minimize the within-group variability, while maximizing the in-between-group variability.[167] Therefore, as discussed in Chapter **2.5.6.2** (p. 153ff.) and depicted in **Table 18**, it is solely the **mean sample uncertainty** that has to be taken into account when subdividing the Volga and calculating the number of samples needed to form a data sub-set.

Starting from Table 33, it is our decision, what amount of variability introduced by the measurement process (i.e. sample uncertainty) we are willing and able to accept – a merely arbitrary choice. These issues have been discussed in Chapter **2.5.6** (p. 146ff.), and one of the rules of thumb says, that the uncertainty of the measurement process as a whole ‘*should not contribute more than 20% of the total variance of the analyte across all the samples in a particular survey*’ (Ramsey, 2002). Despite the fact that this may be a practitioners approach towards the uncertainty of the measurement process, it is of little help since the geochemical variance ‘produced’ by subdividing the data set is fully arbitrary; depending on our decision what samples to pool.

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[167] Note: ‘traditional’ clustering-techniques are less appropriate, since they assign the samples to the respective cluster-centers regardless of their geographic origin. I.e., they lead to a ‘top-down’-interpretation of the results, which could also be obtained by simply using percentiles for classification, but is not suitable to distinguish different stretches of the river.

Based on Student's t-distribution (see **Equation 4**, p. 81) the number of samples, needed to achieve an arithmetic mean with a given confidence interval (***L***) at a given confidence level ($\boldsymbol{t_{df,\alpha/2}}$)[168], can be estimated as follows (see also Chapter **2.5.6.2**, p.153ff.):

$$\sqrt{n} = \frac{t_{df,\alpha/2}\sigma}{\pm L/2}$$

The number of samples needed to achieve a confidence interval equivalent to the respective expanded measurement uncertainty of a parameter, as well as the (arbitrarily chosen) confidence intervals of ± 25% and ± 10% are presented in Table 34. Note: this calculation does NOT account for the (a priori unknown) geochemical variability of a group of samples; it solely incorporates the 'artificial' uncertainty introduced by the measurement process.

Table 34 Number of samples needed to achieve an arithmetic mean with various confidence intervals at a 95% confidence level (shaded grey: less than 20 samples needed, in italic: more than 50 samples needed)

Note:	**uncertainty**			**expanded uncertainty (coverage factor: 2)**		
				number of samples needed to achieve confidence interval [%]		
	measurement uncertainty [%] for x>LOD	**mean sampling uncertainty [%]**	**mean sample uncertainty [%] for x>LOD**	**equivalent to the *expanded* measurement uncertainty**	**±25**	**±10**
Ag	18	91	**93**	*107*	*55*	*346*
Al [%]	52	19	**55**	**4**	**19**	*121*
As	19	68	**71**	*56*	**32**	*202*
Ba	7	30	**31**	*78*	**6**	**38**
Ca [%]	11	31	**33**	**36**	**7**	**44**
Cd	20	65	**68**	**46**	**30**	*185*
Co	8	15	**17**	**18**	**2**	**12**
Cr	17	18	**25**	**9**	**4**	**25**
Cu	8	38	**39**	*95*	**10**	*61*
Fe [%]	9	14	**17**	**14**	**2**	**12**
Hg	19	79	**81**	*73*	**42**	*262*
K [%]	8	26	**27**	**46**	**5**	**29**
Li	8	25	**26**	**42**	**4**	**27**
Mg [%]	13	16	**21**	**10**	**3**	**18**
Mn [%]	8	106	**106**	*702*	*72*	*449*
Mo	15	56	**58**	*59*	**21**	*134*
Na	9	33	**34**	*57*	**7**	**46**
Ni	15	18	**23**	**10**	**4**	**22**
P_2O_5 [%]	7	38	**39**	*124*	**10**	*61*
Pb	11	26	**28**	**26**	**5**	**31**
Sc	10	20	**22**	**19**	**3**	**19**
Sr	8	25	**26**	**42**	**4**	**27**
V	8	20	**22**	**30**	**3**	**19**
Y	12	13	**18**	**9**	**2**	**13**
Zn	9	32	**33**	*54*	**7**	**44**
C_{total} [%]	5	31	**31**	*154*	**6**	**38**
S_{total} [%]	33	105	**110**	**45**	*78*	*488*
$LOI^{550°C}$ [%]	5	21	**22**	*77*	**3**	**19**

Table 34 also highlights the weak point in using the expanded measurement uncertainty as differentiating factor between groups of samples: the less uncertain the measurement, the more samples are needed to achieve the thereby defined confidence interval (assuming a given sampling uncertainty).

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[168] Usually, as in this study, a confidence level of 95% is used.

On the other hand, the whole concept of the expanded uncertainty emerged, because nobody is interested in the precision of a measurement, but in the performance of the entire measurement process according to the ‘real world’ – e.g. a conventionally true value and/or a ‘state-of-the-art’ measurement process. Since the measurement-, as well as the sampling-uncertainty will vary within different studies, a down-to-earth-approach seems more rational, albeit less concise:

- The pooling-process is subjective – as is any other approach towards a (statistical) classification.
- The (expanded) uncertainty of the measurement process is known, thus its amount can be calculated for a given group – this amount will differ amongst diverse studies.
- The geochemical variance is an artifact of the sampling-, and pooling-process – this amount will differ amongst diverse studies and interpretations.
- The overall-variance is a mixture of both, the uncertainty of the measurement process and the geochemical variance – with no apparent chance to differentiate their respective shares, since e.g. the geochemical variance is already an artifact of the sampling-scheme (strictly speaking a component of the measurement process).
- Shortcomings in the study-design[169], the laboratory-performance and/or the pooling-process will result in elevated overall-variances of the results – as will a large genuine geochemical variance.
- Currently no indication for what can be considered a reasonable (geochemical) variance of a given sediment-stratum (and a given parameter) is readily available – far from it, most studies simply ignore variance.

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[169] However, these shortcomings will influence the result solely in case they are included in the calculation of the uncertainty budget – which is rarely done. Otherwise one will end up with the most simple ‘solution’: oversimplification.

4.6.1 Proposals on how to interpret the added-up z-score plots

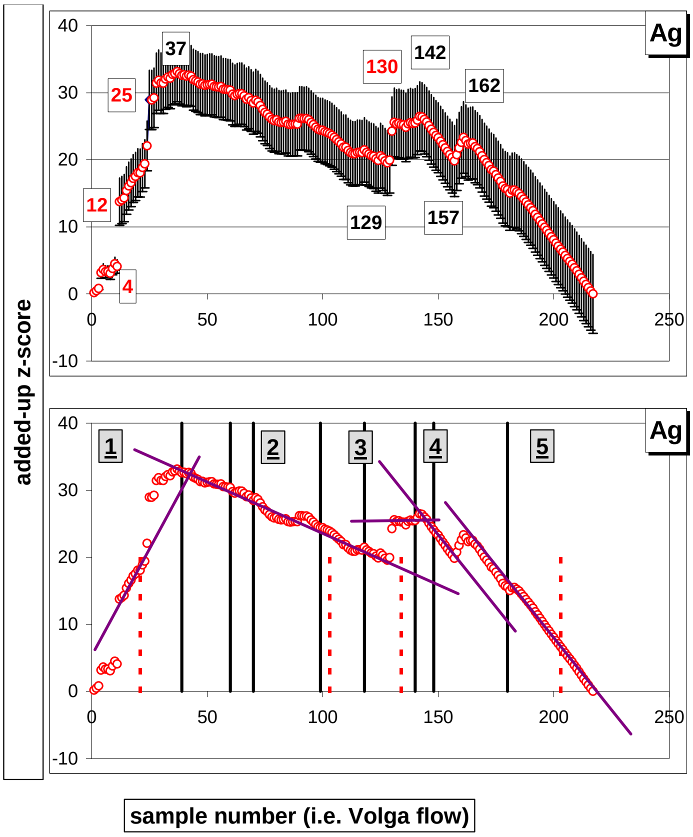
Instead of trying to achieve a given level of confidence (or a given level of uncertainty) one can also pool the data as one pleases, and calculate the level of confidence (uncertainty) afterwards – based on the several times cited finding that a result is either precise or certain.

This intuitive approach in conjunction with a realistic uncertainty budget can never be all wrong:

- ‘Misclassification’ of samples will lead to a higher variance – i.e. a less precise result.
- ‘Less-than-perfect’ sampled stretches either fit the respective flanking stretches – if so it seems reasonable to assign them to these stretches; or they do not fit – if so no conclusion with respect to this stretch is possible.
- The number of samples needed for a (statistically) sound description of a given stretch is determined by the amount of (natural) variance, not the length of the stretch and/or the area.
- However, it has been stated oftentimes, that in no way this study is appropriate to identify, let alone quantify the degree of pollution of Volga sediments with respect to point sources and exploratory data analysis can not ‘repair’ the underlying major uncertainty bound to the data – the inappropriate sampling scheme.
- Nevertheless, realistic estimates of the mean of a given property for a given stretch can be calculated, as well as the identification of areas of potential concern is possible – be it because of (unusual) elevated concentrations or a ‘less-than-perfect’ sampling density.

The outcomes of this approach to subdivide the Volga sediments are depicted on the following pages for the following parameters:

- **The metals monitored as a matter of routine in Germany:**
  - **Cd**, **Cr, Cu**, **Hg**, **Ni**, **Pb**, **Zn**, as well as the metalloid **As**, which is routinely monitored, although no classification system has been established yet.
- **Elements whose respective overall mean exceeds the span usually considered as ‘geogenic background’ (cf. Figure 81; p. 208):**
  - Ag and phosphorous.
  - Mn has been omitted due to its low toxicity and therefore little concern.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 98 Suggested subdivision of the Volga sediments regarding Ag (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 37	0 531	0.58	0.25	34	No. 4, 12, 25
2	38 129	546 1805	0.33	0.14	89	
3	131 142	1826 2280	0.49	0.24	11	No. 130
4	143 156	2280 2635	0.18	0.06	14	
5	162 217	2655 3605	0.19	0.10	56	No. 157-161
Volgograd - Astrakhan	184 217	3098 3605	0.17	0.03	34	

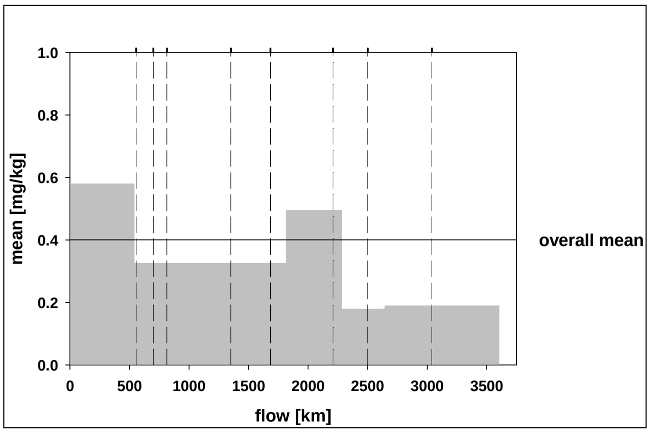


Figure 99 Subdivision of the Volga sediments with respect to Ag according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Ag

Volga sediments overall mean ±σ [mg/kg]: 0.39 ±0.47
Mean expanded measurement uncertainty[170] [%]: 35
Mean expanded sample uncertainty[171] [%]: 186

No. of extremes (high) as defined by interquartile range[172]: 13
No. of extremes (jump discontinuities) removed: 9
Removed samples:

No. 4: –
No. 12: Selisharowka
No. 25: downstream city of Tver
No. 130: wastewater treatment plant near Kazan
No. 157-161: city of Saratov

Mean of the stretch (area) with the lowest content ±σ [mg/kg]: 0.17 ±0.03 (n=34)
Mean of the stretch (area) with the highest content ±σ [mg/kg]: 0.58 ±0.25 (n=34)
Ratio of the areas with the highest/lowest content: 3.4
Ratio of the overall mean/area with the lowest content: 2.3

'Geogenic background'-range according to Table 27 [mg/kg]: 0.050 – 0.07
Ratio of the highest/lowest 'geogenic background': 1.4
Ratio of the Volga sediments overall mean/'geogenic background': 7.8 – 5.6
Ratio of the area with the highest content/'geogenic background': 11.6 – 8.3
Ratio of the area with the lowest content/'geogenic background': 3.4 – 2.4

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[170] Cf. Figure 25; p. 86.

[171] Cf. Table 33; p. 247.

[172] Cf. Table 26; p. 183.

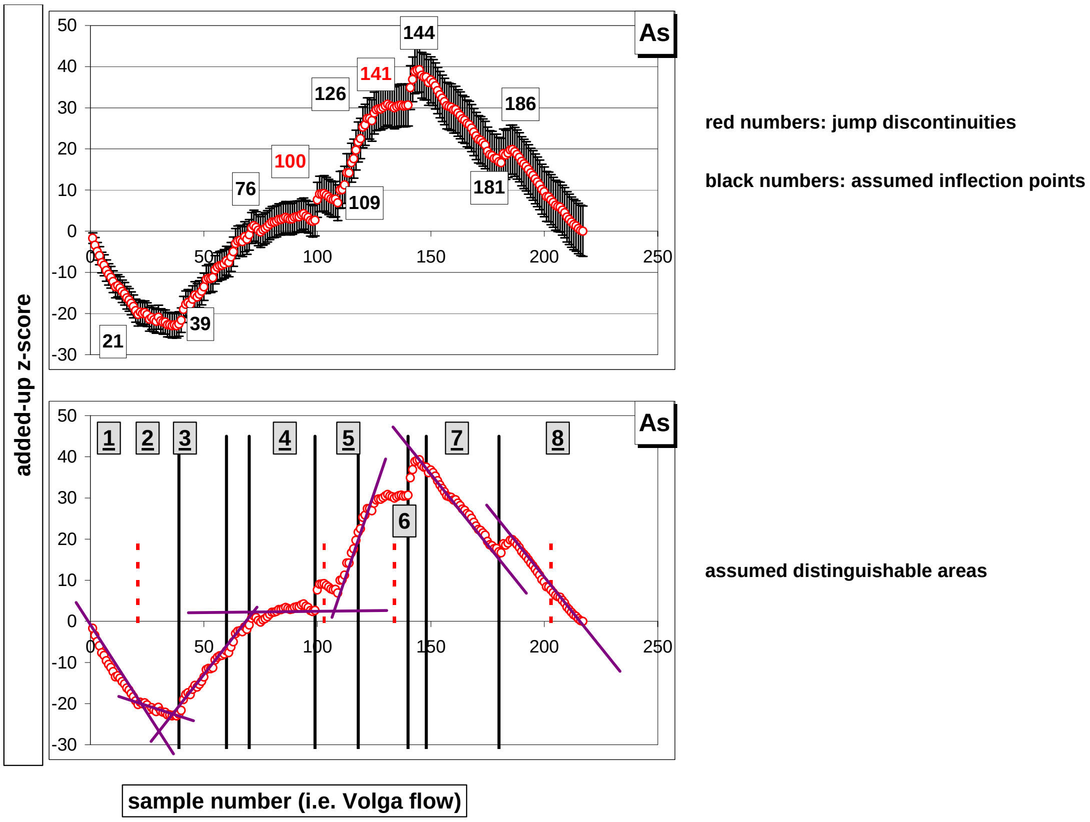

Figure 100 Suggested subdivision of the Volga sediments regarding As (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	 Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 21	0 443	5	2	21	
2	22 39	448 555	8	2	18	
3	40 76	563 904	10	3	37	
4	77 109	916 1350	8	2	33	No. 100
5	110 126	1468 1735	13	4	16	
6	127 140	1790 2209	8	1	14	No. 141, 142, 143
7	144 183	2412 3075	6	2	40	
8	184 217	3098 3605	6	1	34	
Volgograd - Astrakhan	184 217	3098 3605	6	1	34	

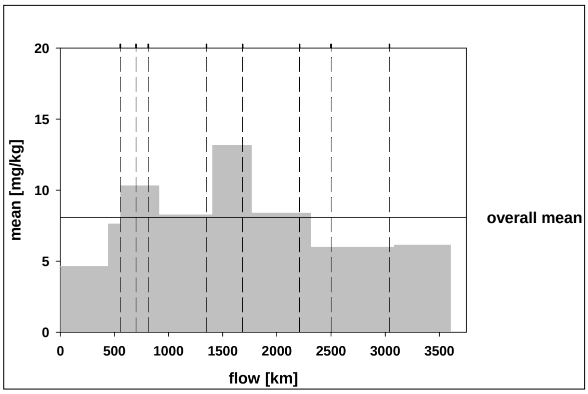

Figure 101 Subdivision of the Volga sediments with respect to As according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: As

Volga sediments overall mean ±σ [mg/kg]:	8 ±4
Mean expanded measurement uncertainty[173] [%]:	38
Mean expanded sample uncertainty[174] [%]:	142

No. of extremes (high) as defined by interquartile range[175]:	10
No. of extremes (jump discontinuities) removed:	4

Removed samples:

No. 100:	–
No. 141:	Togliatti harbor
No. 142, 143:	Samara harbor

Mean of the stretch (area) with the lowest content ±σ [mg/kg]:	6 ±1 (n=34)
Mean of the stretch (area) with the highest content ±σ [mg/kg]:	13 ±4 (n=16)
Ratio of the areas with the highest/lowest content:	2.2
Ratio of the overall mean/area with the lowest content:	1.3

‘Geogenic background’-range according to Table 27 [mg/kg]:	1.5 – 13
Ratio of the highest/lowest ‘geogenic background’:	8.7
Ratio of the Volga sediments overall mean/’geogenic background’:	5.3 – 0.6
Ratio of the area with the highest content/’geogenic background’:	8.7 – 1.0
Ratio of the area with the lowest content/’geogenic background’:	4.0 – 0.5

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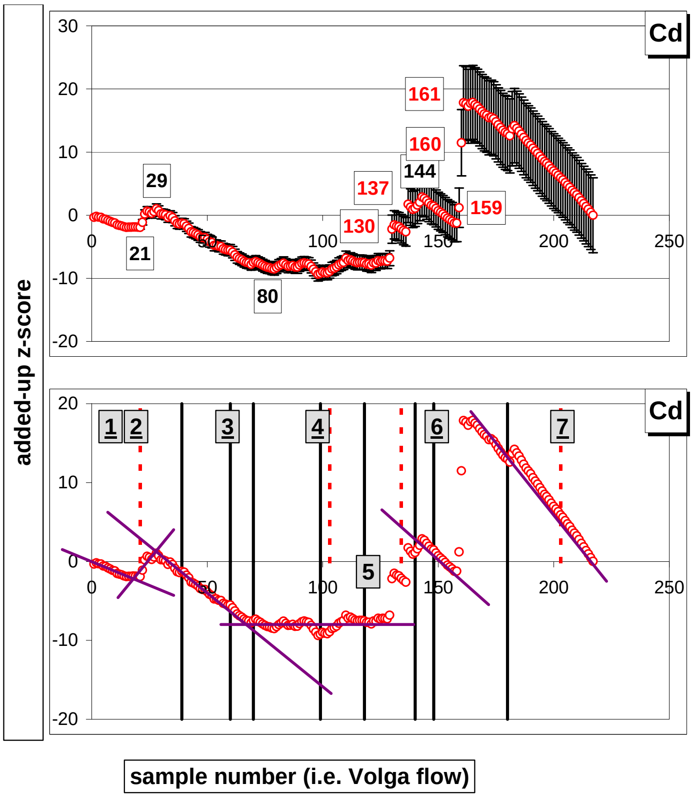
[173] Cf. Figure 25; p. 86.

[174] Cf. Table 33; p. 247.

[175] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 102 Suggested subdivision of the Volga sediments regarding Cd (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	 Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 21	0 443	0.42	0.11	21	
2	22 28	448 492	0.88	0.52	7	
3	29 80	496 960	0.34	0.17	52	
4	81 129	985 1805	0.52	0.22	49	
5	132 143	1856 2280	0.50	0.36	11	No. 103, 131, 137
6	144 157	2412 2645	0.24	0.08	13	No. 158-161
7	162 217	2655 3605	0.21	0.25	56	
Volgograd - Astrakhan	184 217	3098 3605	0.13	0.05	34	

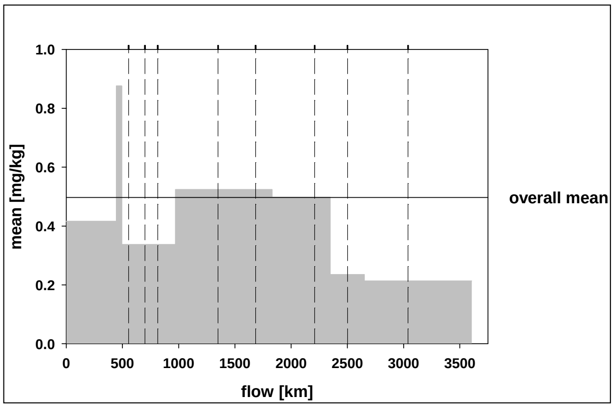


Figure 103 Subdivision of the Volga sediments with respect to Cd according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Cd

Volga sediments overall mean ±σ [mg/kg]: 0.50 ±0.81

Mean expanded measurement uncertainty[176] [%]: 40

Mean expanded sample uncertainty[177] [%]: 136

No. of extremes (high) as defined by interquartile range[178]: 11

No. of extremes (jump discontinuities) removed: 7

Removed samples:

No. 100: –
No. 131: –
No. 137: river port of Ulianovek City
No. 158-161: city of Saratov

Mean of the stretch (area) with the lowest content ±σ [mg/kg]: 0.13 ±0.05 (n=34)

Mean of the stretch (area) with the highest content ±σ [mg/kg]: 0.52 ±0.22 (n=49)

Ratio of the areas with the highest/lowest content: 4.0

Ratio of the overall mean/area with the lowest content: 3.9

‘Geogenic background’-range according to Table 27 [mg/kg]: 0.075 – 0.30

Ratio of the highest/lowest ‘geogenic background’: 4.0

Ratio of the Volga sediments overall mean/’geogenic background’: 5.3 – 1.7

Ratio of the area with the highest content/’geogenic background’: 8.7 – 1.7

Ratio of the area with the lowest content/’geogenic background’: 4.0 – 0.4

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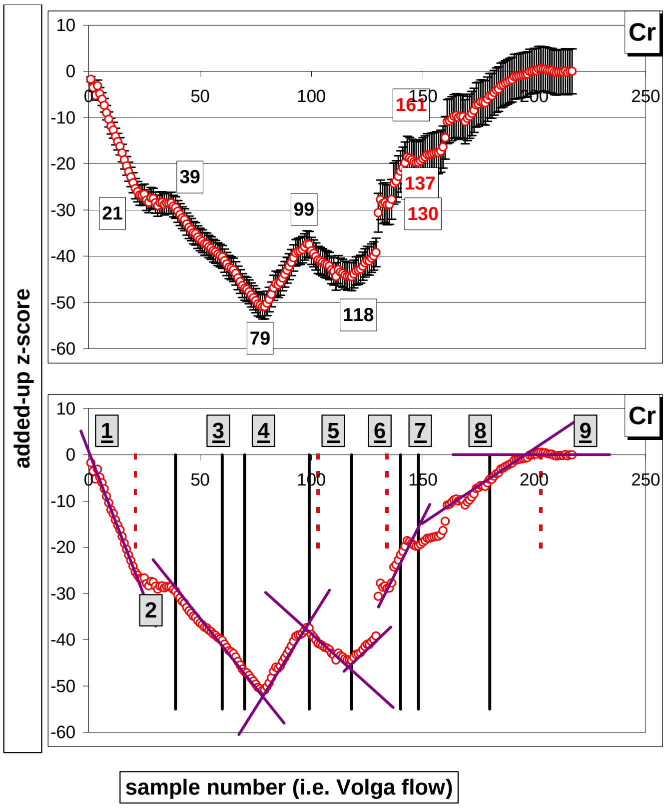
[176] Cf. Figure 25; p. 86.

[177] Cf. Table 33; p. 247.

[178] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 104 Suggested subdivision of the Volga sediments regarding Cr (for dotted and straight vertical lines see Figure 94).

	Range					
Area	**Sample**	**Km**	**Mean**	**Std.-dev. (s)**	**n**	**Removed samples**
1	1 21	0 443	**46**	**20**	21	
2	22 39	448 555	**70**	**14**	18	
3	40 79	563 955	**62**	**6**	41	
4	80 99	960 1350	**92**	**10**	20	
5	100 118	1364 1684	**67**	**14**	19	
6	119 129	1693 1805	**87**	**7**	11	
7	131 159	1826 2663	**85**	**17**	28	No. 130, 137, 160
8	162 203	2655 3528	**82**	**9**	42	No. 161
9	204 217	3528 3605	**74**	**4**	14	
Volgograd - Astrakhan	184 217	3098 3605	**78**	**6**	34	

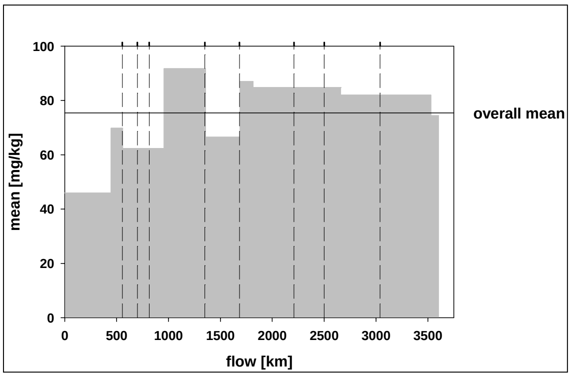


Figure 105 Subdivision of the Volga sediments with respect to Cr according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Cr

Volga sediments overall mean ±σ [mg/kg]: 76 ±23

Mean expanded measurement uncertainty[179] [%]: 34

Mean expanded sample uncertainty[180] [%]: 50

No. of extremes (high) as defined by interquartile range[181]: 10

No. of extremes (jump discontinuities) removed: 4

Removed samples:

No. 130: wastewater treatment plant near Kazan

No. 137: river port of Ulianovek City

No. 160, 161: downstream city of Saratov near a refinery

Mean of the stretch (area) with the lowest content ±σ [mg/kg]: 46 ±20 (n=21)

Mean of the stretch (area) with the highest content ±σ [mg/kg]: 92 ±10 (n=20)

Ratio of the areas with the highest/lowest content: 2.0

Ratio of the overall mean/area with the lowest content: 1.7

‘Geogenic background’-range according to Table 27 [mg/kg]: 35 – 112

Ratio of the highest/lowest ‘geogenic background’: 3.2

Ratio of the Volga sediments overall mean/’geogenic background’: 2.2 – 0.7

Ratio of the area with the highest content/’geogenic background’: 2.6 – 0.8

Ratio of the area with the lowest content/’geogenic background’: 1.3 – 0.4

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[179] Cf. Figure 25; p. 86.

[180] Cf. Table 33; p. 247.

[181] Cf. Table 26; p. 183.

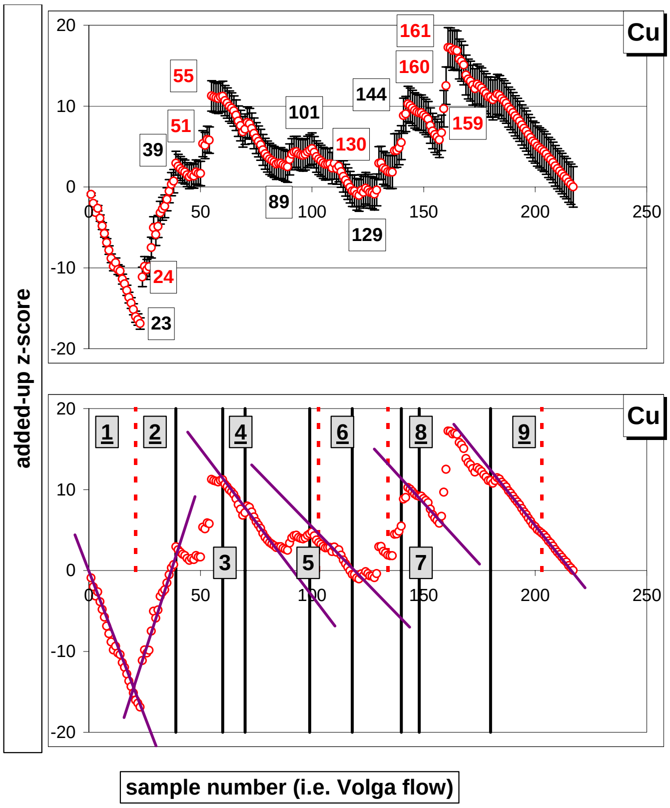

Figure 106 Suggested subdivision of the Volga sediments regarding Cu (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	 Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 23	0 449	26	11	23	
2	25 39	456 555	64	22	15	No. 24
3	40 54	563 641	42	8	14	No. 51, 55
4	56 89	663 1091	37	7	34	
5	90 100	1096 1364	48	8	11	
6	101 129	1394 1805	39	8	29	No 130
7	131 143	1826 2280	46	11	11	No. 137, 141
8	144 157	2412 2645	36	5	14	
9	162 217	2655 3605	36	6	56	No. 158-161
Volgograd - Astrakhan	184 217	3098 3605	35	2	34	

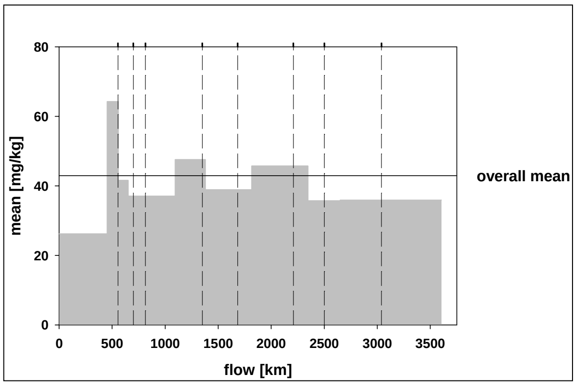

Figure 107 Subdivision of the Volga sediments with respect to Cu according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Cu

Volga sediments overall mean ±σ [mg/kg]:	44 ±23
Mean expanded measurement uncertainty[182] [%]:	16
Mean expanded sample uncertainty[183] [%]:	78

No. of extremes (high) as defined by interquartile range[184]:	19
No. of extremes (jump discontinuities) removed:	9

Removed samples:

No. 24:	city of Tver
No. 51, 55:	–
No. 130:	wastewater treatment plant near Kazan
No. 137:	river port of Ulianovek City
No. 141:	Togliatti harbor
No. 158-161:	city of Saratov

Mean of the stretch (area) with the lowest content ±σ [mg/kg]:	26 ±11 (n=23)
Mean of the stretch (area) with the highest content ±σ [mg/kg]:	64 ±22 (n=15)
Ratio of the areas with the highest/lowest content:	2.5
Ratio of the overall mean/area with the lowest content:	1.8

‘Geogenic background’-range according to Table 27 [mg/kg]:	14 – 44
Ratio of the highest/lowest ‘geogenic background’:	3.1
Ratio of the Volga sediments overall mean/’geogenic background’:	3.1 – 1.0
Ratio of the area with the highest content/’geogenic background’:	4.6 – 1.5
Ratio of the area with the lowest content/’geogenic background’:	1.9 – 0.6

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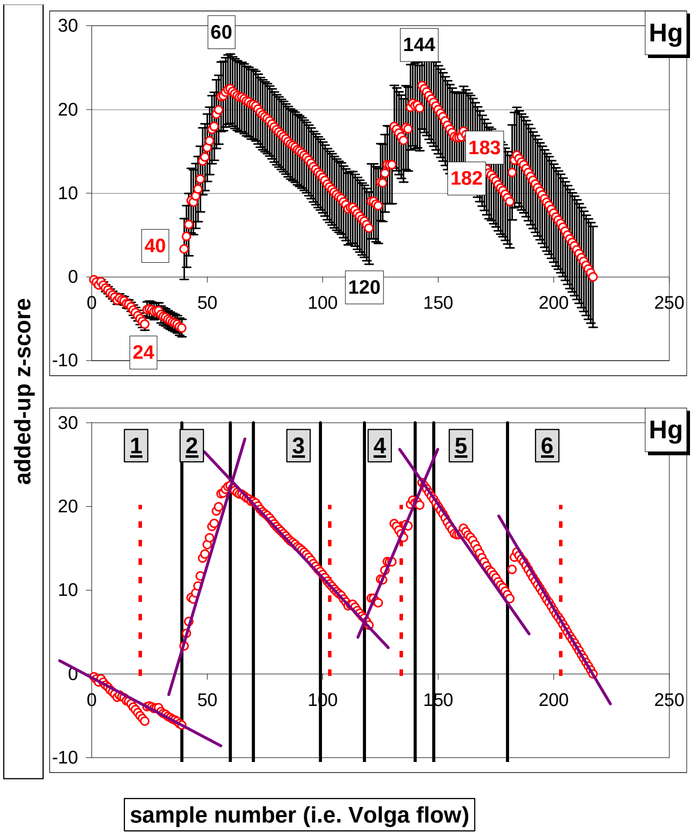
[182] Cf. Figure 25; p. 86.

[183] Cf. Table 33; p. 247.

[184] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 108 Suggested subdivision of the Volga sediments regarding Hg (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	 Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 39	0 555	**0.19**	**0.09**	39	No. 24
2	41 60	573 700	**0.79**	**0.39**	20	No. 40
3	61 120	705 1707	**0.15**	**0.06**	60	
4	121 143	1717 2280	**0.68**	**0.76**	23	
5	144 181	2412 3075	**0.07**	**0.04**	33	No. 157-161
6	184 217	3098 3605	**0.06**	**0.02**	34	No. 182, 183, 184
Volgograd - Astrakhan	184 217	3098 3605	**0.06**	**0.02**	34	

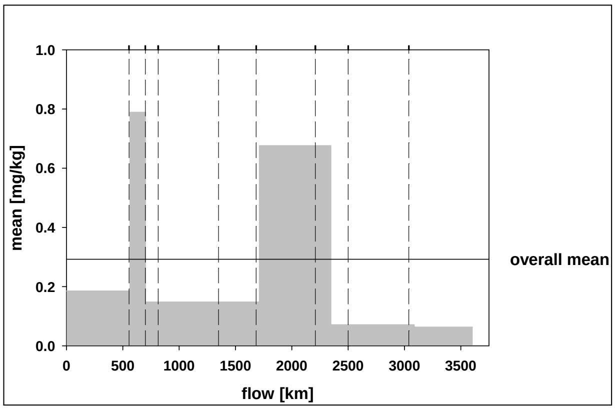


Figure 109 Subdivision of the Volga sediments with respect to Hg according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Hg

Volga sediments overall mean ±σ [mg/kg]: 0.27 ±0.47
Mean expanded measurement uncertainty[185] [%]: 38
Mean expanded sample uncertainty[186] [%]: 162

No. of extremes (high) as defined by interquartile range[187]: 33
No. of extremes (jump discontinuities) removed: 10
Removed samples:
No. 24: city of Tver
No. 40: –
No. 157-161: city of Saratov
No. 182-184: oil storage plant, small town downstream Volgograd

Mean of the stretch (area) with the lowest content ±σ [mg/kg]: 0.06 ±0.02 (n=34)
Mean of the stretch (area) with the highest content ±σ [mg/kg]: 0.79 ±0.39 (n=20)
Ratio of the areas with the highest/lowest content: 13.2
Ratio of the overall mean/area with the lowest content: 4.5

‘Geogenic background’-range according to Table 27 [mg/kg]: 0.0123 – 0.40
Ratio of the highest/lowest ‘geogenic background’: 32
Ratio of the Volga sediments overall mean/’geogenic background’: 22 – 0.7
Ratio of the area with the highest content/’geogenic background’: 64 – 2.0
Ratio of the area with the lowest content/’geogenic background’: 4.9 – 0.2

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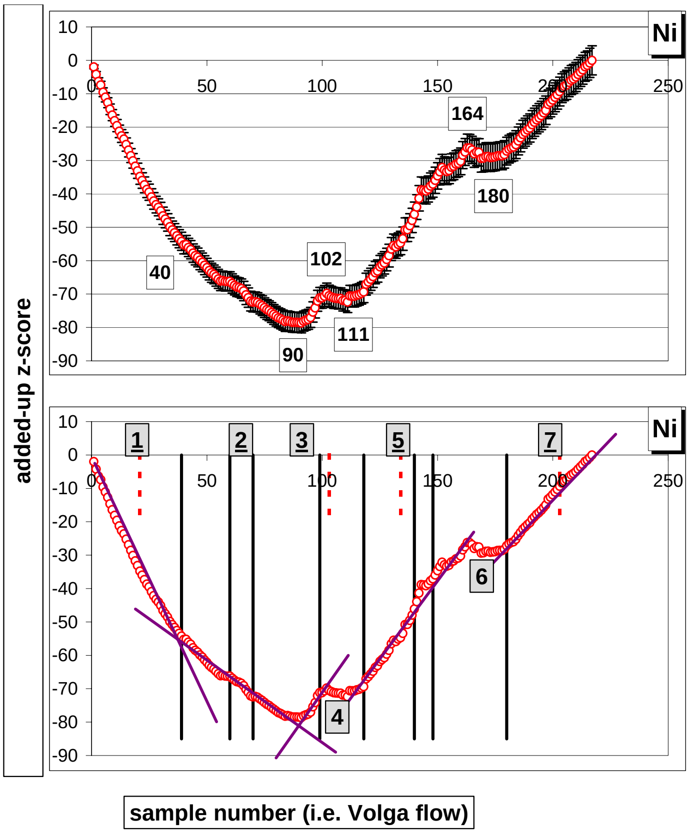
[185] Cf. Figure 25; p. 86.

[186] Cf. Table 33; p. 247.

[187] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 110 Suggested subdivision of the Volga sediments regarding Ni (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	 Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 40	0 563	29	6	40	
2	41 90	564 1096	43	5	50	
3	91 102	1105 1394	62	10	11	
4	103 111	1410 1494	45	4	8	
5	112 163	1565 2660	64	12	52	
6	164 179	2695 3020	48	9	16	
7	180 217	3039 3605	61	4	38	
Volgograd - Astrakhan	184 217	3098 3605	62	4	34	

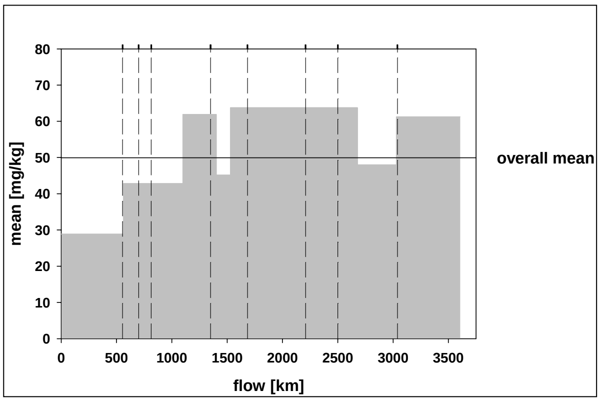


Figure 111 Subdivision of the Volga sediments with respect to Ni according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Ni

Volga sediments overall mean ±σ [mg/kg]:	51 ±15
Mean expanded measurement uncertainty[188] [%]:	30
Mean expanded sample uncertainty[189] [%]:	46
No. of extremes (high) as defined by interquartile range[190]:	0
No. of extremes (jump discontinuities) removed:	0
Removed samples:	none
Mean of the stretch (area) with the lowest content ±σ [mg/kg]:	29 ±6 (n=40)
Mean of the stretch (area) with the highest content ±σ [mg/kg]:	64 ±12 (n=52)
Ratio of the areas with the highest/lowest content:	2.2
Ratio of the overall mean/area with the lowest content:	1.8
‘Geogenic background’-range according to Table 27 [mg/kg]:	19 – 68
Ratio of the highest/lowest ‘geogenic background’:	3.6
Ratio of the Volga sediments overall mean/’geogenic background’:	2.7 – 0.8
Ratio of the area with the highest content/’geogenic background’:	3.4 – 0.9
Ratio of the area with the lowest content/’geogenic background’:	1.5 – 0.4

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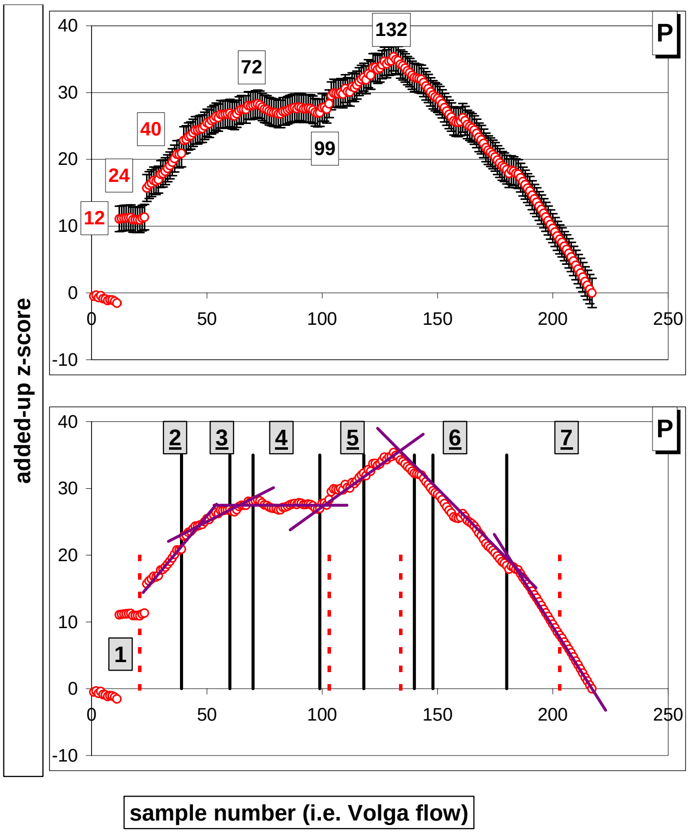
[188] Cf. Figure 25; p. 86.

[189] Cf. Table 33; p. 247.

