Reactive organic species on natural dust

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Abstract

Annually 1000-3000 Tg mineral dust aerosol are emitted into the atmosphere, and transported over the oceans from one continent to the other. During the transport dust particles interact with components in the marine atmosphere and also with seawater as they fall into the ocean. Increased methyl iodide concentrations were observed during a field campaign on the Atlantic Ocean when dust storms occurred.

Volatile halogenated organic compounds (VHOC) are photolyzed to produce reactive halogen species which are responsible for ozone depletion. An abiotic production mechanism for VHOC, involving humic-like substance (HULIS), iron and halide, was supposed to produce methyl iodide through the interaction of dust particles with seawater as all necessary ingredients were present. The main goal of this study was to test this hypothesis and to further elucidate the process. For this, simple dust-seawater addition experiments in headspace glasses were conducted in the laboratory, following a purge-and-trap GC-MS analysis of the headspace gas.

Dust samples were collected in the source regions in southern Algeria and the Gobi Desert and, as representatives for aeolian dust, samples from Cape Verde Island and Lanzarote Island were used. To exclude the biological contribution, sterilized samples were also employed in this study. As assumed, methyl iodide was produced abiotically and the concentration increased tenfold after addition of Fe (III) within half an hour. Methylene chloride was also produced abiotically along with methyl iodide. In contrast to methyl iodide and methylene chloride, methyl chloride and isoprene were produced biologically, provided the production occurred after at least 24 hours of interaction of only non-sterilized samples with seawater. If the microorganisms responsible for the production of isoprene are common soil organisms found everywhere in the world, this process can be the reason for a hitherto not fully explained increase in atmospheric isoprene concentration during wet seasons, especially when the rain falls practically everyday. The results of this study show the importance of natural dust aerosols for the production and emission of volatile organic compounds to the atmosphere and open interesting questions for further studies.

Kurzfassung

Interkontinentale Staubstürme transportieren jährlich riesige Mengen (1000-3000 Tg) an feinstem Mineralstaub, vorwiegend aus den Wüsten, über den ganzen Globus. Während dieses Transportes reagieren die Mineralstaubpartikel über den Meeren mit Komponenten der ozeanischen Atmosphäre, sowie mit dem Meerwasser. Bei Feldmessungen im Atlantik wurden jeweils nach Sandstürmen erhöhte Methyliodid Konzentrationen gemessen.

Methyliodid und andere leichtflüchtige halogenorganische Verbindungen produzieren unter Einwirkung von UV-Strahlung reaktive Halogenverbindungen, die maßgeblich für die Zerstörung der Ozonschicht verantwortlich sind. Es wurde vermutet, dass Methyliodid infolge des abiotischen Prozesses gebildet wird, der zwischen organischem Material, Fe (III) und Halogenid stattfindet, da durch die Wechselwirkung von Staubpartikeln mit Ozeanwasser eigentlich alle für die Bildung von Methyliodid notwendigen Bestandteile vorhanden sind.

Zielsetzung der vorliegenden Arbeit war es, diese Vermutung über die Bildung von Methyliodid zu überprüfen, und den Prozess genauer zu untersuchen. Dafür wurden Mineralstaub und Seewasser in Headspace-Gläsern gemischt und danach die Gasphase mit Purge-und-Trap GC-MS analysiert. Die Mineralstaub-Bodenproben wurden aus der Sahara im Süden Algeriens und aus der Wüste Gobi genommen, und repräsentativ für den durch Stürme übertragenen Mineralstaub, wurden Proben von den Kapverdischen Inseln und von Lanzarote verwendet. Um eine biologische Produktion von Methyliodid ausschliessen zu können, wurden die Proben teilweise auch sterilisiert. Bei den Untersuchungen wurde dann, wie erwartet Methyliodid abiotisch produziert, und nach Zugabe von Fe (III) stieg die Konzentration um das Zehnfache innerhalb von 30 Minuten. Ebenso bildete sich auch Methylenchlorid.

Im Gegensatz zu Methyliodid und Methylenchlorid, entstanden Methylchlorid und Isopren nur biologisch. Sie wurden frühestens nach 24 Stunden, und auch nur in unsterilisierten Proben mit Meerwasser gebildet. Falls die, für die Produktion von Isopren in Frage kommenden Mikroorganismen den üblichen Bodenorganismen entsprechen, die man überall auf der Welt finden kann, könnte dieser Prozess ein Grund für das bisher nicht völlig geklärte Ansteigen von Isopren in der Atmosphäre in Regenzeiten sein.

Die Ergebnisse dieser Arbeit zeigen, dass Mineralstaub eine grosse Bedeutung für die Produktion und Emission von leichtflüchtigen halogenorganischen Verbindungen in der Atmosphäre hat, und es ergeben sich interessante Fragen für zukünftige Untersuchungen.

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ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectroscopy
amu	atomic mass unit
CFCs	chlorofluorocarbons
C/S	carbon sulfur
DOC	dissolved organic carbon
DOAS	Differential Optical Absorption Spectroscopy
DIN	Deutsches Institut für Normung
DMADP	dimethylallyl diphosphate
d	density
d	diameter
ECD	Electron Capture Detector
EMMA	Energy-dispersive Miniprobe Multielement Analyzer
GHG	Green house gas
GF-AAS	Graphite furnace Atomic Absorption Spectroscopy
GC	Gas Chromatography
GC-ECD	Gas Chromatography- Electron Capture Detector
GC-MS	Gas Chromatography-Mass Spectrometry
HPLC-MS	High Performance Liquid Chromatography- Mass Spectrometry
HULIS	humic-like substance
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
IC	Ion Chromatography
IC	inorganic carbon
IR	Infra red
LLD	Lower limit of detection
MACR	methacrolein
MBL	marine boundary layer
MS	Mass Spectrometry
MVK	methyl vinyl ketone
NDIR	non dispersive infra red
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance

OES	Optical Emission Spectroscopy
PANs	peroxyacyl nitrate
ppm	parts per million
pptv	parts per trillion per volume
SOA	Secondary organic aerosol
TOC	total organic carbon
UV	ultra violet
VHOC	volatile halogenated organic compound
VOC	volatile organic compound
XRF	X-ray fluorescence

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1 INTRODUCTION AND RESEARCH OBJECTIVES

This thesis deals with the investigation of the production and the production mechanism of volatile organic compounds through the interaction of dust samples with seawater.

Methyl iodide was measured during the field campaign on the island of Tenerife in July, August 2002 by the group of Williams [*Williams, et al.*, 2007]. Higher methyl iodide mixing ratios were found during dust events than the other times. After observing the same trend during another field campaign on the Atlantic Ocean the same year, a question arose "Does methyl iodide have something to do with dust?"

On the other hand, Frank Keppler and the group in Heidelberg found a new abiotic production mechanism for halogenated organics in soils and sediments [*Keppler*, 2000]. In the presence of halide ions and an electron acceptor such as Fe (III), organic matter in soils and sediments is oxidized to give halogenated compounds.

Ocean is rich in halide ions, dust is rich in Fe (III), and both ocean and dust contain certain amounts of organics. So since we have all the necessary ingredients, our first answer to the question "Does methyl iodide have something to do with dust?" was "It is possible that methyl iodide and dust have some connection."

The main goal of my work was to test this hypothesis and to further elucidate the process. Photolysis of Volatile Halogenated Organic Compounds (VHOCs) produces reactive halogen species that are responsible for the ozone depletion not only in the stratosphere [*Molina and Rowland*, 1974] but also in the troposphere [*Barrie, et al.*, 1988], influencing significantly the oxidation capacity of our atmosphere. In 1974 as Molina and Rowland found out that the chlorofluorocarbons (CFCs) were responsible for the stratospheric ozone hole, the intensive research on VHOC in our environment started. Besides the anthropogenic sources, there are lots of natural sources like ocean, biomass burning, fungi, salt marshes, etc. However, all the known sources and their emission rates are not enough to explain the concentration measured in the atmosphere. So there are still some missing sources [*Butler*, 2000].

Soil, which stores 1500-2200 Gt organic carbon as humus, can be one of the missing sources. In 2000 Frank Keppler and others here in our institute found an abiotic mechanism for the production of VHOC in soils and sediments. Halide ions can be alkylated during the oxidation of organic matter by an electron acceptor such as Fe (III) [*Keppler, et al.*, 2000].

About 33% of the world land area is arid and semi-arid regions [*Usher, et al.*, 2003]. Since the soil in these regions contain very low amount of organics, it is unlikely that the VHOC could be produced there. However, enormous amounts (1-3 billion tons) of desert dust fly up into the sky each year and travel vast distances over the oceans from one continent to the other [*Husar*, 2004]. Mineral dust plays different roles in our environment. Rain forest in Amazonia would not have existed without Saharan dust aerosols that bring nutrient there [*Swap, et al.*, 1992]. It is the main source of major nutrient element iron, in the ocean, which enables the growth of phytoplankton in oligotrophic water [*Jickells, et al.*, 2005]. Dust aerosols affect climate through both direct and indirect radiative forcing [*Li, et al.*, 1996; *Tegen, et al.*, 1996]. Viable fungi and bacteria are transported with soil dust interhemispherically [*Prospero, et al.*, 2005]. Respirable mineral dust aerosols can cause health problems especially when associated with bacteria and microbes [*Usher, et al.*, 2003]. Pollutants are adsorbed onto the mineral dust particles and transported long distances [*Erel, et al.*, 2006]. Different kinds of heterogeneous and multi-phase reactions take place on the surface of mineral aerosols [*Usher, et al.*, 2003].

The production of VHOC from the reaction of mineral dust particles with atmospheric components in the marine boundary layer and with seawater is not yet investigated and is the main research goal of this PhD project. With this work we try to answer several questions:

- How significant is the process of VHOC formation from the multiphase reaction on mineral dust in marine atmosphere and in the ocean?
- Which VHOC and which other Volatile Organic Compounds (VOCs) are produced?
- Through which mechanism are those compounds formed?
- Which constituents play the most important role in the formation of those compounds?

For this, dust-seawater addition experiments in headspace glass vials were conducted in the laboratory, following a purge-and-trap GC-MS analysis of the headspace gas.

Methyl iodide, methylene chloride and isoprene were produced through the interaction of dust samples from the Sahara and Gobi Desert with both seawater and distilled water, methyl chloride was produced through the interaction of dust samples with only seawater. It is proved that the natural dust samples are important contributors of volatile organic compounds to the atmosphere and further studies in this field are urged.

2 EXPERIMENTAL SECTION

2.1 Samples

Total of nine fine Saharan dust samples were collected directly from the ground in Tamanrasset (22° 47′ N, 5° 31′ E, 1362 m) in the Hoggar region of southern Algeria. The sites were located within a radius of 10-20 km from Tamanrasset. The samples were taken from places without anthropogenic influence. They are denoted as Sahara 1 - Sahara 9 or S1 - S9 in the following chapters. Two samples from the Gobi Desert were also collected from the ground in Dalanzadgad city (43° 33′ N, 104° 25′ E) in south Gobi province in Mongolia. One site was a sand dune located 85 km away from the city. This sample is denoted as Mongolia 1 or M1. The other site was directly in the city center. This sample was wind blown and was accumulated at the bottom of the fences which typically every family has around its houses. The anthropogenic influence could not be excluded since the sample was collected in the city. This sample is denoted as Mongolia 2 or M2. To compare dust samples from the source region with that which have already gone aeolian transport, further samples were taken from Cape Verde Island and Lanzarote Island (Canary Islands). The sample from Lanzarote Island is one of the eight composite samples collected in the northern part of the Island (29° 13′ N, 13° 27′ E) [*Maciejczyk*, 2005]. It is denoted as Lanzarote 6 or L6. The sample from Cape Verde Island (16° 45′ N, 22° 57′ W) was generously provided by Professor Gaudichet from LISA, UMR-CNRS 7583 University of Paris. The sample was collected by bulk filtration on 0.4 μm pore-size Nuclepore filter with an average flow rate of 0.8 m^3/h [*Caquineau, et al.*, 1998]. This sample is denoted as Cape Verde or CV. All samples were sieved and only fine particles with diameter smaller than 63 μm were used for the experiments. Also some samples were sterilized in an autoclave under 0.1 MPa pressure at 120 ^{0}C for 1 hour to exclude the microbiological contribution to the production of VOCs. The names of all samples used in this study and their denotations are listed in Table 1.

Table 1. List of the samples used in this study

No.	Place	Denotation	
1	Guelta Oued Imeleoulaouene	Sahara 1	S1
2	Oued Imeleoulaouene	Sahara 2	S2
3	Oued Tehéggart	Sahara 3	S3
4	Oued Tamanrasset	Sahara 4	S4
5	A fila Oued Imeleoulaouene	Sahara 5	S5
6	Oued Adaouda	Sahara 6	S6
7	Oued Sêrsouf	Sahara 7	S7
8	Oued Ézernene	Sahara 8	S8
9	Oued Tindé	Sahara 9	S9
10	Sand dune in Gobi	Mongolia 1	M1
11	Dalanzadgad city	Mongolia 2	M2
12	Lanzarote Island	Lanzarote 6	L6
13	Cape Verde Island	Cape Verde	CV

2.2 Chemicals

Isoprene (99 %, d = 0.68 g/ml, Aldrich)

VOC-Mix 21 (200 mg/l, Ehrenstorfer)

Methyl iodide (10 ng/µl, Ehrenstorfer)

Iron (III) sulfate (>76 % Fluka)

Iron (II) sulfate (>76 % Fluka)

Standard for calcium carbonate (12 % C, LECO Corporation)

Standard 501-005 for Sulfur in coal (1.00±0.02 %, LECO Corporation)

Hydrochloric acid (25 %, d = 1.12 g/ml, AppliChem)

Sodium carbonate (99.9 %, Merck)

Sodium bicarbonate (99.5 %, Merck)

Potassium hydrogen phthalate ($C_8H_5KO_4$) (99.5 %, Merck)

Standard of several mixed cations (1000 mg/l, CertiPUR Merck)

Standard of silicon (1000 mg/l, CertiPUR Merck)

Nitric acid (65 %, d = 1.39 g/ml, Fluka)

Standards of chloride, bromide, nitrate, nitrite, sulfate and phosphate (1000 mg/l, CertiPUR Merck)

2.3 Analytical methods

2.3.1 X-ray fluorescence (XRF)

An in-house designed Energy-dispersive Miniprobe Multielement Analyzer (EMMA) XRF was used to determine the total of 24 major (Al, Si, S, Cl, K, Ca, Ti and Fe) and trace (Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Pb and Th) elements in dust samples. The description and details about this sensitive, rapid and non-destructive method is described elsewhere [*Cheburkin and Shotyk*, 1996].

2.3.2 Carbon, Sulfur analysis

Carbon and sulfur contents of the dry samples were determined by means of C/S Analyzer (LECO SC-144DR). About 200 mg of dust sample was burned at 1350^0C under oxygen atmosphere and the products of this combustion, carbon dioxide and sulfur dioxide were measured with infra red detector. Calcium carbonate was used as carbon standard and sulfur containing coal, 501-005, as sulfur standard.

2.3.3 Water content and total organic content

The water content of the samples was determined using a standard method DIN 18121 Part 1. Fresh dust samples were weighed in crucibles whose weights were constant and were heated at 105^0C until their weights got constant. The mass difference of fresh and dry samples gives the water content of dust samples. After determining the water content, the same samples were heated at 550^0C for an hour, and were weighed. The procedure was repeated until their weight got constant. The mass difference of dry sample and the sample heated at 550^0C gives the amount of total organic matter in the sample.

2.3.4 TOC

Dissolved total, organic and inorganic carbons were determined by means of Shimadzu-5000 Total Organic Carbon (TOC) analyzer. Because dust samples contain very small amount of organic carbon, in order to get solutions with concentrations above the detection limit of the instrument, dust samples were mixed with Milli-Q water in ratio of 1:3 instead of usual 1:10 ratio. After shaking 10 g of dust samples in 30 ml of Milli-Q water for 24 hours, the samples were centrifuged and filtered through 0.45 μm filter. Inorganic carbon standard was prepared by dissolving 0.350 g sodium bicarbonate and 0.441 g of sodium carbonate in 100 ml of Milli-Q water. The concentration of resulting mother solution was 1000 mg/l. Total carbon standard was prepared by dissolving 0.2125 g of potassium hydrogen phthalate ($C_8H_5KO_4$) in 100 ml of Milli-Q water. The concentration of resulting mother solution was also 1000 mg/l. For total carbon determination, the standards with concentrations of 25, 50, 75 and 100 mg/l, and for inorganic carbon determination, the standards with concentrations of 10, 20, 50 and 100 mg/l were prepared. To determine total dissolved carbon, the samples were converted to carbon dioxide by burning them at 680^0C with oxygen. After drying, and absorbing the halogens, the carbon dioxide was analyzed with non-dispersive infra red (NDIR) detector. To determine total dissolved inorganic carbon, the samples were acidified with ortho-phosphoric acid and the resulting carbon dioxide, which is only of inorganic origin, was also detected with NDIR detector. And the total organic carbon was calculated from the difference of total and inorganic carbon.

2.3.5 Anions

Fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate ions were determined by means of ion chromatography DIONEX 120. The sample extracts were prepared by shaking dust samples in Milli-Q water in ratio of 1:3 for 24 hours and filtering through 0.45 μm cellulose filter. A pre-column AG14A and a separating column AS14A 4 x 250 mm were used. The flow rate was 1 ml/min. The eluent solution was a mixture of 8 mmol/l of Na_2CO_3 and 1 mmol/l of $NaHCO_3$. Two types of detectors, UV-208 nm and conductivity meter, were used to determine the anions. For the determination of fluoride, nitrite and bromide, standards with concentrations of 0.5, 1, 3 and 5 mg/l, for the determination of chloride and phosphate, standards with concentrations of 5, 10, 30 and 50 mg/l, and for the determination of nitrate and sulphate, standards with concentrations of 10, 30, 60 and 100 mg/l, were prepared.

2.3.6 Cations

Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si and Sr were determined by means of Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). The sample extracts were prepared by shaking the dust samples in Milli-Q water in various ratios for certain times. The main purposes were to determine the solubility of different metals from dust samples, and to see whether a bulk density had a substantial effect on the solubility. I started with the ratio of 1:10, and after 5 minutes the samples were centrifuged, and 10 ml of extracts were taken from the supernatants. The extracts were filtered through 0.45 µm cellulose filter, and were acidified with 50 µl of concentrated nitric acid for the cation analysis. The extracts were filtered for the analysis accuracy only. Actually, there were no sample losses due to this process, so the calculations were made according to that. 10 ml of Milli-Q water was added to the original samples to keep the 1:10 ratio, and the samples were shaken further for 15 more minutes, which means 20 minutes after the start. Again the samples were centrifuged and 10 ml of extracts were taken out, and were acidified for ICP-OES analysis. 10 ml of Milli-Q water was added to the original sample, and was shaken further for 20 more minutes. Total of 8 extracts were prepared for each sample after 5 min, 20 min, 40 min, 1 hour, 2 hours, 5 hours, 17 hours and 24 hours, respectively. Parallel extracts were obtained by shaking the samples directly for 24 hours in ratios 1:3 and 1:10 in order to compare the effect of bulk density on the solubility of metals from the dust samples. For the quantification of the cations, standards solution CertiPUR (1000 mg/l), which contains several cations, and the standard solution CertiPUR Silicon (1000 mg/l) were used. As a control, an international standard NIST 1643E was used.

2.3.7 pH

The pH of the sample extracts was determined with pH-meter Mettler Toledo 320. The pH-meter was calibrated with the standard solution of pH 7.0.

2.4 Determination of volatile organic compounds

For the determination of volatile organic compounds in the reaction vials, a headspace technique with either GC-ECD or a purge-and-trap GC-MS system was used. The headspace technique is an effective method of sample preparation and injection to the GC system. The volatile and semi-volatile organics in headspace gas of tightly closed vials are analyzed by GC after an establishment of equilibrium in the headspace. There are two types of headspace technique: static and dynamic. In static headspace technique, after the establishment of equilibrium, certain amount of headspace gas is taken by syringe, and is injected to the GC. This method was used in combination with GC-ECD system. In dynamic headspace technique, which is mostly called a purge-and-trap, the headspace gas is continuously purged and concentrated on the cooled trap, and the pre-concentrated sample is then transferred to the GC by thermal desorption. Because the sample is pre-concentrated before it comes to the GC column, a purge-and-trap is a widely used, effective method for the identification and quantification of ultra trace amounts of compounds.

2.4.1 GC-ECD

The volatile halogenated organic compounds were analyzed by means of Gas Chromatography with Electron Capture Detector (GC-ECD). The GC-ECD used for this study composed of Auto sampler Combi PAL with agitator and heatable syringe, Gas Chromatograph Fison HRGC 8265 with split/splitless injector Carlo Erba SSL71, a separating column SGE BP 624 with film thickness of 3 μm and an electron capture detector Carlo Erba HT 25. Electron capture detector has a radioactive beta particle (electron) emitter. It is mostly a metal foil containing 10 milli Curie Ni-63. The emitted electrons are attracted to the positively charged anode, generating a steady current. When the sample is transferred to the detector by means of carrier gas, the electron absorbing compounds capture electrons from the detector, thus reducing the current. The amounts of the compounds are proportional to the reduction of the current signal. The ECD is very sensitive to the electron absorbing compounds, for example halogenated volatile organics.

The samples were shaken for certain hours at 20-50^{0}C in the agitator and certain amounts of headspace gas were then injected to the Gas Chromatograph. The various compounds were then identified and quantified by their retention times. Because we used only retention times for identification, it was sometimes difficult to differ among the compounds with same or close retention times. So we used the GC-ECD analysis results qualitatively to choose the most productive samples for further analysis with a purge-and-trap GC-MS.

2.4.2 A purge-and-trap GC-MS

A purge-and-trap unit, Tekmar LSC 2000, was connected upstream to the Gas Chromatograph Varian Star 3400 cx and the ion trap Mass Spectrometer Varian Saturn 2000. The volatile organic compounds in the headspace glass vials were purged with He (flow rate 30 ml/min) for 4 minutes, and were pre-concentrated on a trap filled with Tenax TA 60/80 which was cooled at -90 ^{0}C with liquid nitrogen. A water trap filled with magnesium perchlorate was connected upstream to the pre concentration trap. After short dry purge step (2 s), desorption of volatile organics from the pre concentration trap was done at 180 ^{0}C for 4 minutes. During the desorption step, the capillary column of the gas chromatograph was cooled at -90 ^{0}C with liquid nitrogen to reconcentrate the volatile organics at the beginning of the column. Gas chromatographic separation was carried out on a column SGE BP624 (I.D. 0.53 mm, O.D. 0.68 mm, length 25 m) using the temperature program as shown in Figure 1.

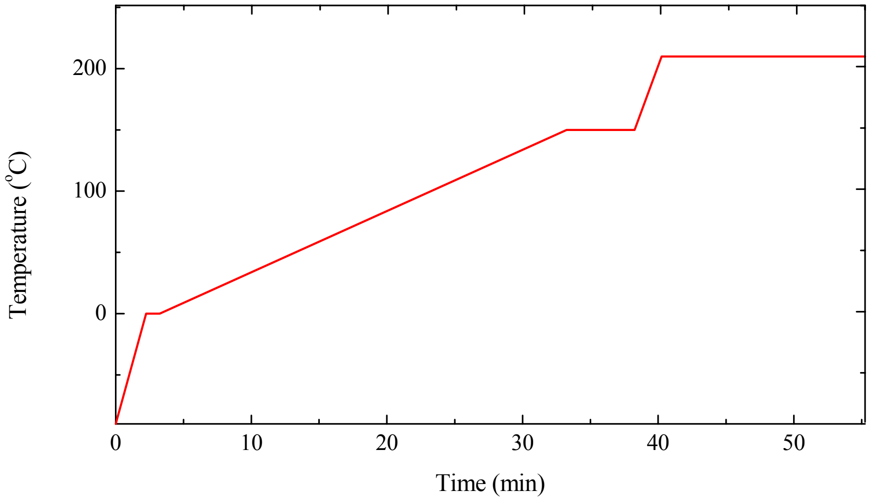

Figure 1. Temperature program of GC oven.

Initial oven temperature was -90^{0}C, and then it was heat up at the rate of 40 ^{0}C/min until 0 ^{0}C and was held for 1 min. After that, the oven was heat up at the rate of 5 ^{0}C/min until 150 ^{0}C and was held for 5 min. Finally, it was further heat up at the rate of 30 ^{0}C/min until 210 ^{0}C and was held for 15 min. Mass spectrometric detection was done in scan mode over a range of 45-280 amu. Because GC-MS gives both the retention time and the mass for identification, it was easier and more suitable to quantify the compounds compared to GC-ECD.

3 CHARACTERIZATION OF SAMPLES

3.1 Results and Discussion of XRF analysis

The detailed results of XRF analysis are shown in Table 2. There are some elements whose concentrations changed related to an aeolian transport of dust samples. Clearly seen in Figures 2 and 3 are the increased concentrations of calcium and bromine in the samples from Cape Verde Island (CV) and Lanzarote Island (L6) that have undergone aeolian transport.

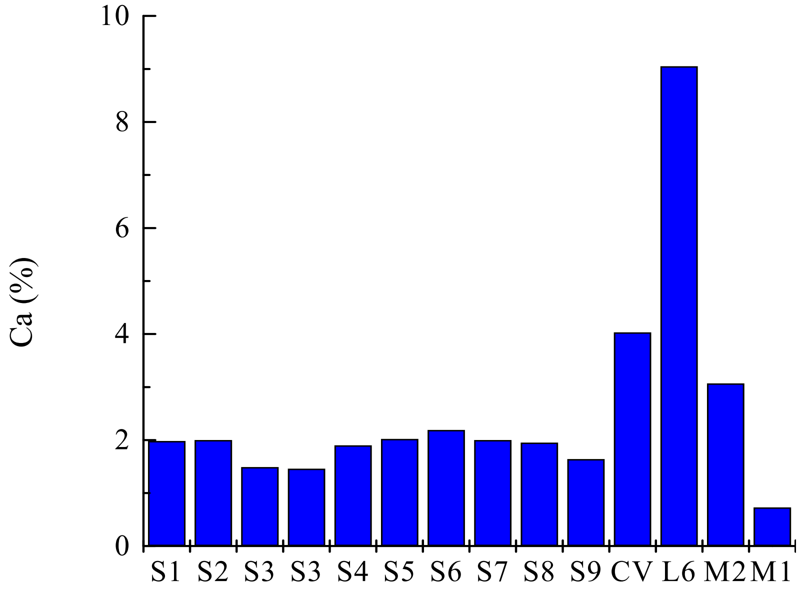

Figure 2. Calcium concentration in the samples.

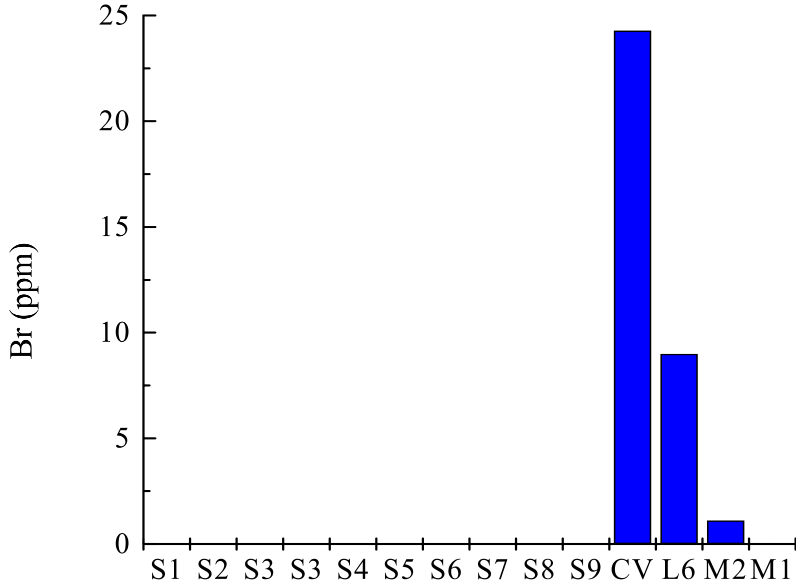

Figure 3. Bromine concentration in the samples.

Table 2. Results of XRF analysis

Sample	K, %	Rb, ppm	Ca, %	Sr, ppm	Al, %	Ga, ppm	Si, %	Pb, ppm
LLD	**0,001**	**1**	**0,001**	**1**	**0,5**	**1,5**	**0,3**	**2**
S1	2,25	133,44	1,98	268,02	8,49	18,74	30,87	22,05
S2	2,00	118,03	2,00	299,08	7,88	17,92	26,61	17,93
S3	2,31	106,59	1,49	262,16	8,35	15,27	31,00	18,45
S3	2,24	116,51	1,46	293,61	6,61	18,19	30,93	19,27
S4	2,22	102,72	1,90	290,53	8,31	16,11	28,54	14,48
S5	2,07	135,88	2,02	261,62	8,27	18,19	27,66	21,62
S6	2,37	154,80	2,19	268,42	8,80	24,86	28,64	19,97
S7	2,16	132,05	2,00	286,04	7,74	19,17	30,34	21,36
S8	2,19	107,30	1,95	256,54	8,95	17,65	27,80	16,92
S9	2,08	107,90	1,64	263,62	6,85	18,93	31,00	20,31
CV	1,94	59,47	4,03	336,58	8,72	19,63	23,57	7,98
L6	3,05	70,32	9,05	276,74	10,21	14,68	27,27	12,48
M1	3,27	105,52	0,73	183,71	6,92	7,65	31,00	12,26
M2	2,20	69,30	3,07	294,95	7,69	15,09	28,48	27,10

Sample	As, ppm	S, ppm	Cl, ppm	Br, ppm	Cu, ppm	Zn, ppm	Y, ppm	Th, ppm
LLD	**1,5**	**300**	**200**	**1**	**2**	**1,5**	**2**	**2,5**
S1	0,00	0,00	0,00	0,00	26,21	104,97	34,65	7,76
S2	5,96	0,00	0,00	0,00	22,71	116,71	32,92	10,96
S3	0,00	0,00	0,00	0,00	16,13	66,19	23,58	5,86
S3	3,04	0,00	0,00	0,00	16,34	74,32	24,24	6,34
S4	2,07	0,00	0,00	0,00	22,64	90,07	22,38	8,14
S5	0,00	0,00	0,00	0,00	31,39	99,49	30,94	9,20
S6	3,59	0,00	0,00	0,00	32,09	102,50	33,99	3,95
S7	1,92	0,00	0,00	0,00	32,40	99,98	32,75	10,35
S8	2,57	0,00	0,00	0,00	28,71	102,85	30,05	3,55
S9	0,00	0,00	0,00	0,00	19,42	73,97	29,19	5,70
CV	4,58	1660,61	3445,76	24,28	47,54	96,40	26,16	3,88
L6	5,66	0,00	0,00	8,99	35,99	68,89	23,48	5,34
M1	2,95	0,00	295,81	0,00	4,19	7,99	8,16	0,00
M2	9,95	497,79	0,00	1,11	28,66	72,99	26,86	4,33

Sample	Ti, %	Zr, ppm	Nb, ppm	Cr, ppm	Mn, ppm	Fe, %	Ni, ppm
LLD	**0,0005**	**2,5**	**2,5**	**1,5**	**1,5**	**0,001**	**3**
S1	0,74	367,18	24,92	115,61	956,45	4,38	32,38
S2	0,99	454,96	46,63	134,29	1119,13	5,67	39,90
S3	0,61	406,44	21,33	79,44	805,37	2,90	25,41
S3	0,62	368,50	20,71	74,78	772,37	3,60	31,93
S4	0,73	333,53	46,26	105,11	944,35	4,73	47,62
S5	1,12	322,37	28,33	147,28	1140,35	4,25	21,01
S6	0,72	388,55	23,52	99,75	974,04	4,46	26,88
S7	0,78	403,80	28,21	104,08	937,55	4,45	25,67
S8	0,78	330,71	28,44	112,14	953,69	4,41	36,01
S9	0,70	413,19	22,96	98,72	804,00	3,95	30,63
CV	2,41	338,19	83,73	275,38	1544,50	7,62	55,19
L6	0,96	256,47	40,15	178,32	679,52	4,52	117,06
M1	0,13	43,31	2,54	9,69	207,24	0,47	4,35
M2	0,53	598,03	12,67	89,05	916,45	3,36	23,93

As the dust is transported farther away from the source region, the overall composition tends to become enriched with clays or micas in whose mineral structures insoluble calcium is bound [*DeBell, et al.*, 2004; *Usher, et al.*, 2003]. This explains why the samples from Cape Verde and Lanzarote Islands have higher calcium concentrations than the samples from Algeria.

For bromine the lowest limit of detection was 1 ppm. It was not detected in all samples collected from the source region but in samples that have undergone aeolian transport. It could be explained by the adsorption of ocean salt aerosols on the dust particles during the transport over the ocean.

In order to see the dependence of elemental concentrations on the size of the samples, three different sized samples Sahara 8 were analyzed. Calcium, lead and arsenic concentrations increased as the size of the samples decreased, and the concentrations of potassium, copper, chromium and manganese decreased with decreasing sample size (Table 3.). In case of calcium, it again demonstrates that calcium, mostly in form of insoluble calcite in mineral dust, is enriched in the fine fraction.

Table 3. Dependence of elemental concentrations on the size of the samples

Sample (S8)	**Ca,** %	**Pb,** ppm	**As,** ppm	**K,** %	**Cu,** ppm	**Cr,** ppm	**Mn,** ppm
d < 0.063 mm	2,01	29,0	6,4	1,98	37,2	105,3	953,8
0.063 mm < **d** < 0.2 mm	1,91	25,4	3,6	2,47	41,3	117,5	1060,0
d > 0.2 mm	1,69	17,8	2,1	3,71	42,5	144,0	1337,1

Trace metals were associated to iron as it is shown for manganese in Figure 4, as it was the case in the work of Guieu et al. [*Guieu and Thomas*, 1996]. There was strong linear correlation ($R^2 = 0.91$). The correlation was also good for chromium, niobium, nickel, titan, strontium, copper and zinc ($R^2 = 0.71$-0.84).

All the other measured elements showed no correlation with iron content, which for lead was also the same for the samples used in the study of Guieu et al. [*Guieu and Thomas*, 1996].

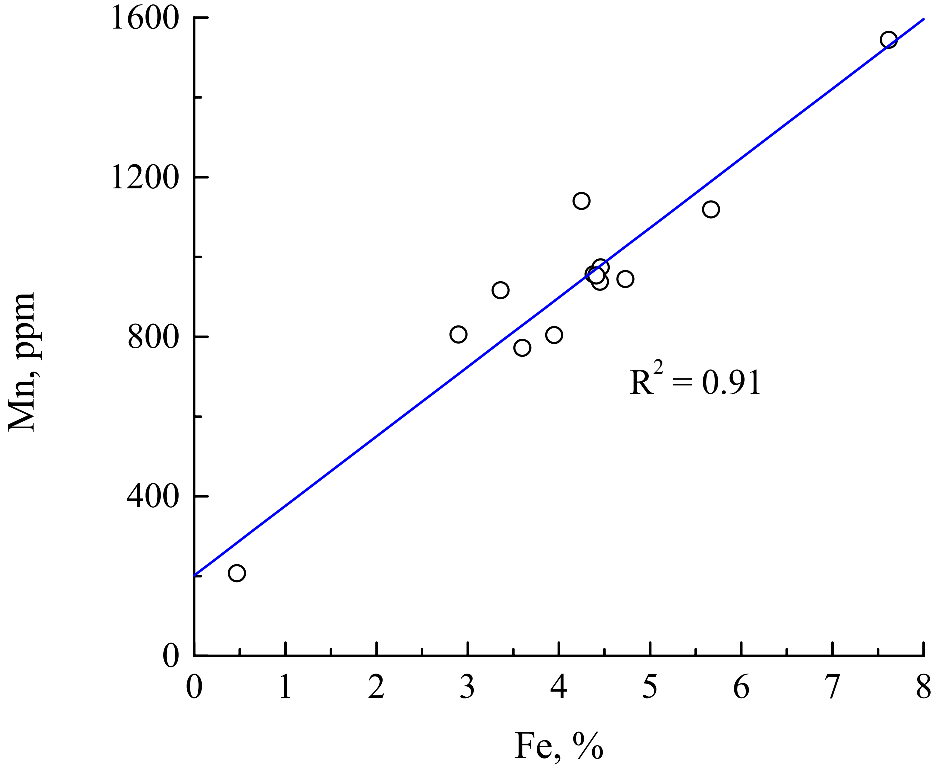

Figure 4. Concentration of manganese versus iron content in dust samples.

3.2 Results and Discussion of Carbon, Sulfur analysis

The carbon, sulfur analysis with C/S analyzer was not suitable for the dust samples because the dust samples contained very small amounts of carbon and sulfur. The carbon standard used for the calibration was pure calcium carbonate which contained 12 % of carbon and the sulfur content of the coal used for the calibration was 1,00 ± 0,02 %. The results of the carbon, sulfur analysis of all the samples are shown in Table 4.

Table 4. Results of carbon, sulfur analysis

Sample	Sulfur, %	Carbon, %
S 1	0,0061	0,2297
S 2	0,0103	0,3258
S 2 > 0.063	0,0041	0,2609
S 2 > 0.125	0,0134	0,6024
S 3	0,0094	0,1806
S 4	0,0060	0,1948
S 5	0,0095	0,1837
S 6	0,0149	0,2740
S 7 < 0.02	0,0099	0,5476
S 7	0,0069	0,1420
S 7 > 0,063	0,0079	0,1465
S 7 > 0,125	0,0022	0,1181
S 7 > 0.2	0,0097	0,1196
S 8	0,0036	0,2521
S 8 > 0,063	0,0127	0,1613
S 8 > 0,125	0,0083	0,1154
S 8 > 0,2	0,0057	0,3001
S 8 > 0.315	0,0062	0,5796
S 9	0,0119	0,1327
CV	0,0887	0,6751
CV > 0.063	0,0826	0,9253
CV > 0.125	0,0575	0,9457
M 1	0,0029	0,0433
M 2	0,0159	1,6838
L 6 < 0.02	0,0147	2,1359
L 6	0,0094	2,9126

The dust samples except the dust sample from Lanzarote Island contained not even 1 % of carbon, and the sulfur content of all the samples except for the dust sample from Cape Verde Island was below 0,02 %. The measurements with more than 200 mg of dust samples failed because of incomplete combustion of the samples. The sulfur content measured with XRF was almost twice as much as that measured with C/S Analyzer. The lower limit of detection of XRF instrument for sulfur was 300 ppm. We consider the measurement of XRF instrument more reliable, because the measured values of C/S Analyzer were far more different from the calibration standard values. In both cases, it is shown that the dust sample collected at the Cape Verde Island contains sea salt aerosol components.

The intended purpose of performing carbon, sulfur analysis with C/S Analyzer was to determine the total, inorganic and organic carbon content of the dust samples in dry samples and then to compare the results with the total dissolved inorganic and organic carbon content of the samples in their leach solutions in order to find out whether or how the carbon contents of the samples affect the formation of volatile organic compounds, when the dust samples interact with ocean water. Unfortunately, the attempt failed because the results of the total carbon content determination turned out to be unreliable. They all fell in the range outside the calibration value (see Table 4), and also the inorganic carbon measurement by means of "Carbonate bomb" instrument developed by Müller and Gastner [*Müller and Gastner*, 1971] was not possible due to insufficient inorganic carbon content of the dust samples.

Carbonate bomb is a closed glass with a pressure measuring instrument. It measures the pressure of the carbon dioxide formed inside the bomb, after the sample reacts with 6 N hydrogen chloride solution. As a standard, calcium carbonate is used. Comparison of the measured pressure with the pressure of carbon dioxide formed from certain amount of standard gives the quantitative results of inorganic carbon content of the sample. The difference between the total carbon and the total inorganic carbon contents gives the amount of total organic carbon of the sample.

The only sample for which the intended measurements were successful was the dust sample collected on the Island of Lanzarote. The results of the total, inorganic and organic carbon measurement of this sample are shown in Table 5 in comparison to the measurement results of Maciejczyk [*Maciejczyk*, 2005]. The difference in results can be explained by the heterogeneity of the sample and also the size of the sample used for the measurement. The sample in the size range of (0.020 < d < 0.063) mm was used in this study. Maciejczyk used the samples in the size range of d < 0.125 mm in her work.

Table 5. Carbon concentration of the sample from Lanzarote Island

Sample	Total carbon, %	Total inorganic carbon, %	Total organic carbon, %	Authors
L 6	2,9126	2,20	0,7126	this study
L 6	2,9905	1,92	1,0705	Maciejczyk

Because the measurement of total organic content of the samples failed with this method, another method was employed for this purpose. Those results are discussed in the next section.

3.3 Results and Discussion of water content and total organic content analysis

The water contents of the dust samples were about 1 % and the total organic contents were about 3 - 4 %. The results of the analysis are shown in Figure 5.

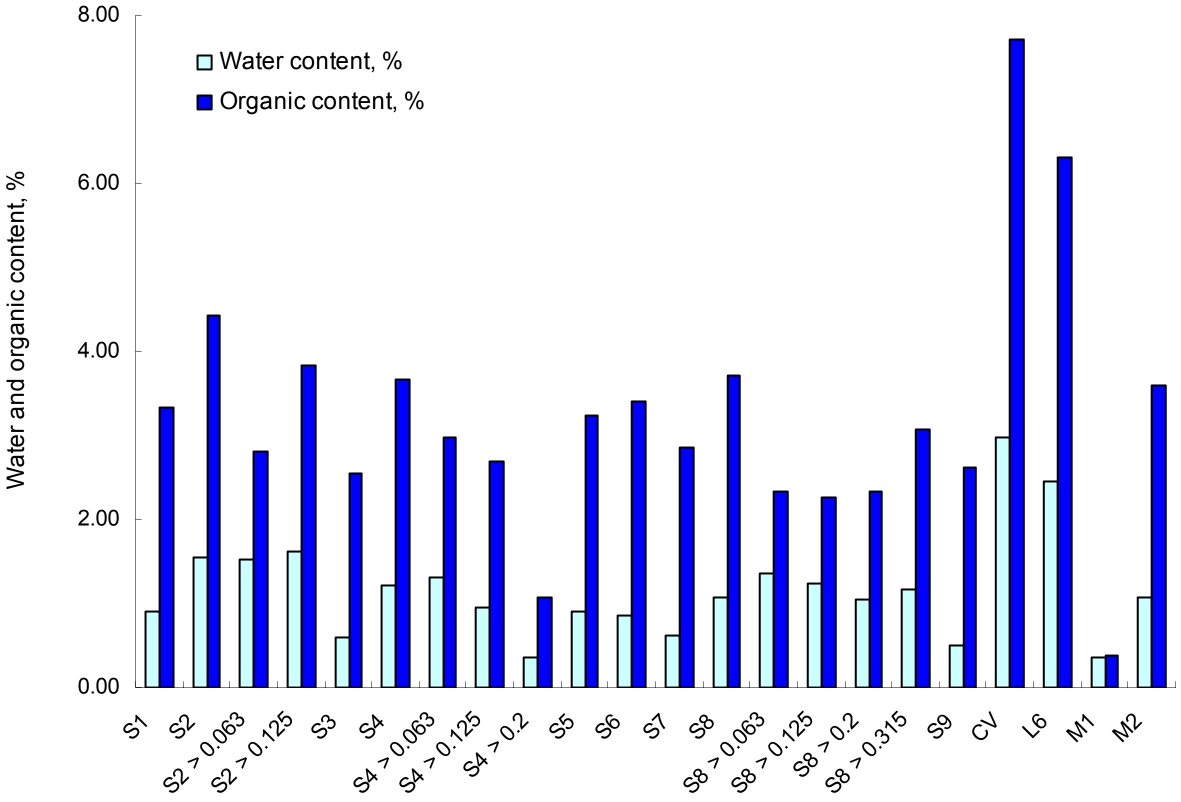

Figure 5. Water and organic content of the samples.

The water and organic content of the samples from Cape Verde and Lanzarote Islands were more than that of the samples collected directly at the source regions. Also the results showed that the dust samples with smallest size contained higher organics than the samples with bigger size. This was seen in samples Sahara 4 and Sahara 8. The structure analysis of organics in the samples would have shown whether the organics originated from the source region, or they were adsorbed onto the dust particles during the transport over long distances. The characterization of the organic compounds in the dust samples was not carried out during this work. But the results of this and the other following analysis approved that the dust samples contain certain sufficient amounts of organics responsible for the formation of some volatile organic compounds.

3.4 Results and Discussion of TOC analysis

The results of the total dissolved organic and inorganic carbon analysis are shown in Figure 6.

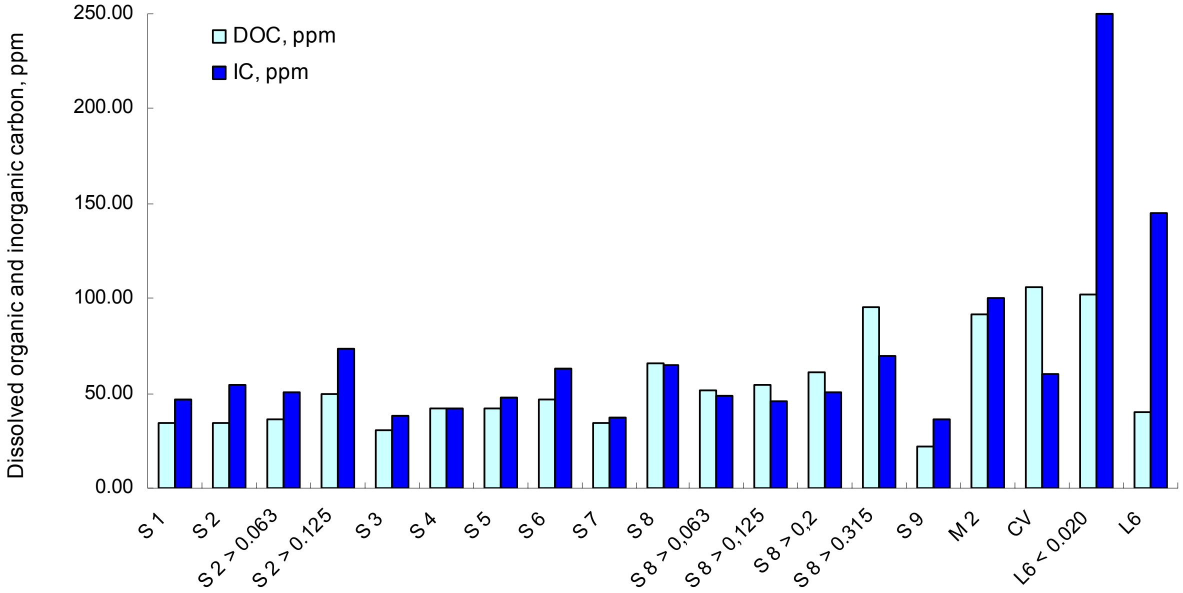

Figure 6. Dissolved organic and inorganic carbon contents of the samples.

It is seen from the figure that the sample from Lanzarote Island contains the highest amount of dissolved inorganic carbon, which supports the result of the carbon analysis of the dry dust sample which was done by means of carbonate bomb instrument. The results of the sample Sahara 8 also correspond with the results of the total organic content analysis. As mentioned previously, the leach solutions were prepared by mixing 10 g of dust sample with 30 ml of Milli-Q water for 24 hours, because dust samples contain lower amounts of organics in comparison to soil samples. Normally, the ratio of 1:10 is used for the analysis of soil sample leach solution. So the question was whether the bulk density had an effect on the solubility of the organics, as it did on the solubility of iron (see Section 3.7). To find out the answer to this question, two leach solutions were prepared from the Lanzarote sample, one by dissolving 2 g of sample in 20 ml of Milli-Q water, and the other by dissolving 10 g of sample in 30 ml of Milli-Q water like all the other samples. The last two columns in Figure 6 represent those two samples. As it is clearly seen from the Figure, the change in the bulk density showed twofold change in dissolved organic and inorganic carbon content. So when the dust particles enter the ocean during dust storms, the dissolved organic and inorganic carbon contents would be higher than these measurement results.

3.5 Results and Discussion of Anion analysis

The results of ion chromatography analysis are shown in Table 6.

Table 6. Results of ion chromatography measurements

Samples	F^- (mg / kg)	Cl^- (mg / kg)	NO_2^- (mg / kg)	Br^- (mg / kg)	NO_3^- (mg / kg)	SO_4^{2-} (mg / kg)
Sahara 1		130,75	5,29		70,25	35,51
Sahara 2	0,41	71,10	6,71	0,15	166,67	49,16
Sahara 2 > 0.063	0,51	56,13	5,41	0,08	127,92	36,27
Sahara 2 > 0.125	0,30	40,20	8,88	0,03	148,90	36,19
Sahara 3		17,35	2,70	0,03	64,88	12,69
Sahara 4	0,27	58,38	4,15	0,04	143,90	48,14
Sahara 5	0,54	105,98	6,14		41,49	21,73
Sahara 6	0,83	44,81	8,07		83,98	138,61
Sahara 7	0,31	31,65			58,52	29,04
Sahara 8		70,80	7,78	0,03	173,83	50,17
Sahara 8 > 0.063	0,35	40,62	4,32		124,72	33,35
Sahara 8 > 0.125		38,16	5,78	0,05	100,55	29,99
Sahara 8 > 0.2	0,31	41,18	2,57		88,24	28,03
Sahara 8 > 0.315	0,21	126,50	13,29	0,20	101,07	32,94
Sahara 9		17,22	3,70		14,96	11,06
Gobi 1	1,22	360,93			50,41	56,02
Gobi 2		30,99			164,70	38,09
Lanzarote	1,14	62,29	9,41	0,05	24,78	13,55
Cape Verde		1627,23		3,74	189,79	1795,45

As it is seen from the table, the sample from Cape Verde Island contains the highest amount of chloride and sulfates, as it was the case of XRF analysis (see Table 5). Bromide could be detected in samples from Lanzarote and Cape Verde Islands and in addition in samples Sahara 2, 3, 4 and 8, which were not detected by XRF analysis (see Figure 3). The samples Sahara 2, 4 and 8 and the samples from the Gobi Desert Mongolia 2 and Cape Verde Island showed higher amounts of nitrate than the other samples. The sample Sahara 6 had higher sulfate content in comparison to the other samples.

The Figure 7 was drawn to see how the dependence of the anion contents on the sample size was. For the samples Sahara 2 and 8, the samples smaller than 0.063 mm diameter contained higher amounts of chloride and sulfate compared to the same samples with bigger size, which also was the case for nitrate, dissolved inorganic carbon, calcium and total organic content of the samples.

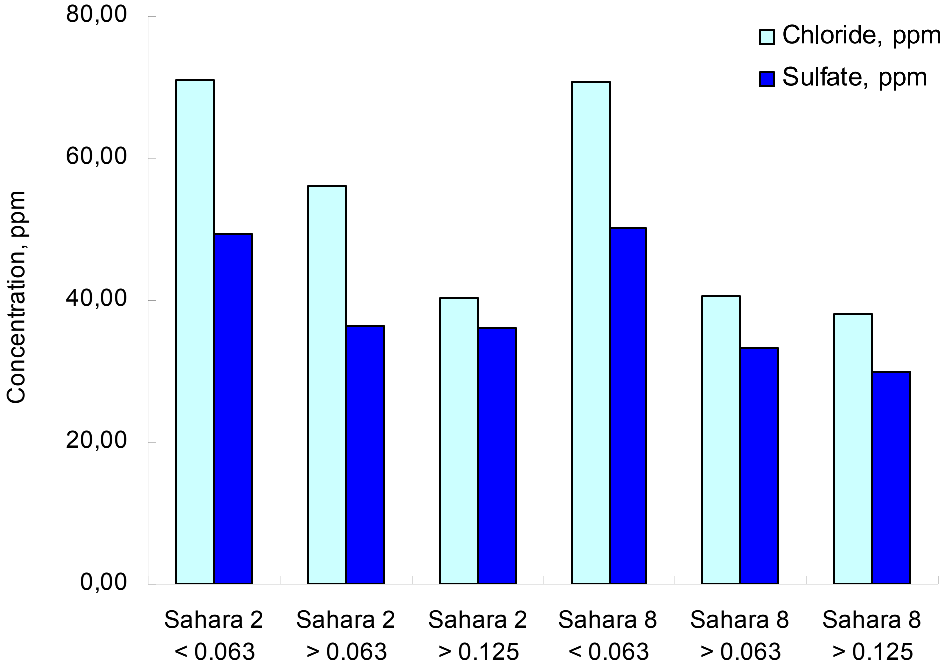

Figure 7. Dependence of anion content on the size of the samples.

If we compare the results of ion chromatography with the results of the XRF analysis for the sample from Cape Verde Island, 47 % of chlorine and 36 % of sulfur were detected as chloride and sulfate. But could all the chloride and sulfate be transferred to the solution when we mixed the samples with Milli-Q water in the ratio of 1:3? To see whether the bulk density had an effect on the dissolution of anions, another set of sample extracts were prepared by mixing the samples with Milli-Q water in ratio of 1:10 and the resulting solutions were analyzed by ion chromatography. The results of this analysis are shown in Table 7 in comparison to the previous analysis results.

Table 7. Dependence of anion dissolution on the bulk density

Samples	Mixing ratio	Cl^-, mg/kg	Br^-, mg/kg	NO_3^-, mg/kg	SO_4^{2-}, mg/kg
Sahara 2	1:10	370,954	0,432	183,223	103,822
	1:3	71,104	0,146	166,674	49,164
Sahara 8	1:10	350,599	0,082	183,057	95,025
	1:3	70,803	0,028	173,826	50,168

According to the results from the Table 7, it is seen that if we increase the sample to water ratio from 1:3 to 1:10, about 5 times more chloride, 4 times more bromide and twice as much as sulfate would dissolve, whereas the amount of nitrate stays almost the same.

If we consider that it implies for all the samples, the ion chromatography analysis of the sample from Cape Verde Island would measure 8136.15 ppm of chloride, 14.96 ppm of bromide and 3590.90 ppm of sulfate, which would be 236 % of chlorine, 62 % of bromine and 72 % of sulfur measured with XRF. In case of chloride, it is just an imaginary number, because at some point, its concentration would reach the maximum, when all the chloride would dissolve if all the chlorine were in form of chloride.

It would have been more convincing if we could show the same comparison results for the samples Sahara 2 and 8, as we did for the sample from Cape Verde Island. Unfortunately, the chlorine and sulfur contents were below the lower detection limit of the instrument in all other samples. But the results we obtained show that it is certainly better to use 1:10 ratio to prepare the dust sample extracts for the ion chromatography analysis.

3.6 Results and Discussion of Cation analysis

The raw results of ICP-OES analysis for fourteen cations are shown in Table 8.

Table 8. Results of ICP-OES analysis

Time	Ca^{2+}, mg/l	K^{+}, mg/l	Na^{+}, mg/l	Si^{4+}, mg/l	Fe^{2+}, mg/l	Al^{3+}, mg/l	Mg^{2+}, mg/l
				S 2			
5 min	7,3124	3,0585	6,4080	2,6465	0,38124	0,58368	0,81812
20 min	7,8432	3,3593	5,6194	3,9590	0,46268	0,77903	0,93240
40 min	8,1770	3,4418	5,2113	4,2563	0,34424	0,59133	0,96626
1 hour	8,4915	3,8925	5,8423	8,5752	1,48550	2,66800	1,36940
2 hours	9,0943	3,9334	4,0084	9,6843	1,67040	3,02140	1,38690
5 hours	9,2848	3,4534	4,3049	6,8405	0,65964	1,22290	1,17210
17 hours	10,6710	3,3638	4,3663	5,8781	0,31567	0,54628	1,33860
24 hours	11,1460	3,4977	3,2434	7,0289	0,55231	0,98527	1,55450
				S 8			
5 min	8,5359	3,0967	4,3615	1,4428	0,11602	0,19051	0,68755
20 min	9,0667	3,5145	4,4694	3,7525	0,59031	0,99165	0,80852
40 min	8,6578	3,2738	4,1366	3,1787	0,22293	0,40727	0,70625
1 hour	8,3129	3,5152	3,5678	5,2453	0,74352	1,38240	0,82366
2 hours	8,5528	3,4109	3,1706	5,1169	0,59962	1,09530	0,78470
5 hours	8,9891	3,2132	2,5082	4,5633	0,25995	0,50326	0,75600
17 hours	12,1050	3,8444	2,9285	11,3750	1,98590	3,76760	1,57850
24 hours	11,7650	4,7025	2,9399	16,2480	3,33600	6,06230	1,68160

Time	Co^{2+}, mg/l	Cr^{3+}, mg/l	Cu^{2+}, mg/l	Mn^{2+}, mg/l	Ni^{2+}, mg/l	Pb^{2+}, mg/l	Sr^{2+}, mg/l
				S 2			
5 min	0,001010	0,002321	0,002405	0,010121	0,000556	0,001196	0,047461
20 min	0,001281	0,002323	0,002675	0,010150	0,000837	0,001431	0,052495
40 min	0,001065	0,001875	0,002460	0,009126	0,000540	0,001411	0,055096
1 hour	0,001533	0,003744	0,002013	0,025458	0,002084	0,001397	0,059341
2 hours	0,001810	0,003768	0,001621	0,027674	0,002135	0,002185	0,062574
5 hours	0,001008	0,002048	0,001735	0,011302	0,000844	0,001411	0,062714
17 hours	0,001074	0,001389	0,003033	0,021563	0,001133	0,001695	0,071414
24 hours	0,001326	0,001515	0,002527	0,044190	0,001050	0,003011	0,074316
				S 8			
5 min	0,000639	0,000810	0,004176	0,006082	0,000558	0,001302	0,054635
20 min	0,001596	0,001303	0,004271	0,015103	0,000768	0,001858	0,059059
40 min	0,000890	0,000732	0,003602	0,007258	0,001018	0,003829	0,056342
1 hour	0,000899	0,001545	0,003515	0,015223	0,000848	0,002190	0,056362
2 hours	0,000764	0,001171	0,002910	0,011847	0,000583	0,001905	0,056434
5 hours	0,000492	0,001108	0,003331	0,008753	0,000513	0,002892	0,058503
17 hours	0,002853	0,003793	0,003809	0,047224	0,002215	0,002487	0,080783
24 hours	0,002492	0,004652	0,003718	0,046729	0,002840	0,003962	0,080174

From those fourteen cations, five were chosen to analyze the solubility of them in Milli-Q water in dependence of the time and bulk density. Especially, the dissolution of iron from Saharan dust aerosol in seawater is very important to determine, since it was shown that iron was essential for the abiotic production of volatile halogenated organics in soils and sediments. In addition, the results of manganese, potassium, calcium and aluminum dissolution experiments are discussed.

Shown in Figure 8 are the percentages of dissolved iron from the samples Sahara 2 and 8 during 24-hour leaching experiment. For the sample Sahara 8 after 24 hours 0.1 % of total iron was dissolved in Milli-Q water. But for the sample Sahara 2 only 0.03 % of the total iron was dissolved. For both samples, percentage of dissolved iron increased until 2 hours of leaching, which was the maximum amount for the sample Sahara 2. The decrease in percentage of dissolved iron after 2 hours of leaching and for the sample Sahara 2 also after 5 hours of leaching indicates the existence of equilibrium state between the dissolved iron and the iron in particle phase and the permanent shift of this equilibrium state.

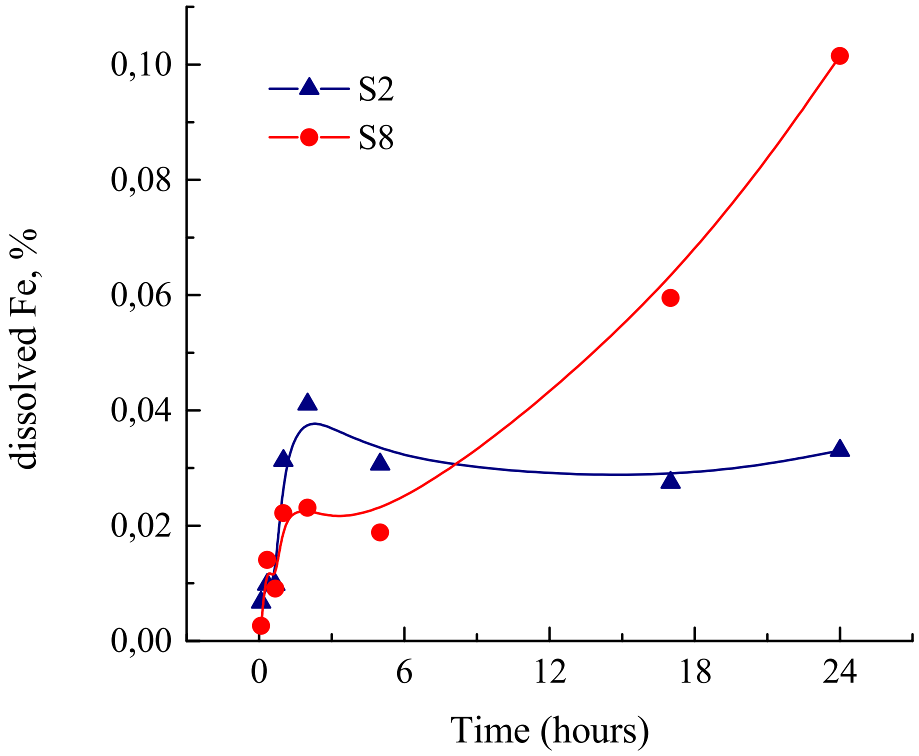

Figure 8. Percentage of dissolved iron during 24-hour leaching experiment.

Exactly the same pattern can be seen for the dissolved manganese and aluminum in Figures 9 and 10. For sample Sahara 8 the amount of dissolved manganese and aluminum reached their maximum percentages after 24 hours and they were 0.08 % and 0.09 %, respectively. For sample Sahara 2 the maximum percentage of dissolved manganese reached after 24 hours and was 0.06 %. But the amount of dissolved aluminum reached its maximum after 2 hours of leaching and was 0.05 %. For sample Sahara 8, the percentage of dissolved iron, manganese and aluminum correlated linearly with the time of leaching ($R^2=0.96$). The difference between the samples Sahara 2 and Sahara 8 could not be explained by the sample characterization experiment results we had. We suggest that it is the difference in the mineralogy of the samples which unfortunately could not be analyzed in frame of this work.

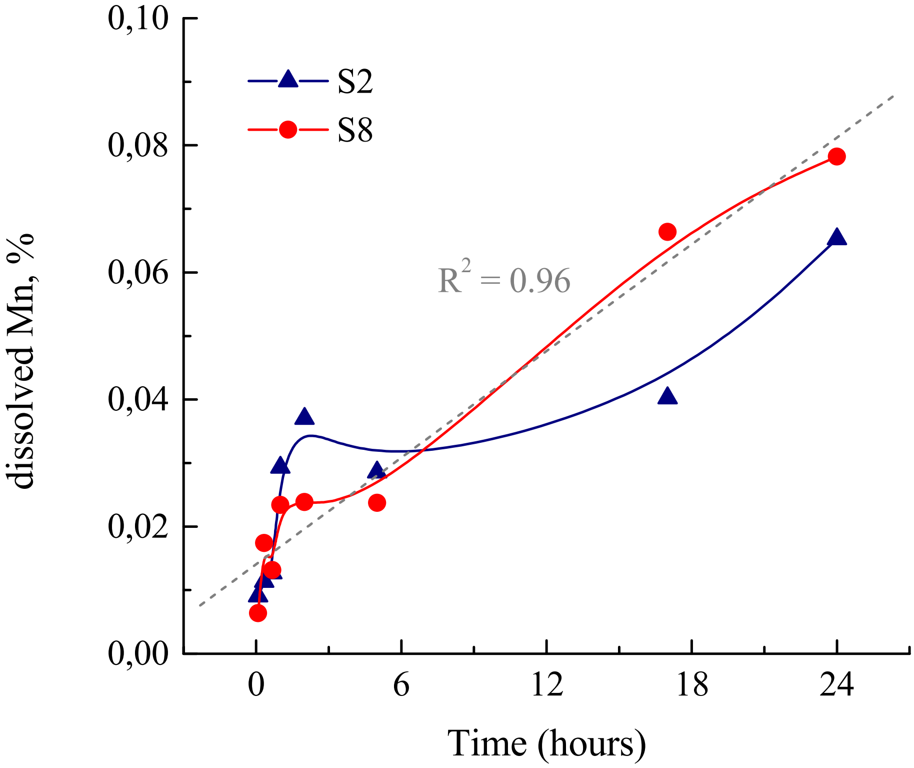

Figure 9. Percentage of dissolved manganese during 24-hour leaching experiment.

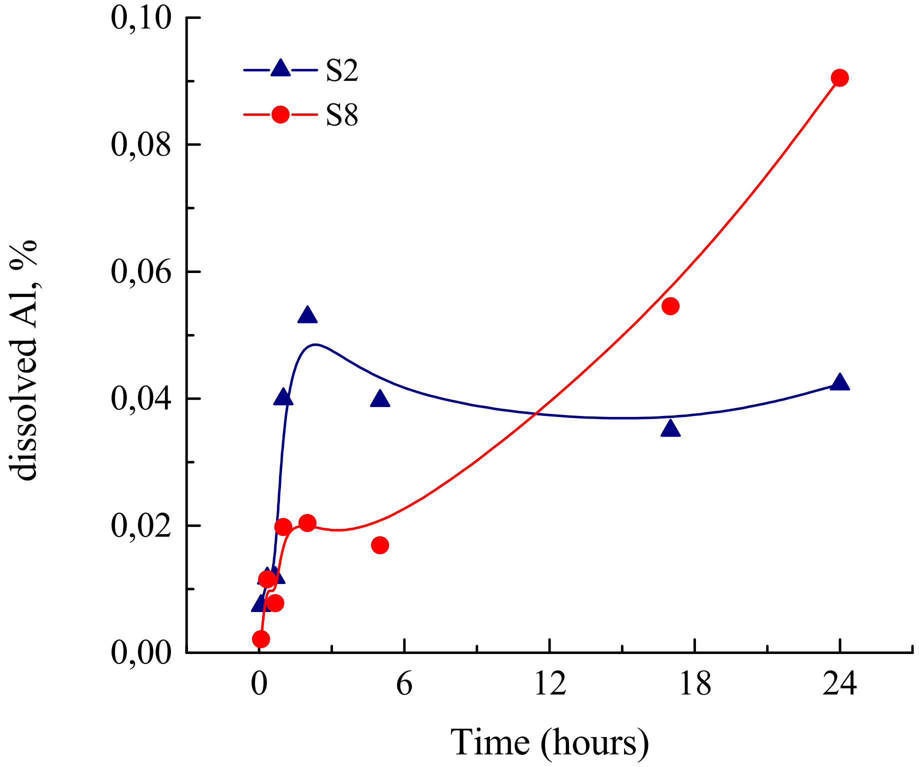

Figure 10. Percentage of dissolved aluminum during 24-hour leaching experiment.

Figures 11 and 12 show the percentages of dissolved calcium and potassium during 24-hour leaching experiment. In contrast to iron, manganese and aluminum, calcium and potassium show the same pattern of dissolution for those two samples. After 24 hours of leaching, about 1.3-1.4 % of calcium and 0.5 % of potassium were dissolved.

The dissolution followed the logarithmic law ($R^2 = 0.96 - 0.98$). In the first 2 hours of leaching half of the calcium and potassium, which were dissolved after 24 hours, were already transferred to the solution.

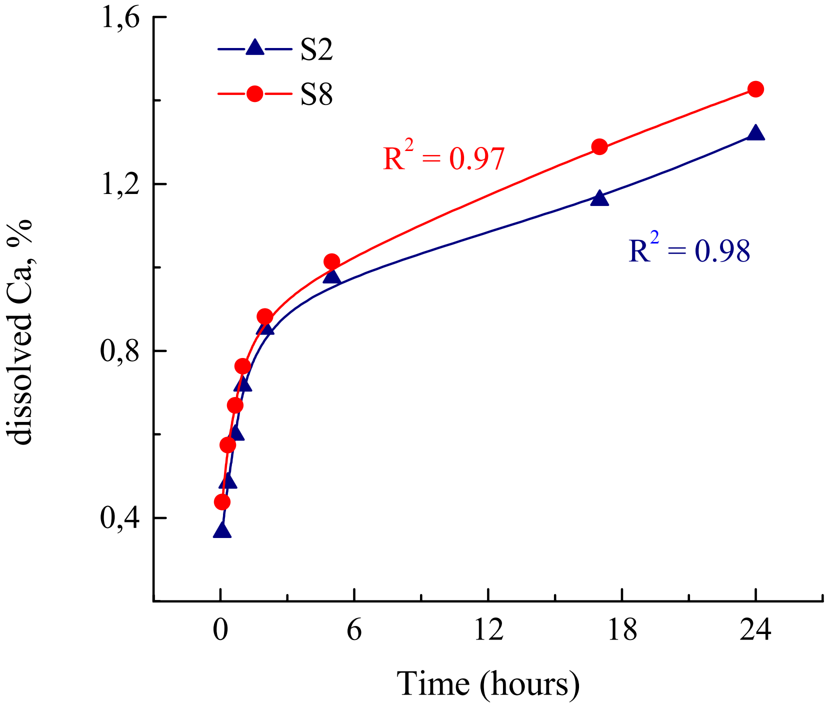

Figure 11. Percentage of dissolved calcium during 24-hour leaching experiment.

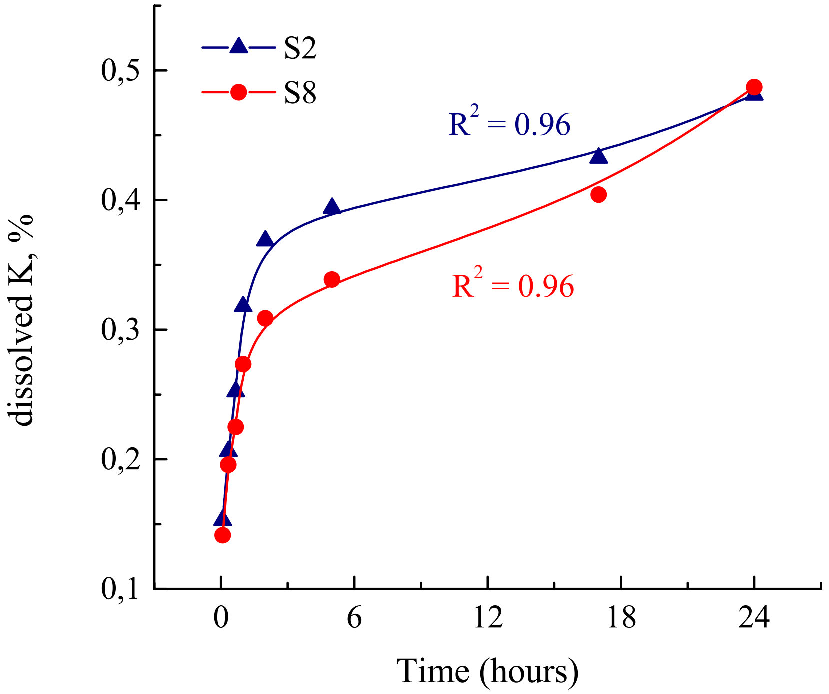

Figure 12. Percentage of dissolved potassium during 24-hour leaching experiment.

Although the bulk density was always kept at ratio 1:10 while shaking the samples with Milli-Q water, every time when the cation analysis was done, 10 ml of the solution was replaced by 10 ml of Milli-Q water, which makes the ratio 1:27.5 after 8 measurements until 24 hours. The effect of this dilution process is clearly seen in Table 9.

Table 9. Effect of the sample to Milli-Q water ratio on the dissolution of some metals after 24 hours of leaching

	Sample to Milli-Q water ratio	Fe^{2+}, %	Mn^{2+}, %	Al^{3+}, %	Ca^{2+}, %	K^{+}, %
S2	1:27.5	0,0330	0,0653	0,0423	1,3182	0,4812
	1:10	0,0065	0,0274	0,0080	0,8348	0,2549
	1:3	0,0033	0,0045	0,0043	0,5150	0,1257
S8	1:27.5	0,2734	0,0782	0,0905	1,4267	0,4872
	1:10	0,1448	0,0171	0,0143	0,9902	0,2356
	1:3	0,0286	0,0016	0,0008	0,7380	0,1196

The bulk densities chosen in this study are far more different than that occur during the common Saharan dust events. But the instrumental availability allowed this range, and the volatile organic compound measurement experiments were also done with these bulk densities. There are no other studies with which we can directly compare our results. There are studies which were carried out in ultra pure water but with bulk densities of 10-1000 mg/l and 15 minutes of leaching, and which were conducted in sea water with 24 hours and 7 days of leaching [*Bonnet and Guieu*, 2004; *Guieu and Thomas*, 1996].

This study showed that there are enough cations coming to the solution when Saharan dust particles are mixed with the solvent. The following experiments are going to show whether these cations are in enough amount to produce the volatile halogenated organics through the anticipated abiotic mechanism.

3.7 Results and Discussion of pH analysis

The sample extracts prepared by mixing 10 g of samples with 30 ml of Milli-Q water for 24 hours and then filtering through 0.45 μm filter showed neutral and slightly basic pH values. The pH measurement results of the sample extracts are shown in Table 10.

Table 10. pH values of the sample extracts

Samples	pH
Sahara 1	7,98
Sahara 2	7,99
Sahara 2 > 0.063	8,08
Sahara 2 > 0.125	8,04
Sahara 3	7,97
Sahara 4	7,92
Sahara 5	8,03
Sahara 6	8,14
Sahara 7	8,04
Cape Verde	8,52
Sahara 8	7,94
Sahara 8 > 0.063	7,97
Sahara 8 > 0.125	7,95
Sahara 8 > 0.2	7,99
Sahara 8 > 0.315	8,04
Sahara 9	8,16
Gobi 1	9,06
Gobi 2	7,91
Lanzarote < 0.02	8,58
Lanzarote	8,47

3.8 Ion balance

The sample characterization analysis was completed. In some analytical methods certified samples were used to check the measurement reliability. Ion balance is the most important control to see whether the water chemistry analysis was in order. Generally the total concentration of anions must equal the total concentration of cations. The analysis is accepted when the error of ion balance does not exceed 5 %.

The cation analysis was conducted on two samples Sahara 2 and 8, so was the ion balance. The Table 11 shows the total cation and the Table 12 shows the total anion concentrations which were used to calculate the ion balance according to the following formula:

$$Ion\,Balance = \frac{Total\,Cation - Total\,Anion}{Total\,Cation + Total\,Anion} * 100\%$$

The ion balance for the sample Sahara 2 was - 3.58 %, for the sample Sahara 8 was - 4.20 %, both of them in the range of acceptable error, which makes the sample characterization analysis reliable.

Table 11. Total cation concentration

Sample	Ca^{2+}, mmol/l	K^{+}, mmol/l	Mg^{2+}, mmol/l	Na^{+}, mmol/l	Al^{3+}, mmol/l	Fe^{2+}, mmol/l	Total
S 2	0,8567	0,2143	0,1763	0,7584	0,0416	0,0111	3,1864
S 8	1,1968	0,2232	0,1725	0,4504	0,0088	0,0026	3,4441

Table 12. Total anion concentration

Sample	Cl^{-}, mmol/l	NO_3^{-}, mmol/l	SO_4^{2-},mmol/l	HCO_3^{-}, mmol/l	Total
S2	0,6685	0,8960	0,1706	1,5169	3,4227
S8	0,6657	0,9345	0,1741	1,7975	3,7459

3.9 Conclusion

The dust samples from Algeria, Cape Verde Island, Lanzarote Island and the Gobi Desert in Mongolia and their leach solutions in Milli-Q water were characterized using several analytical methods. In dry dust samples ($d < 0.063$ mm), elemental composition, water content and total organic content and in their leach solutions, total dissolved organic and inorganic carbon, pH, anions and cations were determined.

Intercomparison of some analytical methods was done. For example, the results of XRF analysis were compared with the results of carbon, sulfur analysis and the Ion Chromatography analysis. The concentrations of the elements determined by means of XRF analysis were similar to the concentrations of the Saharan dust samples, also collected in Algeria, measured by means of acid digestion and following graphite furnace atomic absorption spectrophotometry (GF-AAS) by Guieu et al. [*Guieu and Thomas*, 1996].

The fine sized dust samples contained higher amounts of total organics, calcium, chloride and sulfate. The decreasing bulk density increased the dissolved metal and anion concentrations. The soluble iron fraction, an essential nutrient for the phytoplankton, in case of our study the most important constituent of the abiotic volatile halogenated organic compound formation process, was about 0.03-0.1 %.

The dust samples contained about 4 % of total organics, of which up to 250 ppm were soluble organic carbon. So the sample characterization experiment results approve the possibility of abiotic volatile halogenated organic compound formation process during the interaction of the dust samples from the semi-arid regions with the ocean water, which is a natural pool of halides, since all the required ingredients for this process are present.

Compared to the soil and sediment samples used for the previous studies, the concentrations of some ingredients (iron, organics) were very low. But the following headspace analysis would show whether their concentrations are enough for the process, whether there exists the same mechanism and whether there are other unknown processes taking place.

4 ABIOTIC PRODUCTION OF METHYL IODIDE AND METHYLENE CHLORIDE FROM THE INTERACTION BETWEEN DUST PARTICLES AND SEA WATER

4.1 Summary

The feasibility of abiotic methyl iodide production from the interaction between Saharan dust particles and seawater was investigated. For this, dust-seawater addition experiments were conducted in the laboratory, with subsequent analysis by GC-MS. 4.00 g of fine dust sample (d<0,063mm, 4,7% Fe, 0,19% total carbon), collected from the region of Southern Algeria (Oued Tamanrasset), was suspended in 10 ml of seawater, collected during the ship cruise (METEOR 55) and filtered to 0.2 µm, in 20 ml headspace vials, which were capped immediately after sample preparation. After shaking the samples for certain period, the gas phase was analysed for volatile organics with a purge and trap GC-MS (Tekmar LSC 2000/Varian Star 3400 cx/ Varian Saturn 2000). The same experiments were also done using sterilized dust and water samples. To test the production rates of volatile organics, the following different reaction times were chosen; 20 min, 40 min, 1 hour, 24 hours, 48 hours and 72 hours. Methyl iodide and methylene chloride were produced from both sterilized and non-sterilized samples supporting the abiotic production mechanism. The addition of an electron acceptor Fe (III) increased the amount of methyl iodide produced tenfold. It supports the proposed abiotic production mechanism for volatile halogenated organic compounds involving the humic-like substance (HULIS), an electron acceptor Fe (III) and halide ions.

4.2 Introduction

Methyl iodide was the first organic iodine compound detected in the atmosphere [*Lovelock, et al.*, 1973]. It is the most abundant iodine containing halocarbon [*Richter*, 2003]. The main source of atmospheric methyl iodide is ocean [*Carpenter*, 2003]. It is produced by macroalgae [*Manley and Dastoor*, 1988] and phytoplankton [*Oram and Penkett*, 1994]. Photochemical production of methyl iodide was shown by Moore et al. [*Moore*, 1994] and it was proven by the measurements of Happell and Wallace [*Happell and Wallace*, 1996].

Methyl iodide has an atmospheric concentration of about 0.1-3 pptv over the open ocean [*Carpenter, et al.*, 1999; *Moore and Groszko*, 1999; *Yokouchi, et al.*, 1997]. In the atmosphere, methyl iodide is photolyzed and oxidized by mainly ozone to produce reactive iodine radicals. It has an atmospheric lifetime of only 2-6 days [*Vogt*, 1999]. This short lifetime enables the use of methyl iodide as a tracer of marine convection [*Bell, et al.*, 2002]. In the marine boundary layer, IO and OIO were detected by DOAS (Differential Optical Absorption Spectroscopy) [*Alicke, et al.*, 1999; *Hebestreit, et al.*, 2000]. OIO involves in new particle formation in coastal areas [*Hoffmann, et al.*, 2001].

Although the roles of methyl iodide in the atmosphere are quite well known, there are still uncertainties in its source characteristics and the parameters that control its production [*Carpenter*, 2003]. Atmospheric methyl iodide concentration is shown to have high correlation with surface seawater temperature [*Yokouchi, et al.*, 2001]. Increased methyl iodide concentration was measured after dust storms on the Atlantic Ocean [*Williams, et al.*, 2007].

The results of this chapter show an abiotic production of methyl iodide through the interaction of dust samples with seawater. Also methylene chloride, which has mainly anthropogenic sources, was produced abiotically from this natural source.

4.3 Materials and Methods

Dust samples from the Sahara Desert were collected directly from the ground in Oued Tamanrasset (22° 47′ N, 5° 31′ E, 1362 m) in the Hoggar region of southern Algeria and sea water sample was collected during the ship's cruise (METEOR 55) on the Atlantic Ocean. Dust samples were sieved through 0.063 mm sieve and only fine particles were used for the experiments. Sea water sample was filtered through 0.2 µm filter. 4.00 g of dust sample was added to 10 ml of sea water in a 20 ml headspace glass vial and was capped immediately after sample preparation. After shaking the samples in headspace glass vials for certain period at room temperature, the headspace gas was analyzed with purge-and-trap GC-MS system (Tekmar LSC 2000/Varian Star 3400 cx/Varian Saturn 2000).

For preliminary experiments, six different interaction periods were chosen; 20 minutes, 40 minutes and 1 hour as short interaction and 24 hours, 48 hours and 72 hours as long interaction times. For every period, triplets were measured. For purge-and-trap GC-MS analysis, two needles of purge-and-trap unit, Tekmar LSC 2000, which was connected upstream to the Gas Chromatograph Varian Star 3400 cx, were stuck through the butyl rubber stopper of the headspace glass vial containing the sample. Through one of the needles, helium gas was purged for 4 minutes at the flow rate of 30 ml/min pre-concentrating the headspace gas on the trap filled with Tenax TA 60/80 and cooled at -90 ^{0}C with liquid nitrogen. A water trap filled with magnesium perchlorate was connected upstream to this pre-concentration trap. After 2 seconds of dry purge step, desorption of concentrated volatile organics from the pre-concentration trap was conducted by heating the trap at 180 ^{0}C for 4 minutes. During the desorption step, the capillary column of the gas chromatograph was cooled at -90 ^{0}C with liquid nitrogen to reconcentrate the volatile organics at the beginning of the column. Gas chromatographic separation was carried out on a column SGE BP624 (I.D. 0.53 mm, O.D. 0.68 mm, length 25 m) using the temperature program as shown in Figure 1 (see p.9). Mass spectrometric detection was done in scan mode over a range of 45-280 amu with an ion trap Mass Spectrometer Varian Saturn 2000. Analytical method is also described in detail elsewhere [*Keppler, et al.*, 2005]. For the identification and quantification, methyl iodide standard solution (10 ng/µl) and the standard mix VOC-Mix 20 (200 ng/µl each component) were used. The masses to identify methyl iodide were 127 and 142. The retention time of methyl iodide with the used column was 18.8 min. The masses to identify methylene chloride were 49 and 84. The retention time of methylene chloride with the used column was 19.9 min.

4.4 Results and Discussion

The addition of dust samples collected from the identified source regions in southern Algeria to the filtered Atlantic seawater rapidly produced methyl iodide. This was found for both sterilized and non-sterilized samples. The amount of methyl iodide produced through this interaction was very low and was almost always close to detection limit. However, the experiments with addition of iodide and hydrogen peroxide produced sufficient amounts of methyl iodide to be reliably quantified. The results of the measurements with the addition of iodide and hydrogen peroxide and thus the proof that the methyl iodide is produced abiotically when dust particles interact with seawater are to be found in the works of Maciejczyk and Williams [*Maciejczyk*, 2005; *Williams, et al.*, 2007].

According to Keppler et al. who found the abiotic formation mechanism of volatile halogenated organic compounds in soils and sediments, an electron acceptor Fe (III) is also an important constituent which contributes to this process [*Keppler, et al.*, 2000]. So the addition of Fe (III) was tested to see whether it was also true for the case of dust sample and seawater. In 50 ml headspace glass 0.03 g of dust sample Sahara 5 was put into 30 ml of seawater and was capped immediately afterwards. The sample was then shaken at room temperature for half an hour and the headspace gas was analyzed with purge-and-trap GC-MS. As a blank, 30 ml of seawater without addition of dust sample was measured and the measured concentration of methyl iodide was subtracted from the measured methyl iodide produced from the dust sample. Fe (III) in form of sulfate was added to the mixture of dust sample and seawater. For comparison, the same measurement was done with Fe (II) also in form of sulfate instead of Fe (III). For all the analysis, triplets were done and the average of their results was taken. The final concentration of Fe (III) and Fe (II) in the headspace glass was 0.036 nM. This concentration was chosen, because in iron fertilization experiments which took place on the Pacific and Southern Oceans, they used this concentration to mimic the glacial era concentration of iron in those Oceans [*Wingenter, et al.*, 2004]. Fe (II) sulfate was used for the iron fertilization experiments in the ocean, because Fe (III) is not soluble in pH of ocean water. According to Wingenter et al. the concentration of methyl iodide decreased after addition of iron in the ocean [*Wingenter, et al.*, 2004], whereas another iron fertilization experiment showed about doubled increased concentration of methyl iodide [*Liss, et al.*, 2005]. According to our results, the addition of Fe (II) didn’t show any effect on the concentration of methyl iodide produced through the interaction of dust samples with seawater, but the addition of Fe (III) caused tenfold increase in methyl iodide production within half an hour of interaction. The results are shown in Figure 13. The same was also true for sterilized samples, which excludes biological contribution to the production of methyl iodide.

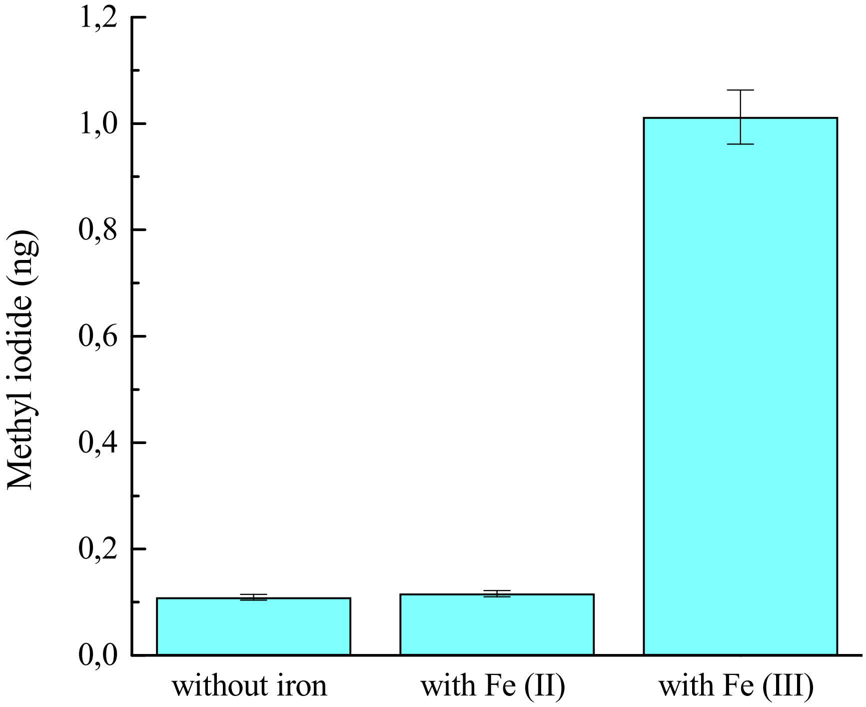

Figure 13. The effect of Fe (II) and Fe (III) addition on the production of methyl iodide through the interaction of dust sample Sahara 5 with seawater.

It is proposed that the humic like substances (HULIS) in dust sample and seawater, iron in dust sample, and iodide in seawater sample are responsible for the production of methyl iodide through abiotic substitution reaction [*Williams, et al.*, 2007]. The methoxy group of HULIS is supposed to give methyl group of the methyl halides produced through the abiotic mechanism and the model substances with methoxy group which is also structural unit of HULIS were tested for their production of methyl halides and indeed showed to produce methyl halides [*Keppler*, 2000; *Maciejczyk*, 2005]. But the production of methyl halides could not be fully explained by this.

It would be helpful to extract the humic substances from the dust samples and to conduct the headspace glass experiments. More helpful would be to determine as much structural units of the humic substances as possible, extracted from the dust samples, using modern analytical techniques like NMR and IR Spectroscopy and to choose the most appropriate model substances for the experiments. Also helpful for fully explaining this abiotic mechanism would be to qualitatively and quantitatively determine as much products of this process as possible in both gas and liquid phase using GC-MS and HPLC-MS. The more products we could determine, the closer we would come to the explanation of the mechanism.

During this work, the headspace gas phase was analyzed by means of purge-and-trap GC-MS covering the mass range of 45-280 amu. Besides isoprene and methyl chloride, whose results are discussed in the following chapters, methylene chloride was identified and quantified along with methyl iodide. As a preliminary experiment, 4 g of Saharan dust samples were put into 10 ml of sea water in a 20 ml headspace glass, which were capped immediately after sample preparation, and were shaken for 20 min, 40 min, 1 hour, 24 hours, 48 hours and 72 hours. For each period, triplets were done. After each period the headspace gas was analysed with GC-MS. The amount of methylene chloride was changing following the polynomial law ($R^2=0.72$) giving the highest amount after 48 hours (Figure 14.).

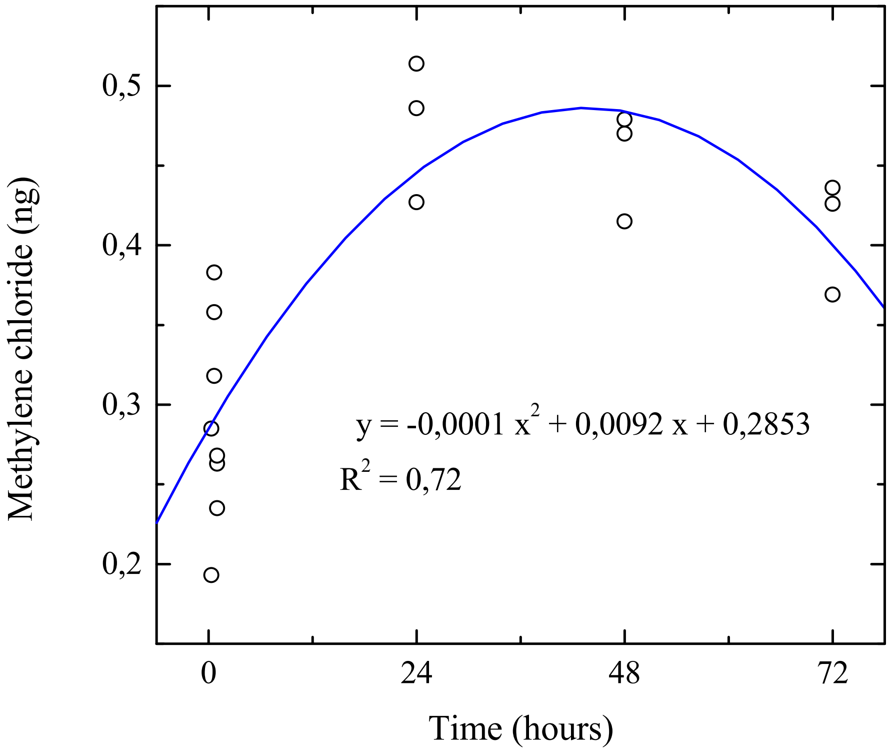

Figure 14. Amount of methylene chloride produced through the interaction of dust sample Sahara 4 with seawater after certain periods. The regression line with the equation is shown.

A continuous measurement of methylene chloride was done from air-tightly closed glass vials, containing 4 g of dust samples in 10 ml of sea water and also from another set of vials containing 4 g of dust samples in 10 ml of distilled water, every 24 hour for 5-7 days using purge-and-trap GC-MS. The amount of methylene chloride was decreasing following the polynomial law ($R^2=0.97$ in seawater and $R^2=0.92$ in distilled water) (Figures 15 and 16.). For every measurement, triplets were done and the average values with the standard errors are shown in the Figures. The decrease in methylene chloride concentration over time could be explained by its degradation.

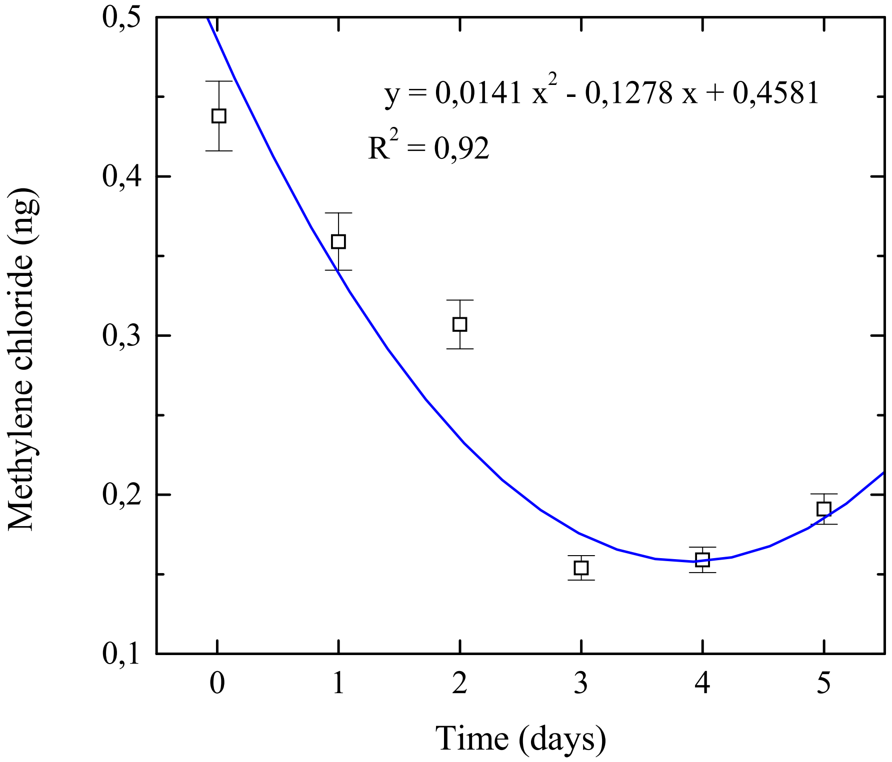

Figure 15. Amount of methylene chloride produced every 24 hour through the interaction of dust sample Sahara 4 with seawater. The regression line with equation is shown.

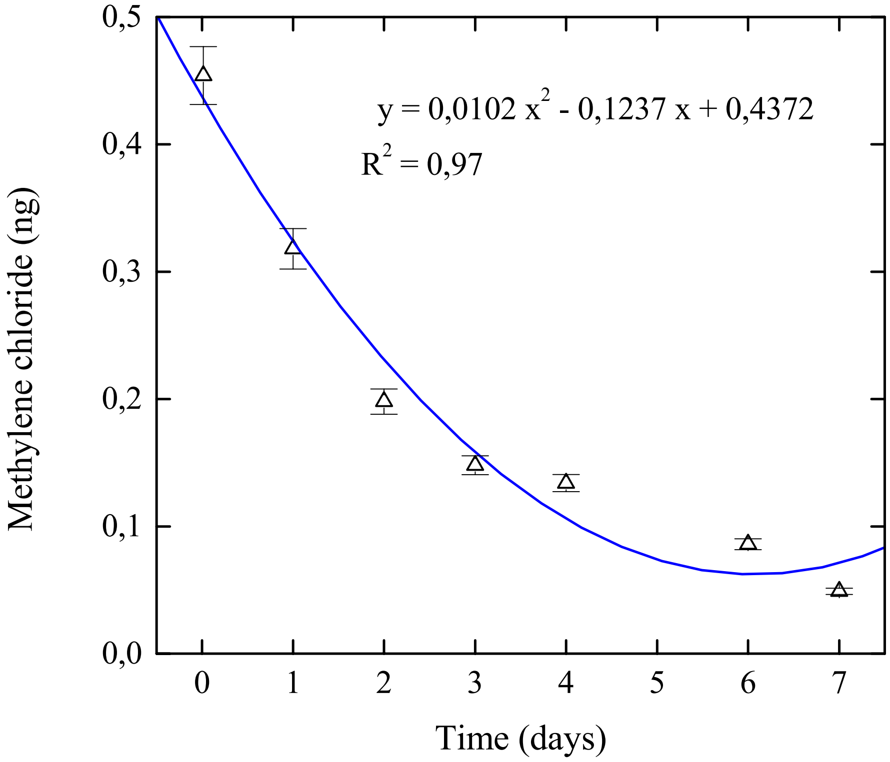

Figure 16. Amount of methylene chloride produced every 24 hour through the interaction of dust sample Sahara 4 with distilled water. The regression line with equation is shown.

The total amount of methylene chloride was increasing also following the polynomial law ($R^2=0.99$ in seawater and in distilled water) with time (Figures 17 and 18.). There was no significant difference between the use of seawater and distilled water as reaction medium.

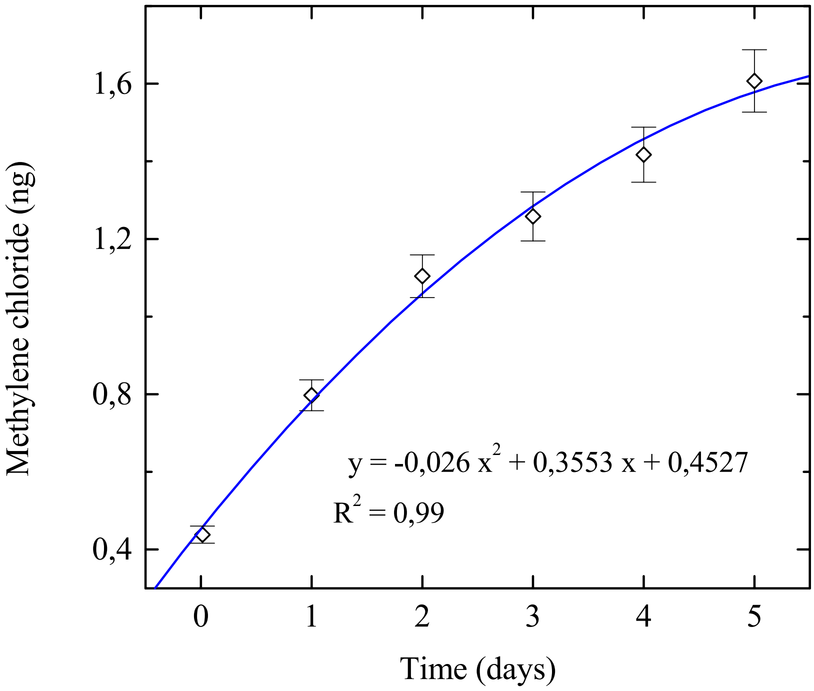

Figure 17. Total amount of methylene chloride produced through the interaction of dust sample Sahara 4 with seawater. The regression line with equation is shown.

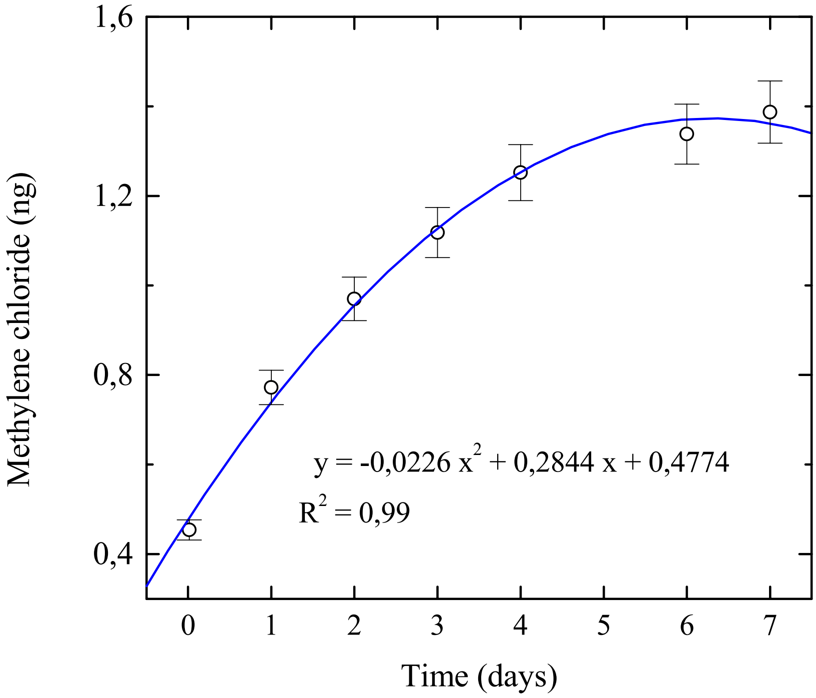

Figure 18. Total amount of methylene chloride produced through the interaction of dust sample Sahara 4 with distilled water. The regression line with equation is shown.

The same experiments were done with sterilized dust and distilled water samples to approve the abiotic production mechanism and to exclude the biological contribution to the production of methylene chloride. The samples were sterilized under 0.1 MPa pressure at 120^0C for 1 hour in an autoclave. A continuous measurement of methylene chloride was done from air-tightly closed glass vials containing 4 g of sterilized dust samples in 10 ml of sterilized distilled water every 24 hour for 4 days using purge-and-trap GC-MS. The amount of methylene chloride was decreasing following the polynomial law ($R^2=1$) (Figure 19.). For every measurement triplets were done and the average values with the standard errors are shown in the Figure.

