HAL
open science

Using 14C, 13C, 18O and 17O isotopic variations to provide insights into the high northern latitude surface CO inventory

T. Röckmann, P. Jöckel, Valérie Gros, M. Bräunlich, G. Possnert, C. A. M. Brenninkmeijer

To cite this version:

T. Röckmann, P. Jöckel, Valérie Gros, M. Bräunlich, G. Possnert, et al.. Using 14C, 13C, 18O and 17O isotopic variations to provide insights into the high northern latitude surface CO inventory. Atmospheric Chemistry and Physics Discussions, 2002, 2 (2), pp.213-248. hal-00300825

HAL Id: hal-00300825

https://hal.science/hal-00300825v1

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Atmos. Chem. Phys. Discuss., 2, 213–248, 2002
www.atmos-chem-phys.org/acpd/2/213/
© European Geophysical Society 2002

Atmospheric Chemistry and Physics Discussions

Using ^{14}C, ^{13}C, ^{18}O and ^{17}O isotopic variations to provide insights into the high northern latitude surface CO inventory

T. Röckmann[1,2], P. Jöckel[2], V. Gros[2], M. Bräunlich[2], G. Possnert[3], and C. A. M. Brenninkmeijer[2]

[1]Max-Planck-Institut für Kernphysik, Bereich Atmosphärenphysik, Heidelberg, Germany
[2]Max-Planck-Institut für Chemie, Abteilung Luftchemie, Mainz, Germany
[3]Uppsala University, Angdströmlaboratoriet, Uppsala, Sweden

Received: 28 January 2001 – Accepted: 20 February 2002 – Published: 7 March 2002

Correspondence to: T. Röckmann (T.Roeckmann@mpi-hd.mpg.de)

© EGS 2002

Abstract

Measurements of the complete isotopic composition of atmospheric CO (^{13}CO, ^{14}CO, $C^{17}O$, $C^{18}O$) have been carried out at the high northern latitude stations Spitsbergen, Norway, and Alert, Canada. The annual changes of the isotope signatures reflect the seasonally varying contributions from the individual CO sources and the OH sink. Short-term variability is small at the remote sampling locations. Nevertheless, the interannual variability is considerable, in particular for the summer minimum. The most prominent event was a strong increase in CO in 1998 that persisted for several months. Using the isotope signatures it is possible to clearly identify extraordinarily strong biomass burning during that season as the cause for this large-scale CO anomaly. In 1997, on the other hand, biomass burning emissions were very low, leading to an unusually low summer minimum and corresponding isotope signatures. The results underscore that monitoring of CO and its isotopic composition at remote high latitude stations is a valuable tool to better understand long-term variations of CO that are representative for the whole high northern latitude region.

1. Introduction

Carbon monoxide is of considerable importance to the chemistry of the global atmosphere for several reasons: Foremost, it is the main reaction partner of the hydroxyl radical (OH), which is responsible for the removal of many natural and anthropogenic contaminants from the troposphere. Because the reaction with CO is responsible for more than half of the total turnover of OH (Crutzen and Zimmermann, 1991), changes in CO can considerably affect mixing ratios of a host of atmospheric constituents that are oxidized by OH, including the greenhouse gas methane. In fact, although not being an effective greenhouse gas itself, it has been shown that the emission of five CO molecules is equivalent to the emission of one CH_4 molecule as regards greenhouse warming (Prather, 1996).

© EGS 2002

In addition to its significance for OH, the reaction CO + OH leads to the formation of HO_2 which, depending on NO_x-levels, can lead either to the production (high NO_x) or destruction (low NO_x) of ozone. Under high NO_x conditions this pathway is a major contributor to ground level photochemical smog.

Through its active role in atmospheric chemistry, CO is also a major player in the global carbon cycle. Most organic compounds – natural or anthropogenic – that are oxidized in the atmosphere are processed via CO to the stable CO_2 molecule. This results in a global turnover of about 2 to 3 Pg/y.

A global increase of CO over the past 200 years has been derived from measurements of CO in air bubbles trapped in polar ice (Haan et al., 1996), changes in the solar absorption spectra from the 1920s to the 1970s (Rinsland and Levine, 1985) and in situ observations at various atmospheric monitoring stations over the last two decades (Khalil and Rasmussen, 1988, 1990, 1994; Novelli et al., 1994a, 1998, 1992). The increase in global CO may have been halted (Khalil and Rasmussen, 1994; Novelli et al., 1994a, 1998), and at present the atmospheric CO budget is being examined in considerable detail using various techniques: In situ measurements are carried out on a global scale and impressive observations from satellites are becoming available (see e.g. MOPITT homepage at http://www.atmosp.physics.utoronto.ca/MOPITT/home.html). Computer models are used to refine source scenarios based on the observed CO distribution, using all available information about atmospheric chemistry and physics (Bergamaschi et al., 2000a, 2000b; Granier et al., 1999). An additional method is isotope analysis. The different isotopic signatures provide independent variables that can help to resolve the contributions of the individual sources and thus to better understand the global CO budget. The major CO sources and their isotopic source signatures are presented in Table 1.

Due to the strong CO sources at the surface and its short chemical lifetime of weeks to months, the mixing ratio and all isotope signatures of tropospheric CO exhibit pronounced temporal and spatial gradients. In this paper, the CO, δ^{13}C, δ^{18}O, Δ^{17}O and

ACPD
2, 213–248, 2002

© EGS 2002

^{14}CO time series from Spitsbergen (79° N) and Alert (82° N) are presented, which are our longest CO isotope records for the northern hemisphere. CO mixing ratios are reported in parts per billion (ppb), i.e. 10^{-9} or nmole/mole. Variations in the stable isotope composition are usually reported in δ- notation as the relative deviation of the ratio of the minor isotope to the abundant isotope, e.g. $^{13}C/^{12}C \equiv {}^{13}R$ in a sample (SA) from an international standard (ST) ratio, i.e. $\delta^{13}C = (^{13}R_{SA}/^{12}R_{ST} - 1) * 1000‰$. In the case of ^{13}C, the standard is Vienna PeeDeeBelemnite (V-PDB), in the case of the oxygen isotopes Vienna Standard Mean Ocean Water (V-SMOW). For ^{17}O, it is useful to introduce the variable $\Delta^{17}O \equiv \delta^{17}O - 0.52 \times \delta^{18}O$, which is a measure (mathematical approximation) for the excess of ^{17}O above what is expected based on the $\delta^{18}O$ value. ^{14}CO values are reported in molecules per cm^3 of air at standard temperature and pressure (Brenninkmeijer, 1993). The activity of the various CO source materials is usually reported in percent Modern Carbon (pMC) (Stuiver and Polach, 1977), and contemporary biomass and organic sources usually have an activity of 120 pMC.

2. Experimental

The air sampling and subsequent CO extraction, conversion and analytical procedures have been extensively described in the literature (Brenninkmeijer, 1993; Brenninkmeijer et al., 2001; Brenninkmeijer and Röckmann, 1997, 1998b; Mak and Brenninkmeijer, 1994; Röckmann, 1998; Rom et al., 2000). At the sampling stations, 1 m^3 air samples are compressed into 10 L aluminum cylinders (Scott Marrin, Riverside, CA) using modified oil-free three-stage piston compressors (RIX industries, Mak and Brenninkmeijer, 1994). The sampling procedure includes low-pressure and high-pressure drying with Drierite™ to prevent condensation of water in the sample cylinders. Zero tests show that the compressors produce less than 0.6 ppb of CO in the compression process, and CO levels in the cylinders are stable over months, i.e. change for most cylinders less than 1 ppb. CO is separated from the large air samples using a laboratory extraction system. First, the air is cleaned from condensable components, in particular

© EGS 2002

CO_2, N_2O and higher hydrocarbons, using high-efficiency, high-capacity Russian-Doll cryogenic traps (Brenninkmeijer, 1991). Subsequently, CO in the clean air matrix is oxidized to CO_2 on Schütze reagent (Brenninkmeijer and Röckmann, 1997; Röckmann, 1998; Schütze, 1949; Smiley, 1965) and the CO-derived CO_2 is collected in an all-glass Russian Doll cryogenic trap (Brenninkmeijer and Röckmann, 1996). The overall yield is then determined in a calibrated manometer and the CO_2 sample transferred to the isotope ratio mass spectrometer (Finnigan MAT 252) for isotope analysis (δ^{13}C and δ^{18}O). After stable isotope determination, the remainder of the sample ($> 90\%$) is recovered for ^{14}CO and/or Δ^{17}O analysis.

This technique is a laborious but absolute method to determine the CO mixing ratio in air at ambient levels, i.e. it does not intrinsically require the use of a reference gas (Brenninkmeijer et al., 2001). Note that a recent intercomparison exercise has revealed a discrepancy between our absolute CO concentrations measurements and the NOAA/CMDL scale in the low concentration range (< 100 ppb). Thorough tests have established the linearity of our system (Brenninkmeijer et al., 2001), and the NOAA/CMDL scale is presently being examined in detail (P. Novelli, personal communication). Above 100 ppb the scales agree well. The reproducibility of our system is better than 1% routine operation, and the absolute precision is better than 2%. The isotopic composition is determined with a standard deviation of ± 0.2‰ and ± 0.3‰ for δ^{13}C and δ^{18}O, respectively, including sampling, preparation and mass spectrometry.

The ^{14}C/^{12}C ratio of the sample is determined by Accelerator Mass Spectrometry (AMS) after dilution of the small samples with nearly ^{14}C-free CO_2 and preparation of a target for AMS from the diluted sample by graphitization (Rom et al., 2000). The overall precision of the experimental procedure including sampling, extraction of CO as CO_2, dilution, preparation of a sample for AMS, and AMS measurement amounts to 0.27 molec.cm^{-3} of air at standard temperature and pressure. An additional error arises due to production of ^{14}CO in the sample cylinders during storage, as recognized recently (Lowe and al, 2002). For storage times of the order of months, the neutron capture reaction ^{14}N(n,p)^{14}C, followed by oxidation of ^{14}C to ^{14}CO leads to non-

© EGS 2002

negligible production of ^{14}CO in high pressure cylinders even at ground level (Lowe and al, 2002; Mak et al., 1999). The production depends not only on the storage time, but also on altitude, latitude and on the actual storage location. To correct for this effect, the global average ^{14}C production rate from (Lingenfelter, 1963) was normalized to the measured ^{14}CO production rate from a cylinder exposure experiment in Antarctica (Mak et al., 1999). The correction amounts to approximately 0.44 molec.cm^{-3} per month of storage at ground level at 80° N. For our sample cylinders, which are shipped approximately every 2 to 5 months from the sampling stations and then analyzed within about two weeks when they arrive at the lab, the average correction is 1.1 molec.cm^{-3}.

The ^{17}O content of a CO-derived CO_2 sample cannot be determined on the CO_2 molecule directly, because both, ^{13}C-substituted and ^{17}O-substituted CO_2 have molecular mass 45 and cannot be resolved on a conventional isotope ratio mass spectrometer. Therefore, an aliquot of the sample is converted to O_2 using a recently developed two-step conversion system (Brenninkmeijer and Röckmann, 1998a). After conversion, $\delta^{17}O$ and $\delta^{18}O$ can be determined independently by monitoring the O_2^+ ions (mass 32, 33 and 34) in the mass spectrometer. Due to a small mass-dependent fractionation during the conversion, the individual $\delta^{17}O$ and $\delta^{18}O$ values have a reproducibility of only 1 and 2‰, respectively, but as these variations are correlated, $\Delta^{17}O$ can be determined with a standard deviation better than 0.2‰.

3. Data presentation and analysis

The CO concentration and isotope records for the two high northern latitude stations Spitsbergen (Norway, 78.5° N, 11.5° W, 475 msl) and Alert (Canada, 81.3° N, 62.3° W, 210 msl) are shown in Fig. 1. Sampling at the Zeppelinfjellet mountain in Ny Ålesund, Spitsbergen, started during the spring 1995 and 1996 ARCTOC campaigns (Barrie and Platt, 1997), at that time specifically in search for ^{13}CO variations during tropospheric ozone depletion events (Röckmann and Brenninkmeijer, 1997; Röckmann et al., 1999a) caused by production of extremely depleted CO via the reaction CH_4 + Cl

© EGS 2002

(see Sect. 3.2). From July 1996 to June 1999, weekly samples were taken on a regular basis by the Norwegian Polar Institute at the Zeppelinfjellet station. In Alert, sampling started in July 1996 and samples were taken approximately weekly until January 1998.

3.1. Seasonal variation

3.1.1. CO mixing ratio

CO mixing ratios at Spitsbergen and Alert are very similar and exhibit a pronounced seasonal cycle with high values in late winter ($\approx$180 ppb) and a minimum in summer ($\approx$80 ppb). This strong seasonal cycle is the result of the relatively short lifetime of CO of the order of weeks to months. On the one hand this is short enough to produce a strong peak to peak amplitude, on the other hand it is long enough to be only little influenced by short time fluctuations at these remote stations, which results in a rather smooth seasonality. The similarity between the Spitsbergen and Alert record shows that the remote high northern latitudes are well-mixed with respect to CO; several Arctic stations show similar CO mixing ratios throughout the year (Novelli et al., 1994b, 1998). Figure 1a also shows the CO time series from Spitsbergen and Alert from the NOAA/CMDL air-sampling network. The data from the two groups show a good agreement. However, the data at the very beginning of our continuous record for Spitsbergen (summer 1996) do not quite capture the seasonal minimum as seen in the record for Alert.

The CO seasonal cycle is to a large degree driven by its main sink, i.e. reaction with OH. When OH levels are low throughout the fall and winter period, CO builds up in the high northern latitude boundary layer, and mixing ratios of about 180 ppb are reached in early spring (Fig. 1a). This CO must originate from the industrial regions at mid-northern latitudes, because there are no in situ CO sources at the high latitudes in winter. Due to reduced convection in the absence of surface heating, mixing with the free troposphere is limited, which results in vertically decreasing CO mixing ratios, as has been established by Conway et al. (1993). Recently, Yurganov et al. (1998)

© EGS 2002

published correlated surface and total column CO mixing ratio measurements revealing that surface values are about 50 ppb higher than average total column values during Arctic winter and spring.

When OH formation starts again after polar sunrise, the main CO sink regains momentum and CO mixing ratios rapidly decline towards the late summer minimum near 80 ppb (Fig. 1a). However, it has already been argued (Röckmann and Brenninkmeijer, 1997) that the in situ destruction of CO at OH levels below 10^5 molec.cm^{-3} in March and April at 80° N (Spivakovsky et al., 2000) is insufficient to cause this rapid CO destruction. Even in a closed box without any sources, OH levels between 2 and 3×10^5 molec.cm^{-3} would be required to produce the observed CO decrease. This confirms that in spring not only chemical destruction causes the fast observed CO decrease. As CO is lower and decreases earlier at lower latitudes, mixing with and import of these air masses leads to a dilution of the high northern latitude CO inventory. Thus, CO that was temporarily stored at the high northern latitudes over winter is transported in spring to lower latitudes again where it is eventually removed. Also mixing with the free troposphere leads to a reduction of the wintertime vertical CO gradient over the Arctic, and by the end of May this gradient has disappeared and the troposphere is vertically well mixed again as regards CO levels (Yurganov et al., 1998).

During spring and summer, not only the dominant CO sink process gains importance, but also CO emissions from natural sources both direct (e.g. biomass burning) and indirect, via oxidation of hydrocarbons and CH_4, increase. The seasonality of these natural CO sources also affects the level of the CO seasonal minimum, which is determined by the competition between the CO + OH sink process and the combined contributions from all sources.

3.1.2. ^{14}CO

As with the CO record, the ^{14}CO time series from Alert and Spitsbergen agree fairly well (Fig. 1b). ^{14}CO values peak at about 25 molec./cm^3 in late winter and bottom out in summer at values around 9 molec./cm^3. The seasonal variations of ^{14}CO and CO

ACPD
2, 213–248, 2002

© EGS 2002

generally follow a very similar pattern, as OH is their primary sink. However, the similarity of the two seasonal cycles cannot be assumed a priori, because both molecules have a very different source distribution, and it is useful to recall the principle factors that influence ^{14}CO abundance before examining the data in detail.

^{14}CO is primarily produced from cosmic radiation in the lower stratosphere and upper troposphere. This ^{14}CO production has no seasonal component, but it is modulated by the 11-year solar cycle, because the solar wind reduces the ability of galactic cosmic ray particles to penetrate the Earth's magnetic field. Consequently the production of ^{14}CO is high during a solar minimum and low during a solar maximum. This inverse modulation of ^{14}CO production by variable solar activity amounts to $\pm 15\%$ (Jöckel, 2000). On short time scales, however, primary ^{14}CO production can be regarded as constant and seasonal variations in cosmogenic ^{14}CO at ground level can only result from variations in transport or OH levels. An additional ^{14}CO source in the troposphere is biogenic CO, which chiefly stems from oxidation of biogenic CH_4 and VOCs, and from biomass burning. This ^{14}C has been circulated through the atmosphere, soils and the terrestrial and marine biosphere as part of the global carbon cycle, and can therefore be regarded as "recycled" ^{14}C. When assigning a modern ^{14}C content of 120 pMC to these biogenic sources, 10 ppb of recycled CO corresponds to 0.38 molec./cm^3 ^{14}CO (Brenninkmeijer, 1993). Note that CO has a higher specific activity than all other atmospheric carbonaceous trace compounds; the ^{14}C level ranges from 400 to 1000 pMC. Therefore, an addition of biogenic, i.e. recycled CO to the atmospheric CO content primarily increases CO mixing ratios, whereas the effect on ^{14}CO is much less. Finally, CO from fossil fuel combustion processes contains no ^{14}CO, and thus contamination of a given CO reservoir with CO from that source can significantly change CO levels without direct effect on the ^{14}CO concentration, as has been shown repeatedly (Brenninkmeijer, 1993; Gros et al., 2001).

To examine relative differences between CO and ^{14}CO in the records, we have normalized the ^{14}CO and CO values by dividing each measured value by the lowest measured ^{14}CO and CO value, respectively, in the record. These normalized data are

© EGS 2002

shown in Fig. 2. Apart from the generally good correlation, clear deviations are discernible. In particular the extraordinarily high CO values in the second half of 1998 (see Sect. 3.3.1) show up below the linear fit line. To eliminate the influence of the strong 1998 CO anomaly as well as several high ^{14}CO values that occurred in 1997, a separate fit has been applied to the 1996 data only, which show relatively little variability. The linear fit through all data has a slope of 1.14 ± 0.05, the slope of the 1996 fit is 1.25 ± 0.10, i.e. the relative annual variation of ^{14}CO is significantly larger (15 to 25%) than that of CO itself. Both molecules share the same sink, therefore the difference must be due to differences in the sources. In summer, the important biogenic CO sources (CH_4 and VOC oxidation) have a much smaller effect on ^{14}CO than on CO. This addition of biogenic CO occurs during the annual minimum of CO and ^{14}CO, and consequently it diminishes the range of annual variation of CO relative to that of ^{14}CO, which can result in the observed slope > 1. Thus, the relationship between ^{14}CO and CO contains interesting information about these difficult to quantify sources, but 3D modeling is needed to investigate this issue in detail.

3.1.3. δ^{13}C

Due to the kinetic isotope effect in the reaction CO + OH, the OH sink induces a variation in δ^{13}C: OH preferentially removes ^{12}CO over ^{13}CO, and the remaining CO becomes enriched in ^{13}C. The kinetic fractionation is strongly pressure dependent and has an average strength of 4 to 5‰ in the lower troposphere (Röckmann et al., 1998b; Smit et al., 1982; Stevens et al., 1980). Consequently in spring, when CO levels decrease after the seasonal maximum, δ^{13}C rapidly rises from values of around -27‰ up to -23‰ within three months (Fig. 1c). In contrast to all other signals, however, the springtime trend does not persist throughout the summer but reverses already in early June. This reversal of the trend for δ^{13}C must be a due to a source effect. Clearly, this source must be strongly depleted in ^{13}C relative to ambient CO so that it can effectively counteract the kinetic fractionation, and it must gain relative importance in summer.

Table 1 shows that CO formed in the oxidation of CH_4 via $CH_4 + OH \rightarrow \ldots \rightarrow CO +$

ACPD
2, 213–248, 2002

© EGS 2002

products has a source value of about -52‰, a very low value compared the other major CO sources with δ^{13}C signatures near -27‰, the typical ^{13}C value of biomass. With atmospheric CH_4 levels being nearly constant at about 1700 ppb, the source strength of CO from CH_4 oxidation depends on OH levels, i.e. at high northern latitudes it is negligible in winter and peaks in summer. As explained above, the same applies to the sink of CO. Thus, although much more CO is formed from CH_4 oxidation in summer than in winter, in summer this amount is also quickly removed again. Assuming an atmosphere in which CH_4 oxidation is the only CO source, the CO cycle can be simply described in a box model by

$$CH_4 \xrightarrow{k_{CH_4+OH}} CO \xrightarrow{k_{CO+OH}} CO_2 \qquad \text{(R1)}$$

and the CO mixing ratio is then given as

$$\frac{[CO]}{[CH_4]} = \frac{k_{CH_4+OH}}{k_{CO+OH}} \qquad (1)$$

Regarding $[CH_4]$ as constant, the equilibrium CO mixing ratio is determined by the ratio of the rate constants and is not a function of OH levels. The rate constant $k_{CO+OH} = 1.5 \times 10^{-13} \times (1 + 0.6 p_{atm})$ (DeMore et al., 1997) is dependent on pressure, but shows almost no temperature dependence at atmospheric pressure (Fulle et al., 1996). Therefore, k_{CO+OH} cannot cause notable seasonal variations in [CO]. However, k_{CH_4+OH}, is strongly temperature dependent ($k_{CH_4+OH} = 2.45 \times 10^{-12} \times \exp(-1775/T)$, DeMore et al., 1997). Thus the seasonal atmospheric temperature variations do result in lower equilibrium CO mixing ratios in winter than in summer. As CO contributions from different sources can be treated as independent, Eq. (1) still applies to the CH_4 derived CO fraction in the natural atmosphere. Thus, the absolute amount of CO from in situ CH_4 oxidation in the troposphere depends on temperature, as indicated in Table 2, and is higher in summer than in winter at high latitudes.

The degree to which this CH_4 derived CO affects the isotopic composition of the ambient CO inventory, however, is determined by the relative, not the absolute contribution of CH_4 derived CO. Given the strong CO seasonality at high northern latitudes,

ACPD
2, 213–248, 2002

© EGS 2002

the relative contribution of CH_4 derived CO increases considerably from about 8% winter (14.3 ppb in a total of $\approx$180 ppb CO at the low winter temperatures, Table 2) to about 29% in summer (23.4 ppb in a total of $\approx$80 ppb CO at moderate summer temperatures, Table 2). CH_4-derived CO is about 25‰ depleted in δ^{13}C relative to the ambient CO, and the additional 21% of this CO will deplete the atmospheric CO pool by $\approx$5‰. This depletion counteracts the kinetic isotope effect in the reaction CO + OH, which itself should lead to an enrichment of $\approx$5‰ for CO decreasing from winter maximum to summer minimum values (ratio of mixing ratios approximately $1/e$). Thus, in early summer the increasing fraction of strongly depleted CO from CH_4 oxidation eventually outweighs the δ^{13}C increase due to the kinetic isotope effect in the reaction CO + OH, and considerably drives down ambient δ^{13}C values. Apparently the extent of the depletion due to the CH_4 oxidation source is slightly larger than the enrichment due to the kinetic isotope effect, as in late summer the overall effect is a moderate depletion of δ^{13}C relative to the late winter values.

In fall and winter, the OH based sink loses importance. Hence, changes in the CO isotopic composition are increasingly less influenced by the kinetic fractionation, but rather reflect the input from the sources. During that time, CO sources shift more and more from natural sources towards combustion sources, as witnessed by the δ^{18}O variations (see below). For δ^{13}C, ambient values in fall are close to the expected source signature from combustion sources of -27‰, except for the very clean year 1997 (see Sect. 3.3.2). Consequently, the δ^{13}C value is relatively constant for the rest of the year until spring, when CO levels decrease again.

3.1.4. δ^{18}O

Even more than δ^{13}C, δ^{18}O is strongly affected by the kinetic isotope fractionation in CO + OH. This reaction involves an inverse isotope effect of about -10‰ for ^{18}O, i.e. here $C^{18}O$ is removed 10‰ faster by OH than $C^{16}O$ (Röckmann et al., 1998b; Stevens et al., 1980). Accordingly, after the seasonal maximum near 11‰ in early spring, δ^{18}O declines quickly concomitant with the strong CO decline (Fig. 1d). In

© EGS 2002

contrast to δ^{13}C, this trend persists until the end of July. Here the increasing CH_4-based source has virtually no effect, because the δ^{18}O value of CH_4 derived CO is close to the ambient summer level. Note, however, that the δ^{18}O values of the CH_4 and NMHC oxidation sources are not well known yet. Our first attempt to determine this source signature (Brenninkmeijer and Röckmann, 1997) is based on an estimate using southern hemisphere isotope data, from which it is clear that δ^{18}O(CO) from CH_4 oxidation must be low (around 0‰, cf. Table 1), and a 3-D inverse modeling study (Bergamaschi et al., 2000a) yielded even lower values.

The δ^{18}O seasonal minimum is reached in July/August at values around -3‰. In fall and winter, two processes contribute to the increasing δ^{18}O trend. First, the kinetic fractionation in CO destruction loses importance as OH levels decrease. Second, CO sources shift from isotopically light natural sources towards isotopically heavy combustion sources. δ^{18}O is plotted vs. the inverse CO mixing ratios in Figure 3. In a simple two-component system where a background reservoir with δ-value δ_{bg} and mixing ratio χ_{bg} is contaminated by a single source with δ-value δ_s and mixing ratio χ_s, the observed delta value is the weighted mean of the two δ-values

$$(\chi_{bg} + \chi_s) * \delta_{obs} = \chi_{bg} * \delta_{bg} + \chi_s * \delta_s \,. \tag{2}$$

Thus, when δ_{obs} is plotted versus $(\chi_{bg}+\chi_s)^{-1}$ the value of the y-axis intercept (infinite contamination, i.e. $(\chi_{bg} + \chi_s) \rightarrow \infty$) corresponds to the isotopic signature of the contaminating source δ_s. Note that kinetic fractionation in the sinks has been neglected in this calculation, although it is clear that also the contaminating CO will be fractionated in its reaction with OH. As the kinetic fractionation is negative for ^{18}O, the intercept will actually be a lower limit for the actual source signature. The linear fit to the fall and winter data from 1996 and 1997 has an intercept at 18.4 ± 0.7‰, only slightly lower than the source signature for high temperature combustion processes (Table 1). Thus the admixture is with fairly unmodified CO from combustion origin. The anomalous behavior in 1998 will be discussed in Sect. 3.3.1. In the atmosphere, the strong winter δ^{18}O increase parallels the increase in CO mixing ratios. The fundamental difference

© EGS 2002

to the δ^{13}C variations is that in the case of δ^{18}O, the isotopic fractionation caused by the dominant source signature (fossil fuel combustion) and the kinetic isotope effect in CO destruction are in phase, whereas for δ^{13}C they counteract each other.

3.1.5. Δ^{17}O

It has been discovered recently (Hodder et al., 1994; Huff and Thiemens, 1996, 1998; Röckmann et al., 1998a, b) that atmospheric CO possesses a significant ^{17}O excess above what is expected based on its ^{18}O content. This anomalous fractionation pattern is often referred to as mass-independent fractionation because it deviates from the general mass dependent relationship approximated by $\delta^{18}\mathrm{O} = 0.52 \times \delta^{17}\mathrm{O}$, which is expected from the established theories for common isotope fractionation. In the case of several atmospheric trace gases, among them CO, a deviation from this relationship has been observed, and the ^{17}O excess is quantified in terms of $\Delta^{17}\mathrm{O} \equiv \delta^{18}\mathrm{O} - 0.52 \times \delta^{17}\mathrm{O}$. Figure 1e shows the extent of the ^{17}O excess of atmospheric CO at high northern latitudes. The strong seasonal signal is clearly anticorrelated to the CO mixing ratio, and Δ^{17}O values vary between 2‰ during the winter minimum and 8‰ during the summer maximum.

It has been shown that the mass independent fractionation in atmospheric CO originates from two processes. One is the production of CO from ozonolysis of unsaturated hydrocarbons (e.g. isoprene) in the atmosphere. The oxygen in the CO product is derived from the ozone precursor, and possesses the strong ^{17}O excess (Röckmann et al., 1998a) that is also found in O_3 (Krankowsky et al., 1995). The dominating effect is however that the fractionation in the CO sink reaction with OH is mass independent (Röckmann et al., 1998b). As mentioned above, the rate constant for reaction with OH is 10‰ faster for $C^{18}O$ than $C^{16}O$. For a strictly mass dependent fractionation, the rate constant for $C^{17}O$ should then be about 5‰ faster, but in fact it is only about 1‰ faster, i.e. very close to $C^{16}O$. Thus, in the reaction with OH the remaining CO accumulates excess ^{17}O with a pseudo-fractionation constant for Δ^{17}O of 4–5‰ (Röckmann et al., 1998b), which is of the right magnitude to explain the atmospheric observations

© EGS 2002

(Fig. 1e). Also the shape of the Δ^{17}O seasonal cycle supports the thesis that the mass independent fractionation in the OH sink is the dominant factor causing the mass independent anomaly. When CO levels decrease in spring, the remaining CO gets progressively enriched in ^{17}O and reaches a seasonal maximum when CO mixing ratios are lowest in summer. The total decrease of CO from the winter maximum at 180 ppb to the summer minimum at 80 ppb corresponds to a reduction of CO to about 40%, i.e. leaving a fraction of close to $1/e$. The concurrent observed isotopic enrichment of about 5‰ is of the right magnitude.

In fall and winter, the reaction with OH loses importance and the atmospheric CO reservoir is topped up with CO primarily from combustion sources, which is mass dependently fractionated. This causes the observed decrease in Δ^{17}O values. Indeed the correlation of Δ^{17}O versus inverse CO mixing ratio reveals that during fall and winter the data follow a dilution line that passes through zero, indicative of a dilution by CO with Δ^{17}O = 0‰ (Röckmann et al., 1998a). This is in agreement with our finding that the δ^{18}O value of the winter CO source is close to 23‰, i.e. CO reaching the observatory in winter is isotopically fairly unmodified, and must originate to a large degree from fossil fuel combustion at mid to high latitudes.

3.2. Short term variability

As mentioned above, short term variability is generally small for the two remote sampling locations, but occasionally the data exhibit some short-term deviation from the general seasonal cycle. Five day 3D-back-trajectories have been calculated by the Atmospheric Environment Service, Canada, for the 1997 data. Using these, one can relate some CO and isotopic excursions to air mass origin, and two clear examples will be presented here. The Alert air sample from 20 March 1997 exhibits an extraordinarily low CO mixing ratio. For this data point back trajectory analysis indicates advection of clean northern Atlantic air from lower latitudes (Fig. 4a). Due to the latitudinal CO gradient in winter and spring, advection of air masses from low latitudes should indeed lead to the observed low CO mixing ratio. Furthermore, a concomitant slightly low δ^{18}O

ACPD
2, 213–248, 2002

© EGS 2002

value, also typical for lower latitudes, is observed.

A significant short-term CO increase in the Spitsbergen record occurred on 26 February 1997. The five day back trajectory shows that this air parcel was advected over major industrialized areas of western Russia (near the Caspian sea) 5 days prior to its arrival at Spitsbergen (Fig. 4b). This makes anthropogenic contamination a plausible cause of the high CO mixing ratio, and also the δ^{18}O value shows a simultaneous small elevation in δ^{18}O, indicating contamination from combustion processes. There are several other instances of simultaneous CO and δ^{18}O elevations, for which the origin of the excursion is not as readily identifiable. The Alert samples from 17 January, 24 January and 13 February 1997, for example, show small ^{18}O elevations. Here, the air parcels passed 5 days before over or near the sparsely populated north eastern part of continental Russia. A similar trajectory was also derived for other samples that show no obvious contamination (e.g. on 13 February, 22 February or 5 March 1997 for Spitsbergen). Thus, the CO mixing ratio and isotopic composition can be a much more reliable indicator for anthropogenic contamination than the trajectory calculations. Clearly, strong CO contaminations can persist for more than five days in an air mass, and furthermore anthropogenic CO sources are often spatially confined to regions that cannot be resolved with trajectory analysis.

On the other hand, the short time variability of the signature that is usually most susceptible to contamination, δ^{18}O, is relatively low in Spitsbergen and Alert for most of the record, apart from the minor deviations as mentioned above. This is in sharp contrast to other sampling stations at lower latitudes (see e.g. Gros et al., 2001), where the ^{18}O composition is often a clear indicator for air mass origin. The absence of strong short time δ^{18}O fluctuations just confirm once more that the high northern latitude stations are remote from major anthropogenic sources. In most cases, the observed signatures are not sensitive to the air mass origin. Thus, the data obtained in this study are representative for the entire high northern latitude region.

The short time variability in the ^{14}CO record at Spitsbergen and Alert is particularly strong in winter and early spring. Here, back trajectory analysis is not very conclusive.

© EGS 2002

We speculate that in particular the two very high values in 1997 may have been caused by stratospheric intrusions (Gros et al., 2001) during that time, because in winter the high northern latitude ^{14}CO background level is already the highest observed near the surface, and even higher values can only originate from higher altitudes.

Generally, $\delta^{13}C$ values rarely exhibit large scatter because CH_4 oxidation, the source with the most prominent $\delta^{13}C$ source signature, shows a very smooth seasonal evolution due to the long CH_4 lifetime. The isotopic source values of the other major sources are close to that of ambient CO, and even large emissions from these sources cannot produce strong $\delta^{13}C$ signals, as witnessed during the 1998 CO anomaly (see Sect. 3.3.1). Furthermore, the $\delta^{13}C$ latitudinal gradient is not very strong in the northern hemisphere, and consequently large scale advection also has little impact on $\delta^{13}C$.

Nevertheless, there is one interesting class of short term $\delta^{13}C$ variations that occurs during polar spring at the Arctic locations. The particular effect has been discussed in detail in Röckmann et al. (1999a), and here it is summarized only. We detected characteristic small ^{13}C depletions at Spitsbergen during tropospheric ozone depletion episodes in Arctic spring. During these episodes, surface ozone levels quickly decline from normal levels of about 40 ppb to values below the detection limit for several hours to days (Barrie and Platt, 1997). Concomitant to these O_3 depletions, the $\delta^{13}C$ values of CO decrease by several tenths of a permil, and return back to background levels when ozone recovers (see Fig. 2 in Röckmann et al., 1999a). These excursions in $\delta^{13}C$ are the result of small quantities of CO being formed according to the reaction $CH_4 + Cl \rightarrow \ldots \rightarrow CO$ + products during ozone depletion events, which are associated with elevated halogen radical levels (mostly Br, but also Cl). In addition to CH_4 being already depleted in ^{13}C relative to CO, the large isotope effect of 70‰ in the reaction CH_4 + Cl (Saueressig et al., 1995) leads to formation of CO with a $\delta^{13}C$ value that is almost 100‰ below that of ambient CO. Thus, even a small addition of about 1 ppb CO from this source can significantly alter the ^{13}C content of the ambient CO content. This effect has not only been shown qualitatively, but the degree of the ^{13}C depletion has been used to estimate the integrated amount of Cl that the air mass must have

© EGS 2002

encountered. The results imply that Cl levels must have been $3 - 7 \times 10^4$ molec./cm^3 over the typical duration of the halogen elevations of about three days (Röckmann et al., 1999a). Thus, the δ^{13}C excursions are a sensitive measure for Cl levels that cannot be measured directly, and the results are in agreement with indirect estimates based on hydrocarbon destruction patterns (Ramacher et al., 1999).

3.3. Interannual variation

3.3.1. Summer-fall 1998

Superimposed on the typical seasonal cycle, interannual variability is evident in the CO data, especially for the summer minimum, as shown in detail in Fig. 5. The most prominent interannual feature is the elevated and surprisingly narrow CO minimum in 1998. From the beginning of July, CO levels do not fall further, and the common minimum values in August are never reached during that summer. Rather, CO already starts increasing rapidly in August 1998, one to two months earlier than in the other years, and then shows an elevation of 20 to 50 ppb for several months. Recalling that the atmosphere at high northern latitudes is well mixed in summer, such a persistent CO excess cannot be a local phenomenon but rather reflects a large-scale CO anomaly in the entire high northern latitude region. Five-day back trajectories calculated for the samples during this period do not show a common air mass origin, which further indicates that the observed CO elevation was a large-scale phenomenon. On the other hand, no similar elevations have been detected at our mid-latitude sampling station Mount Sonnblick in the Austrian Alps (Gros et al., 2001); thus the effect appears to be confined to the high northern latitudes.

Interestingly, the strong CO elevation in summer 1998 even leads to a double shoulder during the 1998/1999 seasonal maximum. This feature is indicative of an additional strong CO source that is out of phase with the CO seasonal cycle, and it is clearly discernible both in our data and the NOAA/CMDL data. After the quick rise in August, mixing ratios actually decrease again in November, when CO usually increases due to

© EGS 2002

low OH levels. The decrease must be due to dynamics, i.e. dilution of the CO excess by mixing with air from lower latitudes. The double shoulder in the observations confines the duration of the additional CO source to a period between July and November 1998, slightly delayed to the typical biomass burning season between May and October. During the spring 1999 maximum, values have recovered almost entirely and are only slightly above the maximum in 1998.

Among the major CO sources, large scale biomass burning is the only one that can be expected to produce such vast quantities of CO for extended periods of time. Indeed, 1998 was an extreme fire year throughout the high northern latitude boreal forest region and the extent of biomass burning even reached catastrophic dimensions in some parts. With a total of 4.7 million hectares burnt in Canada, 1998 is among the five worst years regarding forest fires, whereas only 625 000 and 1.9 million hectares were burnt by wildfires in 1997 and 1996, respectively, the two other burning seasons covered by our study (Johnston, 1999). For Russia, only 2.65 million hectares of burnt forest have been officially reported in 1998, but recent satellite imagery has exposed that the actual area burnt in Russia in 1998 may have been as high as 10 million hectares (Kasishke et al., 1999). In the three major regions (Khabarovsk, Amur, Sakhalin Island), 4% of the entire land area burned. Furthermore, the satellite observations revealed that most of these fires were crown fires, which have recently been shown to emit particularly high amounts of CO (Cofer III et al., 1998). In 1998, boreal forest fire emissions were detected even in the stratosphere: A substantial increase in aerosols stemming from boreal forest fires was detected in the stratosphere during the biomass burning season between May and October at latitudes between 55° N and 70° N (Fromm et al., 2000). It has been shown that CO from biomass burning can significantly influence atmospheric CO mixing ratios in Russia on large scales (Bergamaschi et al., 1998; Crutzen et al., 1996; Röckmann et al., 1999b), that CO from Canadian forest fires can affect concentrations even in the southern United States (Wotawa and Trainer, 2000) and in the free troposphere above northwestern Europe (Forster et al., 2001; Waibel et al., 1999), and that forest fires can increase the entire CO column over Russia (Yurganov et al., 1997).

© EGS 2002

Thus, fire activity in the boreal forests of North America and Asia has far-reaching effects on tropospheric CO levels in the whole high northern latitude region, and a recent evaluation of the NOAA/CMDL data shows a clear correlation of summer CO minima and biomass burning (Wotawa et al., 2001). Both the NOAA/CMDL data and our data show that these high CO levels can persist for several months in the entire northern part of the globe.

The ^{18}O isotope data clearly confirm that the 1998 CO elevation observed in Spitsbergen was due to a particularly strong CO biomass burning contamination. At first sight, relatively little interannual variability is observed in the δ^{18}O data (Fig. 1d). The strong CO anomaly of 1998 is accompanied by only a minor increase in δ^{18}O. However, the correlation of δ^{18}O vs. 1/[CO] for 1998 yields a source signature of 10.8 ± 0.9‰ (Fig. 3) much lower than in the other years. As discussed above, the intercept is actually a lower limit on the source signature, as the kinetic isotope fractionation in the OH based sink has been disregarded in Eq. (2), but the value clearly points to biomass burning. The intercept near 11‰ compares well with results from Siberia derived for both strong (Bergamaschi et al., 1998) and lesser contamination (Röckmann et al., 1999b) with CO from biomass burning. Recent laboratory experiments (Kato et al., 1999) have shown that the δ^{18}O value of CO emitted during biomass burning depends on the fire conditions, and is lower during the smoldering phase when CO emissions are highest, than the burning phase. Our data can also be compared to results from a recent inverse modeling exercise (Bergamaschi et al., 2000a) where source signatures for biomass burning were generally found to be around 10‰. However, this study predicted even lower values for biomass burning north of 30° N, in some scenarios even around 0‰, which is not supported by our data.

Note that in Fig. 3 a few of the δ^{18}O data points from the 1996/1997 seasons fall on the line that is defined by the 1998 data. Figure 5 shows that during August and September 1996, CO summer values are higher than the 1997 data. Actually, it is exactly these data which fall on the "biomass burning-influenced" linear regression line of the 1998 data in Fig. 3. Although the effect is much smaller than in 1998, this

© EGS 2002

indicates that also the slightly elevated CO values in 1996 were caused by biomass burning in the northern boreal forest. Thus, biomass burning has a critical influence on summer minimum CO values at high northern latitudes, as has been shown by (Wotawa et al., 2001). δ^{18}O is a good indicator to detect year-to-year variability of CO emissions from boreal forest burning at high latitudes.

From the two complete seasonal cycles now available we can for the first time examine the interannual variability of Δ^{17}O. As explained above, the seasonal cycles of CO and Δ^{17}O are anticorrelated, because the major sink of CO (reaction with OH) is the major source for Δ^{17}O. This behaviour is now even evident in the interannual pattern. The 1998 summer Δ^{17}O maximum is both much lower and more narrow than in 1997, the opposite behavior than observed for the CO mixing ratio (Fig. 1). Furthermore, as soon as the strong anomalous increase of CO starts in 1998, the Δ^{17}O values show a concurrent strong decrease, and the entire winter 1998/1999 minimum is slightly lower than in 1997/1998. This again confirms that the large CO elevation observed in the second half of 1998 is caused by mass dependently fractionated CO, in agreement with the above explanation that this CO originates from biomass burning.

3.3.2. Summer 1997

The second most significant interannual phenomenon is the exceptionally low and wide summer CO minimum in 1997, reaching values of merely 75 ppb. This feature also persisted for several months, indicating that these levels were characteristic for the entire high northern latitudes in summer 1997. The most likely cause of the low summer minimum is that 1997 was indeed an exceptionally clean year regarding CO source emissions, which is supported by official statistics showing that biomass burning was low throughout the Russian and North American boreal forest in 1997 (Johnston, 1999; Kasishke et al., 1999; Wotawa et al., 2001). The 1997 CO anomaly has a large effect on the δ^{13}C signature during summer 1997, when δ^{13}C values reach almost -29‰. As shown above, the δ^{13}C minimum is primarily determined by the relative fraction of CH_4 derived CO in the total CO reservoir. Due to the exceptional source signature (Table 1),

© EGS 2002

small deviations in this fraction can lead to significant isotopic shifts. The absolute amount of CH_4 derived CO, however, should not exhibit large interannual variation as it only depends on temperature (see above). In 1997, concomitant to δ^{13}C also CO mixing ratios were low (Fig. 5), Thus, the absolute amount of CO from sources other than CH_4 oxidation must have been lower in 1997 than in the other years, and the relative fraction of CH_4 derived CO was consequently higher, causing the observed low δ^{13}C minimum. More quantitatively, the seasonal CO minimum was about 85 ppb in 1996 and 75 ppb in 1997. Keeping the absolute amount of the CH_4 derived CO constant at 23.4 ppb (Table 2), the relative contribution from this strongly depleted source was about 27.5% in 1996 and 31.2% in 1997, a change of $\approx$4%. As the source signature of the CH_4 derived CO is about 25‰ lower than ambient values, this is of the right magnitude to explain the δ^{13}C depletion of 1–1.5‰ during the 1997 minimum.

For δ^{18}O, the additional isotopic depletion that occurs for δ^{13}C in summer 1997 is hardly recognizable. This does not come as a surprise, because the δ^{18}O value of CH_4 derived CO is close to ambient summer levels. For δ^{18}O the main effect is not the different relative amount of CO from CH_4 oxidation, but the fact that CO has been broken down to slightly lower levels in 1997. However, the difference barely discernible above the experimental error. As regards ^{14}CO, the summer minimum in 1997 is low, as observed for the CO data. Although the signal is too small to be evaluated quantitatively, this qualitatively supports the above interpretation that the excess CO observed in other years was produced from biogenic sources.

The 1997 summer Δ^{17}O maximum was very high with values reaching up to 8‰ when CO mixing ratios were extraordinary low. This is in line with the finding that the OH based sink is largely responsible for the seasonality in Δ^{17}O, i.e. in 1997 the CO reservoir was reduced by OH to lower values than in 1998, and thus the remaining CO obtained a higher ^{17}O anomaly.

© EGS 2002

4. Conclusions

The time series of CO mixing ratio and isotopic composition from Spitsbergen and Alert are virtually indistinguishable, showing that the high northern latitudes are a well-mixed reservoir as regards CO. This is confirmed by the relatively smooth seasonality of all signatures with only few occurrences of significant short time variability. Mixing of air between the mid and high northern latitudes plays an important role for the high northern latitude CO seasonal cycle. In winter, large amounts of CO from combustion processes are transported north from the industrial regions. In spring, the observed rapid decline of CO cannot be due to in situ chemical destruction alone, but is also affected by transport down to lower latitudes again and/or vertical exchange with the free troposphere.

A particularly strong, persistent CO elevation of 20 to 50 ppb occurred from July to November 1998. The δ^{18}O isotope signature clearly identifies biomass burning as source of the massive source. This independent isotope evidence is in agreement with the reports about unusually strong forest fire activity throughout the boreal forest region in 1998, and it underscores the crucial role of biomass burning for the CO summer minimum at high latitudes (Wotawa et al., 2001). The additional CO from the forest burning leads to strongly elevated CO mixing ratios in the entire high northern latitude region for several months.

Summer 1997, on the other had, was extremely clean as regards CO mixing ratios, which also shows up in the isotope signatures. Again, the δ^{18}O data indicate that the difference in the CO seasonal minimum between 1996 and 1997 was also due to biomass burning. Thus, biomass burning has a critical effect on summer minimum CO values at high northern latitudes, and it can be detected using the δ^{18}O signature. The data presented here show that monitoring of the isotopic composition of CO at Alert and Spitsbergen provides independent information on the causes of interannual variability of CO in the northern hemisphere.

Acknowledgements. This work would not have been possible without the help of many people

© EGS 2002

at the sampling stations in Spitsbergen and Alert, and we thank Torr Ivan Karlsen, Jan H. Wasseng, Chris R. Lunder and Jan-Ivar Tangen from the Norwegian Institute of Air Research and Kim Holmen from the University of Stockholm, and Korb Whale, Jacinta McNairn, Geoff Jones, Steve Mercer, Peter Ayranto and Christian Piller from the Alert station. Ingeborg Levin from the University of Heidelberg was very helpful in setting up the air sampling in Alert. We also thank Doug Worthy and Victoria Hudec from the Atmospheric Environment Service, Toronto, Canada, for calculation of the back-trajectories. We are grateful to Paul Novelli for providing the records of CO mixing ratios from Alert and Spitsbergen from the NOAA/CMDL network. Temperature data from Ny Ålesund were kindly provided by Siegrid Debatin from the Alfred Wegner Institute in Potsdam, Germany. The European Commission supported the CO-OH-Europe project under grant ENV4-CT96-0318 and the Marie Curie Fellowship of V. Gros under grant EVK2-CT-1999-50003.

References

Barrie, L. A. and Platt, U.: Arctic tropospheric chemistry: An overview, Tellus, 49B, 450–454, 1997.

Bergamaschi, P., Brenninkmeijer, C. A. M., Hahn, M., Röckmann, T., Scharffe, D. H., and Crutzen, P. J.: Isotope analysis based source identification for atmospheric CH_4 and CO across Russia using the Trans-Siberian railroad, J. Geophys. Res., 103, 8227–8235, 1998.

Bergamaschi, P., Hein, R., Brenninkmeijer, C. A. M., and Crutzen, P. J.: Inverse modeling of the global CO cycle: 2. Inversion of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios, J. Geophys. Res., 105, 1909–1927, 2000a.

Bergamaschi, P., Hein, R., Heimann, M., and Crutzen, P. J.: Inverse modeling of the global CO cycle: 1. Inversion of CO mixing ratios, J. Geophys. Res., 105, 14 531–14 546, 2000b.

Brenninkmeijer, C. A. M.: Robust, high efficiency, high-capacity cryogenic trap, Anal. Chem., 63, 1182–1184, 1991.

Brenninkmeijer, C. A. M.: Measurement of the abundance of ^{14}CO in the atmosphere and the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratio of atmospheric CO, with application in New-Zealand and Antarctica, J. Geophys. Res., 98, 10 595–10 614, 1993.

Brenninkmeijer, C. A. M., Köppel, C., Röckmann, T., Scharffe, D. S., Bräunlich, M., and Gros,

© EGS 2002

V.: Absolute measurement of the abundance of atmospheric carbon monoxide, J. Geophys. Res., 106, 10 003–10 010, 2001.

Brenninkmeijer, C. A. M. and Röckmann, T.: Russian doll type cryogenic traps: Improved design and isotope separation effects, Anal. Chem., 68, 3050–3053, 1996.

Brenninkmeijer, C. A. M. and Röckmann, T.: Principal factors determining the $^{18}O/^{16}O$ ratio of atmospheric CO as derived from observations in the southern hemispheric troposphere and lowermost stratosphere, J. Geophys. Res., 102, 25,477–25 485, 1997.

Brenninkmeijer, C. A. M. and Röckmann, T.: A rapid method for the preparation of O_2 from CO_2 for mass spectrometric analysis of $^{17}O/^{16}O$ ratios, Rap. Commun. Mass Spectrom., 12, 479–483, 1998a.

Brenninkmeijer, C. A. M. and Röckmann, T.: Using isotope analysis to improve atmospheric CO budget calculations, in: International Symposium on Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere, (Ed) Murphy, P., 69–77, International Atomic Energy Agency, Vienna, Austria, 1998b.

Brenninkmeijer, C. A. M., Röckmann, T., Bräunlich, M., Jöckel, P., and Bergamaschi, P.: Review of Progress in Isotope Studies of Atmospheric Carbon Monoxide, Chemosphere: Global Change Science, 1, 33–52, 1999.

Cofer III, W. R., Winstead, E. L., Stocks, B. J., Goldammer, J. G., and Cahoon, D. R.: Crown fire emissions of CO_2, CO, H_2, CH_4, and TNMHC from a dense jack pine boreal forest fire, Geophys. Res. Lett., 25, 3919–3922, 1998.

Conway, T. J., Steele, L. P., and Novelli, P. C.: Correlations among atmospheric CO_2, CH_4 and CO in the Arctic, March 1989, Atmos. Environ., 27, 2881–2894, 1993.

Crutzen, P. J., Golitsin, G. S., Elansky, N. F., Brenninkmeijer, C. A. M., Scharffe, D., Belikov, I. B., and Elokhov, A. S.: Observations of minor impurities in the atmosphere over the Russian territory with application of a railroad laboratory car, Dok. Russ. Acad. Sciences, 351, 1289–1293, 1996.

Crutzen, P. J. and Zimmermann, P. H.: The changing photochemistry in the troposphere, Tellus, 43, 136–151, 1991.

DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. L., Howard, C. J., Ravishankara, A. R., Kolb, C. E., and Molina, M. J.: Chemical kinetics and photochemical data for use in stratospheric modeling, JPL Publication, 12, 1997.

Forster, C., Wandinger, U., Wotawa, G., James, P., Mattis, I., Althausen, D., Simmonds, P., O'Doherty, S., Jennings, S. G., Kleefeld, C., Schneider, J., Trickl, T., Kreipl, S., Jager, H.,

© EGS 2002

and Stohl, A.: Transport of boreal forest fire emissions from Canada to Europe, J. Geophys. Res., 106, 22 887–22 906, 2001.

Fromm, M., Alfred, J., Hoppel, K., Hornstein, J., Bevilacqua, R., Shettle, E., Servranckx, R., Li, Z., and Stocks, B.: Observations of boreal forest fire smoke in the stratosphere by POAM III, SAGE II, and lidar in 1998, Geophys. Res. Lett., 27, 1407–1410, 2000.

Fulle, D., Hamann, H. F., Hippler, H., and Troe, J.: High-pressure range of addition reactions of HO. II. Temperature and pressure dependence of the reaction HO + CO $\leftrightarrow$ HOCO $\rightarrow$ CO_2, J. Chem. Phys., 105, 983–1000, 1996.

Granier, C., Müller, J. F., Pétron, G., and Barsseur, G.: A three- dimensional study of the global CO budget, Global Change Science, 1, 255–261, 1999.

Gros, V., Bräunlich, M., Röckmann, T., Jöckel, P., Bergamaschi, P., Brenninkmeijer, C. A. M., Rom, W., Kutschera, W., Kaiser, A., Scheel, H. E., Mandl, M., v. d. Plicht, J., and Possner, G.: Detailed analysis of the isotopic composition of CO and characterization of the air masses arriving at Mt. Sonnblick (Austrian Alps), J. Geophys. Res., 106, 3179–3193, 2001.

Haan, D., Martinerie, P., and Raynaud, D.: Ice core data of atmospheric carbon monoxide over Antarctica and Greenland during the last 200 years, Geophys. Res. Lett., 23, No. 17, 2235–2238, 1996.

Hodder, P. S., Brenninkmeijer, C. A. M., and Thiemens, M. H.: Mass independent fractionation in tropospheric carbon monoxide, ICOG proceedings, US Geological Circulair 1107, 1994.

Huff, A. K. and Thiemens, M. H.: Multiple stable isotope analysis of atmospheric carbon monoxide: Continuing source identification using a mass independent anomaly, in Eos Trans. AGU, Fall Meet. Suppl. Abstracts, pp. F124, San Francisco, 1996.

Huff, A. K. and Thiemens, M. H.: $^{17}O/^{16}O$ and $^{18}O/^{16}O$ isotope measurements of atmospheric carbon monoxide and its sources, Geophys. Res. Lett., 25, 3509–3512, 1998.

Jöckel, P.: Cosmogenic ^{14}CO as tracer for atmospheric chemistry and transport, Ph.D. thesis, Universität Heidelberg, thesis electronically available at http://www.ub.uni-heidelberg.de/archiv/1426, Heidelberg, 2000.

Johnston, T.: Canada Report, International Forest Fire News, 20, 1999.

Kasishke, E. S., Bergen, K., Fennimore, R., Sotelo, F., Stephens, G., Janetos, A., and Shugart, H. H.: Satellite imagery gives clear picture of Russia's boreal forest fires, EOS Transactions of the American Geophysical Union, 80, 141–147, 1999.

Kato, S., Akimoto, H., Röckmann, T., Bräunlich, M., and Brenninkmeijer, C. A. M.: Stable isotopic compositions of carbon monoxide from biomass burning experiments, Atmosph. En-

© EGS 2002

vironm., 33, 4357–4362, 1999.
Khalil, M. A. K. and Rasmussen, R. A.: Carbon monoxide in the earth's atmosphere: indications of a global increase, Nature, 332, 242–245, 1988.
Khalil, M. A. K. and Rasmussen, R. A.: Atmospheric Carbon Monoxide: Latitudinal Distribution of Sources, Geophys. Res. Lett., 17, 1913–1916, 1990.
Khalil, M. A. K. and Rasmussen, R. A.: Global decrease in atmospheric carbon monoxide concentration, Nature, 370, 639–641, 1994.
Krankowsky, D., Bartecki, F., Klees, G. G., Mauersberger, K., Schellenbach, K., and Stehr, J.: Measurement of heavy isotope enrichment in tropospheric ozone, Geophys. Res. Lett., 22, 1713–1716, 1995.
Lingenfelter, R. E.: Production of carbon 14 by cosmic-ray neutrons, Rev. Geophys., 1, 35–55, 1963.
Lowe, D. C., Levchenko, V. A., Moss, R. C., Allan, W., Brailsford, G. W., and Smith, A. M.: Assessment of storage correction required for in situ ^{14}CO production in air sample cylinders, Geophys. Res. Lett., in press, 2002.
Mak, J. E. and Brenninkmeijer, C. A. M.: Compressed air sample technology for isotopic analysis of atmospheric carbon monoxide, J. Atmos. Oceanic Technol., 11, 425–431, 1994.
Mak, J. E., Brenninkmeijer, C. A. M., and Southon, J. R.: Direct measurement of the production rate of ^{14}C near the Earth's surface, Geophys. Res. Lett, 26, 3381–3384, 1999.
Novelli, P., Masarie, K. A., Tans, P. P., and Lang, P. M.: Recent changes in atmospheric carbon monoxide, Science, 263, 1587–1589, 1994a.
Novelli, P. C., Collins, Jr., J. E., Myers, R. C., Sachse, G. W., and Scheel, H. E.: Re-evaluation of the NOAA/CMDL carbon monoxide reference scale and comparisons with CO reference gases at NASA-Langley and the Fraunhofer Institut, J. Geophys. Res., 99, 12 833–12 839, 1994b.
Novelli, P. C., Masarie, K. A., and Lang, P. M.: Distribution and recent trends in carbon monoxide in the lower troposphere, J. Geophys. Res., 103, 19 015–19 033, 1998.
Novelli, P. C., Steele, L. P., and Tans, P. P.: Mixing ratios of carbon monoxide in the troposphere, J. Geophys. Res., 97, 20 731–20 750, 1992.
Prather, M. J.: Time scales in atmospheric chemistry: Theory, GWPs for CH_4 and CO, and runaway growth, Geophys. Res. Lett., 23, 2597–2600, 1996.
Ramacher, B., Rudolph, J., and Koppmann, R.: Hydrocarbon measurements during tropospheric ozone depletion events: Evidence for halogen atom chemistry, J. Geophys. Res.,

© EGS 2002

104, 3633–3653, 1999.
Rinsland, C. P. and Levine, J. S.: Free tropospheric carbon monoxide concentrations in 1950 and 1951 deduced from infrared total column amount measurements, Nature, 318, 250–254, 1985.
Röckmann, T.: Measurement and interpretation of ^{13}C, ^{14}C, ^{17}O and ^{18}O variations in atmospheric carbon monoxide, Ph.D. thesis, University of Heidelberg, Heidelberg, 1998.
Röckmann, T. and Brenninkmeijer, C. A. M.: CO and CO_2 isotopic composition in Spitsbergen during the 1995 ARCTOC campaign, Tellus, 49B, 455–465, 1997.
Röckmann, T., Brenninkmeijer, C. A. M., Crutzen, P. J., and Platt, U.: Short term variations in the $^{13}C/^{12}C$ ratio of CO as a measure of Cl activation during tropospheric ozone depletion events in the Arctic, J. Geophys. Res., 104, 1691–1697, 1999a.
Röckmann, T., Brenninkmeijer, C. A. M., Hahn, M., and Elanksy, N. F.: CO mixing and isotope ratios across Russia; Trans-Siberian Railroad Expedition TROIKA 3, April 1997, Chemosphere, 1, 219–231, 1999b.
Röckmann, T., Brenninkmeijer, C. A. M., Neeb, P., and Crutzen, P. J.: Ozonolysis of nonmethane hydrocarbons as a source of the observed mass independent oxygen isotope enrichment in tropospheric CO, J. Geophys. Res., 103, 1463–1470, 1998a.
Röckmann, T., Brenninkmeijer, C. A. M., Saueressig, G., Bergamaschi, P., Crowley, J., Fischer, H., and Crutzen, P. J.: Mass independent fractionation of oxygen isotopes in atmospheric CO due to the reaction CO + OH, Science, 281, 544–546, 1998b.
Rom, W., Brenninkmeijer, C. A. M., Ramsey, C. B., Kutschera, W., Priller, A., Puchegger, S., Röckmann, T., and Steier, P.: Methodological aspects of CO-C-14 measurements with AMS, Nucl. Instr. Meth. Phys. