Three years of trace gas observations over the EuroSiberian domain derived from aircraft sampling — a concerted action

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ABSTRACT

A three-year trace gas climatology of CO_2 and its stable isotopic ratios, as well as CH_4, N_2O and SF_6, derived from regular vertical aircraft sampling over the Eurasian continent is presented. The four sampling sites range from about 1°E to 89°E in the latitude belt from 48°N to 62°N. The most prominent features of the CO_2 observations are an increase of the seasonal cycle amplitudes of CO_2 and $\delta^{13}C$–CO_2 in the free troposphere (at 3000 m a.s.l.) by more than 60% from Western Europe to Western and Central Siberia. $\delta^{18}O$–CO_2 shows an even larger increase of the seasonal cycle amplitude by a factor of two from Western Europe towards the Ural mountains, which decreases again towards the most eastern site, Zotino. These data reflect a strong influence of carbon exchange fluxes with the continental biosphere. In particular, during autumn and winter $\delta^{18}O$–CO_2 shows a decrease by more than 0.5‰ from Orléans (Western Europe) to Syktyvkar (Ural mountains) and Zotino (West Siberia), mainly caused by soil respiration fluxes depleted in $\delta^{18}O$ with respect to atmospheric CO_2. CH_4 mixing ratios in the free troposphere at 3000 m over Western Siberia are higher by about 20–30 ppb if compared to Western Europe. Wetland emissions seem to be particularly visible in July–September, with largest signals at Zotino in 1998. Annual mean CH_4 mixing ratios decrease slightly from 1998 to 1999 at all Russian sites. In contrast to CO_2 and CH_4, which show significant vertical gradients between 2000 and 3000 m a.s.l., N_2O mixing ratios are vertically very homogeneous and show no significant logitudinal gradient between the Ural mountains and Western Siberia, indicating insignificant emissions of this trace gas from boreal forest ecosystems in Western Siberia. The growth rate of N_2O (1.2–1.3 ppb yr^{-1}) and the seasonal amplitude (0.5–1.1 ppb) are similar at both aircraft sites, Syktyvkar and Zotino. For SF_6 an annual increase of 5% is observed, together with a small seasonal cycle which is in phase with the N_2O cycle, indicating that the seasonality of both trace gases are most probably caused by atmospheric transport processes with a possible contribution from stratosphere–troposphere exchange.

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1. Introduction

The inexorable rise of CO_2 in the atmosphere primarily reflects anthropogenic emissions from fossil fuel and land use changes. The annual average rate of atmospheric CO_2 increase is, however, less than half the anthropogenic emissions, which implies that sinks, probably both in the oceans and on land, currently absorb the other fraction. More than 10 years ago, Keeling et al. (1989), in a modelling study based on observed latitudinal gradients of CO_2 and $^{13}CO_2$, located a large fraction of these sinks in the northern hemisphere, mainly in the North Atlantic ocean, while Tans et al. (1990), in a study based on sea-to-air fluxes inferred from the CO_2 saturation state of surface sea waters and on the latitudinal distribution of atmospheric CO_2, pointed out that a significant sink of carbon must be attributed to the Northern Hemisphere continental biosphere. Since then, atmospheric studies (Fan et al., 1998; Bousquet et al., 1999; Kaminski et al., 1999; Rayner et al., 1999) and ecological measurements (Valentini et al., 2000) tend to support this latter finding by Tans et al. (1990), but the partitioning of the northern land sink between longitudes is still a point of debate.

In the last decade, the global network of atmospheric stations significantly increased at mid to high northern latitudes. However, most of the new stations are located in the marine boundary layer, or on the fringe of continents. As a consequence, the land fluxes remain poorly constrained. Although the atmospheric transport is a superb integrator of the surface fluxes, it is nevertheless difficult to make measurements in the continental atmosphere that are representative of large-scale sources and sinks, say at the regional to continental scale ($> 10^6$ km^2). This is because the sources are spatially heterogeneous and highly variable in time, and because the atmospheric transport is also more variable over vegetated areas than over the oceans (Denning et al., 1996). Therefore, studies aiming to deduce the fluxes from atmospheric measurements are primarily limited by the lack of adequate data. It has been hypothesised (Tans et al., 1996) and further quantified (Gloor et al., 2000) that repeated vertical profiles in the middle of continents will improve the diagnostic power for quantifying the land carbon fluxes.

Our knowledge of the atmospheric CO_2 distri-bution over the extended land masses of European Russia and Siberia is still very limited. Up to date, only one systematic study of vertical aircraft profiling over the Eurasian continent extending from Moscow to Yakutsk was reported by Nakazawa and co-workers (1997a). They made regular observations of CO_2 and its stable isotope ratios as well as CO, CH_4 and N_2O; however, these were limited to the summer periods of 1992, 1993 and 1994. Within the European project EuroSiberian CarbonFlux three new sites for regular aircraft sampling over Russia have been established: Fyodorovskoye, Syktyvkar and Zotino. Together with new data from a parallel aircraft program over Western Europe, at Orléans, these measurements provide important new information on the trace gas climatology over the Eurasian continent from about 1°E to 89°E in the latitude belt of 48°N to 62°N. In this paper, only the results from flask sampling at and above 2000 m a.s.l. are discussed. Also, we will only compare the measurements of greenhouse gases, i.e. CO_2 concentration and stable isotope ratios in CO_2 as well as CH_4, N_2O and SF_6 mixing ratios. For more information on the complete set of trace substances and vertical profiles measured at these sites, see detailed reports by Lloyd et al. (2002), Ramonet et al. (2002a), and Sidorov et al. (2002).

2. Sampling sites and methods

2.1. Flight locations

Figure 1 shows the map of the EuroSiberian study region with the sampling locations. Extending from Western Europe to the Siberian Highlands, the four sampling sites represent considerably different catchment areas which are illustrated by trajectories that extend three days backwards in time starting from the stations at a height of 2500 m a.s.l. The back-trajectories are calculated with the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model of Draxler and Hess (1997) using wind fields from the National Center for Environmental Prediction/National Oceanic and Atmospheric Administration (NCEP/NOAA) medium-range weather forecast model. While the Orléans site largely experiences North Atlantic air masses, the Fyodorovskoye and Syktyvkar sites, although still generally influenced by westerly winds, during
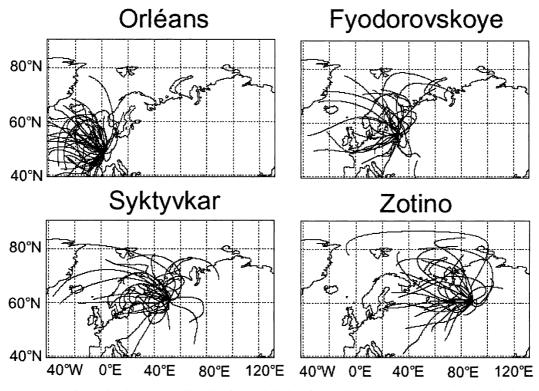
Orléans

Fyodorovskoye

Syktyvkar

Zotino

Fig. 1. Map of Eurasia with the sampling sites for vertical aircraft soundings and 3 d back trajectories calculated for the height level of 2500 m a.s.l. for the individual sampling dates and sites at Orléans, Fyodorovskoye, Syktyvkar and Zotino.

aircraft sampling are more influenced by north western air masses which spent considerable periods of time over north eastern Europe and Scandinavia. By contrast, the most continental Zotino sampling site on the margin of the west wind belt also occasionally observes air masses from north eastern Siberia and from the high Arctic.