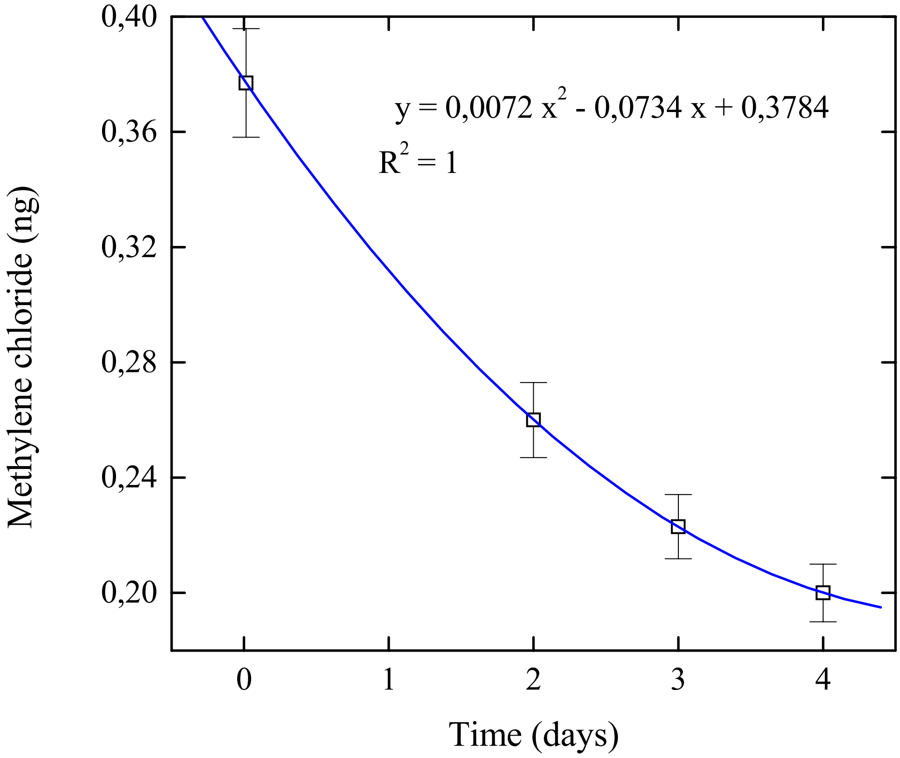

Figure 19. Amount of methylene chloride produced every 24 hour through the interaction of sterilized dust sample Sahara 4 with distilled water. The regression line with equation is shown.

The total amount of methylene chloride was increasing also following the polynomial law (*$R^2=0.99$*) with time (Figure 20.).

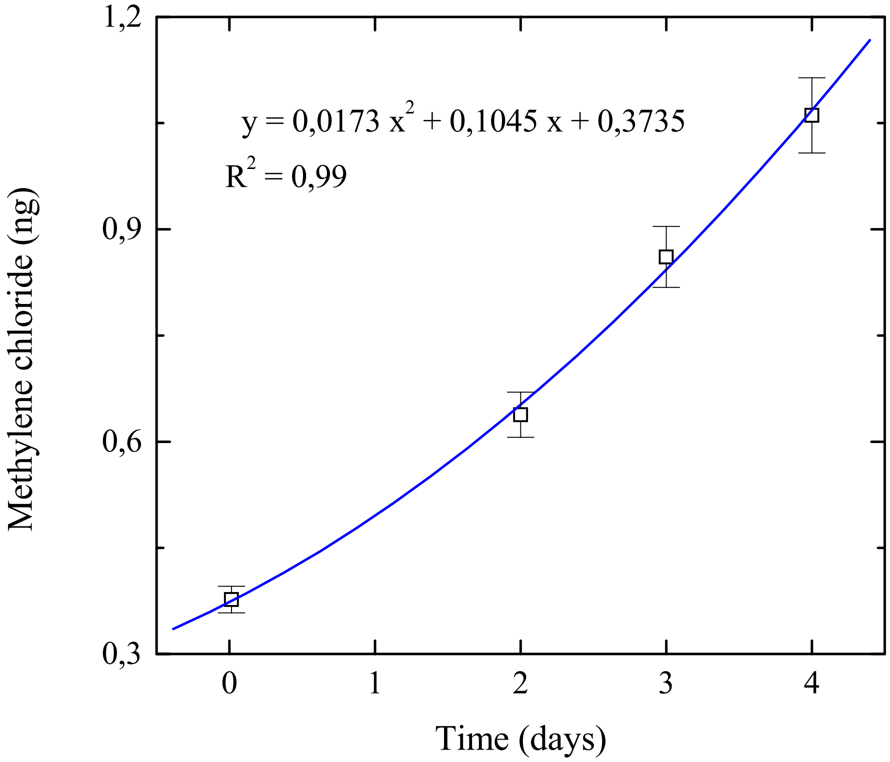

Figure 20. Total amount of methylene chloride produced through the interaction of sterilized dust sample Sahara 4 with distilled water. The regression line with equation is shown.

The GC-MS analysis of sterilized samples also gave methylene chloride, which excludes the biologically mediated methylene chloride production through the interaction of dust particles with seawater. The abiotic production of methylene chloride was presumed to exist [*Law and Sturges*, 2006; *Schöler and Keppler*, 2003]. And the results of these experiments approved this presumption.

4.5 Conclusion

Methyl iodide and methylene chloride were produced through the interaction of dust sample with seawater and distilled water.

There is an abiotic production mechanism for these two volatile halogenated compounds, since the production rate of these compounds from the sterilized samples was as much as that from non-sterilized samples.

The addition of an electron acceptor Fe (III) increased the amount of methyl iodide produced tenfold compared to the amount of methyl iodide produced from the interaction of dust samples with seawater without addition of iron within half an hour, which supports the abiotic mechanism scheme involving HULIS, iron and halide.

5 PRODUCTION OF ISOPRENE FROM THE INTERACTION BETWEEN DUST PARTICLES AND SEA WATER

5.1 Summary

Isoprene is a very important gas for atmospheric chemistry, because it influences the oxidation capacity of the atmosphere by reacting with OH radical, and the radiative balance of the earth by serving as a source for secondary organic aerosol (SOA), and it produces tropospheric pollutant ozone in the presence of NO_x. Plants are the main source of isoprene. The experiments in headspace glass vials conducted in the laboratory during this work show natural dust as a source of isoprene to the atmosphere. Dust samples from the Sahara Desert, Gobi Desert and also the dust sample from Cape Verde Island which has undergone aeolian transport produced isoprene both in the presence of seawater and distilled water. In contrast to methyl iodide and methylene chloride, isoprene production was biologically-mediated, because sterilized samples did not produce it. The concentration of isoprene increased linearly ($R^2=0.96$) until 72 hours of reaction time. 0.398 ng of isoprene was released from 4 g of Saharan dust after 72 hours. There was a positive correlation ($R^2=0.99$) between the amount of dust and the amount of isoprene produced after 48 hours reaction time. Dust samples that have already undergone aeolian transport produced more isoprene compared to the samples collected in the source regions. If those microorganisms in dust samples are common soil organisms, this process would explain until now not fully explained reason for the increased atmospheric isoprene concentration during wet seasons.

5.2 Introduction

In 1860 a scientist and analytical chemist Charles H. Greville Williams first isolated the monomer of natural rubber through dry distillation method and named it "isoprene". Isoprene (2-methyl-1, 3-butadiene) is a photochemically reactive and highly volatile organic compound which is emitted into the atmosphere from biogenic sources, mainly plants. It was only 1957 that Guivi Alexander Sanadze discovered the emission of isoprene from plants [*Sanadze*, 1957] and it was confirmed later by Rasmussen [*Rasmussen*, 1970]. Isoprene is formed in the leaves of the plants through the enzymatic, magnesium ion dependent elimination reaction of diphosphate from dimethylallyl diphosphate (DMADP). The enzyme responsible for this reaction was discovered in 1991 and is called isoprene synthase [*Silver and Fall*, 1991, 1995]. The annual global isoprene flux is estimated to be 506 Tg C/yr [*Guenther, et al.*, 1995]. Isoprene is very important for atmospheric chemistry, air pollution and global warming issue because of the following reasons.

In the daytime isoprene is oxidized to organic peroxides mainly by the reaction with OH radical. In the daytime OH radical is abundant in the atmosphere, since its main source is the destruction of ozone by sunlight and the following reaction of oxygen atom with water molecules. In the nighttime however, isoprene is oxidized mainly by nitrate radical (NO_3) formed by the reaction of NO_2 with ozone [*Starn, et al.*, 1998a]. The emission, chemistry and fate of isoprene and other biogenic volatile organic compounds are reviewed in details elsewhere [*Atkinson*, 1990, 1997, 2000; *Atkinson and Arey*, 2003a; 2003b; *Harley, et al.*, 1999; *Kesselmeier and Staudt*, 1999].

In the presence of NO_x (NO_2+NO), organic peroxides formed from the oxidation of isoprene and other volatile organic compounds react mainly with NO competing with ozone. Nitrogen dioxide (NO_2) produced through this reaction is broken down by sunlight giving oxygen atom which reacts with oxygen molecule in the atmosphere and produces ozone, a pollutant in the troposphere and a third most important greenhouse gas [*Pierce, et al.*, 1998; *Roberts, et al.*, 1995; *Starn, et al.*, 1998b; *Williams, et al.*, 1997]. This oxidation and also the oxidation of the first generation products of isoprene oxidation, methyl vinyl ketone (MVK), methacrolein (MACR) and 3-methyl furan, lead to the formation of organic nitrates and peroxyacyl nitrates (PANs) [*Bertman and Roberts*, 1991; *Chen, et al.*, 1998; *Grossenbacher, et al.*, 2001; *Harley, et al.*, 1999; *Montzka, et al.*, 1993; *Nouaime, et al.*, 1998; *Paulson and Seinfeld*, 1992; *Pegoraro*, 2004; *Pierotti, et al.*, 1990; *Roberts, et al.*, 1998a; *Roberts, et al.*, 2004; *Roberts, et al.*, 2002; *Roberts, et al.*, 2001; *Roberts, et al.*, 2003; *Roberts, et al.*, 1998b; *Tanimoto and Akimoto*, 2001]. The relative stability of PANs enables their long distance transport to remote areas. In remote areas, PANs serve as a source of NO_x, eventually a source of pollutant ozone in the atmosphere [*Shallcross and Monks*, 2000].

Isoprene and its oxidation products are the sources for the secondary organic aerosol (SOA) which plays an important role in the radiation balance of the earth both through direct and indirect means [*Altieri, et al.*, 2006; *Böge, et al.*, 2006; *Carlton, et al.*, 2006; *Claeys, et al.*, 2004a; *Claeys, et al.*, 2004b; *Edney, et al.*, 2005; *Henze and Seinfeld*, 2006; *Kleindienst, et al.*, 2006; *Kroll, et al.*, 2006; *Lane and Pandis*, 2007; *Lim, et al.*, 2005; *Limbeck, et al.*, 2003; *Ruppert and Becker*, 2000; *Surratt, et al.*, 2006; *van Donkelaar, et al.*, 2007].

Isoprene reacts immediately with OH radical in the atmosphere, thus reduces the oxidation capacity of atmosphere and makes the lifetime of second important greenhouse gas (GHG), methane longer.

There are some other sources of isoprene, like sea water [*Bonsang, et al.*, 1992; *Broadgate, et al.*, 1997; *Matsunaga, et al.*, 2002], phytoplankton [*Moore, et al.*, 1994; *Yokouchi, et al.*, 1999], bacteria [*Kuzma, et al.*, 1995; *Wagner, et al.*, 2000; *Wagner, et al.*, 1999], wetland, peatland [*Janson and De Serves*, 1998; *Tiiva, et al.*, 2007] and so on. But compared to the terrestrial emission, the strength of those other sources are negligible. However, due to high reactivity of isoprene, even its small sources have potential to impact the chemistry of the area where it is produced, for example local remote Marine Boundary Layer (MBL) chemistry [*Palmer and Shaw*, 2005].

There is large uncertainty in the emission estimates of isoprene because of scarcity of direct measurements. Indirect emission estimates from satellite measurements are also done [*Palmer and Shaw*, 2005; *Shim, et al.*, 2005]. The current estimates are the results of global models [*Guenther, et al.*, 1995; *Guenther, et al.*, 2006].

This work presents the results of laboratory experiments which show a new interesting source of isoprene.

5.3 Materials and Methods

Dust samples Sahara 4, Sahara 5, Cape Verde and Mongolia 2 were used in the following experiments (see p.4), because they contained higher amounts of organics than the other samples. 4 g sample Sahara 4 was added to 10 ml of seawater in 20 ml headspace glass vial, which was capped immediately after sample preparation. It was shaken at room temperature for certain period and the headspace gas was measured by GC-MS. Later, the amount of dust sample was reduced to 1 g to see the effect of bulk density on the production of isoprene. As it was seen that the bulk density had no big effect on the production, 4 g samples were used for further experiments to better quantify isoprene amounts. For the identification and quantification of isoprene, isoprene standard solution was prepared. Analytical method is described in detail in Chapter 4 (see p.31). The masses to identify isoprene were 53, 67 and 39. The retention time of isoprene with the used column was 17.3 min. The same set of experiments was also done with sterilized samples to exclude the microbiological contribution to the production of isoprene. The samples were sterilized in an autoclave under 0.1 MPa pressure at 120 ^{0}C for one hour.

5.4 Results and Discussion

5.4.1 Production of isoprene

As a preliminary experiment, 4 g of dust samples Sahara 4 were put into 10 ml of sea water in 20 ml headspace glass vials, which were capped immediately after sample preparation, and were shaken for 5 min, 20 min, 40 min, 1 hour, 24 hours, 48 hours and 72 hours. For each period, triplets were done. After each period, the headspace gas was analyzed with GC-MS. We identified isoprene in headspace gas and the amount of isoprene was increasing linearly ($R^2=0.96$) with increasing reaction time till 72 hours, giving 0.398 ng of isoprene after 72 hours (Figure 21.).

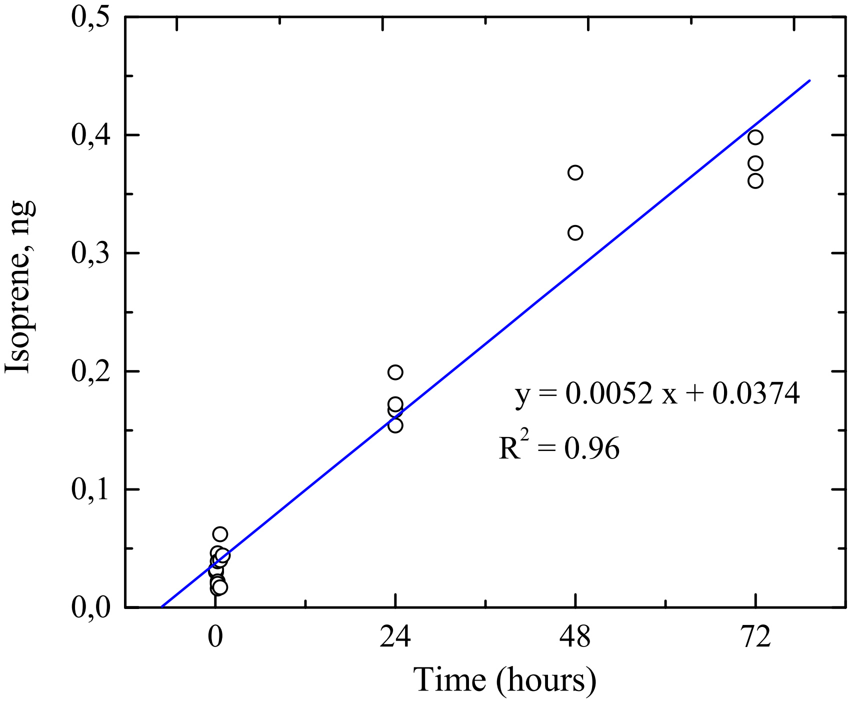

Figure 21. Amount of isoprene produced through the interaction of 4 g of dust samples Sahara 4 with 10 ml of Atlantic Ocean water after certain periods. The regression line with the equation is shown.

The final dust concentration in the 10 m mixed layer of ocean (the bulk density) during strong Saharan dust event is 0.5 mg/l [*Bonnet and Guieu*, 2004]. In this case, the amount of headspace gas produced was always below the detection limit of the instrument. The same experiment was done with 1 g of dust sample in 10 ml of ocean water. The reaction periods were 5 min, 20 min, 40 min, 1 hour, 6 hours, 12 hours and 48 hours, respectively.

For each period, also the triplets were analyzed. The results supported the previous results (Figure 22.). The amount of isoprene produced was increasing linearly (*R^2=0.98*) with reaction time till 48 hours. After same period (48 hours) about 4 times less isoprene was produced than the experiment with 4 g of sample. So we conclude that the bulk density has no relevant effect on the isoprene production whereas it does in dissolution of iron in surface seawater [*Bonnet and Guieu*, 2004].

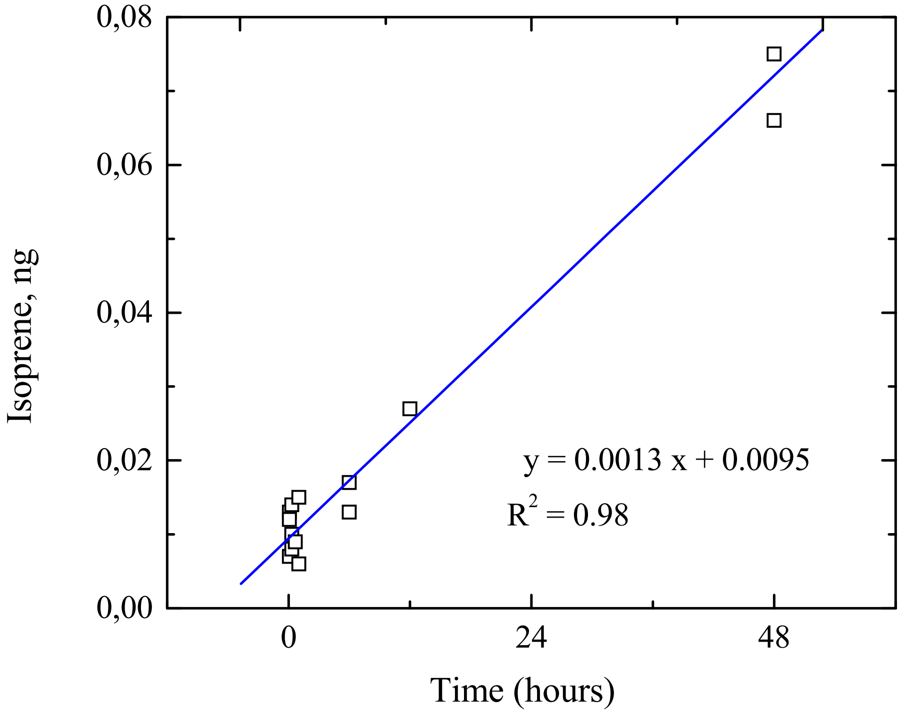

Figure 22. Amount of isoprene produced through the interaction of 1 g of dust samples Sahara 5 with 10 ml of Atlantic Ocean water after certain periods. The regression line with the equation is shown.

5.4.2 Dependence of isoprene amount on the organic content of the dust

The next experiment was done to test the dependence of the amount of isoprene on the amount of dust sample. 0.05 g, 0.10 g, 0.50 g, 1.00 g, 2.00 g and 4.00 g of dust samples from Cape Verde Island were put into 10 ml of sea water and were shaken for 48 hours each. The amount of isoprene produced increased linearly ($R^2=0.99$) with increasing amount of dust sample (Figure 23.), which is also increasing organic content.

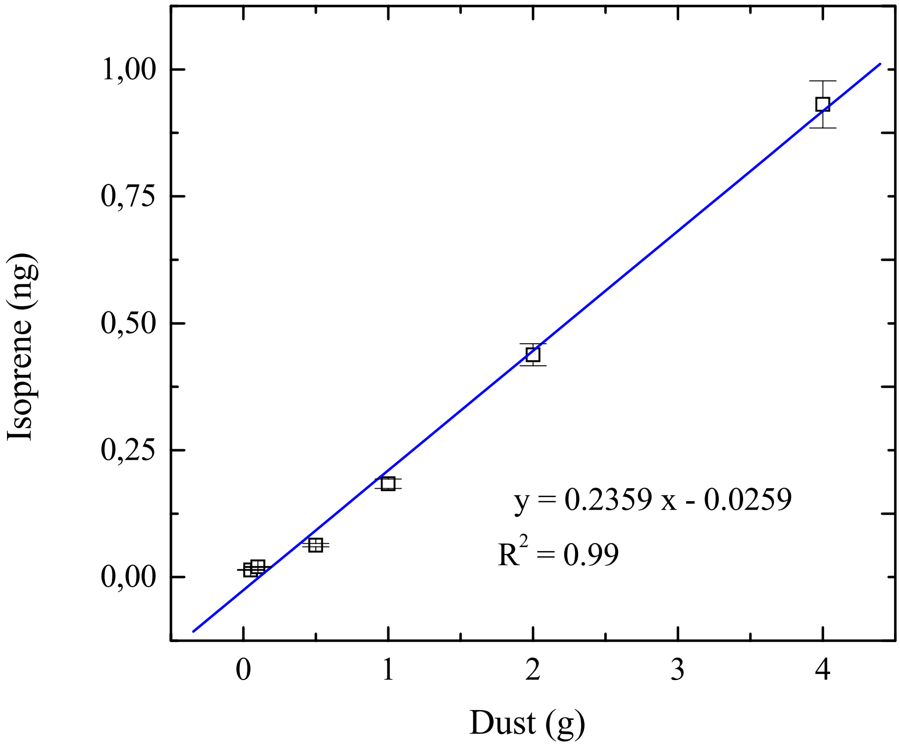

Figure 23. Dependence of isoprene production on the amount of dust. The regression line with the equation is shown.

After 48 hours of reaction time, about 2.5 times more isoprene was produced from 4 g of dust sample from Cape Verde Island (0.931 ng) than that produced from the same amount of dust sample collected directly in the source region in Algeria (0.368 ng). The same was true for the 1 g dust sample from Cape Verde Island (0.184 ng) and Algeria (0.075 ng).

Dust sample which has already gone aeolian transport from Sahara produced more isoprene than the dust sample collected directly from the source region.

It suites well with the ratio of organic content (Ratio=2.3, Cape Verde-7.7%, Algeria-3.4%) and the total dissolved organic content of the samples (Ratio=2.8, Cape Verde-0.11 g/kg, Algeria-0.04 g/kg).

An input of iron containing mineral dust can lead to abiotic production of methyl iodide in the ocean [*Williams, et al.*, 2007]. But a microbiological contribution would be more likely explanation for the production of isoprene [*Fall and Copley*, 2000]. Bacteria produce isoprene [*Kuzma, et al.*, 1995; *Wagner, et al.*, 2000; *Wagner, et al.*, 1999] and viable fungi and bacteria from Africa are transported interhemispherically with soil dust [*McCarthy*, 2001; *Monteil*, 2002; *Prospero, et al.*, 2005]. Also during Asian dust periods, fungal spores are found in the ambient air of west Korea [*Yeo and Kim*, 2002]. The same experiments were done with sterilized dust, sea water and distilled water samples to test our hypothesis of biologically mediated isoprene production. The samples were autoclaved under 0.1 MPa pressure at 120^0C for one hour to exclude the microbiological contribution to the production of isoprene. The GC-MS analysis of those samples gave no isoprene, which supports the biologically mediated isoprene production through the interaction of dust particles with seawater.

5.4.3 Production rate of isoprene and the experiment with distilled water

Since it was shown that there was a biologically mediated isoprene production through the interaction of dust samples with sea water, a question arose "How much is the capability of isoprene production of those microorganisms in dust samples?" To answer this question, continuous measurements of isoprene were done from air-tightly closed glass vials containing 4 g of dust samples in 10 ml of sea water and also from another set of vials containing 4 g of dust samples in 10 ml of distilled water every 24 hour for 5-9 days using purge-and-trap GC-MS. The amount of isoprene was decreasing exponentially ($R^2=0.76$ in seawater and $R^2=0.96$ in distilled water) with time (Figure 24 and 25.) but it was not exhausting.

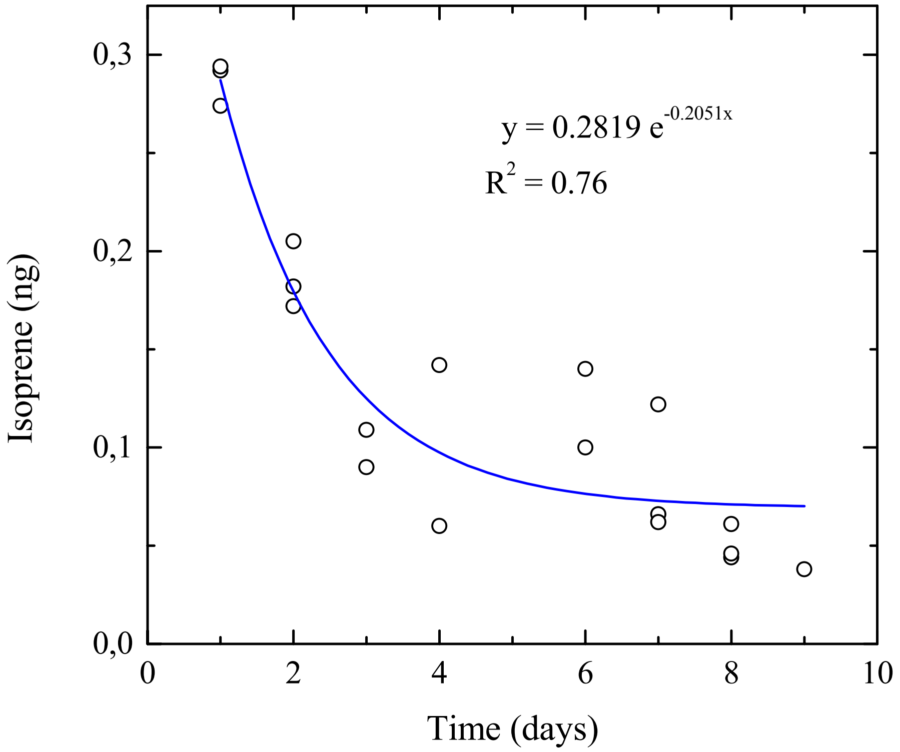

Figure 24. Amount of isoprene produced every 24 hour through the interaction of dust sample Sahara 4 with seawater. The regression line with equation is shown.

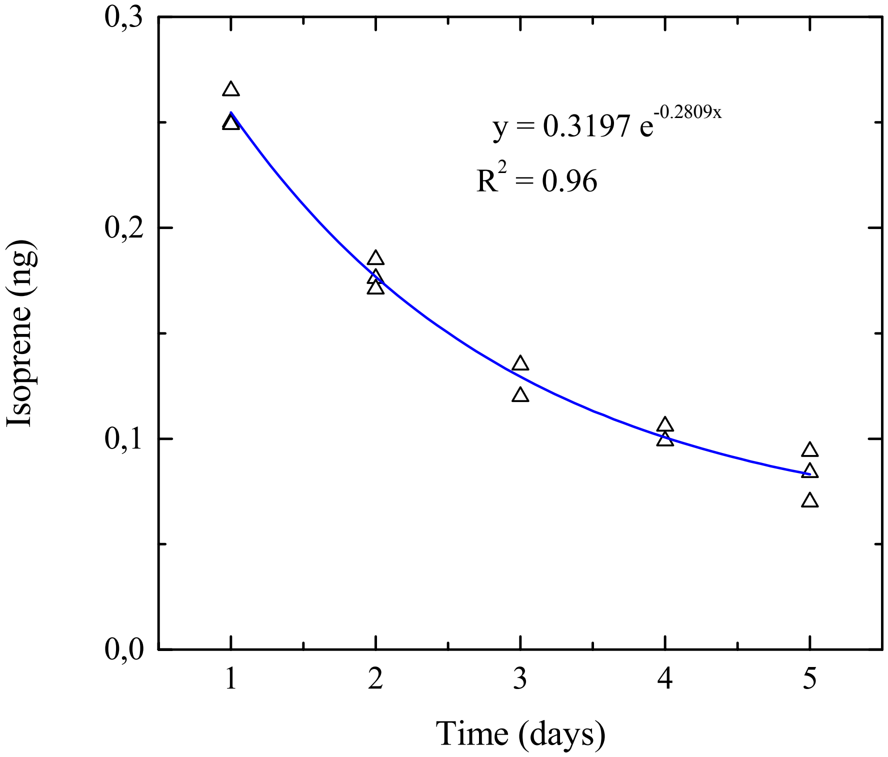

Figure 25. Amount of isoprene produced every 24 hour through the interaction of dust sample Sahara 4 with distilled water. The regression line with equation is shown.

The total amount of isoprene was increasing logarithmically (*R^2=0.99* in seawater and *R^2=0.98* in distilled water) with time (Figure 26 and 27.). There was no significant difference between the uses of seawater and distilled water as reaction medium.

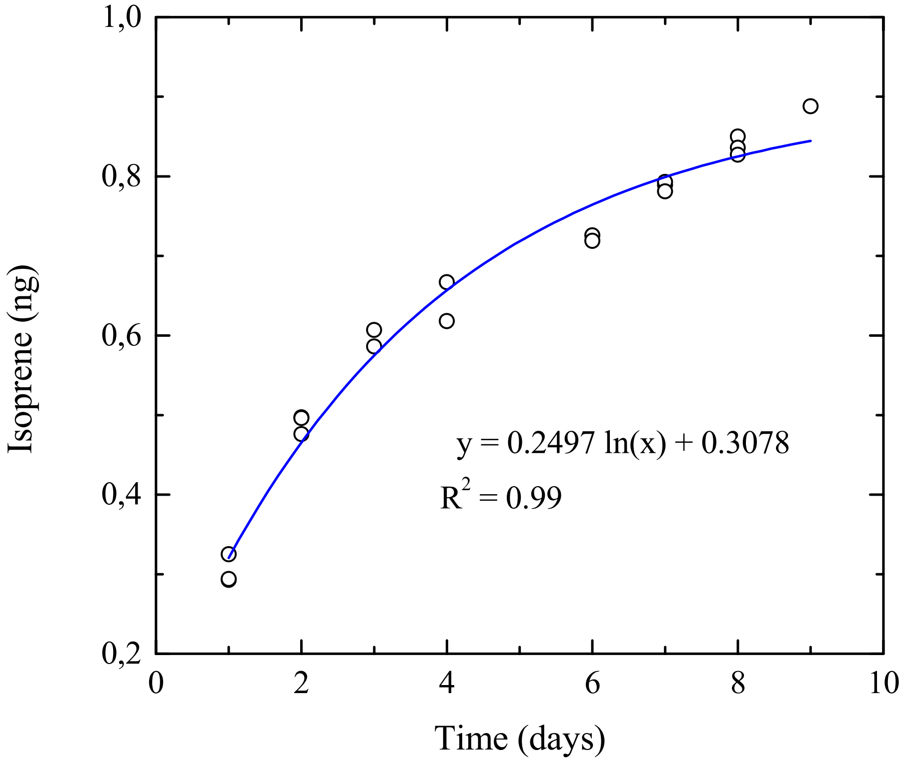

Figure 26. Total amount of isoprene produced through the interaction of dust sample Sahara4 with seawater. The regression line with equation is shown.

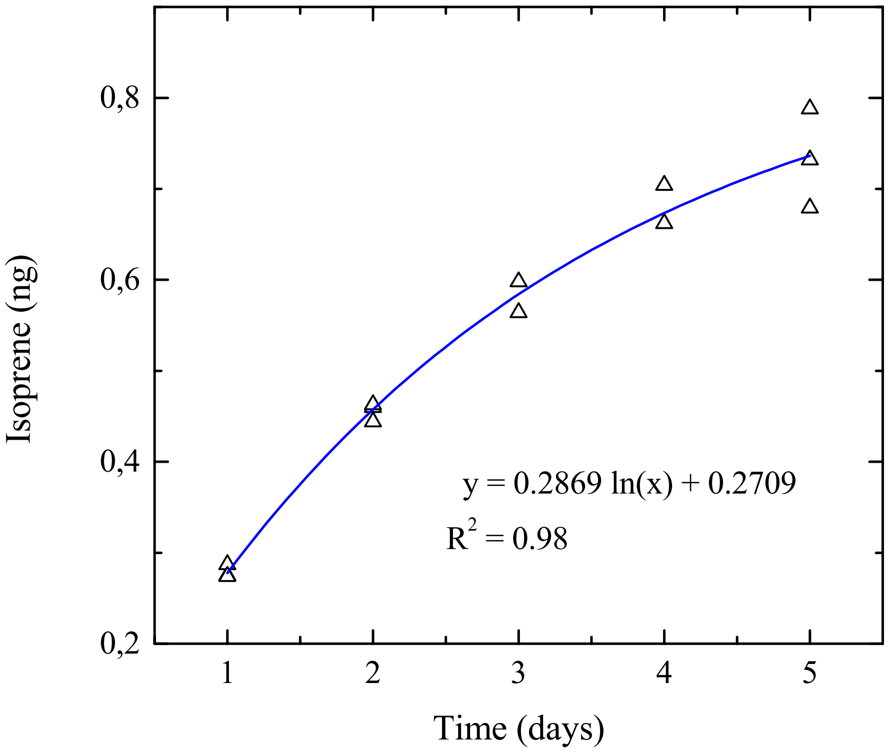

Figure 27. Total amount of isoprene produced through the interaction of dust sample Sahara4 with distilled water. The regression line with equation is shown.

Although we did not have water sample from Pacific Ocean, we were interested in finding out whether dust sample from the Gobi Desert would also produce isoprene when it interacted with water. So the same set of measurements was done with the sample from Gobi Desert in the water sample from Atlantic Ocean and in distilled water.

The sample from Gobi Desert was the one collected in the city center of South Gobi province in Mongolia, which was denoted previously as sample M2. This dust sample was wind blown and was accumulated at the bottom of the fence which typically every family in the city center of the provinces has around its house. So the possibility of anthropogenic pollution was not excluded and it also was shown by XRF and other chemical sample characterization experiments.

In comparison to the dust sample Sahara 4, the sample from Gobi Desert produced 2.5-5 times more isoprene after 24 hours of interaction with seawater and distilled water. Twice more amount of isoprene was produced from the experiment with distilled water than that with sea water. The amount of isoprene produced every 24 hour was decreasing following the polynomial law (*R^2=0.90*) in seawater, and following the potential law (*R^2=0.95*) in distilled water. The results are shown in Figures 28 and 29.

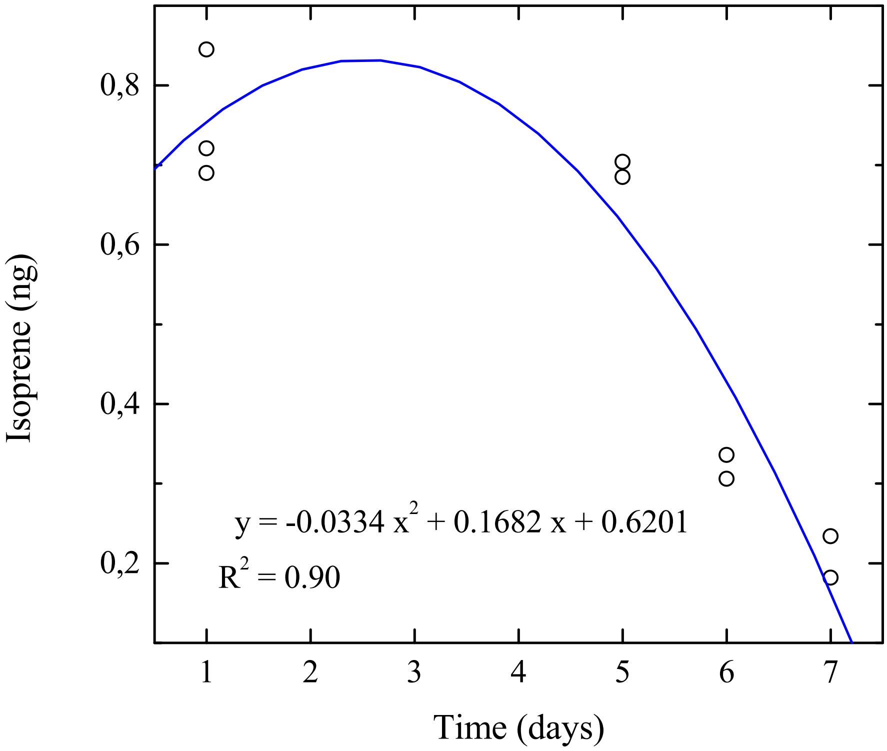

Figure 28. Amount of isoprene produced every 24 hour through the interaction of dust sample from the Gobi Desert with seawater. The regression line with equation is shown.

As shown in Figure 28, the amount of isoprene measured on the 4th day after the first measurement was almost the same or slightly lower than that of the first day, when the dust sample was shaken with sea water.

However, as it is seen in Figure 29, in case of the measurements with distilled water, the amount of isoprene produced on the third day after the first measurement was more than 3 times lower than that of the first time. This could be explained by the existence of both isoprene producing and consuming bacteria in the dust samples and the difference of their activity in different medium. May be the source-sink relationship would be analogous to that seen with methanogens and methanotrophs [*Fall and Copley*, 2000].

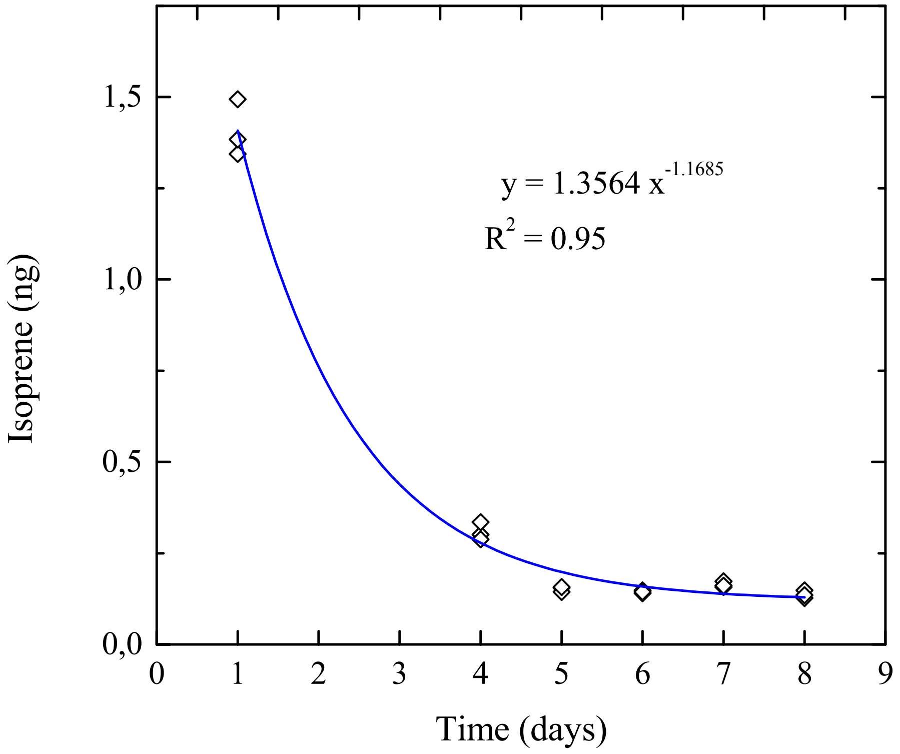

Figure 29. Amount of isoprene produced every 24 hour through the interaction of dust sample from the Gobi Desert with distilled water. The regression line with equation is shown.

As it is seen in Figures 30 and 31, the total amounts of isoprene produced through the interaction of dust samples from the Gobi Desert with sea water and with distilled water were increasing with time exponentially ($R^2=0.98$ in seawater and $R^2=0.94$ in distilled water). The amount of isoprene produced after 7 days was slightly higher in distilled water.

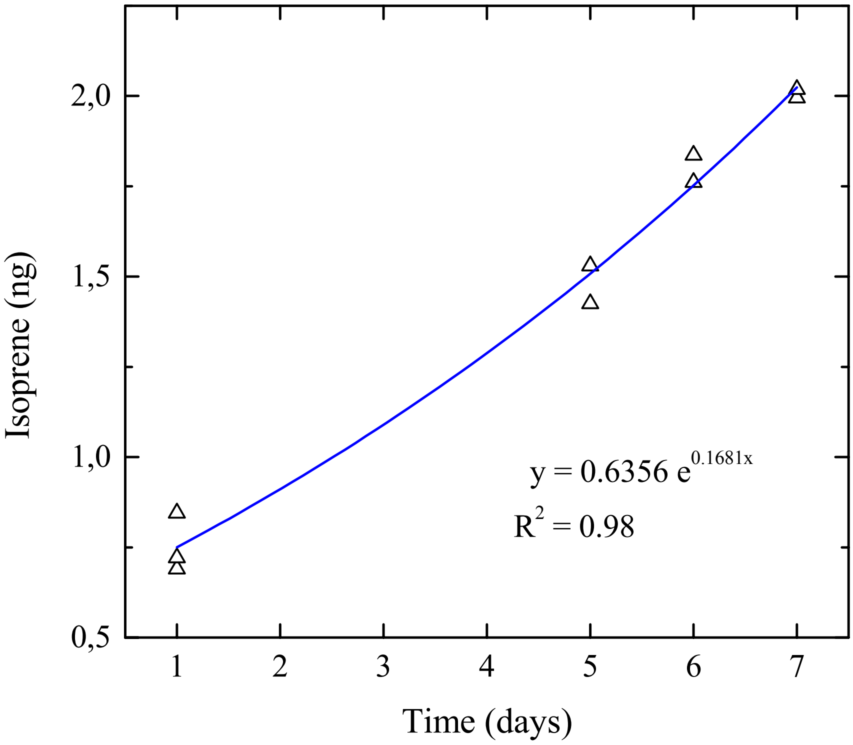

Figure 30. Total amount of isoprene produced through the interaction of dust sample from the Gobi Desert with sea water. The regression line with equation is shown.

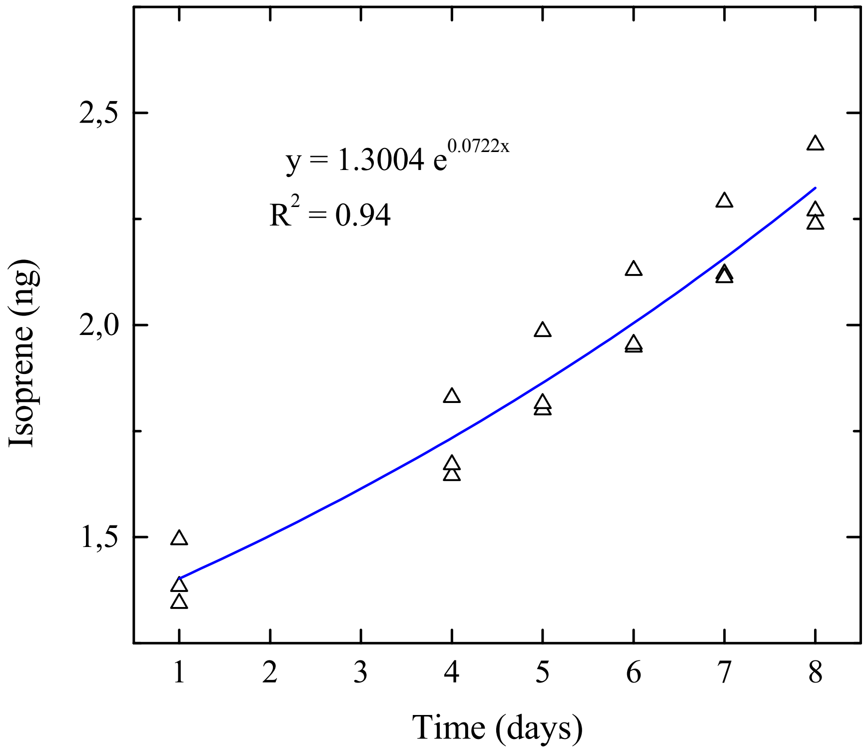

Figure 31. Total amount of isoprene produced through the interaction of dust sample from the Gobi Desert with distilled water. The regression line with equation is shown.

Based on the results of laboratory measurements we could make rough estimate of total amount of isoprene produced during dust storm events annually. It was a very little contribution of isoprene (~ 1500 kg) compared to its plant source. However, this is the case where soil comes into the water and produces isoprene. But on the other hand, how about the case where vice versa occurs, namely when it rains? Of course there would be many other factors influencing the isoprene production of microorganisms in soil. Indeed, there is a study where it shows the consumption of isoprene in soil [*Cleveland and Yavitt*, 1997; *Cleveland and Yavitt*, 1998]. They studied the influence of different factors, such as soil temperature and moisture on the isoprene consumption of soil. In their study, the initial amount of isoprene introduced increased however, when the soil moisture was 100 percent, which supports the results of our measurements.

Isoprene emissions were estimated to be an order of magnitude higher during the November to April wet season, at a level of 23 Tg C, than during the May to October dry season, at a level of 2 Tg C in Tropical Australia [*Ayers and Gillett*, 1988]. It was explained with the increased biomass during this period [*Guenther, et al.*, 1995]. However, microbiological contribution of soil could be high in this region during the wet season, especially, when rain falls on practically every day.

Seasonal emissions of isoprene were measured from an elevated dry site and low wet site on a *Sphagnum* fen in Sweden. The flux from wetter site was generally about 20 times more than that of drier site. The reason for this difference could not be determined in that work [*Janson and De Serves*, 1998].

Diurnal cycles and seasonal variation of isoprene and its oxidation products were measured in the tropical savanna atmosphere. Two times higher levels of isoprene were observed during the wet season. The authors explain the difference with the lower physiological activity of the vegetation during the dry season [*Holzinger, et al.*, 2002].

It is unclear whether soils contribute significantly to atmospheric isoprene [*Fall and Copley*, 2000]. So it is important to find out which kind of microorganisms present in dust samples are responsible for the production of isoprene, whether they are also found in different types of soils and how much would be their contribution to the atmospheric isoprene emission.

5.5 Conclusion

Isoprene was produced through the interaction of dust sample with seawater and distilled water.

There was a positive correlation ($R^2=0.99$) between the amount of dust and the amount of isoprene produced after 48 hours reaction time.

There is a biologically mediated isoprene production when the dust particles come into the sea water, since there was no isoprene production with sterilized samples.

Microbiological contribution of isoprene production in soil, especially during the wet season should be further studied to correctly evaluate and differentiate between the contribution of plant and soil isoprene emission to the atmosphere.

6 PRODUCTION OF METHYL CHLORIDE FROM THE INTERACTION BETWEEN DUST PARTICLES AND SEA WATER

6.1 Summary

Methyl chloride has a lifetime of about 1.5 years. Because of this long lifetime, it reaches stratosphere and the chlorine atom, which destroys the stratospheric ozone layer, is produced through the photolysis of methyl chloride there. The production of methyl chloride from the interaction between Saharan dust particles and seawater was investigated. In the laboratory, the dust samples were added to the seawater samples in 20 ml headspace glass vials and were shaken for certain periods. Then the gas phase products were analyzed by purge-and-trap GC-MS (Tekmar LSC 2000/Varian Star 3400 cx/ Varian Saturn 2000). To test the production rates of methyl chloride, the following different reaction times were chosen; 5 min, 20 min, 40 min, 1 hour, 3 hours, 6 hours, 12 hours, 24 hours, 48 hours and 72 hours.

Methyl chloride was produced through the interaction of dust sample with seawater. The concentration of methyl chloride increased logarithmically ($R^2=0.89$) until 72 hours of reaction time. 1.984 ng of methyl chloride was released from 4 g of Saharan dust after 72 hours. There was a positive correlation ($R^2=0.93$) between the amount of isoprene and the amount of methyl chloride produced after 9 days reaction time.

We suggest that there is a biologically mediated methyl chloride production when the dust particles come into the sea water, since there was no methyl chloride production with sterilized dust and sea water samples.

6.2 Introduction

Methyl chloride (CH_3Cl) is the most abundant chlorine-containing compound in the atmosphere, with globally averaged concentration of about 550 ppt [*Clerbaux and Cunnold*, 2006b; *Li, et al.*, 2001]. It reaches stratosphere where its chlorine atom, released through photolysis, catalytically destroys ozone [*Butler*, 2000].

Tropical forest is the major source of methyl chloride with an annual flux of 820-8200 Gg / yr [*Moore, et al.*, 2005; *Yokouchi, et al.*, 2002; *Yokouchi, et al.*, 2000]. Abiotic conversion of chloride to methyl chloride in senescent and dead leaves at ambient temperatures accounts for 20-2500 Gg / yr of methyl chloride emission [*Hamilton, et al.*, 2003]. Biomass burning is another major source of methyl chloride to the atmosphere with emission estimates of 325-1125 Gg / yr [*Andreae, et al.*, 1996; *Andreae and Merlet*, 2001; *Lobert, et al.*, 1999]. Ocean, which was believed to be the major source of methyl chloride, is a relatively modest source with an annual flux of 380-500 Gg / yr [*Koppmann, et al.*, 1993; *Li, et al.*, 2001; *Moore*, 2000; *Moore, et al.*, 1996; *Tait, et al.*, 1994; *Yvon-Lewis, et al.*, 2004]. Also salt marshes emit large amounts (65-440 Gg / yr) of methyl chloride [*Cox, et al.*, 2004; *Dimmer, et al.*, 2001; *Manley, et al.*, 2006; *Rhew, et al.*, 2002; *Rhew, et al.*, 2000]. Methyl chloride emission by wood-rotting fungi is estimated to be 40-85 Gg / yr [*Dimmer, et al.*, 2001; *Watling and Harper*, 1998]. In addition, ectomycorrhizal fungi have recently been found to emit methyl chloride [*Redeker, et al.*, 2004], but the emission strength has not been estimated yet. Wetlands are significant sources with global annual flux of 48 Gg / yr [*Varner, et al.*, 1999]. Rice paddies emit 2.4-4.9 Gg of methyl chloride per year [*Lee-Taylor and Redeker*, 2005; *Redeker, et al.*, 2002; *Redeker and Cicerone*, 2004; *Redeker, et al.*, 2000]. The decomposition of soil organic matter can act as a source of methyl chloride [*Keppler, et al.*, 2000] but its importance has not been evaluated. Fossil fuel burning, waste incineration and industrial processes also produce methyl chloride, with annual fluxes of 107 Gg / yr, 45 Gg / yr and 10 Gg / yr, respectively [*McCulloch, et al.*, 1999].

The largest sink of methyl chloride in the atmosphere is the reaction with OH radical, which accounts for an annual loss of 3800-4100 Gg [*Lee-Taylor and Brasseur*, 2001; *Yoshida, et al.*, 2004]. Soil is the second largest sink for methyl chloride. Khalil and Rasmussen estimated an uptake of 500 Tg / yr [*Khalil and Rasmussen*, 2000]. Microbiological studies lead to larger sink (1600 Gg / yr) for methyl chloride in soil [*Harper and Hamilton*, 2003; *McAnulla, et al.*, 2001]. Cold ocean water takes up 93-145 Gg of methyl chloride annually [*Moore*, 2000] and again microorganisms are showed to play important role in the degradation process [*Tokarczyk, et al.*, 2003b; *Tokarczyk, et al.*, 2003a]. Reaction with chlorine radicals in the marine boundary layer is another loss process for methyl chloride with estimated sink of 400 Gg / yr [*Keene, et al.*, 1996; *Khalil and Rasmussen*, 1999].

Although above mentioned sources and sinks could be balanced by each other, the large uncertainties in emissions do not exclude another possible sources or sinks [*Clerbaux and Cunnold*, 2006b]. This work presents the results of laboratory experiments which show another interesting source with a possible common mechanism to explain the emission of methyl chloride from some environments.

6.3 Materials and Methods

The standard mix VOC-Mix 20, which contains methyl chloride, was used for the identification and quantification of methyl chloride in the headspace gas by purge-and-trap GC-MS method. The same temperature program as used in Chapters 4 and 5 was employed. The retention time of methyl chloride was 11 min with this program. The masses 49 and 50 in combination with retention time were used for the identification. The samples Sahara 4, Sahara 5 and Mongolia 2 were mixed with seawater from Atlantic Ocean in 20 ml headspace glass vials, shaken for certain periods starting from 5 minutes to 9 days at room temperature and afterwards the headspace gas was analyzed for methyl chloride. The same set of experiments as in Chapters 4 and 5 were done. To differentiate between abiotic and biotic production of methyl chloride, the samples were sterilized and used for the analysis. The sterilization was performed in an autoclave under 0.1 MPa pressure at 120 ^{0}C for 1 hour. The seawater and distilled water samples were measured without addition of dust samples. These samples served as blanks in the quantification.

6.4 Results and Discussion

As a preliminary experiment 4 g of Saharan dust samples were put into 10 ml of seawater in 20 ml headspace glass vials, which were capped immediately after sample preparation, and were shaken for 5 min, 20 min, 40 min, 1 hour, 24 hours, 48 hours and 72 hours. For each period, triplets were prepared. After each period, the headspace gas was analyzed with GC-MS. We identified methyl chloride in headspace gas and the amount of methyl chloride was increasing logarithmically (*$R^2=0.89$*) with increasing reaction time until 72 hours, giving 1.984 ng of methyl chloride after 72 hours (Figure 32.).

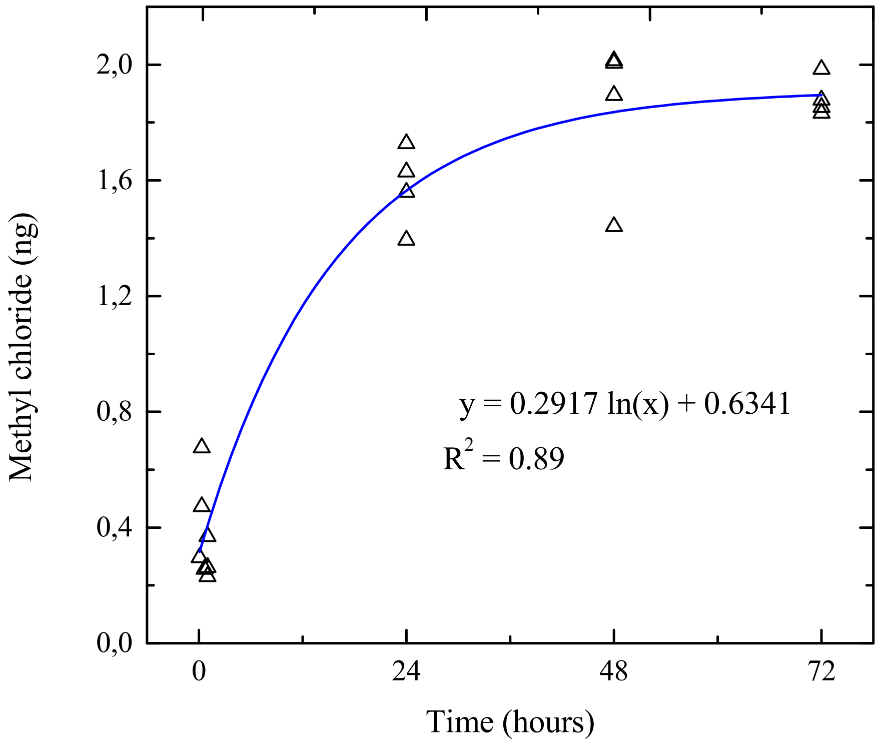

Figure 32. Amount of methyl chloride produced through the interaction of 4 g of dust samples Sahara 4 with seawater after certain periods. The regression line with the equation is shown.

The final dust concentration in the 10 m mixed layer of ocean (the bulk density) during strong Saharan dust event is 0.5 mg / l [*Bonnet and Guieu*, 2004]. An attempt to simulate this condition failed, because the amount of headspace gas produced was always below the detection limit of the instrument. The same set of experiment was done with 1 g of dust sample Sahara 5 in 10 ml of ocean water.

The reaction periods were 5 min, 20 min, 1 hour, 3 hours, 6 hours, 12 hours, 24 hours and 48 hours, respectively. For each period, also triplets were analyzed. The amount of isoprene produced was increasing linearly ($R^2=0.91$) with reaction time until 48 hours, which means after 4 days it will start to produce more methyl chloride than the measurement with 4 g of dust sample (Figure 33.). It means that the bulk density or the final concentration of dust in sea water plays a role in the production of methyl chloride.

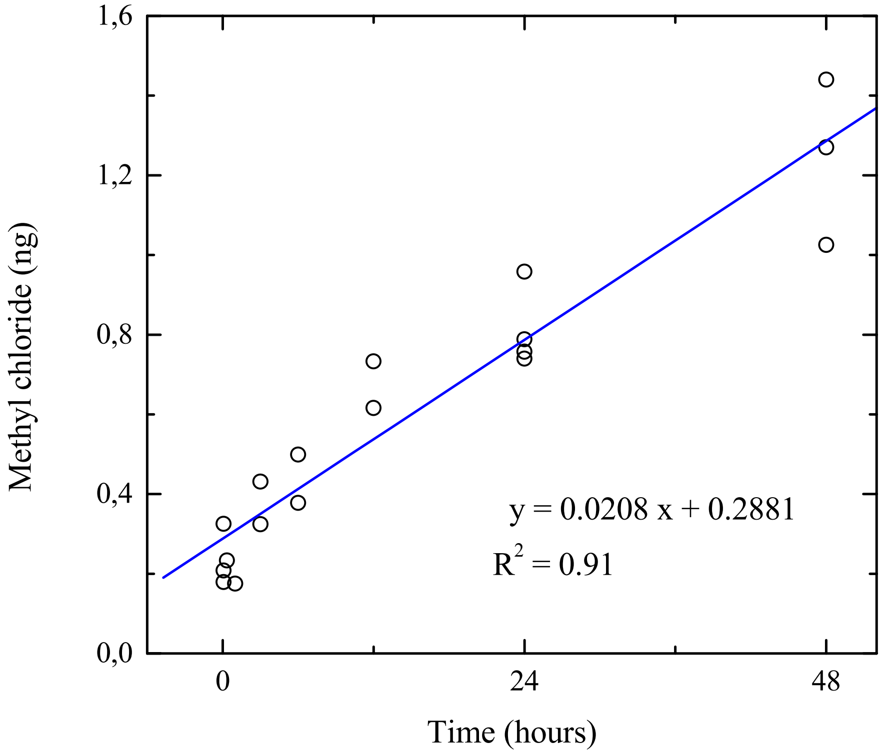

Figure 33. Amount of methyl chloride produced through the interaction of 1 g of dust samples Sahara 5 with seawater after certain periods. The regression line with the equation is shown.

An input of iron containing mineral dust can lead to an abiotic production of methyl iodide in the ocean [*Williams, et al.*, 2007]. To test whether the same mechanism leads to the production of methyl chloride, the same experiments were done with sterilized dust, sea water and distilled water samples. The samples were autoclaved under 0.1 MPa pressure at 120^0C for 1 hour to exclude the microbiological contribution to the production of methyl chloride. The GC-MS analysis of those samples gave no methyl chloride, which shows the biologically mediated methyl chloride production through the interaction of dust particles with sea water. Fungi emit methyl chloride [*Dimmer, et al.*, 2001; *Redeker, et al.*, 2004; *Watling and Harper*, 1998] and viable fungi and bacteria from Africa are transported interhemispherically with soil dust [*Prospero, et al.*, 2005].

Since it was shown that there is a biologically mediated methyl chloride production through the interaction of dust samples with sea water, the following measurements were performed to determine the capability of those microorganisms in dust samples to produce methyl chloride. The continuous measurements of methyl chloride were done from air-tightly closed glass vials containing 4 g of dust samples in 10 ml of sea water (and also distilled water) every 24 hour using purge-and-trap GC-MS. The amount of methyl chloride was decreasing exponentially ($R^2=0.91$ in seawater) with time (Figure 34.).

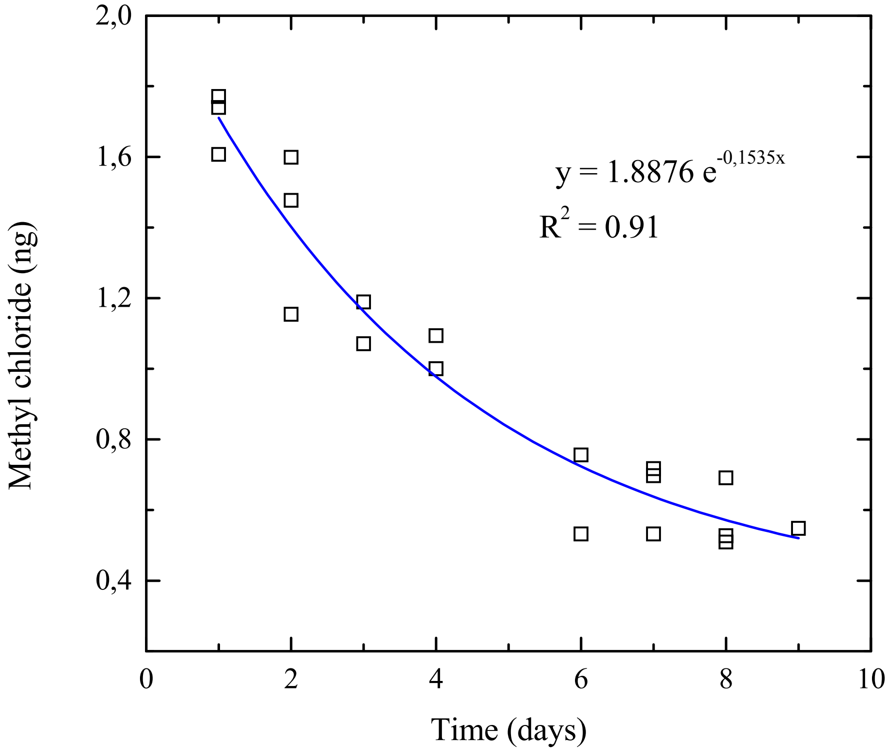

Figure 34. Amount of methyl chloride produced every 24 hour through the interaction of dust sample Sahara 4 with seawater. The regression line with equation is shown.

The total amount of methyl chloride emitted was increasing logarithmically ($R^2=0.89$ in seawater) with time (Figure 35.). The experiment conducted with distilled water gave no methyl chloride, which showed the participation of chloride ion in the process of methyl chloride formation.

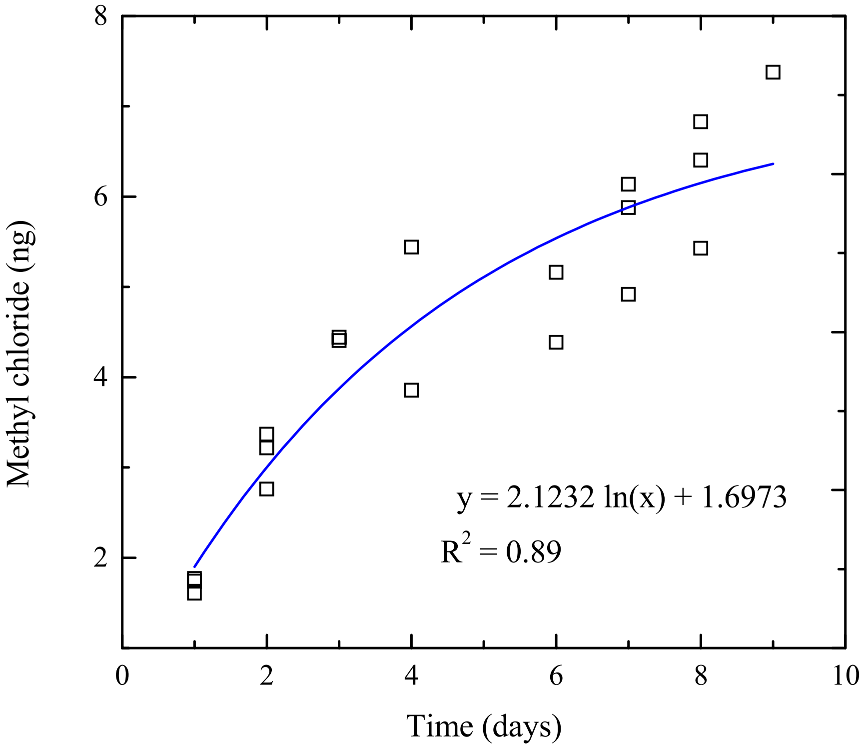

Figure 35. Total amount of methyl chloride produced through the interaction of dust sample Sahara 4 with sea water. The regression line with equation is shown.

Also the measurement with dust samples from the Gobi Desert gave methyl chloride (Figure 36 and 37.). The amount of methyl chloride was decreasing exponentially ($R^2=0.85$ in seawater) with time (Figure 36.).

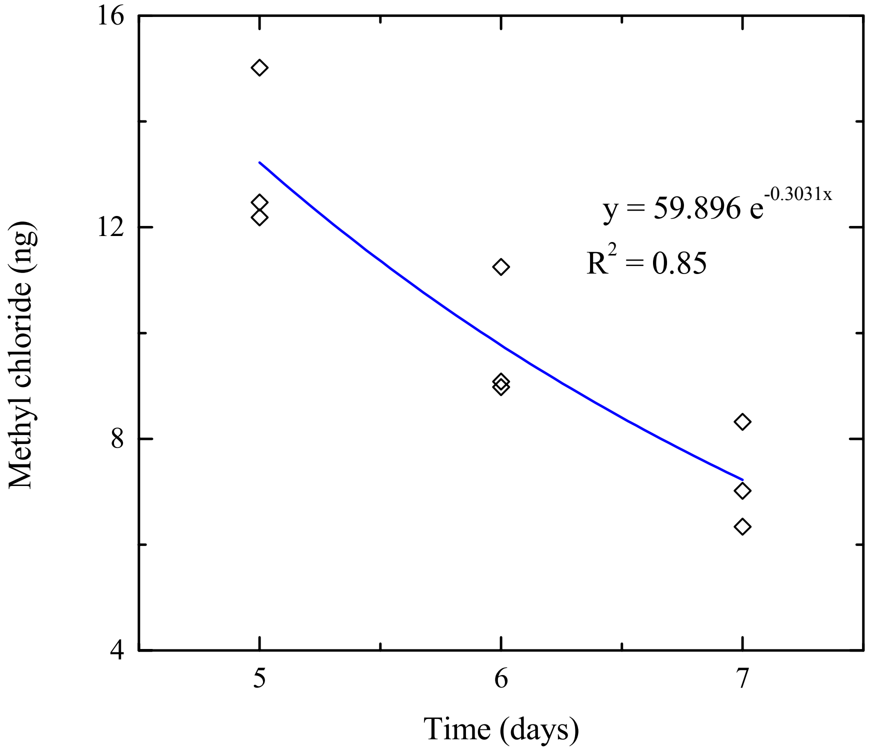

Figure 36. Amount of methyl chloride produced every 24 hour through the interaction of dust sample from the Gobi Desert with seawater. The regression line with equation is shown.

The total amount of methyl chloride emitted was increasing logarithmically ($R^2=0.89$ in seawater) with time (Figure 37.). The amount of the methyl chloride produced was 2-5 times more than that emitted from the same amount of Saharan dust sample after 5-7 days of interaction with sea water. However, the emission of methyl chloride started later than that of Saharan dust sample. After 24 hours of interaction, no methyl chloride was produced from the interaction of dust sample from the Gobi Desert with sea water.

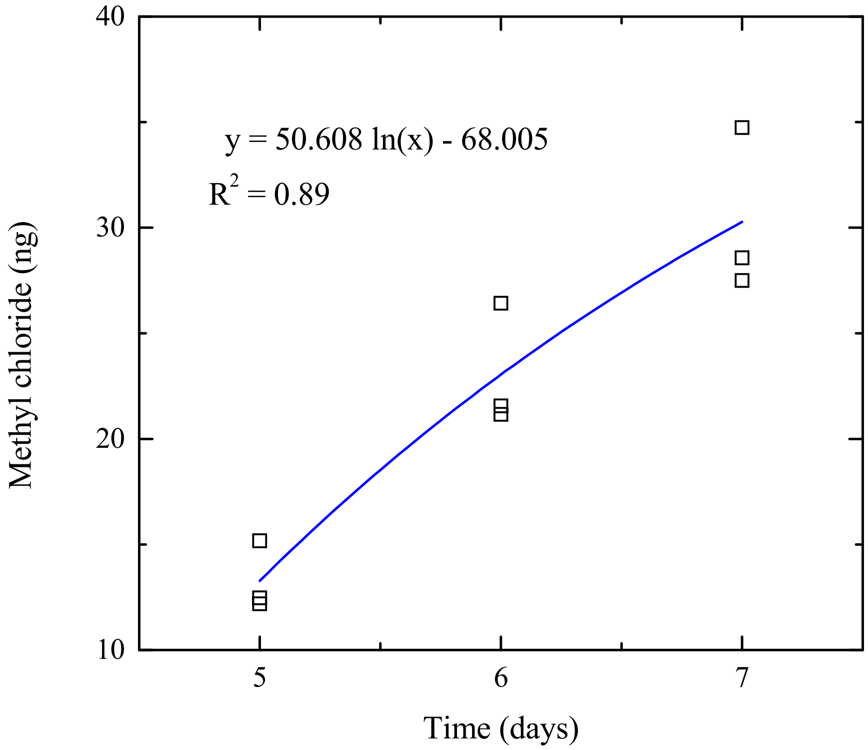

Figure 37. Total amount of methyl chloride produced through the interaction of dust sample from the Gobi Desert with sea water. The regression line with equation is shown.

In both dust samples, our results revealed correlations between the emission rates of methyl chloride and isoprene (Figures 38 and 39.). This suggests again that they are both produced by biologically mediated processes.

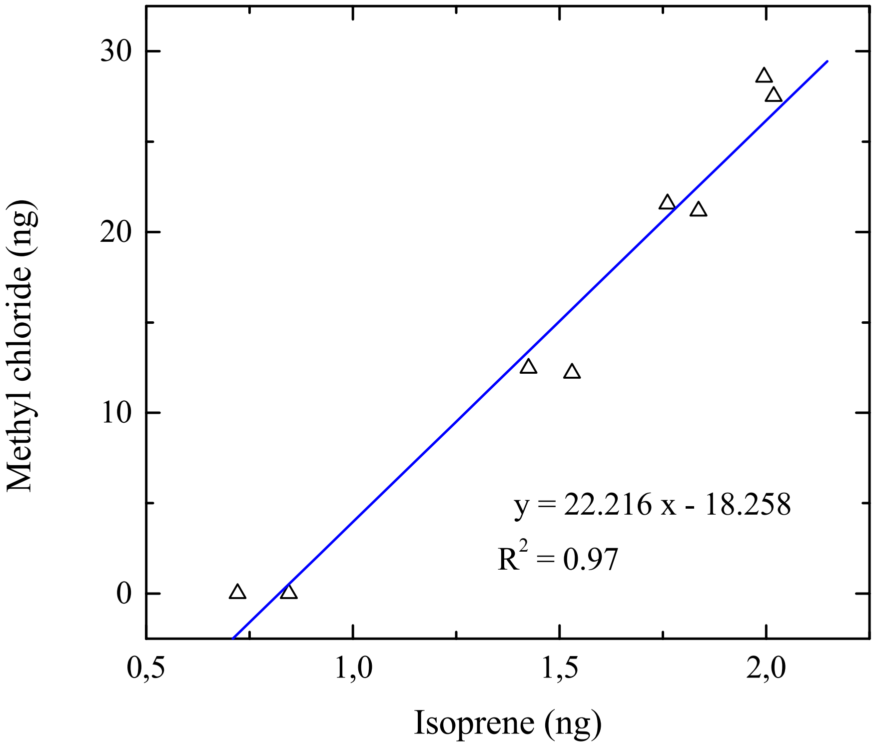

Figure 38. Correlation between the emissions of methyl chloride and isoprene produced through the interaction of dust sample from the Gobi Desert with sea water. The regression line with the equation is shown.

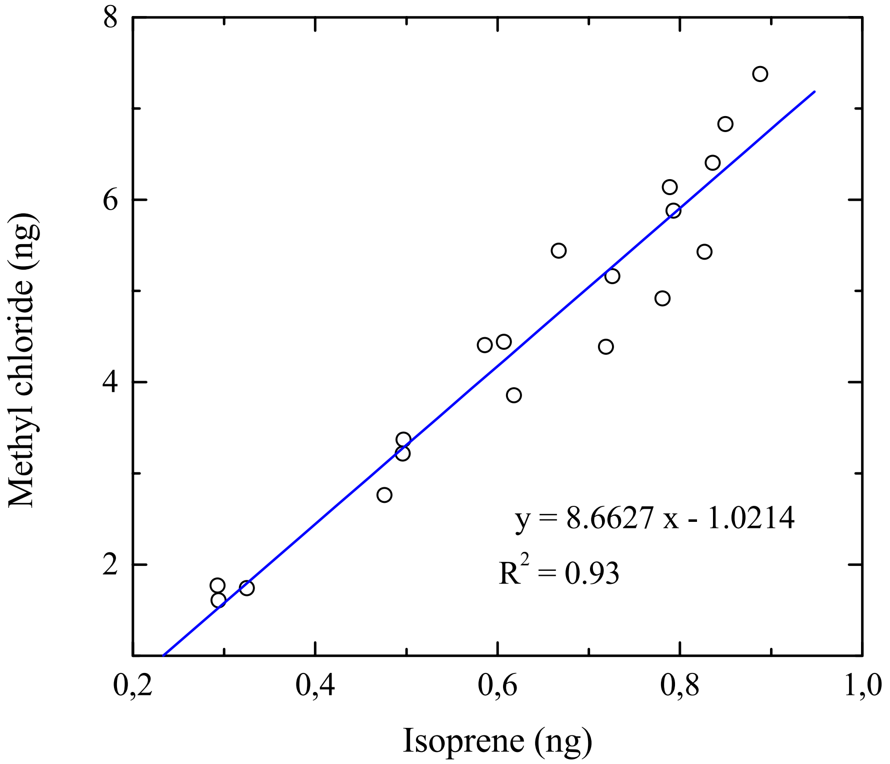

Figure 39. Correlation between the emissions of methyl chloride and isoprene produced through the interaction of dust sample from Sahara with seawater. The regression line with the equation is shown.

Based on the results of laboratory measurements we made an estimate of total amount of methyl chloride (5,3 - 37,5 Mg / yr) produced during dust storm events annually. It is a very little contribution of methyl chloride (0.0001 – 0.001 %) compared to its other known sources. The total methyl chloride source strength is about 4000 Gg/yr [*Clerbaux and Cunnold*, 2006a].

But it seems that this process has a common mechanism with the emission of methyl chloride from coastal and other wetland areas. Unplanted flooded fields emit as much methyl chloride as planted flooded rice fields [*Redeker, et al.*, 2000]. This may be a common feature of saturated, anoxic organic soils [*Varner, et al.*, 1999], but the desert soil would not be really counted as an organic soil. It would be interesting to study which biological organisms are responsible for the methyl chloride emission and which other factors, such as chloride concentration and how they would influence the emission rate. Viable fungi and bacteria from Africa are transported interhemispherically with soil dust [*Prospero, et al.*, 2005]. Dust samples from Cape Verde Island which have already gone aeolian transport, however did not produce methyl chloride after 48 hours of interaction with sea water. So this is an interesting question especially for microbiologists to answer which microorganisms there are originally in desert soil, which of them survive the long range transport and many more questions, like which common features have those regions affected by dust storm, also for the scientists from different disciplines.

6.5 Conclusion

Methyl chloride was produced through the interaction of dust sample with seawater.

There is a biologically mediated methyl chloride production when the dust particles come into the sea water, since there was no methyl chloride production with sterilized samples. Dust samples from the Gobi Desert produced 2-5 times more methyl chloride than the samples from Sahara Desert after 5-7 days interaction time.

There was a very good correlation ($R^2=0.93-0.97$) between the emissions of methyl chloride and isoprene in dust samples.

Microbiological contribution of methyl chloride production in soil in coastal wetland areas especially that are affected by dust storms would be interesting subject for further studies.

7 CONCLUSION AND FUTURE PERSPECTIVES

The results of the headspace glass experiments performed during this study are summarized, and the main conclusions with possible suggestions for further experiments are included in this chapter.

Methyl iodide, methylene chloride and isoprene were produced through the interaction of dust samples from the Sahara and Gobi Desert with both seawater and distilled water, methyl chloride was only produced through the interaction of dust samples with seawater.

As initially hypothesized, methyl iodide was produced abiotically, since sterilized samples produced the same amount. A tenfold increase in methyl iodide production upon addition of Fe (III) within half an hour approves an abiotic production mechanism involving HULIS, iron and halide. The presumption of methylene chloride production through this abiotic mechanism was also approved by the results of this work.

An abiotic production of methyl chloride could not be determined, most likely because the produced amount fell below the detection limit of the instrument. Instead, a biologically mediated methyl chloride and isoprene production was determined. Only non-sterilized samples produced methyl chloride and isoprene, and significant amounts were determined after at least 24 hours of interaction, which reemphasises a biological contribution. Although there was a very good correlation between the produced amounts of methyl chloride and isoprene, 48 hours of interaction of the dust samples from Cape Verde Island with seawater produced only isoprene but not methyl chloride, a possible hint for the responsibility of different types of microorganisms for their production.

Furthermore, methyl chloride was only produced in the presence of seawater which reveals the necessity of halide presence. Contrary to that, the addition of water was enough for isoprene production. The capability of dust samples to produce methyl chloride and isoprene was not finished within 7-9 days which is a typical period for dust particles to stay in 10 m mixed layer of ocean after dust storms.

Dust samples from Cape Verde Island which have undergone aeolian transport produced more isoprene compared to the dust samples directly collected in the source region. It indicates not only the transport of microorganisms during the dust storms, but also gives a hint about either their enrichment as a result of transport or the contribution of local microorganisms to the production of isoprene, or even both. In latter case, it concerns common soil organisms that produce isoprene in the presence of water, which in turn would explain the increase in atmospheric isoprene concentrations during wet seasons compared to dry seasons.

It is also possible for the abiotic production of VHOC to take place on aerosols in marine atmosphere, which would probably be more effective than the process in the ocean. Further study is needed to make an estimate of the significance of this process. It is not excluded that the semi-volatile compounds, which could contribute to the budget of organic aerosols, would be produced through this mechanism. So along with the gas phase products, the liquid phase can be analyzed by HPLC-MS method, which definitely would help to clarify the detailed mechanism of this process. Further important experiments that can contribute for the clarification of the mechanism would be the extraction of humic substances from the dust samples and its structure identification by means of state of the art methods like NMR and IR. This would give a clue of monomer units which can be used as model substances.

There are very few studies on airborne microorganisms from arid regions. So their determination in dust samples from the source regions and in samples that have undergone aeolian transport would give important results about the airborne microorganisms which are responsible for the production of methyl chloride and isoprene. Also, it would give a hint whether this process could take place in every soil environment, and a possibility to estimate the total contribution of this process to the atmospheric isoprene and methyl chloride budget.

The sample from Gobi Desert produced higher amounts of isoprene compared to the sample from Sahara Desert. It suggests the need for experiments with different types of samples from different regions of the world for evaluating the contribution of both abiotic and biotic production mechanisms of volatile and semi-volatile organic compounds.

The natural dust samples from arid and semi-arid regions are proved to be important contributors to the production and emission of volatile organic compounds to the atmosphere and it urges further studies in this field.

8 REFERENCES

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9 APPENDIX

Figure 40. Dust sample from Sahara with seawater in headspace glass vial.

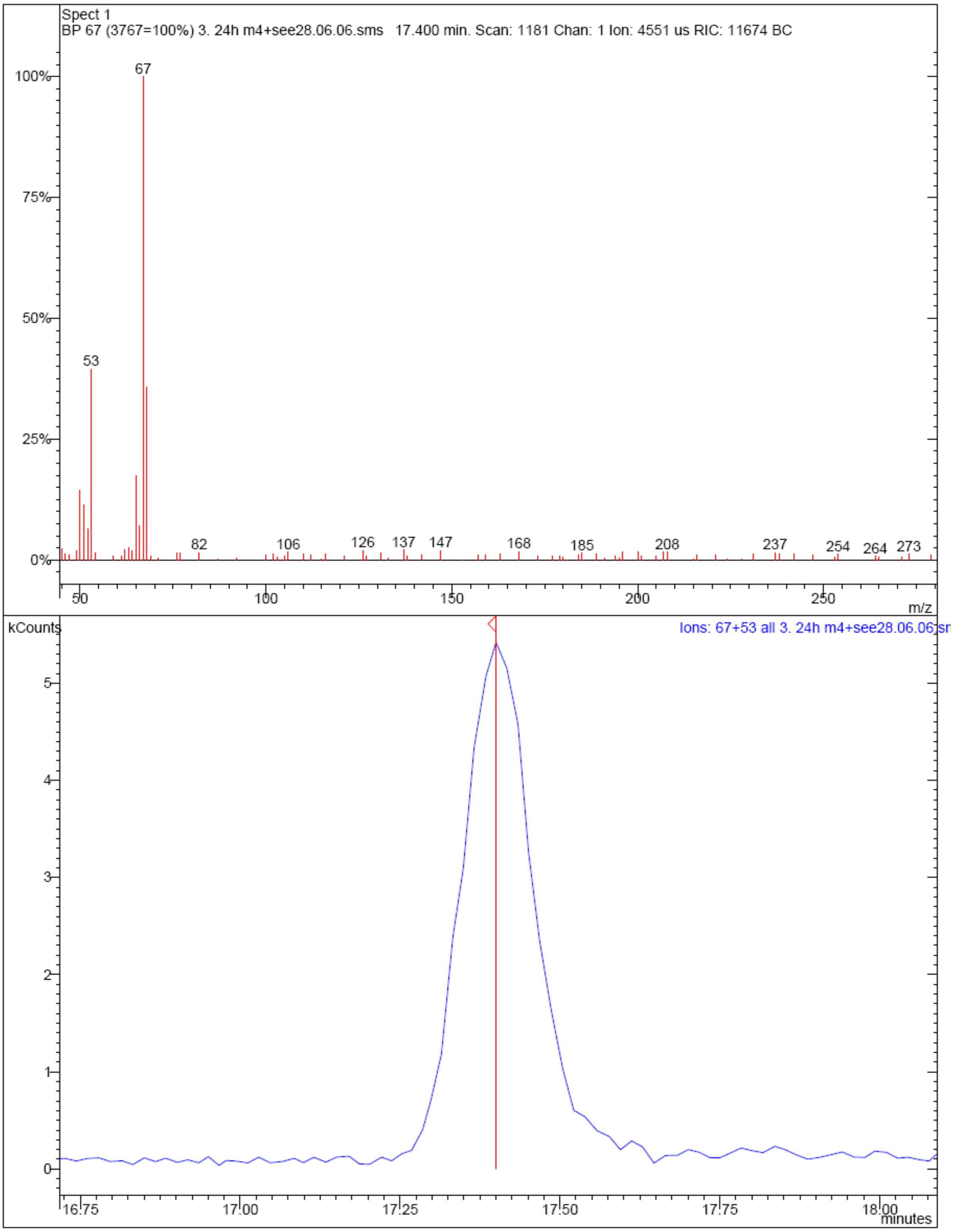

Figure 41. Mass spectrum and chromatogram of isoprene.

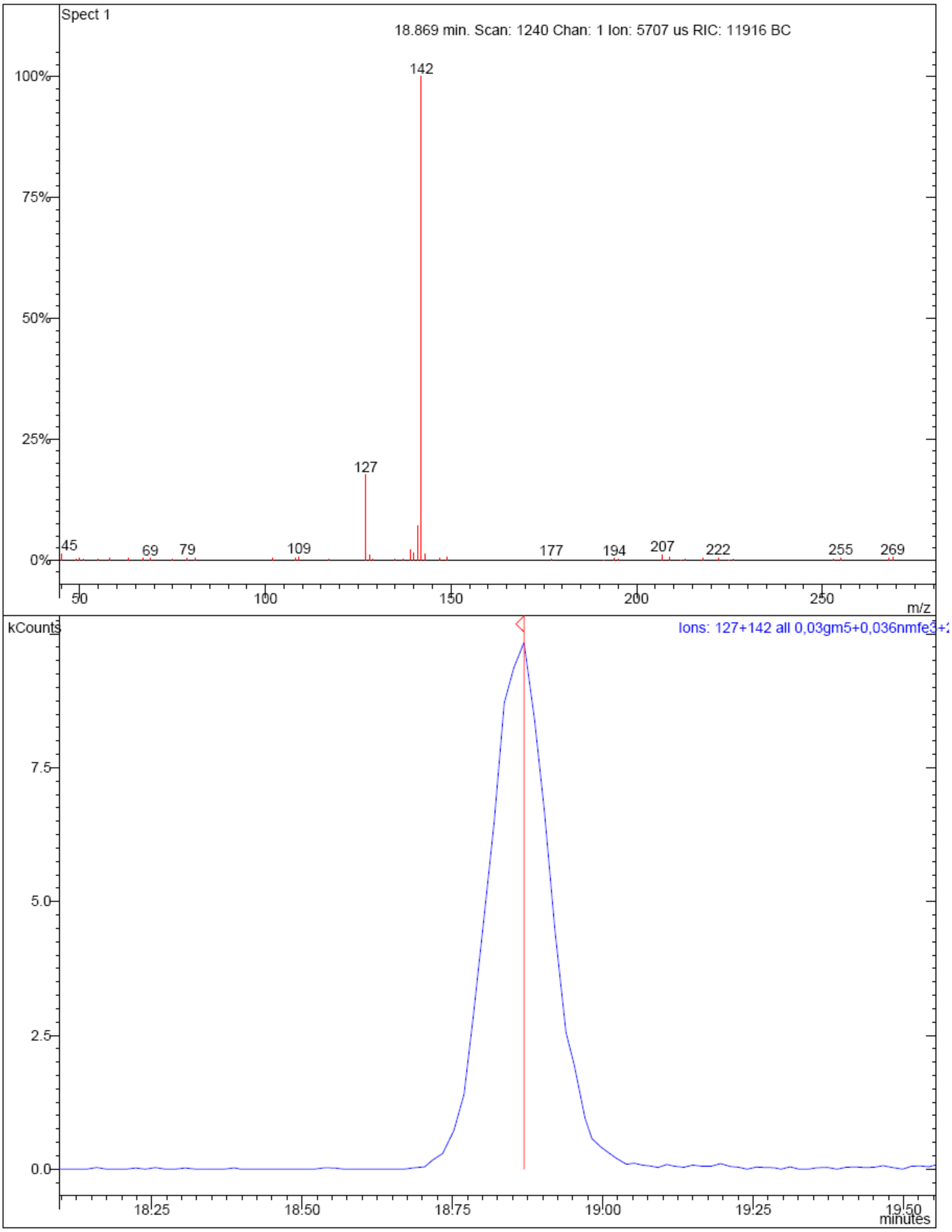

Figure 42. Mass spectrum and chromatogram of methyl iodide.

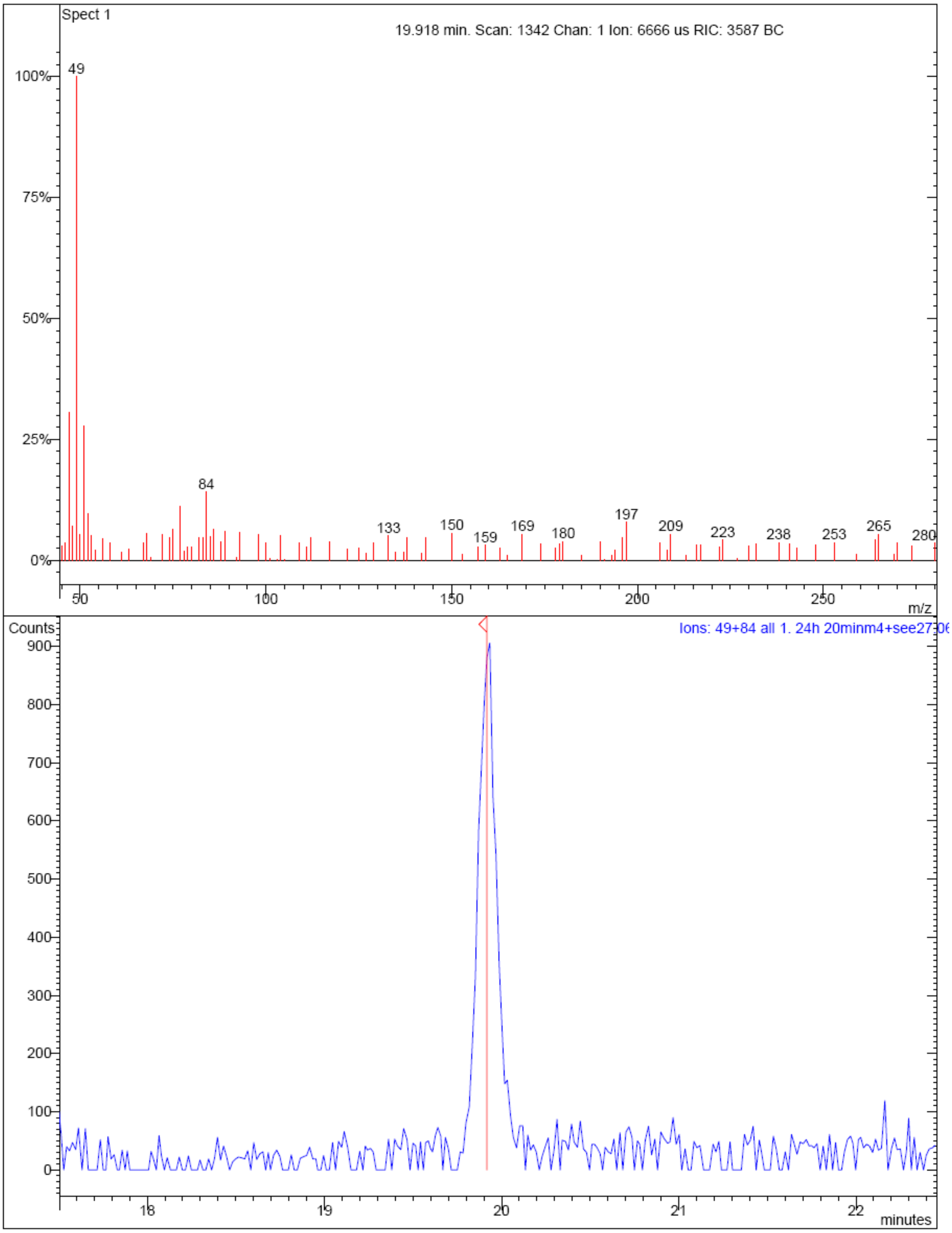

Figure 43. Mass spectrum and chromatogram of methylene chloride.

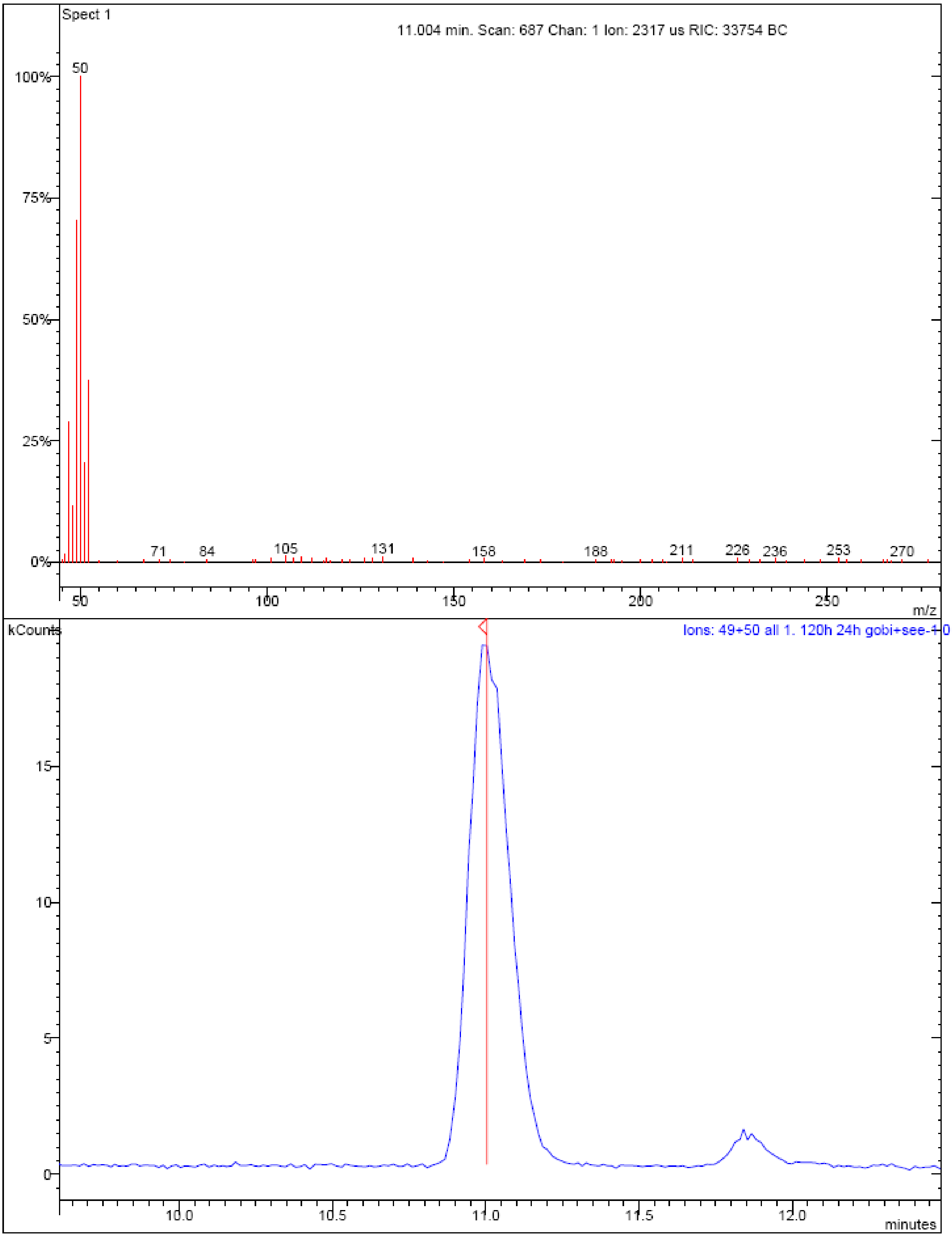

Figure 44. Mass spectrum and chromatogram of methyl chloride.

MEASURED DATA

Table 13. Water and organic content of the samples

No.	Sample	Water content, %	Organic content, %
1	Sahara 1	0,90	3,34
2	Sahara 2	1,55	4,42
3	Sahara 2 > 0.063	1,53	2,81
4	Sahara 2 > 0.125	1,62	3,84
5	Sahara 3	0,60	2,54
6	Sahara 4	1,22	3,67
7	Sahara 4 > 0.063	1,31	2,98
8	Sahara 4 > 0.125	0,95	2,68
9	Sahara 4 > 0.2	0,37	1,06
10	Sahara 5	0,91	3,25
11	Sahara 6	0,86	3,41
12	Sahara 7	0,63	2,85
13	Sahara 8	1,06	3,71
14	Sahara 8 > 0.063	1,36	2,33
15	Sahara 8 > 0.125	1,24	2,26
16	Sahara 8 > 0.2	1,05	2,33
17	Sahara 8 > 0.315	1,16	3,08
18	Sahara 9	0,50	2,61
19	Cape Verde	2,98	7,71
20	Lanzarote 6	2,45	6,31
21	Mongolia 1	0,35	0,38
22	Mongolia 2	1,07	3,59

Table 14. Dissolved organic and inorganic carbon contents of the samples

No.	Samples	DOC, ppm (mg/kg)	IC, ppm (mg/kg)
1	Sahara 1	34,35	46,29
2	Sahara 2	34,08	54,66
3	Sahara 2 > 0.063	36,30	50,10
4	Sahara 2 > 0.125	49,62	73,41
5	Sahara 3	30,75	38,16
6	Sahara 4	41,55	41,91
7	Sahara 5	42,18	47,40
8	Sahara 6	46,77	62,94
9	Sahara 7	34,29	36,93
10	Sahara 8	65,79	64,77
11	Sahara 8 > 0.063	51,87	48,54
12	Sahara 8 > 0.125	54,72	45,45
13	Sahara 8 > 0.2	61,05	50,61
14	Sahara 8 > 0.315	95,04	69,45
15	Sahara 9	21,66	36,33
16	Mongolia 2	91,50	99,81
17	Cape Verde	106,26	60,30
18	Lanzarote 6 < 0.02	101,70	250,10
19	Lanzarote 6	39,78	144,63

Table 15. Effects of Fe (II) and Fe (III) additions on the production of methyl iodide

Sample	Methyl iodide, ng
without iron addition	0,109
with addition of Fe (II)	0,116
with addition of Fe (III)	1,012

Table 16. Amount of Me_2Cl_2 produced through the interaction of 4 g dust sample Sahara 4 with seawater

Time, hours	Methylene chloride, ng
0,33	0,193
0,33	0,285
0,33	0,285
0,66	0,383
0,66	0,358
0,66	0,318
1	0,263
1	0,268
1	0,235
24	0,486
24	0,514
24	0,427
48	0,470
48	0,415
48	0,479
72	0,369
72	0,436
72	0,426

Table 17. Dependence of Me_2Cl_2 concentration on reaction time and medium

Time, days	Methylene chloride, ng		
	Sahara 4 seawater	Sahara 4 distilled water	Sterilized Sahara 4 distilled water
20 min	0,454	0,438	0,446
1	0,318	0,359	
2	0,198	0,307	0,559
3	0,148	0,154	0,835
4	0,134	0,159	1,101
5		0,191	
6	0,086		
7	0,049		

Table 18. Dependence of isoprene amount on the dust amount

Dust sample CV, g	Isoprene, ng
0,05	0,014
0,1	0,020
0,5	0,063
1	0,184
2	0,438
4	0,931

Table 19. Amount of isoprene produced through the interaction of dust samples with seawater

Time, hours	Isoprene, ng	
	4 g Sahara 4	**1 g Sahara 5**
0,083	0,030	0,013
0,083	0,032	0,007
0,33	0,046	0,012
0,33	0,039	0,008
0,33	0,016	0,014
0,33	0,022	0,010
0,33	0,020	0,009
0,66	0,040	0,009
0,66	0,062	0,009
0,66	0,017	
1	0,044	0,006
1		0,015
6		0,013
6		0,017
12		0,027
12		0,027
24	0,154	
24	0,167	
24	0,172	
24	0,199	
48	0,317	0,075
48	0,368	0,075
48		0,066
72	0,398	
72	0,361	
72	0,376	

Table 20. Dependence of isoprene concentration on reaction time and medium

Time, days	Isoprene, ng			
	Sahara 4 seawater	Sahara 4 distilled water	Mongolia 2 seawater	Mongolia 2 distilled water
1	0,484	0,250	0,121	1,344
1	0,484	0,265	0,128	1,384
1	0,484	0,249	0,121	1,494
2	0,969	0,185		
2	0,969	0,176		
2	0,969	0,171		
3	1,453			
3	1,453	0,135		
3		0,120		
4	1,938			0,301
4	1,938	0,106		0,288
4		0,099		0,335
5		0,094	0,090	0,155
5		0,084	0,085	0,144
5		0,070		0,157
6	2,907		0,083	0,148
6	2,907		0,000	0,140
6				0,144
7	3,391		0,065	0,173
7	3,391		0,058	0,157
7	3,391			0,161
8	3,876			0,148
8	3,876			0,127
8	3,876			0,135
9	4,360			

Table 21. Amount of methyl chloride produced through the interaction of dust samples with seawater

Time, hours	Methyl chloride, ng	
	4 g Sahara 4	1 g Sahara 5
0,083	0,296	0,325
0,083		0,179
0,083		0,208
0,33	0,676	0,233
0,33	0,472	
0,66	0,256	
1	0,369	0,175
1	0,262	
1	0,231	
3		0,431
3		0,324
6		0,378
6		0,499
12		0,733
12		0,616
24	1,394	0,757
24	1,559	0,958
24	1,629	0,788
24	1,727	0,740
48	2,005	1,270
48	1,894	1,440
48	1,440	1,025
48	2,014	
72	1,984	
72	1,832	
72	1,852	
72	1,878	

Table 22. Dependence of methyl chloride concentration on reaction time

Time, days	Methyl chloride, ng	
	Sahara 4	Mongolia 2
1	1,771	
1	1,740	
1	1,607	
2	1,599	
2	1,477	
2	1,154	
3	1,071	
3	1,189	
4	1,000	
4	1,094	
5		15,017
5		12,470
5		12,185
6	0,756	11,250
6	0,532	9,083
6		8,977
7	0,697	8,322
7	0,717	7,020
7	0,532	6,339
8	0,691	
8	0,527	
8	0,509	
9	0,548	

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Erklärung gem. § 8 (3) b) und c) der Promotionsordnung der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Ruprecht-Karls-Universität Heidelberg

Ich erkläre hiermit, dass ich die vorgelegte Dissertation selbst verfasst und mich keiner anderen als der von mir ausdrücklich bezeichneten Quellen und Hilfen bedient habe.

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