[190] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 112 Suggested subdivision of the Volga sediments regarding P (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	 Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 23	0 449	0.17	0.03	22	No. 12, 24
2	25 48	456 603	0.22	0.03	23	No. 40
3	49 72	607 826	0.20	0.03	24	
4	73 99	846 1350	0.17	0.03	27	
5	100 132	1364 1856	0.21	0.07	33	
6	132 183	1856 3087	0.11	0.03	86	
7	184 217	3098 3605	0.10	0.01	34	
Volgograd - Astrakhan	184 217	3098 3605	0.10	0.01	34	

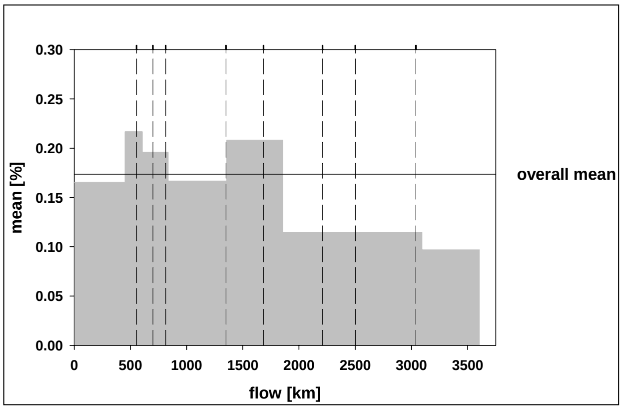


Figure 113 Subdivision of the Volga sediments with respect to P according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: P

Volga sediments overall mean ±σ [%]: 0.17 ±0.13
Mean expanded measurement uncertainty[191] [%]: 14
Mean expanded sample uncertainty[192] [%]: 78

No. of extremes (high) as defined by interquartile range[193]: 5
No. of extremes (jump discontinuities) removed: 3
Removed samples:
No. 12: Selisharowka
No. 24: city of Tver
No. 40: –

Mean of the stretch (area) with the lowest content ±σ [%]: 0.10 ±0.01 (n=34)
Mean of the stretch (area) with the highest content ±σ [%]: 0.22 ±0.03 (n=23)
Ratio of the areas with the highest/lowest content: 2.2
Ratio of the overall mean/area with the lowest content: 1.7

‘Geogenic background’-range according to Table 27 [%]: 0.05 – 0.13
Ratio of the highest/lowest ‘geogenic background’: 2.6
Ratio of the Volga sediments overall mean/’geogenic background’: 3.4 – 1.3
Ratio of the area with the highest content/’geogenic background’: 4.4 – 1.7
Ratio of the area with the lowest content/’geogenic background’: 2.0 – 0.8

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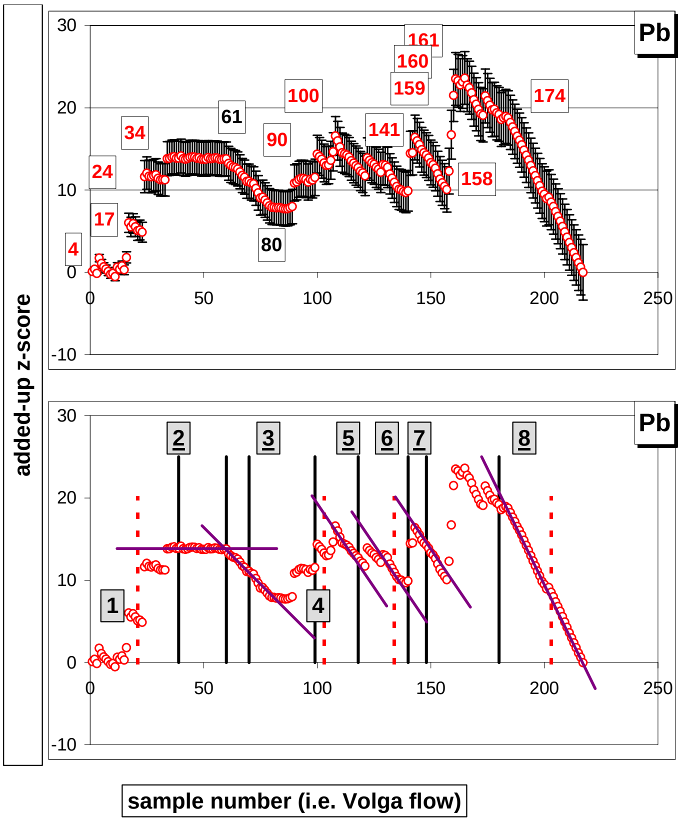
[191] Cf. Figure 25; p. 86.

[192] Cf. Table 33; p. 247.

[193] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 114 Suggested subdivision of the Volga sediments regarding Pb (for dotted and straight vertical lines see Figure 94).

	Range					
Area	Sample	Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 33	0 512	23	8	30	No. 4, 17, 24, 34
2	35 60	526 700	24	2	26	
3	61 80	705 960	19	3	20	
4	81 108	985 1442	26	8	26	No. 90, 100
5	109 121	1468 1717	17	4	13	
6	123 140	1732 2209	20	6	18	No. 122
7	144 157	2412 2645	16	2	14	No. 141, 142, 143
8	162 217	2655 3605	16	5	55	No. 158-161, 174
Volgograd - Astrakhan	184 217	3098 3605	14	3	34	

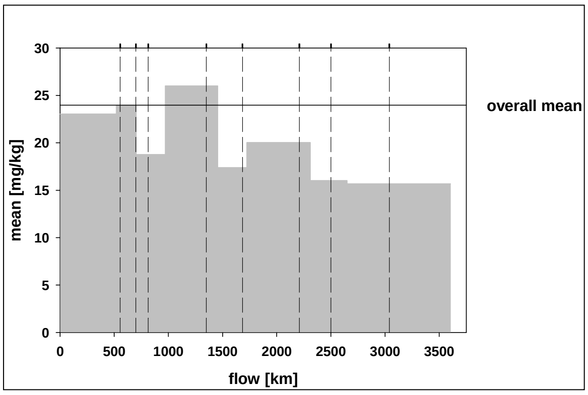


Figure 115 Subdivision of the Volga sediments with respect to Pb according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Pb

Volga sediments overall mean ±σ [mg/kg]: 24 ±16

Mean expanded measurement uncertainty[194] [%]: 22

Mean expanded sample uncertainty[195] [%]: 56

No. of extremes (high) as defined by interquartile range[196]: 19

No. of extremes (jump discontinuities) removed: 15

Removed samples:

No. 4: –
No. 17: downstream city of Rzhev
No. 24: city of Tver
No. 34: –
No. 90: Kineschma harbor
No. 100: wastewater treatment plant near Kazan
No. 122: Butyakova harbor near Zvenigovo
No. 141: Togliatti harbor
No. 142, 143: Samara harbor
No. 158-161: city of Saratov
No. 174: industrial town upstream Volgograd

Mean of the stretch (area) with the lowest content ±σ [mg/kg]: 14 ±3 (n=34)

Mean of the stretch (area) with the highest content ±σ [mg/kg]: 26 ±8 (n=26)

Ratio of the areas with the highest/lowest content: 1.9

Ratio of the overall mean/area with the lowest content: 1.7

‘Geogenic background’-range according to Table 27 [mg/kg]: 17 – 20

Ratio of the highest/lowest ‘geogenic background’: 1.2

Ratio of the Volga sediments overall mean/’geogenic background’: 1.4 – 1.2

Ratio of the area with the highest content/’geogenic background’: 1.5 – 1.3

Ratio of the area with the lowest content/’geogenic background’: 0.8 – 0.7

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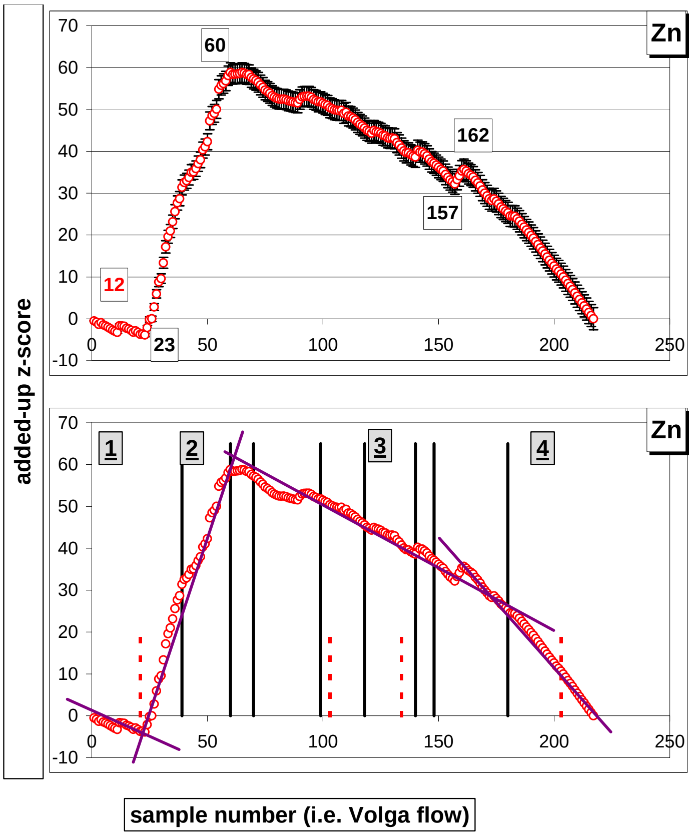
[194] Cf. Figure 25; p. 86.

[195] Cf. Table 33; p. 247.

[196] Cf. Table 26; p. 183.



red numbers: jump discontinuities

black numbers: assumed inflection points

assumed distinguishable areas

Figure 116 Suggested subdivision of the Volga sediments regarding Zn (for dotted and straight vertical lines see Figure 94).

Area	Range Sample	Range Km	Mean	Std.-dev. (s)	n	Removed samples
1	1 23	0 449	138	30	22	No. 12
2	24 60	450 700	365	146	37	
3	61 157	705 2645	135	43	97	No. 158-161
4	162 217	2655 3605	92	25	56	
Volgograd - Astrakhan	184 217	3098 3605	83	8	34	

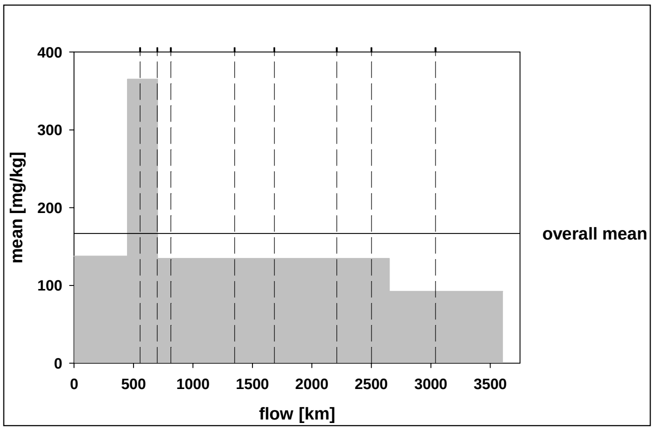


Figure 117 Subdivision of the Volga sediments with respect to Zn according to the above interpretation (vertical lines indicate the Volga chain of reservoirs cf. Figure 94)

Summary: Zn

Volga sediments overall mean ±σ [mg/kg]:	171 ±121
Mean expanded measurement uncertainty[197] [%]:	18
Mean expanded sample uncertainty[198] [%]:	66

No. of extremes (high) as defined by interquartile range[199]:	31
No. of extremes (jump discontinuities) removed:	5

Removed samples:

No. 12:	Selisharowka
No. 158-161:	city of Saratov

Mean of the stretch (area) with the lowest content ±σ [mg/kg]:	83 ±8 (n=34)
Mean of the stretch (area) with the highest content ±σ [mg/kg]:	365 ±146 (n=37)
Ratio of the areas with the highest/lowest content:	4.4
Ratio of the overall mean/area with the lowest content:	2.1

‘Geogenic background’-range according to Table 27 [mg/kg]:	52 – 95
Ratio of the highest/lowest ‘geogenic background’:	1.8
Ratio of the Volga sediments overall mean/’geogenic background’:	3.3 – 1.8
Ratio of the area with the highest content/’geogenic background’:	7.0 – 3.8
Ratio of the area with the lowest content/’geogenic background’:	1.6 – 0.9

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[197] Cf. Figure 25; p. 86.

[198] Cf. Table 33; p. 247.

[199] Cf. Table 26; p. 183.

4.7 Conclusions

4.7.1 Definite conclusions

- **The idea of the Volga River sediments and suspended solids being a major threat towards the ecosystem of the Caspian Sea with respect to the measured parameters is preposterous.**

- **The hypothesis of an extensive pollution of the Volga River sediments can be ruled out – depending on the respective sampling density, but at least on a 200km scale even in the least sampled section on the Middle Volga; typically: on a 20km scale.**

- **No evidence whatsoever can be found to back up the idea of the Volga reservoirs acting as '*storage tanks of pollutants*' (e.g. CEP 1998) in such a way, that their sediments could be considered a 'chemical time bomb'.**

4.7.1.1 Technical rationale

The outcomes of applying the German LAWA-classification system (see Chapter 4.3.2; p.216ff.) to the Volga – because of its use of the same methodology as this study and the up to now absence of a Russian classification system – for the monitored elements are as follows:

- **Silver (Ag)**: no limit values and/or classification exist for silver in sediments within the LAWA field of responsibility, so the results are discussed in the next section.
- **Arsenic (As)**: although no classification system has been established yet within the LAWA field of responsibility, a target value of 40 mg/kg has been set up. In the last resort, the individual measurements meet that target and the respective means of the Volga-sections are well below this target value.
- **Cadmium (Cd)**: even the most heavily polluted stretch on the Volga – approx. 50 km downstream the city of Tver – still complies with the (German) definition of the target concentration (LAWA-class II; moderately contaminated) and already starting within the Saratov reservoir, the sediments have to be considered as uncontaminated up to the Caspian Sea (LAWA-class I; uncontaminated).
- **Chromium (Cr)**: similar to Cd, even the most heavily polluted stretch on the Volga – approx. 400km between the city of Kostroma and Gorkii – matches the German regulatory of the target concentration (LAWA-class II; moderately contaminated). Downstream the Volgograd reservoir, the sediments are uncontaminated per definition (LAWA-class I; uncontaminated).
- **Cupper (Cu)**: owed to the use of an astonishingly low assumed ‘geogenic background’ of just 20 mg/kg within the LAWA-classification system, the most heavily polluted stretch on the Volga – approx. 100km starting from the city of Tver downstream up to the Ivankovo reservoir dam – is classified as ‘moderately to strongly contaminated’ (LAWA-class II-III). Moreover, within this classification system no section of the Volga can be considered as ‘uncontaminated’; while on the other hand except for the above mentioned 100km the sediments are classified as LAWA-class II or better, i.e. comply with the German regulatory of a target concentration.
- **Mercury (Hg)**: analogous to Cd and Cr, the most heavily polluted stretch – approx. 130 km throughout the entire Uglic-reservoir – classifies as ‘moderately polluted’ (LAWA-class II; target), as does the entire Kuibyshev reservoir (approx. 500km). However already starting within the Saratov reservoir, the sediments have to be considered as uncontaminated up to the Caspian Sea (LAWA-class I; uncontaminated).

- **Nickel (Ni)**: more pronounced as with Cu, the astonishingly low assumed ‘geogenic background’ of just 30 mg/kg within the LAWA-classification system, as well as the modifications made to (some of) the class-definitions, results in more than half of the Volga course (1950km out of 3600km) to be classified as ‘moderately to strongly contaminated’ (LAWA-class II-III). Solely the uppermost 500km of the river – up to the city of Tver – would qualify as ‘uncontaminated’ (LAWA-class 0). From a strict technical standpoint, that is what would qualify Ni as the only element within the Volga sediments entering the Caspian Sea markedly above the ‘geogenic background’ (62 mg/kg compared to an assumed ‘LAWA-background’ of 30 mg/kg).
- **Phosphorous (P)**: no limit values and/or classification exist for phosphorous in sediments within the LAWA field of responsibility, so the results are discussed in the next section.
- **Lead (Pb)**: all stretches are well below the LAWA-class II (i.e. target), and already starting within the Cheboksary reservoir, the sediments have to be considered as uncontaminated up to the Caspian Sea (LAWA-class I; uncontaminated).
- **Zink (Zn)**: with the exception of a section of about 250km between the city of Tver and the Uglic reservoir dam that has to be considered as ‘moderately to strongly contaminated’ (LAWA-class II-III), the Volga sediments are largely ‘unpolluted to moderately polluted’ (LAWA-class I-II). What is more, already shortly downstream the city of Saratov up to the Caspian Sea the sediments are classified as ‘uncontaminated’ (LAWA-class I).

4.7.1.2 Scientific rationale

Apart from classification systems used for risk-assessment – as already mentioned a task way beyond the scope of this study – the point of reference will always be the ‘geogenic background’ of a given parameter at a given site.

The real problem is in its definition and determination, and two principle approaches are conceivable (cf. Chapter 4.3.1):

- **the use of an external reference system, e.g. ‘*Clarke-values*’ (Clarke 1924)**
- **derivation from the data set itself**

As already discussed, both approaches have their shortcomings and in fact, none of them can be proven or disproved. Moreover already the idea of a homogeneous ‘geochemical background’ for the entire Volga catchment is little convincing, since the factors controlling the weathering-processes vary notedly throughout the rivers course – e.g. climate, slope (cf. Chapter 4.3.1.1). In other words, even in case the parent material within the Volga catchment would be homogeneous, the weathering products and thus the chemical composition of the sediments should differ.

4.7.1.2.1 External reference system

Applying the I_{geo}-classification-system, based on the Ronov/Vinogradov-values for ‘clay rocks’ of the Russian plate where applicable – else the Turekian/Wedepohl-values have been used (As and Hg) – leads to the following results:

- **Silver (Ag)**: no section of the Volga can be considered ‘uncontaminated’ (I_{geo}-class 0)! Even though downstream the Kujbyshev reservoir up to the Caspian Sea the sediments match the I_{geo}-class 1 (‘uncontaminated to moderately contaminated’) the larger parts of the river are classified as I_{geo}-class 2 or even 3.
- **Arsenic (As)**: all sections of the Volga match I_{geo}-class 0 (‘uncontaminated’).
- **Cadmium (Cd)**: due to the low Cd-contents of Russian ‘clay rocks’ according to Ronov and Migdisov (1996) – 0.095 mg/kg instead of the more commonly assumed 0.3 mg/kg (e.g. Turekian and Wedepohl 1961) – solely the section of the Volga downstream the city of Volgograd up to the Caspian Sea can be considered as ‘uncontaminated’ (I_{geo}-class 0). The most heavily polluted stretch of the Volga – approx. 50 km downstream the city of Tver – already falls into Igeo-class 3 (‘moderately to strongly contaminated’) and most parts of the river have to be classified Igeo-class 2 (‘moderately contaminated’).
- **Chromium (Cr)**: all sections of the Volga match I_{geo}-class 0 (‘uncontaminated’).
- **Cupper (Cu)**: even the most heavily polluted stretch on the Volga – approx. 100km starting from the city of Tver downstream up to the Ivankovo reservoir dam – is classified as ‘Igeo-

class 1 (‘uncontaminated to moderately contaminated’). The same holds true for two other sections, while most parts of the Volga – including the stretch up to the Caspian Sea – qualify as I_{geo}-class 0.

- **Mercury (Hg)**: due to the nowadays often considered ‘too high’ shales-value of 0.4 mg/kg by Turekian and Wedepohl (1961), even the most heavily polluted stretch – approx. 130km throughout the entire Uglic-reservoir – classifies as ‘uncontaminated to moderately contaminated’ (I_{geo}-class 1), as does the entire Kuibyshev reservoir (approx. 500km). All other Volga sections fall into Igeo-class 0 (‘uncontaminated’).
- **Nickel (Ni)**: all sections of the Volga match I_{geo}-class 0 (‘uncontaminated’).
- **Phosphorous (P)**: no section of the Volga can be considered ‘uncontaminated’ (I_{geo}-class 0)!
- **Lead (Pb)**: all sections of the Volga match I_{geo}-class 0 (‘uncontaminated’).
- **Zink (Zn)**: with the exception of a section of about 250km between the city of Tver and the Uglic reservoir dam that has to be considered as ‘moderately contaminated’ (I_{geo}-class 2), the Volga sediments are largely ‘uncontaminated to moderately contaminated’ (I_{geo}-class 1). What is more, already shortly downstream the city of Saratov up to the Caspian Sea the sediments are classified as ‘uncontaminated’ (I_{geo}-class 0).

4.7.1.2.2 Internal reference system

As with the above approaches, no scientific rationale can be given for any reference value (target) derived from the data set itself, although at first sight it seems to be the most straightforward approach. However, as already discussed (Chapter 4.3.1.1) there are several principal problems:

- **‘background’ concentrations can not be approximated in a scientifically sound way from other compartments like the parent material or e.g. sedimentary rocks.**
- **‘background’ concentrations take the form of a range not a single number.**
- **‘background’ concentrations are site-specific and controlled by a large number of variables, usually not (fully) accounted for within a study (e.g. the factors controlling the weathering, as well as the factors controlling the further fate of the weathering products (pH/Eh, salinity, cation exchange capacity, organic carbon, particle size and distribution). Purely ‘technical’ issues also control them, as sample design, number of samples, investigated fraction, analytical method.**

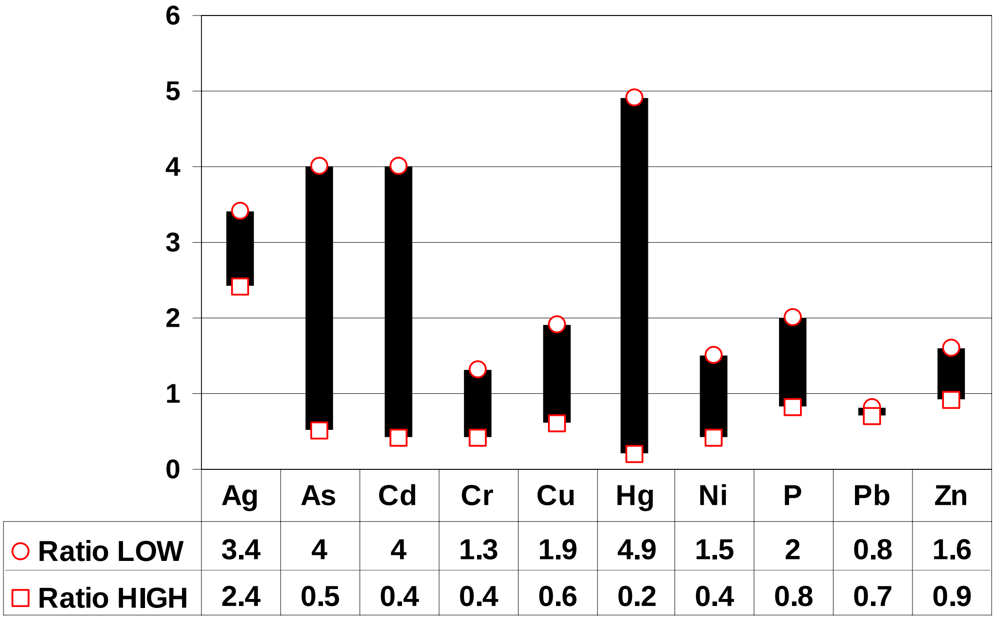
In other words, in almost the same manner as the mean, the standard deviation, and the distribution function of a given parameter are artifacts of the measurement process – particularly the sampling scheme – any kind of calculated or assumed background is an artifact, of fairly unknown validity.

The simplest approach however is to define the area with the lowest content of a given parameter as '*background site*', although following the discussion in Chapter 4.3.1.1 (pp. 210ff.) this approach is as unimpressive as any other is.

In any case, it is the most radical approach when it comes to the search for contamination, since it is virtually impossible to derive reasonable lower values to act as a referee from the data set itself. Moreover, as long as one can – at least with some decency – rule out the contamination of the entire sampled lot, it is also the soundest approach – especially in cases like the River Volga, where at least the parent rock material can be roughly considered homogeneous.

Two parts of the Volga are often referred to as unregulated: the part upstream the Ivankovo reservoir and the part downstream the Volgograd reservoir (cf. Chapter 1.2 p. 15ff). In conjunction with the fact, that these two stretches are also the least populated and industrialized (see Figure 19 and Figure 20), it is little surprising that in either case one of these stretches represents the area with the lowest concentration of a given parameter in the Volga sediments.

Actually, with the exception of Silver (see also discussion in Chapter 4.3.1) the respective average concentrations of the common inorganic COPC's are in good agreement with what is usually considered the '*geogenic background*' (see Table 27).

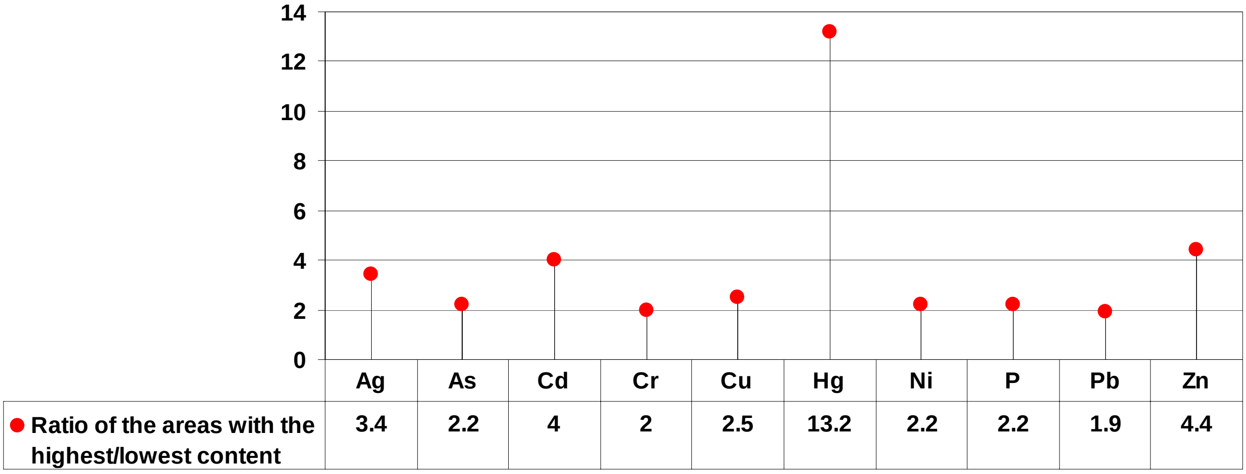


	Ag	As	Cd	Cr	Cu	Hg	Ni	P	Pb	Zn
○ Ratio LOW	3.4	4	4	1.3	1.9	4.9	1.5	2	0.8	1.6
□ Ratio HIGH	2.4	0.5	0.4	0.4	0.6	0.2	0.4	0.8	0.7	0.9

Figure 118 Ratio of the mean of the area with the lowest content on the Volga and the highest and lowest 'geogenic background' as of Table 27 (a ratio of one or below indicates concentrations in Volga sediments equal to, or below an assumed (external) background-level).

According to the LAWA – as well as the original scheme their classification is derived from, the I_{geo}-classes (cf. Chapter 4.3.2; p. 216ff.) –, solely the **average concentration** of a COPC within the sediment body can/should be used to draw conclusions with respect to the magnitude of 'contamination' (or 'anomalies' and/or potential risk). Moreover, their general classification system is based on doubling the respective upper class limit in order to calculate the adjacent upper class limit (starting with the ‘*geogenic background*’ as class I).

Using the average concentration of the respective Volga-stretches with the lowest concentration as a ‘*background*’ and applying the above classification system, results in the description of the whole course of the Volga as practically unpolluted with respect to the major COPC’s.



	Ag	As	Cd	Cr	Cu	Hg	Ni	P	Pb	Zn
● Ratio of the areas with the highest/lowest content	3.4	2.2	4	2	2.5	13.2	2.2	2.2	1.9	4.4

Figure 119 Ratio of the areas on the Volga with the highest/lowest content of a given COPC; see Chapter 4.6.1, p.251ff.)

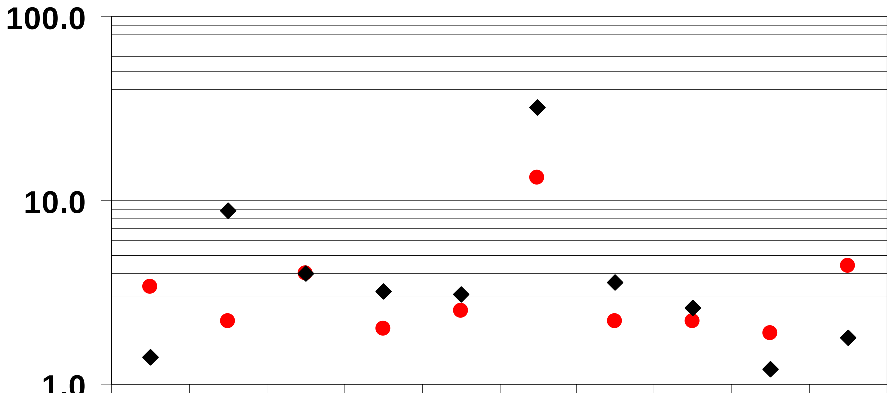
Comparing Figure 119 with the initial definition of the two classification-systems used (Figure 84) reveals that even the stretches on the Volga with the highest content of a given COPC at worst fall into I_{geo}-class 2 (‘*moderately contaminated*’) and LAWA-class II (‘*target*’) respectively – with mercury as the sole exception.

With respect to mercury, about 700km of the Volga have to be considered as ‘*moderately to strongly contaminated*’ (I_{geo}-class 4; LAWA-class II-III; cf. Figure 109, p. 262) when applying the low concentrations (< 0.07 mg/kg) found throughout large sections on the Volga as ‘*geogenic background*’ – even though the concentrations itself are far from frightening (< 0.8 mg/kg).

The above ratios of respective sections with the highest and lowest concentration of a given COPC (Figure 119) get even more impressive, when leaving aside any sort of classification-system, and compare them with ratios of commonly accepted ‘*geogenic backgrounds*’ (cf. Table 27, p. 207). The rationale for this approach –instead of a direct comparison with these background values – is its complete independence from any assumption but the uncertainty of (and in-between) studies based on much larger data sets and diverse methodological approaches towards the characterization of a ‘*normal range*’. As a reminder: it is NOT the scale, but the variance that matters!

As abovementioned, with the exception of silver, the Volga sections with the lowest contents of a given COPC are within the range of what is usually considered the ‘geogenic background’ (cf. Figure 118). In case of (a noticeable) contamination, the ratio of a section with elevated concentration and the respective section with the lowest concentration should at least exceed reasonable (external) uncertainties in the calculation of a benchmark (i.e. the ‘*geogenic background*’).

This uncertainty – or variance – (expressed as the ratio of the highest and the lowest ‘geogenic background’ as of Table 27) is at worst exceeded by a factor of about 2.5 (Ag, Pb, Zn) by the ratio of the Volga sections with the highest / lowest content of a given parameter (Figure 120).



	Ag	As	Cd	Cr	Cu	Hg	Ni	P	Pb	Zn
● **Ratio of the Volga sections with the highest/lowest content**	**3.4**	**2.2**	**4.0**	**2.0**	**2.5**	**13**	**2.2**	**2.2**	**1.9**	**4.4**
◆ **Ratio of the highest/lowest 'geogenic background'**	**1.4**	**8.7**	**4.0**	**3.2**	**3.1**	**32**	**3.6**	**2.6**	**1.2**	**1.8**

Figure 120 Comparison of the ratios derived from the Volga sections with the highest / lowest content of a given parameter and the respective ratios of the highest / lowest ‘geochemical background’ (i.e. uncertainty of its determination) as of Table 27 – please note: logarithmic scale.

Although this can be readily interpreted as some sort of enrichment/pollution, the above mentioned classification systems (Figure 84) would suggest even the worst cases (Ag, Pb, Zn) to be practically negligible – while most other parameters at worst meet the background-uncertainty!

As a reminder: this is the outcome of comparing ratios of the Volga sections with the **highest** ‘pollution’ and sections of a presumed local background, with ratios of ‘geogenic backgrounds’ from different sources!

4.7.2 Summary of the definite conclusions

- Due to the fact, that up to date neither unanimously accepted ‘background values’ for sediments, nor a methodology for their sound determination are available; each and every classification system is based on more or less shaky assumptions.
- Because of the still missing commonly accepted evaluation-criteria with respect to the toxicity towards e.g. ‘aquatic communities’ no quality targets for suspended solids and sediments could have been worked out up to date.
- In other words: neither of the discussed classification systems is suitable for any kind of risk-assessment, nor appropriate to pinpoint, let alone quantify potential enrichment and/or pollution.
- Not only is their respective center of reference questionable, but also their definition of the subsequent classes has no scientific justification whatsoever; and the only rationale for the respective doubling of the antecedent class-limits is the allowance for uncertainties of the measurement process – even though this uncertainty still controls the limits of any quantification.
- While geo-statistical procedures used for prospection purposes more often than not solely rely on the data set of the respective study, in order to delineate ‘abnormal’ regions and codomains; environmental geo-chemistry mostly relies on external benchmarks in order not to run the risk of classifying contaminated samples as ‘background’ samples within their usually smaller-scaled studies.
- Since the underlying difficulty, the lack of knowledge about distribution functions induced by natural processes and their interference with man-made factors, continues to exist, neither approach towards a classification is revisable – although geo-statistical approaches are proven and tested for their (commercial) usability in case of prospection.
- Unsurprisingly, the outcomes of the different classification systems are primarily controlled by the assumed or calculated center of reference – and with no apparent chance to validate them; no strict rating can be given (Table 35).

However, even accepting the respective ‘worst-case’-scenario of Table 35, would qualify the Volga as a river marginally loaded with inorganic contaminants of potential concern.

Table 35 Outcomes of the three used classification approaches (Terminology see Table 30).

	Technical rationale	Scientific rationale	
		external reference	internal reference
	LAWA	I_{geo}	factor relative to background ratio
Ag	not applicable	larger parts of the river 'moderately to strongly contaminated'	2.4
As	all measurements below 'target value'	'uncontaminated'	<1
Cd	target	most parts of the river 'moderately contaminated'	1
Cr	target	'uncontaminated'	<1
Cu	approx. 100 km 'moderately to strongly contaminated'	minor parts 'uncontaminated to moderately contaminated'	<1
Hg	target	approx. 700 km 'uncontaminated to moderately contaminated'	<1
Ni	more than half of the Volga course 'moderately to strongly contaminated'	'uncontaminated'	<1
P	not applicable	most parts of the river 'moderately contaminated'	<1
Pb	target	'uncontaminated'	1.6
Zn	approx. 250 km 'moderately to strongly contaminated'	approx. 250 km 'moderately contaminated'	2.4

Table 36 Possible Volga River 'background'-ranges, using the respective area with the lowest content and the mean sample uncertainty.

mg/kg	'background'	SD	n	mean sample uncertainty [%]	resulting expanded uncertainty [%]		resulting range
Ag	**0.17**	0.03	34	93	**32**		**0.12 - 0.22**
As	**6**	1	34	71	**24**		**5 - 7**
Cd	**0.13**	0.05	34	68	**23**		**0.10 - 0.16**
Cr	**46**	20	21	25	**11**		**41 - 51**
Cu	**26**	11	23	39	**16**		**22 - 30**
Hg	**0.06**	0.02	34	81	**28**		**0.04 - 0.08**
Ni	**29**	6	40	23	**7**		**27 - 31**
P [%]	**0.10**	0.01	34	39	**13**		**0.09 - 0.11**
Pb	**14**	3	34	28	**10**		**13 - 15**
Zn	**83**	8	34	33	**11**		**74 - 92**

coverage factor: 2

4.7.3 Somewhat speculative conclusions

- The measured parameters can be subdivided into two groups (see Chapter 4.5.1.1, pp. 237ff.). However, the reasons for this behavior remain necessarily unknown.[200]
    - Group 1 parameters (see Figure 92) could be interpreted as "anthropogenically influenced; or as predominantly soft (or Type B) cations.
    - Group 2 parameters (see Figure 93) could be interpreted as " geogenic"; or as predominantly hard (Type A) cations.
    - However, since already the notions of hardness and softness are qualitatives, and the respective oxidation degree (i.e. important to classify the intermediate cations) is unknown, the classification of cations will help as much, or as little, as the concept anthropogenic vs. geogenic. The pattern can be described, but not explained.
- However, already the above Table 36 is severely influenced by this classification, since it is in no way justifiable, to use the stretch with the lowest concentration of a given parameter as 'background' for the entire Volga. Note: this will NOT influence the above 'definite conclusions' (Chapter 4.7.1); on the contrary, it makes e.g. the scientific rationale using an internal reference system even more conservative – i.e. regarding the 'worst case'.

- The distribution pattern of most parameters can be 'explained' by the basic characteristics of the Volga River catchment described in Chapter 1 (esp. Figures 19-22).
    - Parameters usually considered as "anthropogenically" influenced, have their highest concentrations in the densely populated and highly industrialized areas, namely of the Upper Volga, where the relative discharge of the Volga is low, and thus thinning-effects less pronounced.
    - At least with the Kama River confluence, the Volga discharge 'prevents' any form of large-area pollution by assumed point sources – simply by the sheer amount of water. E.g. after the Kama confluence, the Volga discharge is about 4 times higher than the River Rhine's discharge near its mouth; i.e. in order to achieve the same extent of pollution on the Volga, there would also have to be 4 times as much waste discharge.

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[200] Although often overlooked, the reasons for this 'inaptitude' are bound to every 'correlational study'. "*Only experimental data can conclusively demonstrate causal relations between variables. …Data from correlational research can only be "interpreted" in causal terms based on some theories that we have, but correlational data cannot conclusively prove causality.*" (Elementary Concepts in Statistics; http://www.statsoft.com/textbook/stathome.html)

- The reported maxima are necessarily pure artifacts. The chances are believed to be good, that a denser sampling plan in the vicinity of the large cities on the Volga banks could lead to higher maxima, while the general findings for the Volga sediments would not change.
- In fact, with respect to inorganic pollutants the Volga can be considered a quite simple riverine system, in which just a few point sources (the major cities) are accountable for the discharge of waste products, while the amount of water and the distance in-between these point sources are sufficient for self-purification to take place. This assumption may be violated in the Upper Volga, up to the Gorki reservoir (less discharge, lower interval of point sources) – hence the main areas under stress are situated there.

- Finally yet importantly, although the sampling of the entire Volga took about 5 years, and the respective sampling plans were less than perfect from a statistical point of view, the resulting shortcomings are believed to be quite negligible. The low sedimentation rates in conjunction with the simple wastewater discharge pattern and the low variance of the measured parameters in-between (potential) point sources excuses almost any mistake – as long as the interpretation is kept simple.
    - Comparing sedimentation rates of several mm/year with sample-supports of about 15 cm diminishes any ‘time-problem’; i.e. the possible claim, the results could have been influenced by changes in sedimentary composition over the last 10 years.
    - Having to deal with apparently just a handful of point sources, and no indications for anything else than (in either case) uncontrollable diffuse sources in-between, clearly reduces the requirements of the sampling plans – making the ones used appropriate.
    - Facing merely low variances – and the little number of ‘outliers’ gives no rise to the assumption of a severely biased data set – further reduces the requirements with regard to the sampling plans and the number of samples needed.

To make a long story short, from a strict scientific standpoint almost anything went wrong within the scope of this study – the conditions for sampling were less than perfect, initial knowledge about the Volga catchment almost nonexistent, and the chances to get hold of any existing (official) data were nil. To make things worse, the rarely accomplished calculation of a realistic uncertainty-budget revealed the necessity to simplify the questions addressed.

However, already this turned out to be sufficient, to disprove way more detailed ‘scientific’ studies claiming an alarming situation on the River Volga – this in fact, should be alarming…

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6 Appendix

Table 37 Description of the samples up to the Ivankovo reservoir.

No.	New No.	Name	E	N	Description	km	Year
1	1	BB1	32.46877	57.25143	Source	0	2000
2	2	BB2	32.57593	57.21622	Source	1	2000
3	3	T7	32.72620	56.93220		50	2000
4	4	T2	32.72050	56.92510		51	2000
5	5	T9	32.73700	56.92900	city of Peno	52	2000
6	6	T10	32.77930	56.91850	city of Peno	53	2000
7	7	T1	32.78150	56.88050		54	2000
8	8	T8	32.79370	56.93180		55	2000
9	9	T6	33.29730	56.90090		115	2000
10	10	T5	33.28150	56.89580		116	2000
11	11	T4	33.30450	56.89890		117	2000
12	12	T3	33.44040	56.85419	Selisharowka	138	2000
13	13	T12	33.82980	56.65710		201	2000
14	14	T13	33.84630	56.64570		202	2000
15	15	T16	34.26250	56.28950	upstream the city of Rshev	329	2000
16	16	T17	34.33710	56.25830	city of Rshev	334	2000
17	17	T20	34.58460	56.18620	downstream the city of Rshev	354	2000
18	18	T18	34.64490	56.19820		359	2000
19	19	T21	34.93910	56.49800		383	2000
20	20	T22	34.95220	56.56400		388	2000
21	21	T23	35.74520	56.84510	upstream the city of Tver	443	2000
22	22	T24	35.89730	56.86120	Tver	448	2000
23	23	T25	35.91260	56.88540	Tver	449	2000
24	24	T27	35.89110	56.85640	Tver	450	2000
25	25	T26	36.01490	56.81610	downstream the city of Tver	456	2000
26	26	T28	36.33460	56.71460		486	2000
27	27	T 29	36.36970	56.69890		489	2001
28	28	T 30	36.41570	56.68510		492	2001
29	29	T 31	36.38692	56.68738		496	2001
30	30	T 32	36.48192	56.65467		496	2001
31	31	T 33	36.48150	56.65435		502	2001
32	32	T 34	36.54588	56.64210		503	2001
33	33	T 35	36.55810	56.63793		512	2001
34	34	T 36	36.76220	56.71020		521	2001
35	35	T 37	36.55810	56.75860		526	2001
36	36	T 38	36.75140	56.79190		530	2001
37	37	T 39	36.79960	56.78985		531	2001
38	38	T 40	36.96185	56.80397		546	2001
39	39	T 41	37.10558	56.73399	Ivankovo-Dam	555	2001
40	39	T 42	37.10608	56.73513	Ivankovo-Dam	555	2001
41	39	T 43	37.10666	56.73628	Ivankovo-Dam	555	2001
42	39	T 44	37.10724	56.73771	Ivankovo-Dam	555	2001
43	39	T 45	37.10872	56.73977	Ivankovo-Dam	555	2001
44	39	T 46	37.10962	56.74118	Ivankovo-Dam	555	2001
45	39	T 47	37.11020	56.74250	Ivankovo-Dam	555	2001
46	39	T 48	37.11159	56.74437	Ivankovo-Dam	555	2001

No. refers to the original data set; *New No.* to the data set adapted for interpretation (see p. 232)

Table 38 Measured parameters of the samples up to the Ivankovo reservoir.

No.	New No.	Ag	Al [%]	As	B	Ba	Ca [%]	Cd	Co	Cr	Cu	Fe [%]	Hg	K [%]	Li	Mg [%]	Mn [%]	Mo	Na [%]	Ni	Pb	Sc	Sr	V	Y	Zn	C [%]	S [%]	P_2O_5 [%]	P [%]	CO_3 [%]	105°	550°
1	1	0.49	1.86	2	13	127	0.39	0.20	11	34	22	2.15	0.11	0.57	21	0.47	0.03	0.9	0.02	20	26	4	21	29	11	109	5.63	0.12	0.25	0.11		1.59	11.57
2	2	0.56	2.12	2	11	212	1.01	0.64	6	31	18	1.60	0.15	0.34	27	0.44	0.03	1.6	0.03	16	29	1	24	30	10	129	12.61	0.25	0.45	0.19			
3	3	0.57	2.41	3	20	251	0.84	0.38	10	33	16	3.20	0.11	0.51	22	0.48	0.12	1.0	0.05	18	15	5	55	31	14	103	5.77	0.13	0.29	0.12		3.43	13.19
4	4	1.60	2.61	4	33	253	1.04	0.48	13	127	55	3.88	0.49	0.70	31	0.55	0.03	2.3	0.11	33	57	5	66	40	20	216	11.65	0.32	0.49	0.21		4.59	23.42
5	5	0.64	2.42	2	24	218	0.52	0.27	8	33	15	2.13	0.08	0.49	21	0.42	0.04	1.0	0.03	17	13	4	32	29	12	104	5.74	0.12	0.25	0.11		3.62	12.42
6	6	0.24	3.22	6	26	261	0.73	0.46	16	48	21	4.23	0.11	0.80	32	0.67	0.14	1.5	0.04	27	17	6	46	44	18	140	4.80	0.09	0.38	0.16		3.77	12.14
7	7	0.39	2.99	4	24	181	0.74	0.33	13	43	22	2.79	0.17	0.72	31	0.61	0.05	1.5	0.04	25	19	5	37	39	13	129	7.77	0.08	0.32	0.14		3.78	17.56
8	8	0.28	2.56	5	24	288	0.75	0.37	11	36	17	4.11	0.12	0.58	23	0.48	0.19	1.2	0.04	20	19	5	41	36	15	130	8.01	0.18	0.44	0.19		4.65	17.33
9	9	0.76	2.89	6	23	292	0.95	0.35	12	40	22	4.28	0.16	0.61	29	0.49	0.12	1.7	0.02	23	18	6	53	38	17	125	9.62	0.21	0.40	0.17		5.09	20.61
10	10	0.77	2.76	4	26	276	0.60	0.43	11	40	20	2.93	0.15	0.51	27	0.45	0.08	1.8	0.02	24	26	5	38	40	16	131	9.18	0.19	0.34	0.15		4.88	19.64
11	11	0.19	3.26	4	28	257	0.77	0.23	14	54	20	3.70	0.11	0.86	34	0.64	0.09	1.7	0.03	27	17	6	46	41	15	134	6.20	0.15	0.30	0.13		4.20	14.70
12	12	5.32	2.17	9	43	225	4.11	0.40	12	42	53	8.00	0.43	0.70	26	0.66	0.75	3.8	0.16	24	44	5	592	38	18	359	11.13	0.78	4.57	1.98			
13	13	0.53	2.91	6	28	290	1.47	0.43	16	48	24	4.35	0.17	0.73	34	0.85	0.14	1.7	0.04	29	20	5	110	44	19	158	7.63	0.16	0.42	0.18		4.31	17.57
14	14	0.55	3.10	5	35	257	2.81	0.37	18	51	38	3.67	0.24	0.86	37	0.95	0.22	1.7	0.05	36	31	6	58	49	21	156	5.79	0.16	0.43	0.18		3.47	13.88
15	15	0.97	2.53	6	28	293	1.22	0.44	14	40	20	3.61	0.11	0.64	27	0.74	0.32	1.3	0.06	25	16	5	45	38	17	115	6.06	0.12	0.40	0.17		3.15	14.31
16	16	0.75	2.34	5	21	270	1.61	0.51	13	39	29	3.05	0.26	0.58	27	1.04	0.15	1.2	0.04	25	50	4	56	35	18	143	5.78	0.12	0.41	0.18		2.83	12.73
17	17	0.64	2.53	6	29	284	1.71	0.50	13	44	25	3.44	0.13	0.67	28	1.05	0.24	1.2	0.04	25	98	5	56	37	17	128	5.87	0.11	0.41	0.18		3.12	13.76
18	18	0.73	2.56	5	26	297	1.58	0.54	13	45	23	2.92	0.09	0.61	30	1.13	0.11	1.2	0.05	26	15	5	52	37	16	112	4.29	0.08	0.30	0.13		3.10	10.63
19	19	0.56	2.46	5	21	271	2.04	0.49	14	47	27	3.23	0.14	0.57	28	1.06	0.25	1.2	0.03	25	31	5	50	38	16	205	5.32	0.13	0.40	0.17		2.80	12.44
20	20	0.68	2.37	4	19	276	1.98	0.47	14	46	25	3.09	0.10	0.55	27	1.14	0.18	2.3	0.03	29	17	4	47	37	16	128	6.07	0.13	0.40	0.17		2.97	13.23
21	21	0.39	2.48	5	19	267	2.20	0.47	13	44	22	3.24	0.10	0.58	28	1.24	0.10	1.1	0.03	24	16	5	44	36	16	110	5.10	0.11	0.39	0.17		2.67	11.53
22	22	0.81	2.37	10	22	328	1.83	1.21	17	60	35	4.31	0.12	0.62	27	0.91	0.34	1.3	0.04	31	25	5	48	41	16	178	5.98	0.13	0.49	0.21		3.06	13.77
23	23	0.68	2.36	7	20	324	2.02	1.66	15	58	32	4.52	0.13	0.62	27	0.94	0.17	1.2	0.06	30	19	5	41	38	15	140	6.37	0.23	0.45	0.19		3.13	14.35
24	24	1.77	2.17	9	29	489	2.34	0.92	12	73	174	4.88	1.19	0.61	26	0.98	0.17	1.4	0.08	29	143	4	85	37	13	374	9.56	0.35	1.84	0.80		3.49	19.34
25	25	3.89	2.67	6	27	259	3.39	0.37	16	81	73	3.67	0.34	0.74	35	1.40	0.10	1.6	0.10	38	32	5	83	47	17	392	6.12	0.24	0.54	0.23		2.71	13.27
26	26	0.39	2.44	4	27	237	3.35	0.28	13	44	34	2.97	0.24	0.77	30	0.96	0.10	1.0	0.04	29	17	5	62	37	16	186	4.79	0.08	0.50	0.21		2.06	10.42
27	27	0.56	2.72	10	30	289	1.47	0.75	17	64	51	4.71	0.20	0.53	30	0.92	0.20	1.3	0.13	31	23	5	57	44	19	498	5.62	0.15	0.54	0.23		3.79	13.22
28	28	1.51	2.81	6	30	283	1.62	0.94	15	99	97	3.84	0.33	0.57	31	1.01	0.08	1.6	0.09	33	27	5	47	42	18	533	6.94	0.18	0.36	0.16		4.24	14.53
29	29	0.63	3.14	7	28	286	1.99	0.21	16	71	99	4.64	0.30	0.70	39	1.13	0.16	2.4	0.15	37	26	6	82	46	19	500	6.26	0.15	0.47	0.20		3.57	14.21
30	30	0.19	3.29	12	25	370	0.92	0.03	15	54	24	5.26	0.06	0.75	37	0.73	0.19	1.6	0.08	34	16	7	71	55	22	259	1.65	0.04	0.68	0.29		2.89	6.40
31	31	0.39	2.56	5	24	239	1.65	0.48	13	59	66	3.57	0.17	0.54	31	0.89	0.10	1.2	0.14	27	20	5	65	37	16	609	6.16	0.21	0.43	0.18		4.17	12.88
32	32	0.72	3.21	7	25	292	1.43	0.40	15	92	82	4.39	0.23	0.66	39	1.00	0.10	1.6	0.09	35	25	6	57	47	19	613	5.62	0.17	0.52	0.22	2.50	4.90	12.30
33	33	0.54	3.46	8	31	311	1.58	0.11	15	76	54	4.67	0.18	0.75	42	0.94	0.19	1.7	0.13	35	23	6	74	49	17	451	6.68	0.17	0.54	0.23		5.35	14.92
34	34	0.32	2.53	6	38	230	1.36	0.76	15	65	50	3.47	0.21	0.40	27	0.80	0.10	1.3	0.10	30	69	5	90	45	14	326	5.40	0.16	0.54	0.24	2.50	3.64	12.64
35	35	0.69	3.52	8	29	345	1.56	0.23	16	82	63	4.71	0.21	0.73	42	1.03	0.16	1.5	0.10	35	24	6	64	52	19	422	5.67	0.20	0.56	0.24	2.50	5.02	12.53
36	36	0.47	3.39	7	26	323	1.29	0.05	16	75	66	4.80	0.23	0.68	41	0.92	0.12	1.6	0.09	37	27	6	57	54	18	451	7.02	0.24	0.58	0.25	2.50	5.26	15.46
37	37	0.55	3.25	9	23	361	1.40	0.11	16	77	63	5.34	0.21	0.67	38	0.98	0.16	1.5	0.08	36	25	6	61	51	19	410	5.41	0.15	0.62	0.27	2.50	5.01	12.49
38	38	0.25	3.19	7	18	289	1.10	0.42	17	59	52	4.26	0.15	0.57	38	0.87	0.15	1.6	0.09	37	21	7	48	51	22	287	3.68	0.19	0.39	0.17	2.50	4.21	9.11
39	39	0.30	4.04	9	34	321	1.18	0.59	19	76	84	5.13	0.23	0.82	42	1.07	0.11	1.7	0.09	41	25	8	51	58	22	487	4.56	0.15	0.48	0.21	2.50	4.43	11.82
40	39	0.33	3.41	14	28	286	1.15	0.77	16	68	146	4.82	0.29	0.63	35	0.97	0.16	1.9	0.08	36	26	7	45	53	20	702	5.56	0.31	0.44	0.19	2.50	4.09	13.22
41	39	0.12	2.91	8	27	242	1.50	0.38	14	52	57	3.87	0.16	0.50	30	1.18	0.10	1.3	0.07	31	19	6	39	44	18	263	4.44	0.14	0.28	0.12	2.50	3.41	10.62
42	39	0.21	3.22	11	35	266	1.26	0.56	16	61	126	4.44	0.21	0.58	34	1.00	0.11	1.6	0.09	33	23	6	46	48	18	586	5.00	0.22	0.38	0.17	2.50	4.43	11.59
43	39	0.25	3.48	11	36	277	1.31	0.64	17	68	128	4.80	0.25	0.69	40	1.02	0.12	1.8	0.10	37	26	7	47	55	20	556	5.06	0.25	0.42	0.18	2.50	4.13	12.22
44	39	0.31	3.55	9	34	295	1.26	0.56	19	70	64	5.10	0.11	0.67	40	0.99	0.16	1.6	0.10	40	24	7	50	55	22	407	4.49	0.14	0.51	0.22	2.50	4.95	11.50
45	39	0.32	3.76	7	34	311	1.21	0.74	19	75	79	5.12	0.22	0.72	43	1.02	0.13	1.8	0.11	41	26	8	49	58	22	479	4.51	0.14	0.48	0.21	2.50	4.28	11.88
46	39	0.33	3.47	8	35	305	1.18	0.68	18	69	64	5.10	0.21	0.66	38	0.94	0.16	1.6	0.09	38	24	7	47	54	21	399	4.83	0.12	0.54	0.24	2.50	4.68	11.93

Table 39 **Description of the samples in-between the Ivankovo and the Gorki reservoir.**

No.	New No.	Name	E	N	Description	km	Year
47	40	TU 49	37.24317	56.78252		563	2001
48	41	TU 50	37.21230	56.76970		564	2001
49	42	TU 51	37.25310	56.79080		573	2001
50	43	TU 52	37.41730	56.88317	downstream the city of Kimry	582	2001
51	44	TU 53	37.51827	56.96743		593	2001
52	45	TU 54	37.48618	56.98633		595	2001
53	46	TU 55	37.44568	57.00325		596	2001
54	47	TU 56	37.43700	57.00592		597	2001
55	48	TU 57	37.51167	57.06585		603	2001
56	49	TU 58	37.51233	57.07260		607	2001
57	50	TU 59	37.64125	57.13008		617	2001
58	51	TU 60	37.65425	57.17027		623	2001
59	52	TU 61	37.65425	57.17027		631	2001
60	53	TU 62	37.72167	57.27100		636	2001
61	54	TU 63	37.79975	57.27618		641	2001
62	55	TU 64	37.87352	57.26018		646	2001
63	56	TU 65	38.01600	57.31492		663	2001
64	57	TU 66	38.08867	57.37967		674	2001
65	58	TU 67	38.14290	57.43160		681	2001
66	59	TU 68	38.26452	57.47147		690	2001
67	60	TU 69	38.28792	57.49797	Uglic Dam	700	2001
68	60	TU 70	38.28770	57.49910	Uglic Dam	700	2001
69	60	TU 71	38.28670	57.50030	Uglic Dam	700	2001
70	60	TU 72	38.28490	57.50190	Uglic Dam	700	2001
71	60	TU 73	38.28260	57.50430	Uglic Dam	700	2001
72	60	Tu 74	38.28040	57.50660	Uglic Dam	700	2001
73	60	TU 75	38.27810	57.50870	Uglic Dam	700	2001
74	61	U 76	38.34300	57.58360	downstream the city of Uglic	705	2001
75	62	U 77	38.37150	57.67190		710	2001
76	63	U 78	38.47650	57.78700		720	2001
77	64	01W 34	38.49055	57.80633		735	2001
78	65	01W 35	38.48770	57.93192		749	2001
79	66	01W 36	38.40697	58.02532		763	2001
80	67	01W 37	38.38213	58.14692		772	2001
81	68	01W 38	38.28988	58.07258		784	2001
82	69	01W 39	38.62842	58.12378		806	2001
83	70	01W 33	38.69813	58.09490	Rybinsk dam	814	2001
84	70	01W 32	38.70078	58.09765	Rybinsk dam	814	2001
85	70	01W 31	38.70095	58.10035	Rybinsk dam	814	2001
86	70	01W 30	38.69140	58.10563	Rybinsk dam	814	2001
87	71	01W 29	38.82948	58.06107	city of Rybinsk	820	2001
88	72	01W 28	38.96978	58.03940	downstream the city of Rybinsk	826	2001
89	73	01W 27	39.16472	58.02153		846	2001
90	74	01W 26	39.43432	57.93313		868	2001
91	75	01W 25	39.70078	57.79263		880	2001
92	76	01W 24	39.86295	57.67053	upstream the city of Jaroslawl	904	2001
93	77	01W 23	39.95110	57.57202	Vakarevo	916	2001
94	78	01W 22	40.05827	57.55675		934	2001
95	79	01W 21	40.77245	57.66738		955	2001
96	80	01W 20	40.57032	57.76680		960	2001
97	81	01W 19	40.87088	57.76117	upstream the city of Kostroma	985	2001
98	82	01W 18	40.90338	57.76720	Kostroma	987	2001
99	83	01W 17	40.99960	57.68940	downstream the city of Kostroma	990	2001
100	84	01W 16	41.10165	57.62138	11	999	2001
101	85	01W 14	41.20177	57.45852	Volgoretchensk-Power Station	1017	2001
102	86	01W 13	41.20008	57.47182	downstream Volgoretchensk	1018	2001
103	87	01W 12	41.54998	57.45577	near Plios	1038	2001
104	88	01W 11	41.83147	57.40462	near Semigorie	1059	2001
105	89	01W 10	42.09263	57.48110	Kineschma	1091	2001
106	90	01W 09	42.17642	57.44213	Kineschma	1096	2001
107	91	01W 08	42.32520	57.46748		1105	2001
108	92	01W 07	42.53113	57.41527		1119	2001
109	93	01W 06	42.80283	57.41380		1139	2001
110	94	01W 05	43.16810	57.38037		1160	2001
111	95	01W 04	43.18935	57.04817		1180	2001
112	96	01W 03	43.16488	56.91498		1205	2001
113	97	01W 02	43.25827	56.75503		1225	2001
114	98	01W 01	43.22675	56.69943		1230	2001
115	99	1	43.41147	56.68843	Gorki dam	1350	1997
116	99	2	43.31258	56.65622	Gorki dam	1350	1997
117	99	3	43.31602	56.64752	Gorki dam	1350	1997
118	99	4	43.35142	56.64777	Gorki dam	1350	1997
119	99	5	43.35867	56.65075	Gorki dam	1350	1997
120	99	6	43.36997	56.65935	Gorki dam	1350	1997
121	99	7	43.38668	56.66983	Gorki dam	1350	1997
122	99	8	43.39933	56.67985	Gorki dam	1350	1997

No. refers to the original data set; *New No.* to the data set adapted for interpretation (see p. 232)

Table 40 Measured parameters of the samples in-between the Ivankovo and the Gorki reservoir.

No.	New No.	Ag	Al [%]	As	B	Ba	Ca [%]	Cd	Co	Cr	Cu	Fe [%]	Hg	K [%]	Li	Mg [%]	Mn [%]	Mo	Na [%]	Ni	Pb	Sc	Sr	V	Y	Zn	C [%]	S [%]	P_2O_5 [%]	P [%]	CO_3 [%]	105°	550°
47	40	0.44	3.11	11	24	306	2.27	0.42	14	56	34	5.21	5.19	0.63	39	0.94	0.15	1.4	0.14	35	28	6	136	48	16	301	4.79	0.30	1.05	0.46		4.98	11.48
48	41	0.29	3.30	17	25	225	2.44	0.15	21	59	36	4.77	1.07	0.68	42	1.10	0.18	2.0	0.11	51	18	7	84	61	23	213	3.31	0.45	0.44	0.19		3.98	7.72
49	42	0.49	3.29	13	23	350	1.95	0.20	17	58	37	5.33	1.03	0.67	41	1.09	0.41	1.6	0.10	37	23	6	75	53	20	259	4.54	0.30	0.55	0.24	5.50	4.18	10.49
50	43	0.34	3.55	10	21	334	1.23	0.01	18	65	39	5.27	1.77	0.70	41	0.92	0.22	1.7	0.11	40	26	7	63	56	21	313	3.89	0.22	0.45	0.19		4.15	10.01
51	44	0.12	3.08	6	18	272	1.33	0.38	15	53	35	4.40	0.20	0.48	44	0.92	0.10	1.6	0.10	35	27	6	58	50	15	178	5.17	0.34	0.54	0.23	2.50	4.54	11.68
52	45	0.31	3.22	13	21	329	1.44	0.34	19	58	37	5.73	0.68	0.63	38	0.89	0.21	1.5	0.09	38	24	7	62	55	22	258	3.48	0.28	0.52	0.22	2.50	4.44	9.11
53	46	0.31	3.38	12	24	302	1.40	0.32	19	63	48	5.26	0.71	0.68	41	0.96	0.17	1.6	0.10	42	24	7	59	57	23	306	3.62	0.45	0.41	0.18	2.50	3.96	8.78
54	47	0.25	3.39	6	25	310	1.13	0.23	17	60	40	4.96	0.92	0.62	44	0.89	0.12	1.6	0.09	37	22	7	55	52	19	273	4.70	0.27	0.45	0.20	2.50	3.91	11.26
55	48	0.41	3.43	10	27	308	1.20	0.38	17	69	55	5.11	1.40	0.66	42	0.94	0.16	1.7	0.10	40	25	7	56	56	21	442	3.72	0.34	0.43	0.18	2.50	3.88	9.71
56	49	0.29	3.37	11	23	345	1.17	0.50	18	58	39	5.82	0.55	0.59	42	0.85	0.19	1.6	0.10	37	21	7	53	56	19	252	5.10	0.33	0.54	0.23		4.52	12.06
57	50	0.44	3.48	12	28	349	1.11	0.23	18	63	43	5.31	0.88	0.66	42	0.87	0.29	1.6	0.10	39	24	7	58	55	19	312	5.09	0.27	0.55	0.24	2.50	4.36	12.14
58	51	0.44	3.28	14	23	477	1.06	0.22	17	66	127	4.77	0.71	0.58	40	0.92	0.16	1.7	0.09	37	24	7	51	54	18	752	1.70	0.15	0.36	0.15	2.50	5.10	10.06
59	52	0.41	3.38	9	21	420	1.10	0.38	18	62	38	5.33	0.99	0.59	40	0.85	0.27	1.5	0.09	40	27	7	56	55	20	314	4.82	0.24	0.55	0.24	2.50	6.24	12.51
60	53	0.25	3.49	8	20	293	1.09	0.10	17	72	60	4.80	0.49	0.66	44	1.00	0.11	1.7	0.10	42	22	7	45	58	19	229	3.06	0.18	0.48	0.21	2.50	4.92	8.74
61	54	0.37	3.31	9	19	323	1.17	0.49	18	63	41	5.17	1.05	0.60	40	0.97	0.19	1.6	0.09	40	24	7	52	55	19	279	4.13	0.17	0.52	0.22	2.50	5.40	10.75
62	55	0.39	3.17	15	19	261	1.46	0.35	17	67	168	4.64	0.56	0.60	40	1.20	0.15	1.6	0.10	39	25	7	46	54	17	728	3.69	0.26	0.35	0.15	2.50	4.75	9.28
63	56	0.44	3.31	10	17	329	1.23	0.47	18	63	40	0.54	1.10	0.62	38	0.99	0.28	1.5	0.09	41	24	7	53	54	20	274	4.20	0.10	0.57	0.25	2.50	5.12	10.91
64	57	0.21	3.82	9	28	266	1.29	0.18	19	68	41	5.00	0.34	0.79	49	1.28	0.13	1.8	0.10	52	21	8	48	67	20	217			0.38	0.17	2.50	5.25	8.82
65	58	0.38	3.37	8	22	329	1.17	0.39	20	64	41	5.12	0.52	0.61	41	1.09	0.26	1.6	0.09	47	24	7	47	58	21	241	2.94	0.13	0.43	0.18	2.50	5.44	9.93
66	59	0.36	3.30	9	18	318	1.22	0.40	20	67	48	2.36	0.46	0.61	42	1.17	0.19	1.7	0.09	49	25	7	47	62	20	316	3.38	0.16	0.41	0.18	2.50	5.45	9.59
67	60	0.38	3.56	10	32	293	1.38	0.52	22	69	45	5.25	0.41	0.70	43	1.28	0.29	1.7	0.10	51	24	8	44	64	20	266	3.32	0.19	0.42	0.18	2.50	5.04	9.26
68	60	0.36	3.53	11	35	271	1.50	0.56	21	70	48	5.21	0.40	0.73	44	1.33	0.23	1.7	0.11	50	24	8	45	65	19	289	3.28	0.21	0.45	0.20	2.50	4.91	9.20
69	60	0.41	3.33	10	27	283	1.38	0.52	22	65	43	5.18	0.39	0.66	41	1.25	0.30	1.7	0.09	48	24	7	41	61	20	244	3.34	0.15	0.46	0.20	2.50	4.86	9.21
70	60	0.31	3.41	11	34	271	1.55	0.63	20	68	45	5.00	0.21	0.68	43	1.27	0.25	2.5	0.11	52	24	7	43	63	19	266	3.40	0.17	0.43	0.19	2.50	5.38	9.31
71	60	0.47	4.18	12	34	371	1.13	0.41	26	73	43	5.66	0.27	0.83	50	1.18	0.44	2.0	0.11	54	25	9	48	76	23	206	2.67	0.09	0.46	0.20	2.50	5.69	8.84
72	60	0.34	3.37	10	32	278	1.39	0.45	21	66	43	5.15	0.39	0.67	42	1.26	0.25	1.7	0.10	50	24	7	42	62	20	250	3.08	0.13	0.44	0.19	2.50	5.17	9.36
73	60	0.32	3.59	10	28	276	1.46	0.50	22	68	44	5.11	0.37	0.73	44	1.31	0.23	1.8	0.10	51	24	8	43	65	20	250	3.30	0.18	0.40	0.17	2.50	4.72	9.29
74	61	0.11	2.93	7	24	189	2.00	0.20	17	56	31	3.80	0.12	0.58	36	1.41	0.07	1.4	0.09	40	15	6	41	54	16	115	3.07	0.14	0.29	0.13	6.00	3.20	7.57
75	62	0.28	3.07	13	22	294	1.50	0.12	18	58	36	4.83	0.16	0.60	39	1.26	0.17	1.5	0.09	41	19	7	47	58	19	173	3.34	0.13	0.37	0.16	2.50	4.18	8.80
76	63	0.50	3.07	13	15	345	1.41	0.15	20	59	34	5.32	0.17	0.60	37	1.10	0.38	1.5	0.09	43	21	6	50	58	21	174	3.45	0.12	0.50	0.22		4.86	9.65
77	64	0.46	3.79	15	28	327	1.42	0.30	22	69	38	5.31	0.20	0.72	41	1.31	0.37	1.8	0.10	47	22	7	54	69	20	180	3.74	0.09	0.56	0.24		5.21	10.31
78	65	0.39	3.75	10	30	315	1.34	0.34	20	67	35	5.20	0.29	0.71	40	1.23	0.25	1.7	0.09	44	21	7	49	63	19	191	4.10	0.14	0.47	0.20		5.03	10.82
79	66	0.24	3.18	9	19	250	1.11	0.27	18	57	31	4.33	0.19	0.52	34	0.98	0.15	1.5	0.09	39	18	6	40	54	17	151	3.12	0.12	0.40	0.17		4.42	8.60
80	67	0.15	3.03	7	17	259	0.97	0.34	14	51	26	3.86	0.15	0.41	32	0.73	0.14	1.4	0.09	33	16	5	40	48	14	130	7.27	0.16	0.40	0.17		5.35	15.63
81	68	0.50	3.23	12	16	320	1.33	0.44	17	56	31	4.73	0.23	0.50	33	0.91	0.40	1.4	0.10	37	20	6	52	54	15	160	6.89	0.13	0.59	0.26		5.68	15.75
82	69	0.19	3.39	6	14	241	0.87	0.28	14	55	25	3.79	0.16	0.42	40	0.72	0.14	1.5	0.09	34	15	6	41	54	14	86	7.56	0.14	0.38	0.17		5.14	16.60
83	70	0.14	3.65	14	41	243	1.28	0.34	21	67	66	4.74	0.31	0.71	43	1.08	0.10	1.9	0.10	51	26	7	43	68	16	138	6.72	0.52	0.39	0.17	2.50	4.10	14.49
84	70	0.16	3.20	13	29	237	1.35	2.22	20	60	63	4.47	0.40	0.55	38	0.99	0.13	1.6	0.09	49	24	6	42	62	16	126	6.37	0.44	0.37	0.16	2.50	4.14	13.71
85	70	0.26	3.21	10	22	278	1.26	0.25	17	57	38	4.63	0.23	0.53	37	0.89	0.21	1.5	0.09	43	24	6	44	59	16	121	7.15	0.39	0.44	0.19	2.50	4.50	15.57
86	70	0.27	3.43	10	25	267	1.17	0.29	16	58	34	4.72	0.17	0.57	38	0.92	0.22	1.5	0.09	41	22	6	45	58	15	114	7.21	0.13	0.50	0.21	2.50	4.37	16.43
87	71	0.61	3.33	14	27	239	1.54	0.63	18	71	62	4.80	0.19	0.57	40	1.12	0.31	1.8	0.09	52	20	6	47	57	14	128	7.95	0.28	0.44	0.19	2.50	4.55	16.71
88	72	0.26	3.13	10	24	204	1.47	0.32	18	62	39	4.33	0.11	0.50	38	1.12	0.18	1.5	0.12	46	22	6	48	55	14	113	6.93	0.14	0.43	0.19		4.82	15.87
89	73	0.14	3.23	7	22	206	1.57	0.34	17	60	30	4.14	0.09	0.54	40	1.27	0.10	1.5	0.12	43	14	6	51	57	14	94	4.68	0.13	0.35	0.15		4.07	11.19
90	74	0.12	3.18	6	18	218	1.32	0.30	17	60	29	3.97	0.14	0.48	41	1.22	0.07	1.5	0.12	43	14	6	50	57	16	101	3.79	0.17	0.30	0.13		4.08	9.43
91	75	0.17	3.13	7	22	184	1.69	0.35	16	60	30	3.71	0.17	0.57	39	1.33	0.11	1.5	0.10	41	13	6	45	54	14	91	5.27	0.13	0.30	0.13		3.89	11.16
92	76	0.27	2.72	10	20	177	1.72	0.36	17	59	33	4.01	0.18	0.46	36	1.16	0.22	1.5	0.12	41	25	5	45	52	13	123	5.59	0.13	0.37	0.16		4.18	12.24
93	77	0.17	2.98	9	20	177	1.38	0.44	17	69	34	3.91	0.15	0.48	39	1.09	0.12	1.6	0.10	44	18	6	47	58	14	117	6.58	0.28	0.32	0.14	2.50	4.56	13.83
94	78	0.23	2.90	10	19	169	1.49	0.37	17	66	29	4.12	0.11	0.49	36	1.23	0.11	1.5	0.10	42	18	6	52	59	16	105	4.79	0.16	0.36	0.15		4.01	10.76
95	79	0.31	3.05	10	19	185	1.50	0.44	17	76	32	3.98	0.09	0.51	38	1.21	0.16	1.5	0.09	42	18	6	52	57	15	122	5.52	0.19	0.37	0.16		4.34	11.88
96	80	0.46	3.11	10	18	206	1.46	0.71	17	93	35	4.03	0.13	0.50	39	1.19	0.21	1.6	0.10	42	21	6	53	55	14	135	6.69	0.19	0.40	0.17		4.63	14.28
97	81	0.23	3.11	8	20	215	1.25	0.75	17	95	36	4.29	0.15	0.49	40	1.08	0.08	1.8	0.10	43	24	6	41	55	15	147	4.91	0.29	0.34	0.15	2.50	4.38	11.81
98	82	0.37	3.45	9	31	216	1.22	0.67	19	103	38	4.55	0.15	0.58	43	1.14	0.11	1.8	0.10	45	23	6	51	61	15	160	6.04	0.20	0.41	0.18	2.50	4.71	13.90
99	83	0.42	3.06	10	20	207	1.33	0.72	18	110	39	4.42	0.16	0.46	38	1.03	0.19	1.6	0.10	44	25	6	46	53	14	173	6.64	0.20	0.52	0.22	2.50	5.60	14.98
100	84	0.46	3.49	8	19	250	1.24	0.23	18	98	38	4.26	0.14	0.53	43	1.08	0.19	1.8	0.09	44	23	6	50	59	14	152	6.77	0.26	0.41	0.18		5.36	15.11
101	85	0.18	2.99	9	19	200	1.14	0.27	19	69	45	4.39	0.13	0.48	37	1.08	0.09	1.4	0.09	53	23	6	40	62	15	133	2.98	0.09	0.46	0.20	2.50	4.26	8.44
102	86	0.36	3.11	9	21	209	1.24	0.53	19	87	43	4.42	0.15	0.48	39	1.07	0.16	1.5	0.11	47	23	6	43	60	14	150	5.05	0.15	0.46	0.20		4.62	12.50
103	87	0.43	3.79	7	21	257	1.14	0.57	18	99	38	4.50	0.20	0.60	46	1.16	0.15	1.9	0.10	46	24	7	51	63	15	151	6.04	0.20	0.44	0.19		4.96	13.94
104	88	0.41	3.75	7	22	254	1.35	0.29	19	95	40	4.53	0.18	0.60	45	1.23	0.17	1.8	0.10	50	26	7	52	65	15	152	5.65	0.21	0.43	0.19		5.29	13.29
105	89	0.40	3.86	9	24	257	1.21	0.50	19	97	40	4.50	0.14	0.63	46	1.23	0.12	1.9	0.10	50	27	7	52	68	15	152	5.52	0.27	0.35	0.15		5.33	13.05
106	90	0.85	3.04	9	24	271	1.59	0.78	19	95	64	4.60	0.21	0.45	37	0.98	0.16	1.7	0.11	49	74	6	47	63	15	267	6.65	0.28	0.48	0.21		5.61	15.03
107	91	0.40	3.53	9	20	232	1.00	0.73	18	97	58	4.47	0.18	0.58	43	1.14	0.10	2.0	0.09	48	26	7	42	64	15	238	4.98	0.31	0.38	0.16		4.72	12.00
108	92	0.37	3.92	8	26	276	1.26	0.57	21	100	49	4.52	0.15	0.66	48	1.21	0.12	2.1	0.10	58	29	8	51	73	16	180			0.33	0.14		4.18	12.49
109	93	0.41	4.05	10	26	258	1.12	0.41	20	102	44	4.57	0.15	0.67	48	1.22	0.14	1.9	0.09	54	26	8	54	72	16	170	5.16	0.15	0.41	0.18		4.52	12.72
110	94	0.30	3.89	9	25	264	0.73	0.42	22	82	37	4.82	0.12	0.61	48	0.94	0.13	1.9	0.10	54	24	8	49	72	14	167	4.01	0.11	0.41	0.18		4.18	11.02
111	95	0.21	4.15	6	27	242	0.99	0.16	21	78	40	4.55	0.11	0.65	47	1.30	0.06	2.0	0.11	59	22	8	49	70	15	135	4.77	0.25	0.39	0.17		4.33	12.69
112	96	0.23	4.17	7	28	203	1.39	0.09	20	83	41	4.44	0.08	0.71	44	1.85	0.15	1.9	0.11	74	18	9	50	72	15	110	2.89	0.07	0.34	0.15		4.44	8.72
113	97	0.22	4.31	5	30	246	1.14	0.15	21	90	46	4.73	0.13	0.79	48	1.59	0.08	2.0	0.11	69	30	9	49	78	16	142	3.35	0.15	0.28	0.12		4.49	9.74
114	98	0.23	4.35	7	29	238	1.01	0.14	22	90	50	4.89	0.11	0.75	46	1.67	0.09	2.2	0.10	81	22	9	50	80	16	125	3.35	0.14	0.36	0.16		5.05	10.17
115	99	0.18	3.34	8	5	243	0.64	0.51	20	73	39	5.10	0.13	0.48	34	1.02	0.07	5.7	0.06	75	19	8	39	66	19	144	2.98	0.20	0.34	0.15	2.50	4.70	7.56
116	99	0.38	3.15	12	4	347	0.77	0.59	21	73	46	6.26	0.14	0.49	32	1.10	0.34	1.7	0.06	61	30	6	45	62	14	174	5.12	0.16	0.52	0.23	2.50	4.70	12.53
117	99	0.33	2.87	9		272	0.71	0.54	22	71	47	5.46	0.15	0.39	29	1.06	0.28	1.5	0.07	66	33	6	41	58	15	171	4.59	0.13	0.37	0.16	2.50	4.70	10.76
118	99	0.51	2.70	7		327	0.89	0.53	21	65	49	5.08	0.13	0.34	25	0.97	0.46	1.3	0.09	65	31	5	46	56	16	160	6.49	0.17	0.42	0.18	2.50	4.70	16.00
119	99	0.30	3.20	8	3	250	0.77	0.60	21	75	52	5.38	0.17	0.49	32	1.09	0.22	1.7	0.07	66	32	7	43	63	16	182	5.69	0.12	0.38	0.16	2.50	4.70	14.86
120	99	0.42	3.21	11	6	327	0.86	0.73	21	80	50	5.77	0.16	0.49	32	1.01	0.40	1.7	0.07	61	32	6	49	64	15	180	6.79	0.14	0.47	0.20	2.50	4.70	16.45
121	99	0.35	3.35	10	12	304	0.85	0.59	21	71	47	5.39	0.15	0.53	34	1.00	0.31	1.7	0.07	58	30	7	48	64	14	180	7.62	0.15	0.44	0.19	2.50	4.70	16.48
122	99	0.25	3.29	9	11	268	0.83	0.82	19	71	51	5.14	0.15	0.50	32	0.98	0.13	1.8	0.07	57	29	7	46	64	15	179	8.56	0.36	0.44	0.19	2.50	4.70	17.65

Table 41 **Description of the samples in-between the Gorki and the Saratov reservoir.**

No.	New No.	Name	E	N	Description	km	Year
123	100	9	43.52867	56.57085		1364	1997
124	101	10	43.85350	56.39950		1394	1997
125	102	10A	43.85350	56.39950		1394	1997
126	103	12	44.03240	56.33920		1410	1997
127	104	13	44.18210	56.25460		1419	1997
128	105	14	44.32222	56.17855		1442	1997
129	106	15 A	44.32222	56.17855		1442	1997
130	107	15 B	44.32222	56.17855		1442	1997
131	108	15 C	44.32222	56.17855		1442	1997
132	109	16A	44.77110	56.06580	entrance harbour Rabotky, sandy mud and sand	1468	1997
133	110	16B	44.77110	56.06580	entrance harbour Rabotky, sandy mud and sand	1468	1997
134	111	17	45.03675	56.05285	Lyskowo, mud	1494	1997
135	112	Volga 1	45.94643	56.16175		1565	1999
136	113	Volga 2	47.21893	56.18008	~100m from left bank Opposite to Cheboksary	1668	1999
137	114	Volga 3	47.23338	56.17748	~50m from left bank Near Sosnovka	1670	1999
138	115	18A	47.26400	56.15843	closest to harbour entrance, very sandy	1672	1997
139	116	18B	47.27092	56.16413	about middle of river, extremely muddy	1672	1997
140	117	18C	47.27635	56.16808	toward left bank, very sandy	1672	1997
141	118	19	47.39763	56.13633	Cheboksary dam	1684	1997
142	118	20	47.42947	56.14033	Cheboksary dam	1684	1997
143	118	21	47.43358	56.14417	Cheboksary dam	1684	1997
144	118	22A	47.43718	56.14842	Cheboksary dam	1684	1997
145	118	22B1	47.43718	56.14842	Cheboksary dam	1684	1997
146	118	22B2	47.43718	56.14842	Cheboksary dam	1684	1997
147	118	23	47.44108	56.15550	Cheboksary dam	1684	1997
148	118	24A	47.44333	56.15927	Cheboksary dam	1684	1997
149	118	24B	47.44333	56.15927	Cheboksary dam	1684	1997
150	119	Volga 4	47.58092	56.11525	200m below mouth Tsivil river	1693	1999
151	120	Bolshaya Kokshaga	47.81093	56.13477	20m from right bank	1707	1999
152	121	Volga 5	47.91623	56.07825	Behind the Urakovsky Island	1717	1999
153	122	Volga 6	48.00023	55.97817	Butyakova harbor near Zvenigovo	1731	1999
154	123	Lopatinsky 1	48.01650	55.95800	Lopatinskij channel	1732	1999
155	124	Lopatinsky 2	48.02050	55.95750	Lopatinskij Island-Lake	1732	1999
156	125	Volga 7	48.00263	55.97930	Near Lopatinskij Island	1733	1999
157	126	Volga 8	48.00027	55.96793	Volga's current flow between Lopatinsky Island and left bank (Volzhsk town); Near the paper factory of Volzhsk	1735	1999
158	127	Volga 10	48.56898	55.82717		1790	1999
159	128	Volga 9	48.74510	55.78752	70 m from left bank	1795	1999
160	129	Kazan harbor	49.09547	55.78250	Locomotiv harbor	1805	1999
161	130	Volga 11	49.04748	55.72558	500m downstream from wastewater-treatment plant outlet	1815	1999
162	131	Volga 12	48.99728	55.61065	500m to left bank. Borovoe Matyshino	1826	1999
163	132	Volga 13	49.10127	55.35720	right bank. Krasnovidovo	1856	1999
164	133	Volga 14	49.26617	55.26730	Volzhsco-Kamsky reservation area	1873	1999
165	134	Volga 15	49.17055	55.14655	Kyibyshevscy harbor	1893	1999
166	135	Volga 16	48.88760	54.88097	20m to right bank	1933	1999
167	136	Volga 17	48.42350	54.42185	1 km to right bank	2075	1999
168	137	Volga 18	48.38372	54.26822	500m to right bank. River port of Ulianovek City	2085	1999
169	138	Volga 19	49.15445	53.46793		2185	1999
170	139	Volga 20	49.24470	53.44308		2190	1999
171	140	Volga 21	49.44622	53.47052	Kuibyshev dam	2209	1999
172	140	Volga 22	49.44857	53.46680	Kuibyshev dam	2209	1999
173	140	Volga 23	49.44917	53.46377	Kuibyshev dam	2209	1999
174	140	Volga 24	49.44803	53.45908	Kuibyshev dam	2209	1999
175	140	Volga 25	49.44870	53.45248	Kuibyshev dam	2209	1999
176	140	Volga 26	49.45197	53.44692	Kuibyshev dam	2209	1999
177	141	Volga 27	49.48442	53.46760	Togliatti harbor	2210	1999
178	142	Volga 28	50.06962	53.17068	Samara harbor	2280	1999
179	143	Volga 29	50.08713	53.17728	Samara harbor 2	2280	1999
180	144	WG 1	48.34163	52.71785		2412	1998
181	145	WG 2	48.32342	52.70443		2415	1998
182	146	WG 3	48.25760	52.51168		2435	1998
183	147	WG 4	48.11993	52.45027		2445	1998
184	148	WG 5	47.74817	52.06075	Saratov dam	2501	1998
185	148	WG 6	47.74975	52.05658	Saratov dam	2501	1998
186	148	WG 7	47.75170	52.05390	Saratov dam	2501	1998
187	148	WG 8	47.75530	52.05090	Saratov dam	2501	1998
188	148	WG 9	47.75900	52.04760	Saratov dam	2501	1998
189	148	WG 10	47.76230	52.04460	Saratov dam	2501	1998
190	148	WG 11	47.40500	52.03300	Saratov dam	2501	1998

No. refers to the original data set; *New No.* to the data set adapted for interpretation (see p. 232)

Table 42 Measured parameters of the samples in-between the Gorki and the Saratov reservoir.

No.	New No.	Ag	Al [%]	As	B	Ba	Ca [%]	Cd	Co	Cr	Cu	Fe [%]	Hg	K [%]	Li	Mg [%]	Mn [%]	Mo	Na [%]	Ni	Pb	Sc	Sr	V	Y	Zn	C [%]	S [%]	P_2O_5 [%]	P [%]	CO_3 [%]	105°	550°
123	100			26				0.72		43	48	7.14	0.12		28		0.45				74					124			0.65	0.28	2.50		
124	101	0.27	2.99	13	6	238	1.31	0.38	23	62	33	5.77	0.10	0.53	35	1.55	0.22	1.5	0.07	58	19	7	50	60	16	130	2.71	0.13	0.42	0.18	2.50	4.70	7.81
125	102	0.34	3.07	8	4	214	1.57	0.47	22	59	31	4.82	0.07	0.51	34	1.74	0.20	1.5	0.09	61	18	7	57	58	15	142	2.56	0.09	0.31	0.13	2.50	4.70	7.79
126	103	0.32	2.81	8	12	170	2.16	0.71	14	58	36	4.48	0.12	0.53	27	0.98	0.17	1.3	0.08	40	16	5	156	44	13	101	4.25	0.22	0.66	0.29	2.50	4.70	9.76
127	104	0.29	3.11	7	14	227	1.82	0.84	15	71	38	4.86	0.14	0.58	30	1.07	0.10	1.5	0.15	45	18	6	114	53	15	141	3.29	0.49	0.80	0.35	2.50	4.70	7.72
128	105	0.24	3.20	7	13	209	1.17	0.60	17	67	37	5.12	0.12	0.56	33	1.25	0.13	1.6	0.08	46	25	6	66	56	14	135	3.42	0.26	0.54	0.23	2.50	4.70	7.69
129	106	0.23	3.07	6	10	205	1.11	0.68	17	67	39	5.04	0.14	0.51	33	1.30	0.09	1.6	0.08	48	34	7	57	54	14	152	2.77	0.57	0.38	0.16	2.50	4.70	6.77
130	107	0.23	3.12	7	10	213	0.96	0.81	17	72	43	4.92	0.16	0.51	33	1.22	0.10	1.5	0.07	49	42	7	49	58	15	161	2.56	0.35	0.38	0.16		4.70	20.01
131	108	0.24	3.12	8	11	210	1.06	0.67	18	68	44	5.34	0.19	0.52	33	1.20	0.10	1.6	0.06	50	58	7	55	61	15	174	2.72	0.33	0.46	0.20		4.70	5.94
132	109	0.16	2.85	5	13	152	2.24	0.63	14	55	31	3.63	0.08	0.65	32	1.85	0.06	1.4	0.08	41	14	6	115	46	13	82	2.81	0.18	0.33	0.15	7.00	4.70	4.71
133	110			19				1.10		67	56	5.13	0.12		20		0.47				11					191			0.66	0.29	2.50		
134	111	0.16	2.82	9	17	161	3.88	0.18	13	49	28	3.21	0.04	0.71	35	2.61	0.07	1.5	0.10	43	12	6	218	47	12	68	3.64	0.32	0.26	0.11	12.00	4.70	5.37
135	112	0.24	4.87	12	25	238	1.45	0.60	24	112	50	5.41	0.37	0.89	48	1.45	0.15	2.1	0.10	77	21	10	120	94	20	149			0.37	0.16	2.50		
136	113	0.31	3.18	19	1	355	0.75	0.33	16	62	28	8.57	0.30	0.24	35	0.77	0.14	2.3	0.08	49	22	6	78	73	12	124	3.66	0.25	0.67	0.29	2.50	4.70	10.45
137	114							0.35		69	29	6.23	0.12				0.11				20					117	4.94	0.55	0.35	0.15		6.20	12.99
138	115	0.51	3.04	17	14	299	1.58	0.41	18	65	32	4.83	0.10	0.62	30	1.23	0.45	1.6	0.13	55	16	6	131	61	14	98	4.25	0.13	0.53	0.23	2.50	4.70	10.08
139	116	0.40	3.12	12	9	300	1.10	0.54	18	70	33	5.53	0.12	0.58	30	1.14	0.39	1.5	0.08	53	19	6	104	61	15	114	4.04	0.27	0.57	0.25	2.50	4.70	12.13
140	117	0.37	3.55	15	16	298	1.08	0.49	19	75	33	5.58	0.11	0.68	34	1.18	0.37	1.8	0.09	56	19	7	113	68	15	121	3.75	0.07	0.52	0.22	2.50	4.70	11.44
141	118			14				0.34		66	39	4.68	0.10				0.55			68	32					110			0.56	0.24	2.50		
142	118	0.48	3.32	9	15	302	1.59	0.40	18	68	32	4.57	0.09	0.66	32	1.23	0.43	1.7	0.14	58	17	7	114	65	14	101	4.91	0.27	0.46	0.20	2.50	4.70	11.66
143	118	0.75	3.23	15	12	361	1.56	0.52	21	68	32	4.78	0.11	0.60	29	1.25	0.83	1.8	0.14	59	18	7	135	65	15	122	4.18	0.11	0.56	0.24	2.50	4.70	10.17
144	118	0.21	3.74	6	16	244	0.80	0.37	17	70	29	4.88	0.10	0.65	36	1.09	0.14	1.8	0.08	49	16	7	80	66	14	106	3.82	0.16	0.35	0.15		4.70	10.32
145	118	0.27	3.80	11	18	241	1.00	0.71	19	85	41	5.35	0.16	0.74	37	1.29	0.19	1.9	0.08	60	19	8	78	70	16	127	3.08	0.22	0.48	0.21	2.50	4.70	9.51
146	118	0.18	3.90	7	13	234	0.49	0.25	16	68	26	4.38	0.07	0.53	39	0.99	0.07	2.0	0.07	47	16	8	50	67	14	91	3.39	0.03	0.25	0.11	2.50	4.70	9.42
147	118	0.47	3.51	14	24	303	1.07	0.58	18	77	33	5.63	0.17	0.71	36	1.05	0.34	1.6	0.08	54	20	7	105	72	15	121	4.32	0.19	0.58	0.25	2.50	4.70	13.07
148	118	0.64	3.87	20	25	297	0.96	0.52	20	84	35	5.87	0.21	0.82	39	1.09	0.44	1.8	0.09	58	21	8	101	80	17	127	3.37	0.08	0.58	0.25	2.50	4.70	10.18
149	118	1.87	3.40	40	23	376	1.17	0.40	18	72	29	5.47	0.37	0.70	33	0.98	0.72	2.1	0.08	48	19	6	140	72	15	98	4.15	0.10	0.66	0.29	2.50	4.70	12.30
150	119	0.21	4.50	11	28	197	1.54	0.32	27	89	42	4.69	0.08	0.76	49	1.37	0.12	1.9	0.08	85	16	10	95	84	17	102	1.66	0.04	0.27	0.12	2.50	4.70	6.56
151	120	0.28	4.77	18	30	347	1.10	0.50	22	92	34	7.52	0.08	0.81	45	1.16	0.17	2.0	0.09	61	20	10	98	87	17	135	3.51	0.17	0.70	0.30	2.50	6.72	10.74
152	121	0.28	3.09	10	10	183	1.18	0.31	19	78	40	4.79	1.95	0.47	30	1.15	0.12	1.3	0.07	62	18	7	92	62	16	118	2.37	0.04	0.32	0.14	2.50	4.70	7.17
153	122	0.36	3.46	14	17	265	1.31	0.83	19	82	57	7.12	0.29	0.63	40	1.17	0.16	1.8	0.07	63	63	8	89	79	16	243	3.59	0.32	0.78	0.34	2.50	4.70	10.22
154	123	0.20	4.66	8	28	237	1.21	0.47	23	91	38	5.77	0.11	0.82	46	1.36	0.09	2.1	0.09	67	19	10	99	80	18	134	3.32	0.20	0.41	0.18	2.50	4.70	8.34
155	124	0.28	3.63	6	20	290	2.82	0.84	16	92	54	4.43	0.19	0.63	39	1.10	0.09	3.9	0.13	58	19	7	164	66	15	148	6.81	0.98	0.31	0.13	2.50	4.70	12.17
156	125	0.76	4.08	15	20	290	1.48	0.38	25	88	37	4.90	1.77	0.71	39	1.29	0.61	1.8	0.12	70	21	8	143	79	18	134	3.94	0.12	0.47	0.20	2.50		
157	126	0.24	3.26	11	12	197	1.95	0.60	18	73	37	5.79	0.25	0.50	31	1.08	0.19	1.2	0.11	59	18	9	162	76	17	115	3.88	0.23	0.56	0.24	2.50	4.70	11.40
158	127	0.17	4.15	9	17	212	1.12	0.48	19	91	42	5.35	0.88	0.68	36	1.30	0.09	1.7	0.10	59	20	8	99	75	15	150	3.08	0.24	0.56	0.24	2.50	4.70	8.19
159	128	0.24	4.22	8	36	228	2.90	0.47	19	87	39	4.15	0.83	0.87	48	1.85	0.12	2.0	0.08	65	17	9	122	75	15	113	3.39	0.19	0.28	0.12		4.70	8.79
160	129	0.61	4.35	9	26	257	1.62	0.91	20	94	55	5.38	0.26	0.80	48	1.35	0.16	2.1	0.08	68	41	9	158	78	16	151	3.52	0.23	0.53	0.23	2.50	6.41	10.42
161	130	2.61	3.56	10	14	217	1.48	4.60	21	284	118	5.02	0.30	0.46	30	1.20	0.15	2.5	0.06	80	22	8	113	67	17	177	2.46	0.12	0.42	0.18	2.50	4.70	7.74
162	131	1.07	4.20	9	15	235	1.11	1.11	22	144	44	5.47	2.66	0.61	37	1.31	0.12	1.6	0.09	66	19	8	106	74	17	146	2.50	0.13	0.60	0.26	2.50	4.70	7.75
163	132	0.26	2.99	7	40	127	11.20	0.30	13	55	29	2.90	0.13	0.73	51	4.98	0.12	1.9	0.13	45	10	6	144	51	10	58	5.95	0.09	0.26	0.11	38.00	4.70	5.20
164	133	0.46	3.32	7	13	191	0.89	0.43	18	81	39	4.58	0.06	0.50	29	1.15	0.12	1.3	0.06	60	15	8	88	61	16	101	2.15	0.09	0.35	0.15	2.50	4.70	6.67
165	134	0.32	3.39	7	18	150	2.64	0.20	17	64	37	3.55	0.06	0.62	32	1.82	0.08	1.3	0.07	57	15	8	87	63	15	80	2.02	0.04	0.22	0.10	12.50	4.70	4.06
166	135	0.38	3.83	9	24	205	3.64	0.26	18	77	41	4.22	0.07	0.77	40	3.13	0.21	1.5	0.11	69	15	8	117	67	14	90	3.82	0.07	0.32	0.14	2.50	4.70	7.64
167	136	0.21	5.01	9	21	264	1.16	0.30	27	103	43	5.70	1.09	0.85	45	1.60	0.14	2.1	0.11	91	18	11	105	102	19	114	2.63	0.12	0.29	0.13	2.50	4.70	8.19
168	137	0.67	3.79	8	38	193	0.79	4.39	20	159	103	4.61	0.21	0.68	59	1.04	0.05	3.1	0.06	51	23	10	90	94	16	164	1.74	0.13	0.27	0.12	2.50	4.70	4.06
169	138	0.48	3.86	7	26	299	1.26	0.11	20	87	44	5.47	1.64	0.72	42	1.27	0.27	1.8	0.10	68	21	9	118	86	17	113	2.81	0.20	0.31	0.13	2.50	4.70	7.63
170	139	0.34	4.65	8	29	278	1.20	0.16	22	101	50	5.28	0.54	0.92	52	1.39	0.20	2.2	0.10	73	22	10	122	102	17	128	2.34	0.15	0.27	0.12	2.50	4.70	7.55
171	140	0.39	4.68	7	35	287	1.51	0.64	22	99	56	5.11	0.10	0.91	46	1.52	0.11	2.3	0.09	77	26	11	125	94	19	126	3.16	0.39	0.26	0.11	2.50	4.70	7.85
172	140	0.41	4.25	10	27	323	1.30	0.72	21	94	66	5.64	0.13	0.79	41	1.42	0.16	2.1	0.07	75	30	10	122	87	19	148	3.01	0.37	0.29	0.12	2.50	4.70	8.01
173	140	0.43	4.86	8	44	314	1.38	0.80	23	109	64	5.68	0.21	1.10	62	1.49	0.16	2.7	0.12	82	29	11	123	103	19	157	3.04	0.42	0.30	0.13	2.50	4.70	8.30
174	140	0.52	5.12	9	46	352	1.37	0.65	23	107	54	5.55	0.10	1.06	62	1.46	0.33	2.4	0.09	82	29	11	126	105	20	135	2.66	0.13	0.29	0.13	2.50	4.70	8.36
175	140	0.58	4.85	10	40	399	1.36	0.59	23	99	51	5.63	0.11	0.96	48	1.42	0.53	2.1	0.09	78	27	11	138	102	20	128	3.08	0.11	0.37	0.16	2.50	4.70	9.28
176	140	0.30	4.43	8	47	311	1.32	0.59	21	104	57	5.23	0.18	0.97	59	1.41	0.18	2.4	0.09	79	25	11	118	97	19	149	2.55	0.26	0.27	0.12	2.50	4.70	7.33
177	141	0.62	4.06	23	24	611	2.63	0.92	27	94	119	6.75	0.34	0.75	36	1.94	0.11	2.2	0.17	83	104	9	130	97	17	359	5.35	0.60	0.37	0.16	2.50		
178	142	0.69	4.65	15	31	288	4.35	0.92	22	102	48	4.63	0.10	0.91	49	1.82	0.49	2.0	0.14	90	25	9	217	78	15	114	4.19	0.11	0.37	0.16	2.50	4.70	9.12
179	143	0.35	4.50	15	27	244	3.60	1.22	18	105	71	5.06	1.68	0.89	42	1.91	0.10	2.1	0.13	88	57	10	173	92	15	168	4.18	0.23	0.37	0.16	8.00	4.70	7.45
180	144	0.22	3.79	9	40	126	0.92	0.33	23	70	38	4.67	0.09	0.73	61	0.99	0.13	3.5	0.11	48	17	11	103	101	16	118	1.47	0.05	0.24	0.10	2.50	4.79	6.79
181	145	0.20	3.61	9	29	138	0.99	0.15	21	67	36	4.47	0.10	0.72	56	0.97	0.11	3.8	0.13	47	16	11	111	95	15	111	1.46	0.04	0.23	0.10	2.50	4.63	6.24
182	146	0.14	3.19	3	15	162	2.30	0.19	16	65	36	3.08	0.06	0.65	26	1.17	0.07	1.4	0.11	59	13	8	123	60	13	81	3.26	0.16	0.27	0.12	2.50	4.23	9.07
183	147	0.12	3.51	7	15	164	2.61	0.16	22	71	38	4.06	0.08	0.75	38	1.43	0.11	1.8	0.12	64	18	10	119	78	15	88	2.01	0.04	0.23	0.10	2.50	4.55	6.31
184	148	0.22	3.85	12	30	164	0.88	0.39	22	77	45	5.04	0.14	0.74	50	0.98	0.11	9.6	0.12	58	21	11	116	106	17	164	2.52	0.45	0.30	0.13	2.50	4.42	7.76
185	148	0.15	4.15	7	28	180	0.94	0.35	22	82	42	4.72	0.08	0.80	52	1.13	0.08	6.0	0.12	61	19	12	112	105	17	124	2.33	0.25	0.25	0.11	2.50	4.62	7.99
186	148	0.23	3.41	8	15	152	0.90	0.25	20	70	39	4.94	0.08	0.66	44	0.99	0.08	5.6	0.12	56	18	10	110	89	16	117	2.35	0.23	0.26	0.11	2.50	4.39	7.78
187	148	0.16	3.79	8	1	174	0.92	0.28	20	78	38	4.91	0.06	0.74	47	1.02	0.09	3.0	0.11	58	19	11	115	86	16	118	2.37	0.21	0.25	0.11	2.50	4.87	8.14
188	148	0.14	4.00	8	26	171	0.97	0.98	21	78	41	4.82	0.05	0.77	52	1.04	0.11	6.5	0.11	57	19	11	116	105	17	119	2.42	0.26	0.26	0.11	2.50	4.44	8.18
189	148	0.15	3.87	6	21	177	0.94	0.27	21	79	40	4.73	0.06	0.76	46	1.11	0.09	4.9	0.10	60	19	11	114	95	17	118	2.40	0.19	0.24	0.10	2.50	4.47	8.18
190	148	0.14	3.57	6	17	176	0.99	0.32	20	75	41	4.55	0.09	0.70	44	1.08	0.10	4.6	0.09	59	19	11	106	91	16	119	2.25	0.30	0.23	0.10	2.50	4.59	7.72

Table 43 **Description of the samples in-between the Saratov and the Volgograd reservoir.**

No.	New No.	Name	E	N	Description	km	Year
191	149	WG 12	47.84010	52.05580		2530	1998
192	150	WG 13	46.93600	51.81100	Bolz	2570	1998
193	151	WG 14	46.74160	51.72027	Markx-town	2593	1998
194	152	WG 15	46.63085	51.71235	Karaman-Vol	2600	1998
195	153	WG 16	46.53917	51.81568	Tereschka	2605	1998
196	154	WG 17	46.49567	51.79772	Usowja	2620	1998
197	155	WG 18	46.32702	51.77983	Tschardim	2630	1998
198	156	WG 19	46.30030	51.69477		2635	1998
199	157	WG 20	46.20583	51.65443	Drain Heven	2645	1998
200	158	WG 21	46.03200	51.52075	city of Saratov	2660	1998
201	159	WG 22	45.99680	51.50908	city of Saratov	2661	1998
202	160	WG 23	45.96250	51.48427	city of Saratov	2663	1998
203	161	WG 24	45.96143	51.44602	city of Saratov	2665	1998
204	162	WG 25	46.19258	51.51458		2655	1998
205	163	WG 26	46.09800	51.53017		2660	1998
206	164	WG 27	45.82275	51.33975		2695	1998
207	165	WG 28	45.77677	51.23427		2705	1998
208	166	WG 29	45.81692	51.12352		2718	1998
209	167	WG 30	46.03102	50.85055		2755	1998
210	168	WG 31	45.91710	50.83400	Salotoe	2765	1998
211	169	WG 32	45.65692	50.73342		2788	1998
212	170	WG 33	45.85868	50.42512		2826	1998
213	171	WG 34	45.62700	50.24915		2854	1998
214	172	WG 35	45.49992	50.15842		2868	1998
215	173	WG 50	45.41377	50.08300	Kamtchin	2877	1998
216	174	WG 36	45.39543	50.09813	Tameschitt	2877	1998
217	175	WG 37	45.32783	49.82583		2908	1998
218	176	WG 38	45.08413	49.54968		2945	1998
219	177	WG 39	44.88517	49.17827		2988	1998
220	178	WG 40	44.82733	49.04708		3003	1998
221	179	WG 41	44.66080	48.86542		3020	1998
222	180	WG 42	44.66080	48.86527	Volgograd dam	3039	1998
223	180	WG 43	44.66338	48.86335	Volgograd dam	3039	1998
224	180	WG 44	44.66668	48.86167	Volgograd dam	3039	1998
225	180	WG 45	44.67347	48.85902	Volgograd dam	3039	1998
226	180	WG 46	44.67697	48.85685	Volgograd dam	3039	1998
227	180	WG 47	44.68150	48.85355	Volgograd dam	3039	1998
228	180	WG 48	44.68447	48.85068	Volgograd dam	3039	1998
229	180	WG 49	44.69142	48.84627	Volgograd dam	3039	1998

No. refers to the original data set; *New No.* to the data set adapted for interpretation (see p. 232)

Table 44 **Measured parameters of the samples in-between the Saratov and the Volgograd reservoir.**

No.	New No.	Ag	Al [%]	As	B	Ba	Ca [%]	Cd	Co	Cr	Cu	Fe [%]	Hg	K [%]	Li	Mg [%]	Mn [%]	Mo	Na [%]	Ni	Pb	Sc	Sr	V	Y	Zn	C [%]	S [%]	P_2O_5 [%]	P [%]	CO_3 [%]	105°	550°
191	149	0.17	4.35	3	18	204	1.64	0.17	19	83	43	4.24	0.07	0.91	35	1.43	0.12	1.7	0.11	67	18	11	118	80	16	112	3.27	0.17	0.31	0.13	2.50	5.13	9.67
192	150	0.23	4.31	10	15	186	1.14	0.16	21	86	36	4.84	0.06	0.74	39	1.27	0.19	2.1	0.11	70	14	12	112	91	16	106	1.64	0.05	0.32	0.14	2.50	5.47	7.01
193	151	0.13	4.06	6	10	210	1.20	0.29	20	86	38	4.63	0.07	0.71	32	1.30	0.11	1.6	0.14	69	19	11	91	78	16	113	2.23	0.30	0.29	0.13	2.50	4.98	8.01
194	152	0.14	4.17	5	10	198	1.13	0.25	20	87	37	4.49	0.07	0.78	35	1.36	0.11	1.8	0.11	69	16	11	100	80	16	115	2.04	0.14	0.24	0.10	2.50	4.78	7.39
195	153	0.15	3.08	4	15	110	6.33	0.20	12	75	25	3.37	0.03	0.84	23	0.84	0.06	1.8	0.10	38	12	7	201	66	12	77	4.32	0.19	0.22	0.09	15.00	4.81	9.11
196	154	0.14	3.51	5	18	153	3.77	0.21	14	79	28	3.42	0.03	0.87	27	0.94	0.09	2.0	0.10	44	13	8	158	75	14	83	3.73	0.13	0.23	0.10	10.00	4.75	8.59
197	155	0.16	3.39	5	12	183	1.40	0.28	17	78	33	3.75	0.05	0.69	31	1.03	0.08	1.9	0.11	54	16	9	101	75	14	102	2.72	0.27	0.23	0.10	2.50	4.36	8.12
198	156	0.18	3.66	5	10	187	1.15	0.28	19	79	36	4.43	0.08	0.66	32	1.22	0.12	1.7	0.11	64	17	10	104	73	16	110	2.70	0.17	0.27	0.12	2.50	4.55	9.05
199	157	0.13	3.60	5	12	164	1.81	0.22	17	76	35	3.98	0.04	0.80	35	1.29	0.07	1.8	0.11	55	17	10	107	73	15	103	2.22	0.45	0.20	0.09	2.50	5.22	7.39
200	158	0.87	3.84	7	21	228	3.34	0.51	16	83	63	3.90	0.23	0.80	37	1.40	0.07	2.4	0.16	60	63	9	146	113	15	293	4.53	0.30	0.35	0.15	6.50	5.12	11.26
201	159	0.91	3.59	7	20	223	2.67	2.68	15	97	111	3.81	0.30	0.74	33	1.46	0.07	2.4	0.12	53	102	9	123	78	14	271	4.92	0.20	0.38	0.17	2.50	5.28	11.82
202	160	0.83	2.57	6	21	295	6.27	9.65	12	124	108	3.09	0.34	0.75	24	1.83	0.05	2.6	0.13	59	108	6	192	53	14	303	6.38	0.35	0.45	0.20	16.00	4.09	10.99
203	161	0.77	3.15	8	18	216	4.57	6.17	16	161	151	4.10	0.65	0.70	31	1.21	0.07	3.1	0.17	78	59	7	206	110	14	209	6.14	0.41	0.57	0.25	9.00		
204	162	0.16	3.81	5	13	185	1.55	0.33	18	80	42	4.49	0.07	0.82	33	1.38	0.06	1.9	0.20	64	20	10	78	72	16	121	2.29	0.38	0.26	0.11	2.50	5.28	8.00
205	163	0.14	4.24	6	21	179	0.89	0.15	21	86	35	4.27	0.08	0.74	37	1.32	0.08	1.8	0.06	70	15	11	86	87	16	98	1.50	0.03	0.22	0.09	2.50	5.28	6.57
206	164	0.47	3.58	5	40	178	1.87	0.92	16	88	45	3.67	0.15	0.97	33	1.05	0.08	2.3	0.11	49	30	9	189	76	14	124	3.22	0.09	0.31	0.14	2.50	5.25	9.48
207	165	0.42	3.12	7	33	182	1.62	0.62	15	79	40	3.60	0.11	0.87	28	0.95	0.08	2.4	0.08	41	32	8	188	68	15	117	2.84	0.12	0.32	0.14	2.50	5.34	8.71
208	166	0.12	2.64	5	40	107	6.41	0.19	9	66	20	2.71	0.02	1.06	24	0.80	0.03	3.7	0.13	32	9	6	309	50	11	72	3.74	0.12	0.29	0.12	13.50	4.59	8.03
209	167	0.25	3.99	7	27	192	2.99	0.26	20	82	37	3.83	0.03	1.06	35	1.38	0.14	2.1	0.10	58	19	10	170	80	16	95	2.06	0.05	0.24	0.10	7.00	4.74	6.98
210	168	0.16	3.68	5	26	158	3.07	0.12	18	73	32	3.68	0.02	1.06	33	1.46	0.07	1.7	0.10	49	13	9	141	71	16	81	1.65	0.03	0.21	0.09	9.00	3.76	5.36
211	169	0.10	2.19	5	39	98	14.00	0.13	8	49	15	2.31	0.02	1.04	19	0.64	0.03	1.7	0.10	23	10	5	325	47	11	51	4.36	0.09	0.28	0.12	26.00	3.45	5.88
212	170	0.11	3.95	5	29	167	1.90	0.18	15	92	31	3.68	0.03	0.99	30	1.20	0.07	1.9	0.07	51	14	10	126	84	16	85	1.77	0.05	0.22	0.10	2.50	4.72	6.06
213	171	0.17	4.61	5	33	223	1.84	0.31	23	86	37	4.57	0.03	1.38	41	1.62	0.08	2.1	0.11	56	13	11	110	89	18	91	0.88	0.03	0.20	0.09	2.50	4.15	5.14
214	172	0.18	3.67	7	31	179	2.20	0.13	17	90	32	4.07	0.05	1.08	31	1.34	0.10	2.4	0.09	51	14	9	136	83	16	85	1.52	0.05	0.26	0.11	2.50	4.19	5.74
215	173	0.10	3.64	6	26	153	1.69	0.59	14	92	33	4.21	0.18	0.97	27	1.05	0.05	2.1	0.07	44	21	9	114	76	15	119	3.58	0.20	0.30	0.13	5.00	3.36	9.55
216	174	0.28	3.54	6	27	233	2.65	0.26	16	104	56	3.96	0.09	1.02	28	1.22	0.07	2.2	0.09	52	65	9	146	83	17	211	2.22	0.13	0.29	0.13	2.50	4.21	6.85
217	175	0.14	4.12	3	33	213	1.76	0.07	20	80	38	4.04	0.11	1.27	36	1.48	0.07	1.6	0.10	52	14	10	115	79	17	95	1.49	0.06	0.28	0.12	2.50	3.58	5.49
218	176	0.14	4.59	5	36	191	1.95	0.07	22	86	37	4.44	0.06	1.40	41	1.62	0.09	1.8	0.11	54	14	11	121	89	18	96	1.04	0.03	0.24	0.11	5.00	4.00	5.25
219	177	0.16	3.91	7	21	162	1.83	0.11	16	75	34	4.07	0.08	1.01	32	1.28	0.07	1.8	0.07	51	14	9	105	76	16	84	1.57	0.06	0.26	0.11	2.50	4.54	5.97
220	178	0.05	3.44	6	13	181	1.71	0.13	19	71	36	4.31	0.14	1.03	28	1.25	0.08	1.5	0.08	49	25	9	133	74	17	110	1.53	0.06	0.26	0.11	2.50	3.82	5.79
221	179	0.20	4.04	8	39	197	1.60	0.19	24	95	33	4.45	0.06	1.24	31	1.22	0.17	2.1	0.10	56	17	10	167	105	19	108	2.04	0.12	0.33	0.14	2.50	4.07	7.57
222	180	0.27	4.41	6	41	281	0.98	0.36	23	98	40	5.07	0.08	1.27	35	1.29	0.27	2.1	0.10	60	21	11	164	108	20	113	1.88	0.10	0.32	0.14	2.50	4.40	7.53
223	180	0.28	4.31	8	38	266	0.91	0.35	23	97	42	4.91	0.09	1.23	35	1.32	0.20	2.0	0.09	64	20	11	150	102	20	120	1.82	0.10	0.32	0.14	2.50	4.73	7.30
224	180	0.51	4.12	5	30	326	1.05	0.43	21	92	42	4.70	0.08	1.15	34	1.29	0.52	2.0	0.08	65	22	11	144	93	19	118	2.10	0.12	0.32	0.14	2.50	4.61	7.71
225	180	0.34	4.59	4	34	299	0.91	0.36	22	97	44	4.88	0.07	1.24	38	1.38	0.32	1.9	0.09	71	22	11	128	98	20	127	1.80	0.08	0.27	0.12	2.50	4.17	7.59
226	180	0.19	4.73	4	32	246	0.88	0.41	22	98	46	4.86	0.07	1.27	39	1.43	0.13	1.8	0.09	68	21	12	120	97	20	133	1.57	0.07	0.24	0.10	2.50	3.61	7.69
227	180	0.26	4.48	4	30	254	0.89	0.37	22	94	46	4.81	0.08	1.21	38	1.44	0.14	1.8	0.09	67	20	11	107	93	19	124	1.67	0.10	0.24	0.11	2.50	3.76	7.64
228	180	0.44	4.30	6	26	305	1.01	0.31	22	89	42	4.94	0.05	1.19	38	1.45	0.40	1.8	0.08	68	20	11	117	90	19	114	1.86	0.05	0.32	0.14	2.50	3.94	8.11
229	180	0.27	4.28	4	25	227	1.28	0.15	22	83	40	4.81	0.07	1.19	38	1.57	0.23	1.7	0.09	62	17	11	102	84	18	105	1.31	0.03	0.25	0.11	2.50	3.29	6.88

Table 45 **Description of the samples downstream the Volgograd reservoir.**

No.	New No.	Name	E	N	Description	km	Year
230	181	VA 01	44.52255	48.53692	Volgograd left bank	3075	2000
231	182	VA 02	44.68155	48.51155	Oil storage plant 40m from right bank	3086	2000
232	183	VA 03	44.68118	48.51068	Oil storage plant 35m from right bank	3087	2000
233	184	VA 04	44.82175	48.47835	Next to Svetly Yar 30m from right bank	3098	2000
234	185	VA 05	45.16157	48.47532	Mouth of Pocrovsky(?) harbour 20m from left bank	3120	2000
235	186	VA 06	45.20745	48.45475	Mouth of Krutovsky harbour 20m from right bank	3130	2000
236	187	VA 07	45.52673	48.44923	Vyazovoy Island 15m from right bank	3159	2000
237	188	VA 08	45.69060	48.40898	Harbour near Kapustin Yar 45m from the bank	3176	2000
238	189	VA 09	46.15747	48.25012	Close to Ahtubinsk (Vladimirsky harbour) 50m from left bank 1,5km from mouth of harbour	3223	2000
239	190	VA 10	46.16042	48.23675	Vladimirsky harbour 45m from left bank 500m from the mouth	3223	2000
240	191	VA 11	46.38670	47.84628	25m from left bank	3283	2000
241	192	VA 12	46.62125	47.64450	Opposite Vetlayanka village 75m from right bank	3323	2000
242	193	VA 13	47.10920	47.31597	50m from left bank	3381	2000
243	194	VA 14	47.49810	47.01612	Opposite Seroghazovka village 30m from left bank	3436	2000
244	195	VA 15	47.76505	46.78382	Near Baranovsky Island (30m)	3483	2000
245	196	VA 16	47.89047	46.64728	Opposite Raznochinovka village (down Narimanov town) 30m from right bank	3502	2000
246	197	VA 17	47.90437	46.60205	10m from left bank	3505	2000
247	198	VA 18	48.01972	46.50108	Opposite Rastopulovka village right bank	3523	2000
248	199	VA 19	48.02990	46.50290	Rastopulovka village 40m from left bank	3523	2000
249	200	VA 20	48.01215	46.40725	30m from right bank	3536	2000
250	201	VA 21	47.99565	46.33022	Down the rail bridge left bank	3545	2000
251	202	VA 22	47.97005	46.29225	Home of Gosnadzor	3550	2000
252	203	VA 23	47.97643	46.46915	Trans. Astrakhan	3528	2000
253	203	VA 24	47.97798	46.47023	Trans. Astrakhan	3528	2000
254	203	VA 25	47.98193	46.47148	Trans. Astrakhan	3528	2000
255	203	VA 26	47.98472	46.47217	Trans. Astrakhan	3528	2000
256	203	VA 27	47.98733	46.47260	Trans. Astrakhan	3528	2000
257	204	Kern I-1	47.97643	46.46915		3528	2000
258	205	Kern II-1	47.97643	46.46915		3528	2000
259	206	VA 31	47.86992	46.20478	Volga-Kaspian channel Ship-building-plant right bank	3528	2000
260	207	Back	47.81893	46.16210		3535	2000
261	208	VA 32	47.82413	46.15300	Volga-Kaspian channel 45m from left bank	3536	2000
262	209	VA 33	47.74453	46.10165	Volga-Kaspian channel at Ikryanoe town 20m from right bank	3544	2000
263	210	*VA 34*	47.69880	45.99555	after Yamnoye town 20m from left bank	3557	2000
264	211	VA 35	47.66533	45.93982	Volga-Kaspian channel 20m from left bank	3568	2000
265	212	VA 36	47.64660	45.85395	Volga-Kaspian channel at Fyodorovka town 35m from right bank	3579	2000
266	213	VA 37	47.54175	45.82537	Volga-Kaspian channel 25m from left bank	3589	2000
267	214	VA 38	47.52792	45.79817	Volga-Kaspian channel right bank	3592	2000
268	215	VA 39	47.56357	45.77235	Volga-Kaspian channel 50m from right bank	3598	2000
269	216	Kern III-1	47.56357	45.77235		3598	2000
270	217	VA 40	47.64307	45.73072	Volga-Kaspian channel left bank	3605	2000

No. refers to the original data set; *New No.* to the data set adapted for interpretation (see p. 232)

Table 46 Measured parameters of the samples downstream the Volgograd reservoir.

No.	New No.	Ag	Al [%]	As	B	Ba	Ca [%]	Cd	Co	Cr	Cu	Fe [%]	Hg	K [%]	Li	Mg [%]	Mn [%]	Mo	Na [%]	Ni	Pb	Sc	Sr	V	Y	Zn	C [%]	S [%]	P_2O_5 [%]	P [%]	CO_3 [%]	105°	550°
230	181	0.13	3.48	7	21	152	1.35	0.17	16	75	35	3.80	0.06	0.84	41	1.28	0.05	1.7	0.09	59	13	8	106	68	15	82	1.27	0.00	0.22	0.10	6.00	4.13	6.37
231	182	0.62	3.33	16	35	245	1.77	1.49	19	92	50	5.32	2.10	0.98	38	1.24	0.20	2.0	0.18	56	28	7	140	74	16	160	3.11	0.12	0.55	0.24		2.47	10.89
232	183	0.42	3.08	7	28	228	2.00	0.95	17	89	51	4.27	1.06	0.91	38	1.22	0.10	1.9	0.14	53	27	7	144	66	17	156	2.88	0.20	0.35	0.15	5.00	3.32	9.14
233	184	0.26	3.53	10	28	202	1.43	0.11	21	81	39	4.35	0.60	0.86	41	1.25	0.15	1.7	0.13	61	21	9	107	72	15	100	1.86	0.06	0.29	0.13		3.57	7.81
234	185	0.27	4.28	11	28	197	1.07	0.12	20	94	34	4.91	0.07	0.94	48	1.31	0.13	1.9	0.16	67	14	11	132	80	14	99	1.49	0.06	0.36	0.16		4.39	8.09
235	186	0.19	3.58	8	25	162	1.66	0.05	19	80	37	4.14	0.09	0.81	44	1.34	0.10	1.7	0.11	64	14	9	114	71	14	83	1.37	0.04	0.22	0.10	5.50	4.32	6.48
236	187	0.19	4.03	6	31	183	1.40	0.05	21	84	36	4.49	0.12	0.97	47	1.41	0.10	1.8	0.14	66	15	10	114	79	15	87	1.15	0.04	0.20	0.09		3.87	6.55
237	188	0.17	3.67	6	22	173	0.93	0.06	18	81	32	4.20	0.05	0.77	40	1.13	0.09	1.6	0.11	59	14	9	102	68	15	86	1.35	0.08	0.25	0.11		3.44	6.37
238	189	0.18	3.78	6	22	175	1.06	0.16	18	82	36	4.42	0.05	0.81	40	1.18	0.09	1.7	0.09	60	16	9	97	70	14	93	1.31	0.09	0.23	0.10	5.00	3.56	6.40
239	190	0.19	3.75	5	25	171	1.10	0.19	17	81	35	4.28	0.05	0.82	41	1.16	0.11	1.6	0.10	59	14	9	99	68	14	86	1.72	0.13	0.27	0.12		3.95	6.79
240	191	0.18	4.32	6	30	191	0.88	0.05	18	91	34	4.59	0.05	0.91	47	1.26	0.07	1.9	0.12	65	13	11	112	79	15	91	0.82	0.03	0.19	0.08		7.35	5.32
241	192	0.13	3.67	6	27	146	1.79	0.12	18	76	35	3.86	0.06	0.87	43	1.34	0.08	1.6	0.09	60	13	9	107	71	14	78	1.31	0.03	0.22	0.09	2.50	2.54	6.02
242	193	0.16	3.63	5	25	147	1.31	0.15	18	79	35	4.07	0.07	0.81	41	1.27	0.08	1.6	0.11	61	14	9	102	68	14	80	1.42	0.03	0.24	0.11		5.48	5.85
243	194	0.16	3.72	5	22	140	1.27	0.10	18	78	33	3.97	0.07	0.91	42	1.32	0.08	1.5	0.10	59	13	9	89	67	14	77	1.46	0.06	0.21	0.09		5.00	5.74
244	195	0.16	3.74	6	30	138	1.55	0.11	18	79	34	4.02	0.07	0.94	45	1.38	0.08	1.6	0.09	60	13	9	95	70	15	80	1.42	0.07	0.23	0.10	2.50	5.15	5.61
245	196	0.15	3.67	5	28	146	1.83	0.13	18	76	35	3.91	0.06	0.84	43	1.32	0.08	1.7	0.10	62	13	9	104	70	14	80	1.69	0.10	0.22	0.09		5.04	6.10
246	197	0.16	3.74	5	27	151	1.36	0.23	18	79	33	3.84	0.06	0.86	43	1.30	0.09	1.7	0.09	62	13	9	99	69	15	81	1.64	0.09	0.22	0.10		4.79	6.36
247	198	0.17	3.55	5	27	141	1.76	0.15	19	89	35	3.83	0.10	0.79	42	1.34	0.10	3.2	0.10	77	13	9	110	69	14	82	1.83	0.09	0.22	0.10	2.50	5.46	6.48
248	199	0.15	3.65	4	28	146	1.25	0.11	17	76	33	3.70	0.05	0.85	42	1.27	0.07	1.6	0.09	58	13	9	93	68	14	79	1.49	0.09	0.21	0.09		4.85	5.70
249	200	0.17	3.79	6	29	158	1.64	0.15	18	79	38	4.18	0.06	0.89	46	1.41	0.07	1.8	0.20	62	17	9	110	73	14	90	1.48	0.15	0.21	0.09		5.48	6.34
250	201	0.15	3.56	4	26	146	1.47	0.20	18	75	34	3.91	0.05	0.80	42	1.27	0.08	1.6	0.09	62	15	9	100	66	14	83	1.84	0.13	0.21	0.09	2.50	4.95	6.68
251	202	0.17	4.02	8	31	167	1.25	0.18	18	84	38	4.21	0.10	0.99	47	1.39	0.08	1.7	0.09	61	27	10	92	74	15	103	1.39	0.08	0.21	0.09		4.77	5.84
252	203	0.15	3.48	5	27	133	1.52	0.16	17	72	33	3.95	0.06	0.71	38	1.42	0.09	1.4	0.08	58	13	8	91	69	13	83	1.34	0.08	0.22	0.10	2.50	5.33	5.56
253	203	0.20	4.22	5	32	145	2.10	0.16	21	87	42	3.72	0.08	0.88	49	1.80	0.08	1.7	0.11	73	15	9	116	83	16	100	1.76	0.10	0.26	0.11		5.09	6.48
254	203	0.15	3.76	6	30	144	1.93	0.14	20	78	37	3.67	0.08	0.76	42	1.62	0.10	1.5	0.10	68	14	9	105	74	15	90	1.79	0.10	0.25	0.11		4.88	6.48
255	203	0.18	3.74	6	26	143	1.83	0.18	19	78	35	3.74	0.12	0.79	42	1.59	0.11	1.6	0.10	65	14	9	107	75	14	86	1.82	0.10	0.22	0.10	2.50	5.14	6.80
256	203	0.16	3.26	6	31	127	1.47	0.16	19	68	40	3.48	0.11	0.69	33	1.35	0.07	1.3	0.20	61	11	7	102	65	12	81			0.21	0.09			
257	204	0.18	3.38	6	21	138	1.83	0.20	18	73	38	3.72	0.05	0.66	40	1.52	0.08	1.5	0.10	65	14	8	108	68	15	86	1.37	0.08	0.25	0.11		5.21	5.01
258	205	0.15	3.66	6	24	138	1.69	0.14	17	75	36	4.03	0.05	0.89	43	1.38	0.08	1.6	0.09	59	13	9	102	68	14	76	1.38	0.09	0.21	0.09		4.78	5.21
259	206	0.18	3.31	7	20	151	1.89	0.12	16	70	33	3.89	0.04	0.82	41	1.35	0.09	1.4	0.25	57	14	8	106	62	14	75	1.58	0.09	0.24	0.11	2.50	4.07	6.61
260	207	0.18	3.61	8	45	142	2.29	0.19	19	74	37	4.10	0.05	0.90	46	1.49	0.07	1.9	0.23	62	14	9	147	70	14	88	1.28	0.17	0.21	0.09	6.00	4.70	5.69
261	208	0.18	3.71	5	33	129	2.30	0.08	17	74	35	3.88	0.08	0.96	46	1.43	0.09	1.6	0.11	60	13	9	121	68	14	77	1.85	0.15	0.21	0.09	5.00	4.40	6.42
262	209	0.15	3.44	6	24	127	2.43	0.17	16	69	34	3.69	0.07	0.89	42	1.42	0.08	1.5	0.10	56	12	8	122	62	14	72	1.80	0.17	0.20	0.09		4.19	5.93
263	210	0.15	3.51	4	23	127	2.39	0.19	17	72	35	3.81	0.06	0.91	43	1.41	0.07	1.5	0.11	59	13	8	119	64	14	74	1.80	0.18	0.19	0.08		4.34	6.09
264	211	0.14	3.96	6	38	142	2.70	0.09	18	78	36	3.86	0.05	1.02	49	1.47	0.08	1.8	0.12	62	13	9	143	75	14	79	1.71	0.16	0.20	0.09		3.92	6.00
265	212	0.14	3.80	6	32	136	2.47	0.07	17	76	36	3.84	0.04	0.93	47	1.43	0.08	1.7	0.10	60	13	9	137	71	14	76	1.94	0.17	0.21	0.09	6.00	4.11	6.21
266	213	0.14	3.75	6	32	127	2.45	0.11	17	75	35	3.83	0.06	0.98	47	1.45	0.08	1.6	0.11	60	13	9	118	69	14	78	1.71	0.15	0.20	0.09		4.12	5.85
267	214	0.16	4.05	7	37	141	3.07	0.08	18	80	37	4.06	0.04	1.04	50	1.53	0.07	1.8	0.15	63	14	9	155	80	14	77	1.85	0.19	0.18	0.08		5.69	5.42
268	215	0.16	3.37	6	25	121	2.55	0.12	16	69	33	3.65	0.06	0.87	42	1.40	0.07	1.5	0.10	56	13	8	117	62	13	71	1.89	0.15	0.22	0.09		4.64	5.25
269	216	0.15	3.99	6	36	158	2.31	0.07	18	81	37	4.22	0.05	1.07	49	1.49	0.07	1.8	0.11	62	15	10	120	75	15	83	1.67	0.21	0.20	0.09		4.60	5.68
270	217	0.17	3.89	7	34	135	2.62	0.08	18	75	35	3.94	0.05	0.98	48	1.48	0.08	1.8	0.12	61	13	9	147	74	13	76	1.85	0.18	0.21	0.09	6.00	5.35	5.57

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„Anmerkung: Fragen zur Dankesliste

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2. *Eins ist sicher: Jeder der Dank verdient, ist der nagenden Ungewissheit, die diese Fragen erzeugen, gewachsen!!! selber groß!“*

Kinderzimmer Productions (1999)

Erklärung gem. § 8 (3) b) und c) der Promotionsordnung

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