The Orléans aircraft program is operated by the Laboratoire des Sciences du Climat et de l'Environnement, CE Saclay (LSCE), in co-operation with Meteo France since 1996. The flight location is at 1°E, 48°N, about 300 km south of Paris over an area of agricultural land and forests. Regular vertical aircraft profiles for flask sampling are performed every 2–3 wk from 100 to 3000 m a.s.l. Flasks are analysed at LSCE for CO_2 concentration and stable isotope ratios ($^{13}C/^{12}C$ and $^{18}O/^{16}O$) in CO_2, as well as for CO and CH_4 mixing ratios.

The Fyodorovskoye aircraft program is oper-

ated by the Svertsov Institute for Evolutionary and Ecological Problems (IPEE) in close co-operation with Max-Planck-Institut für Biogeochemie (MPI-BGC). The flight location for Fyodorovskoye is at 33°E, 56°N about 300 km north-west of Moscow. Vertical profiles of continuous CO_2 NDIR, temperature and relative humidity measurements as well as flask sampling from 100 to 3000 m are performed every 2–4 wk. The sampling location is over the Central Forest Reserve at Fyodorovskoye in Central European Russia, the southern taiga, where continuous ground measurement sites in a forest and a bog have been established within EuroSiberian CarbonFlux (Schulze et al., 2002). Flask samples have been analysed by LSCE for CO_2 concentration and stable isotope ratios in CO_2, as well as for CO and CH_4 mixing ratios. Due to several logistical and sampling problems, the records at this site contain large gaps, and complete seasonal cycles of trace gases from flask sampling are not

yet available. For this first summary of the climatology of greenhouse gases over the EuroSiberian region, we will only compare individual 3000 m profile data points from Fyodorovskoye with the other aircraft data. A more detailed report summarising results from flasks and in situ profile measurements is given by Ramonet et al. (2002a).

The Syktyvkar aircraft program is operated by IPEE in close cooperation with MPI-BGC. Flights are performed 400 km west of the Ural mountains over the Vychegodsko-Mezenskoj plain, about 100 km south east (52°E, 61°N) of the city of Syktyvkar (160 000 inhabitants), the capital of the Republic of Komi. The area belongs to the northern European taiga, dominating vegetation in this area is pine forest (*Pinus sylvestris*). Vertical profiles of continuous CO_2 NDIR soundings as well as temperature and relative humidity are measured every 2–4 wk. Duplicate flasks are collected here only at 2000, 2500 and 3000 m a.s.l. Flask samples have been analysed by the Institut für Umweltphysik, Universität Heidelberg (UHEI-IUP) for CO_2 concentration and stable isotope ratios in CO_2, as well as for CH_4, N_2O and SF_6 mixing ratios.

The Zotino aircraft program is operated by the Institute of Forest, Siberian Branch, Russian Academy of Sciences (IF SB RAS) and MPI-BGC. The flight location for Zotino is at 89°E, 61°N, about 600 km north of the city of Krasnoyarsk close to the small village Zotino located on the west bank of the Yenisei river. It is situated at the eastern edge of the West Siberian Lowland, an extended (3×10^6 km^2) poorly drained area covered by 55% bogs and about 40% forests (Schulze et al., 2002). The whole region belongs to the Siberian taiga (boreal coniferous forest). Vertical profiles of CO_2, measured with continuous NDIR, temperature and relative humidity, are obtained every 2–4 wk, and air samples are collected in glass flasks between 100 and 3000 m a.s.l. Flask samples collected between June 1998 and July 2000 have been analysed by CSIRO Atmospheric Research (CAR) for CO_2 concentration and stable isotope ratios in CO_2, as well as for CO, CH_4, N_2O and H_2 mixing ratios. Flask samples collected from July 2000 onwards were analysed by MPI-BGC in a newly commissioned facility.

2.2. Flask sampling

At the Orléans site, vertical profiling for flask sampling was performed with light aircraft Piper

ARROW up to June 1999 and Piper AZTEC from Meteo France afterwards, whereas at the Russian sites, local Antonov-AN2 bi-plane aircraft were used. Separate air intake lines (6 mm dekabon tubing) for continuous NDIR CO_2 measurements (LiCor 6152) and for flask sampling systems were installed in the wings of the respective aircraft. Whole air samples were collected into pre-conditioned 1-L cylindrical flasks made of Pyrex glass with PFA O-ring valves (Glass Expansion, Australia) at both ends. Drying of the air was performed via magnesium perchlorate. Flasks were flushed for more than 5 min at a flow rate of ca. 4 L min^{-1}, and pressurised to 1 atmosphere above ambient pressure at final filling (pump: KNF-Neuberger, Germany, N86KNDC with EPDM membrane).

Drying of the air with magnesium perchlorate under conditions of changing pressure may influence the CO_2 mixing ratio ending up in the flask. In our sampling system, the drying unit is located upstream of the pump unit, therewith experiencing only pressure changes according to the vertical atmospheric pressure change. Two different experiments have been performed to test possible systematic biases caused by the drying agent, one in the laboratory, simulating inlet pressure drops similar to those experienced during aircraft flights up to 8.5 km (Langenfelds et al., 1996), and two tests during real aircraft flights (Ramonet et al., 2002b). The laboratory tests resulted in no detectable changes associated to pressure changes while the tests performed during aircraft flights when comparing samples collected in parallel, with and without magnesium perchlorate showed differences between pairs of samples collected dry respectively wet of "dry–wet" $= -0.23 \pm 0.3$ ($n = 4$) during the first flight and of "dry–wet" $= -0.10 \pm 0.3$ ($n = 4$) during the second flight. Within the standard deviation of this comparison, no significant offset could be observed. Any possible bias in the mixing ratios from aircraft samples reported here are thus probably smaller than -0.25 ppm.

2.3. Flask analysis

Laboratories responsible for flask analysis were LSCE at Orléans and Fyodorovskoye, UHEI-IUP at Syktyvkar and CAR and MPI-BGC at Zotino. At LSCE, CO_2 concentration analysis was

performed by NDIR (Hartmann & Braun, Germany, URAS-3G), whereas at UHEI-IUP, CAR, and at MPI-BGC gas chromatographic (GC) systems with a nickel catalyst for conversion of CO_2 into CH_4, and flame ionisation detectors (FID) were used. Stable isotope ratios in CO_2 were measured in all four laboratories by isotope ratio mass spectrometry (IRMS, Finnigan-252, Bremen, Germany), after cryogenic extraction of CO_2 from the whole air samples. For description of the CO_2 concentration and isotopic measurement procedures see Francey et al. (1996), Bourg and Ciais (1998, 1999), Neubert (1998), Ramonet et al. (1999), and Jordan and Brand (2001). In all laboratories, CH_4 was analysed by GC-FID (Levin et al., 1999; Jordan and Brand, 2001; Langenfelds et al., 2001; Werner et al., 2001). The N_2O mixing ratio was analysed by the GC electron capture detector technique (ECD) in all flasks from Syktyvkar and Zotino by UHEI-IUP, CAR and MPI-BGC (Jordan and Brand, 2001; Langenfelds et al., 2001; Schmidt et al., 2001). SF_6 was only measured in flasks from Syktyvkar by UHEI-IUP also using GC-ECD technique (Maiss et al., 1994).

2.4. Calibrations and drift corrections

For the CO_2 mixing ratio, all data are reported in the WMO CO_2 mole fraction scale maintained at NOAA/CCGG, Boulder, CO, USA. Laboratory standards (CO_2 in natural air) were obtained from NOAA/CCGG. Stable isotope ratios in CO_2 are reported on the Vienna-PDB-CO_2 scale. Respective carbonate reference standard material (NBS-19) is provided by the International Atomic Energy Agency (IAEA), Vienna. These standards have to be chemically processed to yield carbon dioxide gas for calibration of the respective working gases (pure CO_2) at the mass spectrometers. For $\delta^{18}O$, calibration of the mass spectrometer can also be obtained through water standards (V-SMOW) which are equilibrated with CO_2. The V-SMOW scale is then mathematically converted to the V-PDB-CO_2 scale. In this kind of calibration, chemical or physical processing of primary reference material is necessary for the transfer of the V-PDB (and the V-SMOW) scale to atmospheric CO_2 samples. Through these processes, laboratory biases may be introduced which may cause systematic calibration errors of laborat-

ory working standards (pure CO_2) and finally to the whole-air standards used to check the extraction procedures in the individual laboratory. This is particularly true for $\delta^{18}O$. However, whole-air standards such as those for CO_2 mixing ratios are not yet available for stable isotope ratios in CO_2; therefore, using carbonate or water standards transferred to CO_2 is the only "absolute" way to provide calibration of isotope ratio measurements in atmospheric CO_2. To date, MPI-BGC $\delta^{18}O$ data are calibrated against a whole air standard using the value assigned to it by CAR. All isotope ratio data are corrected for interference with N_2O. The absolute calibration procedures used in the individual labarotories are reported in the detailed descriptions of the data from the individual sites (Lloyd et al., 2002; Ramonet et al., 2002a; Sidorov et al., 2002).

For CH_4 all laboratories relate their mixing ratios to the NOAA/CCGG scale. For N_2O no internationally agreed calibration scale is available. CAR and MPI-BGC relate their standards to the scale that is maintained at CAR and derived from a suite of mixtures gravimetrically prepared by NOAA/CMDL, while UHEI-IUP is preliminarily linked to the SIO93 scale maintained at Scripps Institution of Oceanography for the ALE/GAGE and AGAGE programs (Weiss et al., 1981; Schmidt et al., 2001). The scale factor linking these scales has been precisely determined through regular exchange by CAR and SIO of high-pressure cylinders used as calibration standards in the AGAGE program to 0.992 52, equivalent to a difference of 2.4 ppb (CAR-SIO93) at a N_2O mixing ratio of 315 ppb. The Zotino data presented here have been adjusted to the SIO93 scale. Preliminary results from a flask intercomparison between CAR and UHEI-IUP during the period 1998–2000 performed with stainless steel containers (2.5 L Sirocans, $n = 16$) and with glass flasks identical to those used in this program ($n = 10$) showed a mean difference of 0.7 and 0.5 ppb, respectively, with UHEI-IUP data being higher. This not yet finally confirmed scale difference must be kept in mind when comparing Zotino and Syktyvkar N_2O flask data. SF_6 data from UHEI-IUP are reported relative to a diluted gravimetric standard gas provided by Messer Griesheim, Mannheim, Germany. The dilution procedure is described by Maiss et al. (1996). Its absolute accuracy is better than 1%.

Based on long-term tests performed at CAR and MPI-BGC, all CO_2 and N_2O mixing ratios presented here have been corrected for drift during storage. Experiments were performed by "sausage filling" of multiple flasks from a high-pressure cylinder with precisely determined mixing ratios, to a pressure typical of field samples. These storage tests will be described in detail on the EuroSiberian CarbonFlux web site (*http:// www.bgc-jena.mpg.de/ ∼ martin.heimann/eurosib/*), a brief summary is presented here. At CAR, test flask samples were each analysed once only, at various times up to 7 months after collection, while at MPI-BGC the same samples were re-analysed on multiple occasions up to 1 yr after collection. For CO_2, both laboratories observed an initial offset of -0.06 ppm, and a subsequent drift of -0.0012 ppm per day of storage. For 100 d of storage this corresponds to a total correction of $+0.18$ ppm. For N_2O, ignoring any initial offset which was not as well resolved relative to experimental precision, at least in the CAR tests, drift rates of -0.0035 and -0.0033 ppb per day were observed by CAR and MPI-BGC, respectively. The CAR value has been used to correct all data presented here. No significant drifts were observed for CH_4. Although the stable isotopes of CO_2 were not included in these tests, their stability has been previously monitored by CAR in their 0.5 L glass flasks, fitted with the same types of taps and O-rings. No significant drifts were observed in $\delta^{13}C$. No consistent drifts were observed in $\delta^{18}O$ although in isolated cases, individual flasks did exhibit large drifts that were probably related to elevated moisture levels (see also Gemery et al., 1996).

2.5. Laboratory intercomparison

Besides relating our measurements of greenhouse gases to common international standards (where available), quality control and intercomparison of the individual laboratories participating in this joint project is crucial to achieve comparable and reliable results. Within the EuroSiberian CarbonFlux project, a number of intercomparison exercises have been performed: exchange of pure CO_2 samples for isotopic analysis as well as exchange of high-pressure cylinders and flasks identically filled with tank air. In addition, intercomparison was performed through duplicate measurement of flask pairs by two different laboratories. All these intercomparison results are summarised by Levin et al. (2002). The mean differences and standard deviations for CO_2 analyses between pairs of laboratories did not exceed 0.20 ± 0.45 ppm in CO_2 mixing ratio, 0.06 ± 0.03‰ in $\delta^{13}C$ and 0.15 ± 0.17‰ in $\delta^{18}O$ analyses. Nevertheless, these differences are large when considering the observed gradients between different sites, and need to be reduced in future work. Concerning CH_4 concentration, the laboratories compare within their internal pair reproducibility, i.e. $\pm(2-5)$ ppb. For N_2O the laboratories compare to better than ± 0.7 ppb. Special care was taken to assure the continuity of the record at the Zotino site when transferring the analysis from CAR to MPI-BGC. A total of 100 flasks was analysed in both laboratories with mean differences and standard deviations of individual comparisons (MPI–BGC–CAR) of -0.11 ppm (± 0.15 ppm) for CO_2 analyses, 0.03 ppb (± 1.94 ppb) for CH_4 and -0.09 ppb (± 0.30 ppb) for N_2O.

2.6. Data selection and typical pair reproducibility

Except for the Fyodorovskoye sampling site, where serious contamination of the samples occurred from November 1998 until June 1999, the quality of the flask samples was good. Contamination of samples through leakage in the air intake line, which occurred at Fyodorovskoye but also at Syktyvkar during two flights in October 1999, was easily detected by extremely high CO_2 and elevated CH_4 mixing ratios. For all sites CO_2 results with pair differences larger than 0.5 ppm and $\delta^{13}C$–CO_2 differences larger than 0.1‰ have been rejected from the records. For the $^{18}O/^{16}O$ ratio of CO_2, reliable drying of the samples is essential. On some occasions this was not achieved, and manifested itself in pair differences for $\delta^{18}O$ larger than 0.15‰. These $\delta^{18}O$ data have also been removed from the data sets. For the remaining samples, the mean pair reproducibility for the individual stations is given in Table 1.

2.7. Curve-fitting procedures

To derive the amplitude and phase of the seasonal cycles as well as annual means for the different components at the different sites, har-

Table 1. *Pair reproducibility and its standard deviation for trace components analysed in aircraft flasks*

	Orléans	Fyodorovskoye	Syktyvkar	Zotino
CO_2 (ppm)	0.084 ± 0.074	0.10 ± 0.08	0.080 ± 0.073	0.10 ± 0.09
$\delta^{13}C$–CO_2 (‰)	0.012 ± 0.012	0.011 ± 0.009	0.008 ± 0.008	0.011 ± 0.013
$\delta^{18}O$–CO_2 (‰)	0.029 ± 0.027	0.024 ± 0.21	0.035 ± 0.027	0.033 ± 0.026
CH_4 (ppb)	6.8 ± 9.7	4.5 ± 4.3	1.6 ± 1.4	1.1 ± 0.9
N_2O (ppb)	—	—	0.20 ± 0.16	0.11 ± 0.10
SF_6 (ppt)	—	—	0.009 ± 0.008	—

monic fit curves have been calculated through the data. Linear trends and seasonal cycles using two harmonics and digital filtering (cut-off period 6 months) have been calculated with a fitting routine from Nakazawa et al. (1997b). Due to occasional data gaps of several weeks up to months, annual mean values were calculated from the fitted harmonic curves and not from the data themselves. At all Russian stations except for Fyodorovskoye, complete annual cycles of observations exist only for 1999 and 2000; therefore, for these two years only mean values have been calculated and are compared in Section 3.3.
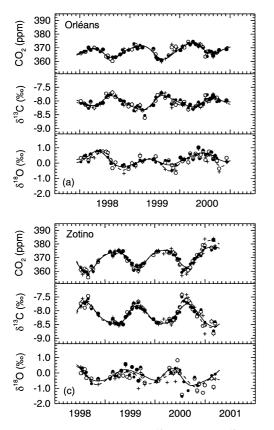
3. Results

3.1. Carbon dioxide mixing ratios and $^{13}C/^{12}C$ ratio in atmospheric CO_2

Figures 2a–2c show the three year-long records of CO_2 mixing ratio, $\delta^{13}C$–CO_2, and $\delta^{18}O$–CO_2 from the three aircraft sites Orléans, Syktyvkar, and Zotino. At all three sites, very regular seasonal cycles are observed at all three height levels and in all three components. At the two Russian sites, the CO_2 and $\delta^{13}C$ amplitudes decrease with height from 2000 to 3000 m. As expected, the sign of CO_2 and $\delta^{13}C$ vertical gradients changes between summer, with a net ground level sink of CO_2, and winter, with a net source. For Syktyvkar, in a number of profiles, the CO_2 concentration gradient between 2000, 2500 and 3000 m was larger than 1 ppm, enough to derive with confidence the $\delta^{13}C$ signature of the source CO_2 and/or the discrimination of the sink responsible for this gradient. From a two-component mixing approach according to Keeling (1961) we calculated this source signature for individual profiles (Fig. 2b, lowest panel). The most depleted source signatures are observed during winter, possibly containing

some contributions from fossil fuel emissions. The maximum summer sink $\delta^{13}C$ signature of -21 ± 3‰ corresponds to an ecosystem discrimination Δ of -13.5‰, assuming a mean summer CBL $\delta^{13}C$–CO_2 of -7.5‰. Mean values of the apparent source signature for summer (June to October) are -25.9 ± 1.0‰ and for winter -30.8 ± 0.9‰. Similar seasonal differences of the apparent source signature in the order of 4–5‰ have been found at mid-northern latitude sites by Bakwin et al. (1995, 1998). Lloyd et al. (2002), inspecting vertical profiles at Zotino extending from 100 up to 3000 m, also observed winter situations with source $\delta^{13}C$–CO_2 as depleted as -31.6‰. These situations could be clearly identified as "polluted" by enhanced CO mixing ratios. Again during the winter season, however, they also frequently observed CO_2 increases in the boundary layer which are not elevated in CO, and therefore postulated to be caused by soil emissions of respiratory CO_2 with source signatures ranging from $\delta^{13}C = -26.8$ to -28.9‰.

Figure 3 shows the correlation of de-trended $\delta^{13}C$ and $1/[CO_2]$ at all four sites for free tropospheric air observed at the respective 3000 m height level for all data. The apparent source signatures change from Orléans with $\delta^{13}C(\text{source}) = -24.8 \pm 1.4$‰ to Fyodorovskoye with $\delta^{13}C(\text{source}) = -26.0 \pm 1.0$‰, Syktyvkar with $\delta^{13}C(\text{source}) = -27.8 \pm 0.3$‰, and Zotino with $\delta^{13}C(\text{source}) = -27.1 \pm 0.4$‰. It is obvious from Fig. 3 that the scatter in the Keeling plots is larger at the two western sites Orléans and Fyodorovskoye than at the more continental stations. Except for occasional long-range transport of polluted air, the source distributions around Syktyvkar and Zotino are probably more homogeneous than further to the west, where sources from sea-to-air fluxes, natural ecosystems, agricultural land, and anthropogenic emissions all
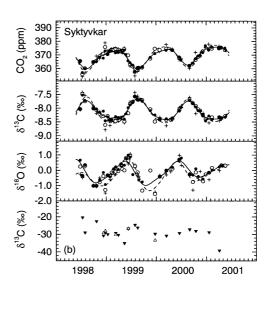
Fig. 2. (a) CO_2 mixing ratio, $\delta^{13}C–CO_2$ and $\delta^{18}O–CO_2$ observed in aircraft samples over Orléans, France ($1°E$, $48°N$) at three height levels, 2000 m (crosses), 2500 m (open circles) and 3000 m (closed circles). Dashed lines are harmonic fit curves through the 2000 m data, solid lines harmonic fit curves through the 3000 m data. (b) Same as (a) but for the Russian site Syktyvkar ($52°E$, $61°N$). The lowest panel shows apparent source signatures calculated from individual profiles where CO_2 gradients between 3000 m and 2000 m (closed symbols) and 2500 m (open symbols) were larger than 1 ppm. (c) Same as (a) but for the Siberian site Zotino ($89°E$, $61°N$).

substantially contribute to the seasonality and variability. There is a slight gradient in the annual mean source signature along a transect from Orléans over Fyodorovskoye towards Syktyvkar and Zotino. Possibly, the presence of considerable areas of introduced C4 agricultural species such as maize and sorghum in Western Europe (Orléans) contribute to this gradient by reducing the overall extent of ^{13}C discrimination (Lloyd and Farquhar, 1994). The change of mean source signature in the order of -1 to $-2‰$ observed between Fyodorovskoye and the two sites further to the north-east (Syktyvkar and Zotino) is, however, also consistent with the difference observed (and modelled) between temperate to cool and cold forest ecosystems by Kaplan et al. (2002).

3.2. $^{18}O/^{16}O$ ratio in atmospheric CO_2

The $\delta^{18}O–CO_2$ records at all three sites (Figs. 2 and 4) also show a regular seasonality, however with a phase shift of about two months compared to $\delta^{13}C$, the $\delta^{18}O$ maximum occurring earlier in the year (May/June instead of July/August). Most visible at Syktyvkar, this maximum coincides with the maximum draw-down rate of CO_2 mixing ratio in the atmosphere, i.e. when the net uptake of CO_2 by plant assimilation (NEP) reaches maximum values (Arneth et al., 2002; Milyukova et al., 2002). Therefore, this $\delta^{18}O–CO_2$ maximum is most probably caused by strong photosynthetic activity and exchange of ^{18}O with leaf water in the plants, which is generally enriched due to evapotranspir-
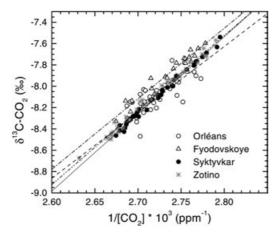
Fig. 3. "Keeling Plot" from detrended data normalised to 1999 of the inverse CO_2 mixing ratios and $\delta^{13}C$–CO_2 to derive the mean $\delta^{13}C$ source signatures driving the respective seasonal cycles at the four aircraft sites at 3000 m a.s.l. (Orléans: dashed line, $\delta^{13}C_{source} = -24.8 \pm 1.4‰$; Fyodorovskoye: dotted-dashed line, $\delta^{13}C_{source} = -26.0 \pm 1.0‰$; Syktyvkar: solid line, $\delta^{13}C_{source} = -27.8 \pm 0.3‰$; Zotino: dashed–dot–dot line, $\delta^{13}C_{source} = -27.1 \pm 0.4‰$).

ation in $\delta^{18}O$–H_2O by about 10–20‰ if compared to the source (ground) water supply (Bariac et al., 1994; Langendörfer et al., 2002). The strong decrease in the atmospheric $\delta^{18}O$–CO_2 signal during the remaining summer and autumn season can be interpreted as a dominating influence of soil respiration CO_2 fluxes over assimilation fluxes on the tropospheric $\delta^{18}O$–CO_2. Measurements in a Canadian boreal forest showed that CO_2 originating from soil respiration is depleted in $\delta^{18}O$ compared to atmospheric CO_2 by about 5–20‰ (Flanagan et al., 1997), and, from aircraft sampling in the nocturnal boundary layer in early morning during the intensive campaign in Zotino, July 1998, a $\delta^{18}O$–CO_2 value for respired CO_2 of $-15‰$ has been obtained (Styles et al., 2002). At Syktyvkar and Zotino, throughout the year, $\delta^{18}O$ seems to be slightly more depleted at the lower level (2000 m) than at 3000 m, supporting the hypothesis of dominating influence from a generally depleted CO_2 source and sink at ground level. This behaviour is less pronounced at Orléans than at the two Russian sites. Support for this also comes from the data presented by Lloyd et al. (2002). They observed that for the Zotino site, $\delta^{18}O$–CO_2 within the atmospheric boundary layer

is always depleted with respect to the free troposphere, irrespective of whether the overall CO_2 profile indicated the underlying terrestrial surface to be a source or a sink of CO_2.

In autumn and early winter, most visible at Zotino in the second half of 2000, very depleted $\delta^{18}O$ values are observed at the Russian sites. If these measurements are not affected by sampling or measurement problems, then the most plausible explanation is that they indicate strong ^{18}O equilibration processes (gross CO_2 exchange) at ground surfaces rather than net CO_2 emissions (i.e. from fossil fuels or net soil respiration).

3.3. Comparison of CO_2 and stable isotopic results between sites for free tropospheric conditions (3000 m a.s.l.)

From examination of the continuous vertical profiles of CO_2, relative humidity, and temperature, in most situations it is possible to determine the height of the atmospheric boundary layer (ABL) during individual flights (Lloyd et al., 2002; Ramonet et al., 2002a; Sidorov et al., 2002). Due to radiative/convective processes over the continents, this ABL height changes from 300–500 m during winter to 1500–2800 m in summer. Measurements within the ABL, even during the day, are still largely affected by regional short-term ground level processes while, as a first-order approach, the 3000 m level represents the large-scale background situation of the lower troposphere. Representative gradients over the EuroSiberian region can, therefore, be derived primarily from the data at the 3000 m level. For CO_2 and its stable isotope ratios, Fig. 4 shows the comparison of observations at all four sites. (Note that for Fyodorovskoye harmonic fit curves have not been calculated due to data gaps.) The amplitudes of the seasonal cycles in all three components increase from Orléans towards Syktyvkar and Zotino (Table 2). The annual mean values show a significant increase in the CO_2 mixing ratio and a corresponding decrease in $\delta^{13}C$–CO_2, from Syktyvkar towards Zotino in 1999, which indicates change of mean air mass origin and/or large net flux changes in the longitude band from Syktyvkar to Zotino, i.e. from about 50 to 90°E, where large areas are covered by wetlands. The $\delta^{13}C$ source signature of this flux is calculated to have a value of $-27.6‰$, very similar to the source signature
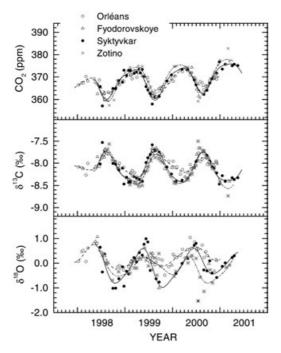
Fig. 4. Comparison of CO_2 mixing ratio (upper panel), $\delta^{13}C$–CO_2 (middle panel) and $\delta^{18}O$–CO_2 (lower panel) at the four aircraft sites for the 3000 m level. The lines are harmonic fit curves through the respective data (Orléans: dashed line; Syktyvkar: solid line; Zotino: dashed–dot–dot line).

derived from the annual cycles at the two stations (Fig. 3). However, a positive gradient between Zotino and Syktyvkar of 1–2 ppm does not support the existence of strong ecosystem uptake, at least in Western and Central Siberia, as calculated by Bousquet et al. (1999).

One interesting feature of our observations is the $\delta^{18}O$–CO_2 gradient between Orléans and the two continental sites, Syktyvkar and Zotino, in autumn and winter of the order of -0.5 to -1.0‰. A substantial gradient towards more continental longitudes within Eurasia, at least during times when the continents are a net source of CO_2, was certainly expected from the well known gradient of $\delta^{18}O$ in precipitation water (IAEA, 1969–1998; Sonntag et al., 1983). As a consequence of depleted precipitation, surface ground water has been modelled to show a decrease of the order of 10–20‰ between the Atlantic coast and the continental area around Syktyvkar and Zotino (Farquhar

et al., 1993; Ciais et al., 1997; Cuntz et al., 2002). Our atmospheric $\delta^{18}O$–CO_2 observations, for the first time, manifest this gradient as being transferred through surface vegetation interaction into the isotopic abundance of atmospheric CO_2 in the respective area.

From the observed signal we can roughly estimate the respiration flux that must be involved in this proces. We assume a mean residence time of air masses reaching central Eurasia to about 5 d (see trajectories in Fig. 1), and a well mixed lower tropospheric air mass layer M of 3000 m thickness (our observation level) which is influenced by the surface flux. The change in $\delta^{18}O$–CO_2 ($\Delta\delta^{18}O_{air}/\Delta t$) between Orléans and central Eurasia is given by the mass balance equation:

$$M\frac{\Delta\delta^{18}O_{air}}{\Delta t} = A\Delta_{leaves} + R(\delta^{18}O_{soil} - \delta^{18}O_{air} - \varepsilon_{soil})$$

(1)

where A and R are the gross carbon fluxes of photosynthesis and ecosystem respiration, respectively, Δ_{leaves} is the leaf isotope discrimination and $\delta^{18}O_{soil}$ and ε_{soil}, respectively, the isotopic composition of soil-respired CO_2 and the diffusive soil–atmosphere fractionation [7.2‰ after Miller et al. (1999)]. Assuming A to be zero in late autumn and early winter, and a $\delta^{18}O_{soil}$ of -12‰ from a global modelling study (Cuntz et al., 2002), we can estimate the respiration flux R to 0.25 mol CO_2 m^{-2} d^{-1} or 3 μmol m^{-2} s^{-1} during this time of the year. This value is in reasonable agreement with eddy flux measurements in the same region at that time of the year (Milyukova et al., 2002). However, this flux would, if the emitted CO_2 remained in the mixing layer over 5 d (as was assumed for $\delta^{18}O$ in our simple approach) cause a continental gradient in the order of 10 ppm. As we only observe a CO_2 increase of less than 4 ppm between Orléans and Zotino (associated with the $\delta^{18}O$ gradient of -0.5‰) our mass balance equation is probably too simple. Processes such as vertical mixing into the free troposphere (above 3000 m) which reduce the concentration increase have to be considered; but also possible ^{18}O equilibration of atmospheric CO_2 with soil surface water by invasion into the topsoil (Tans, 1998) may increase the $\delta^{18}O$ gradient without altering the CO_2 gradient.

Table 2. *Average peak-to-peak amplitudes (1998–2001) and annual mean values 1999 and 2000 of trace gas components measured at the EuroSiberian aircraft sites*[a]

	Orléans	Syktyvkar	Zotino
CO_2 (ppm)			
Peak-to-peak amplitude	8.36 (83, 243)	12.4 (68, 232)	13.06 (66, 238)
Annual mean 1999	367.16 ± 0.61	367.60 ± 0.29	369.66 ± 0.39
Annual mean 2000	369.59 ± 0.37	369.57 ± 0.31	370.61 ± 0.56
$\delta^{13}C$ (‰)			
Peak-to-peak amplitude	0.36 (237, 86)	0.67 (230, 60)	0.67 (239, 74)
Annual mean 1999	−8.062 ± 0.035	−8.112 ± 0.017	−8.184 ± 0.017
Annual mean 2000	−8.043 ± 0.018	−8.136 ± 0.015	−8.146 ± 0.040
$\delta^{18}O$ (‰)			
Peak-to-peak amplitude	0.84 (162, 310)	1.30 (141, 298)	0.80 (143, 340)
Annual mean 1999	−0.04 ± 0.05	−0.22 ± 0.08	−0.09 ± 0.09
Annual mean 2000	0.25 ± 0.05	−0.02 ± 0.07	−0.33 ± 0.13
CH_4 (ppb)			
Peak-to-peak amplitude	—	17.0 (32, 244)	33.9 (43, 192)
Annual mean 1999	—	1815.4 ± 1.3	1826.9 ± 3.1
Annual mean 2000	—	1821.1 ± 4.1	1823.8 ± 2.7
N_2O (ppb)			
Peak-to-peak amplitude	—	0.50 (3, 232)	1.08 (50, 199)
Annual mean 1999	—	314.23 ± 0.09	313.45 ± 0.09
Annual mean 2000	—	315.40 ± 0.06	314.76 ± 0.04
SF_6 (ppt)			
Peak-to-peak amplitude	—	0.060 (55, 263)	—
Annual mean 1999	—	4.499 ± 0.005	—
Annual mean 2000	—	4.719 ± 0.007	—

[a] The numbers in parentheses are the respective Julian days of the seasonal cycle maximum and minimum.

3.4. Methane mixing ratio

Our main objective when starting this aircraft program was to investigate the carbon balance over Russia. Concerning gross carbon fluxes between the biosphere and the atmosphere, this exchange (to more than 98%) is dominated by carbon dioxide. However, in the taiga and tundra regions of the West Siberian Lowland with its extended wetland areas, net carbon fluxes associated with anaerobic decomposition of organic material and eventual emissions of methane cannot be neglected. Estimated ranges of CH_4 emissions from this area are between 10 and 30 Tg CH_4 per year (0.007–0.022 PgC yr^{-1}), depending on the study (Aselmann and Crutzen, 1989; Bartlett and Harriss, 1993; Christensen et al., 1996). This corresponds to a carbon source to the atmosphere in the order of 10% of the absolute value of a postulated net CO_2 uptake in the order

of 0.1 PgC yr^{-1} by the biosphere in the same area (i.e. Bousquet et al., 1999). Moreover, with regard to the climatic impact of CH_4, when using a time horizon of 100 yr, its global warming potential is higher by a factor of 21 compared to CO_2 (IPCC, 1996). Thus, considering only the area of the West Siberian Lowland, the warming effect of its net CH_4 emissions would still be about twice that of the potential "cooling" effect by the postulated CO_2 sink!

Most of the flasks collected during aircraft profiling have been analysed for CH_4 mixing ratio, with the results from the free tropospheric samples at 3000 m being presented in Fig. 5 (upper panel). As expected for mid-northern latitudes, the data from the Russian sites show a seasonality, with maximum concentrations during autumn and winter and a minimum in summer. However, particularly in 1998 the scatter of the data is rather

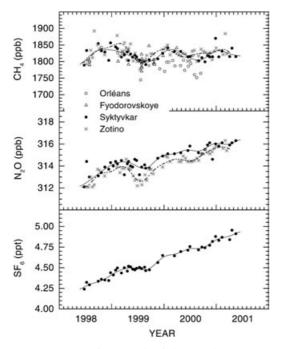*Fig. 5.* Concentration records of the greenhouse gases CH_4 (upper panel), N_2O (middle panel) and SF_6 (lowest panel) derived from aircraft samples at Orléans, Fyodorovskoye, Syktyvkar, and Zotino. The lines are harmonic fit curves through the Syktyvkar (solid line) and Zotino (dashed–dot–dot line) data. The N_2O shift between Syktyvkar and Zotino is most probably due to different calibration scales used in the two laboratories.

large. A large variability of CH_4 mixing ratios has been observed earlier by Tohjima et al. (1997) during transect flights over Siberia in July 1993. The seasonal peak-to-peak amplitudes at Syktyvkar and Zotino are up to 40 ppb in 1998/1999. Due to occasionally high concentrations at Zotino, annual mean values are up to 10 ppb higher at Zotino than at Syktyvkar during that period. Orléans data from Western Europe seem to be lower again by about 20–30 ppb. There is obviously a significant CH_4 accumulation over Central Eurasia, most probably due to wetland emissions (late summer and autumn); however, influences from anthropogenic sources such as natural gas production and distribution cannot be excluded [a source of 17 Tg CH_4 yr^{-1} after Hein et al. (1997)]. Assuming a mean residence time of air masses of 3 d between Syktyvkar and Zotino,

a CH_4 gradient of 10 ppb, as observed in 1999 between the two sites, representing a well mixed air column up to 3000 m, requires a methane source to the atmosphere of about 7 mg CH_4 $m^{-2} d^{-1}$. This flux may reflect emissions either from the widespread area of wetlands over the West Siberian Lowland or from large fields of natural gas exploited from the Northern Ob river basin. Our estimated emission is close to the mean summer season (June–October) methane flux density estimated for the Hudson Bay Lowlands in Northern Canada, which ranges from about 2 mg CH_4 $m^{-2} d^{-1}$ in October to a maximum of 13 mg CH_4 $m^{-2} d^{-1}$ in August (Worthy et al., 2000). Also remarkable is that CH_4 mixing ratios measured during individual flights in autumn 1999 are much less scattered than in autumn 1998, where occasionally very high mixing ratios up to 1890 ppb are observed at Zotino even at 3000 m. This high scatter in 1998 is possibly due to higher regional wetland emissions in 1998 compared to 1999. Globally speaking, 1998 was the warmest year of the last century, and also in marine background air an anomalous growth rate was observed, particularly in high northern latitudes by Dlugokencky et al. (2001), which they partly attribute to anomalously high wetland emissions. Examination of long-term weather records for the town of Surgut, located near the centre of the West Siberian Lowland, suggests that this may have also been the case in the extensive wetlands of that region. The mean temperature for July 1998 was 21.4 °C, higher than any value recorded between 1885 and 1983 in the long-term database for Surgut of Razuvayev et al. (1993). The highest July average temperature previously reported (excluding 1984 to 1993 for which we do not have data available) was 20.8 °C in 1886. This compares to an average July temperature in Surgut (calculated using 1885–1983 data) of 17.1 °C, and a July 1999 temperature of 18.1 °C.

3.5. Sulfur hexafluoride mixing ratio

Sulfur hexafluoride (SF_6) is a chemically very stable and purely anthropogenic greenhouse gas, which is industrially used mainly in electrical insulation and switching, and for degassing and purifying of molten reactive metals (Maiss and Brenninkmeijer, 1998). Destruction of SF_6 occurs only in the very high stratosphere and in the

mesosphere. Since the 1970s, atmospheric SF_6 has been increasing globally at a rate of more than 6% per year (Maiss et al., 1996; Geller et al., 1997). SF_6 mixing ratios have only been analysed in the Syktyvkar flasks (Fig. 5, lowest panel). As observed globally, this greenhouse gas is still strongly increasing at a recent rate of about 5% per year. SF_6 shows a regular seasonality which is strikingly in parallel to N_2O (Fig. 5, middle panel). This seasonal cycle must be associated with atmospheric transport patterns, as the purely anthropogenic sources of SF_6 have no seasonality (see discussion in Section 3.6).

3.6. Nitrous oxide mixing ratio

Nitrous oxide (N_2O) is a greenhouse gas with natural and anthropogenic sources (Ehhalt et al., 2001). Major emissions are from natural tropical soils as well as from the ocean. Fertilised soils are a large anthropogenic source in mid-northern latitudes as well as a number of industrial processes. N_2O mixing ratios were determined in all flasks from Syktyvkar and Zotino. Figure 5 (middle panel) shows the results at both sites for the highest flight level. Both aircraft records show a pronounced seasonality with a peak-to-peak amplitude between 0.5 and 1.1 ppb. The mean growth rate is 1.2–1.3 ppb yr^{-1}. The mean N_2O level at Syktyvkar is higher than at Zotino by 0.7 ppb. This difference has the same magnitude as the preliminarily determined scale difference between CAR/MPI-BGC and UHEI-IUP of 0.5–0.7 ppb [Section 2.4 and Levin et al. (2002)]. Therefore, although still preliminary, we conclude that there is no significant N_2O difference in the free troposphere between Syktyvkar and Zotino. The N_2O results from the 2000 and 2500 m levels [not shown here but presented by Lloyd et al. (2002) and Sidorov et al. (2002)] do not differ from the free troposphere values which, in combination with the missing gradient between Syktyvkar and Zotino suggests that, contrary to fertilised soils and soils exposed to nitrogen deposition (Bouwman et al., 1995), natural soils in boreal regions are probably not a large source of N_2O.

As mentioned earlier, the phasing of the seasonal cycle of N_2O is very similar to that of SF_6. This suggests that similar processes may be the driving modulating force for the observed seasonal cycles

of both gases. SF_6 has no seasonally varying sources, while for N_2O, natural and anthropogenic emissions from soils were observed to be highest during spring and summer (Flessa et al., 1995; Schmidt et al., 2001). This should lead to maximum concentrations in the free troposphere in summer and autumn. By contrast, concentrations of N_2O (and SF_6) tend to be more or less constant or even decreasing during summer. Therefore, rather than being due to seasonally varying sources, the observed seasonality of both gases is more likely due to atmospheric mixing processes. One process possibly contributing to the seasonal cycles of both greenhouse gases is a seasonally varying stratosphere–troposphere exchange. N_2O is destroyed by photolysis at wavelengths between 180 and 230 nm in the stratosphere, it has no known sinks in the troposphere (Ehhalt et al., 2001). Due to the photolytical sink process, a steep vertical gradient of N_2O is observed in the stratosphere with mixing ratios decreasing to only 10% of the tropospheric value above 25 km. Similarly, SF_6 mixing ratios decrease with height by almost 50% (Harnisch et al., 1998; Strunk et al., 2000). If the seasonal cycles of N_2O and SF_6 were both due to a springtime input of stratospheric air intrusions into the troposphere, the ratio between the driving stratosphere–troposphere gradients and the amplitudes in the troposphere of both gases should be similar. The troposphere minus lower stratosphere (250–100 hPa) difference for N_2O in high northern latitudes is about 40 ppb, while the respective gradient for SF_6 is about 0.6 ppt (Strunk et al., 2000). The observed peak-to-peak amplitudes of the seasonal cycles at Syktyvkar are 0.5 ± 0.3 ppb for N_2O and 0.060 ± 0.035 ppt for SF_6. From this we derive ratios between gradient and seasonal amplitude differing by a factor of about 6–7 between N_2O and SF_6. In fact, the seasonal amplitude of SF_6 in the southern hemisphere, which was largely attributed by Levin and Hesshaimer (1996) to stratosphere–troposphere exchange, is only about 0.02 ppt, one third of that observed at Syktyvkar. Consequently, other processes must contribute to the seasonal cycle of SF_6. One of these may be the seasonal change of the circulation pattern, but this process can only contribute to the seasonal cycle of a trace gas in mid-to-high latitudes if that gas also has a significant latitudinal gradient. This is only the case for SF_6, which

shows an increase of about 0.2 ppt from 70°N to 50°N (Maiss et al., 1996). All in all, this suggests that the origin of the tropospheric seasonal cycle of N_2O is still not readily explicable, but that stratosphere–troposphere exchange which shows the correct phasing (Appenzeller et al., 1996) may make a significant contribution to the observed seasonal pattern observed over Western Siberia.

4. Conclusions

The EuroSiberian aircraft program, started in 1998, has provided a unique set of trace gas observations over the Eurasian continent which will serve as an invaluable source of information to investigate quantitatively the associated bio-geochemical cycles with these entities. From the first results presented here we can conclude that the observed gradients in CO_2 and stable isotopic ratios in the vertical and across the Eurasian continent are small. As expected, the seasonal amplitudes of CO_2 concentration and stable isotope ratios in CO_2 increase towards more continental sites due to large seasonal CO_2 exchange fluxes with the continental biosphere. However, the largest changes in amplitude are observed between Orléans (Western Europe) and Syktyvkar, while the further increase in amplitude between Syktyvkar and Zotino is not significant. Also, the mean CO_2 concentration and isotope ratios gradients within the Eurasian continent, i.e. between Syktyvkar and Zotino, are very small. The same is true for CH_4. Here, probably due to net emissions from wetlands and natural gas production, we observe the largest gradient between Western Europe and Russia. Although still preliminary, no horizontal N_2O gradient is observed between Syktyvkar and Zotino. From this and from vertical profiles of N_2O which show no gradient between 2000 and 3000 m, we infer that the natural boreal forest areas are probably neither a significant source nor a sink of N_2O to the atmosphere. N_2O and SF_6 show small seasonal cycles over Eurosiberia which must be associated to the transport pattern in the sub-polar atmosphere. To validate transport patterns of models (Denning et al., 1999), SF_6 measurements along the west–east transect Orléans–Syktyvkar–Zotino would be highly desirable.

The observed small atmospheric signals make high demands on measurement accuracy, and, as in our case of a concerted program with several participating laboratories, on inter-laboratory comparability. In fact, the latter may be the limiting component of a cooperative network, if these data are to be used successfully in model inversion estimates to derive net Eurasian trace gas fluxes. On the other hand, the interannual variability of horizontal gradients is considerable and our 3-yr observations can only provide a snapshot of the long-term climatology over this extended continental area. Much longer observational records are definitely necessary to provide reliable answers to the urgent questions of the role of the great land masses of the Eurasian continent in global budgets of atmospheric greenhouse gases.

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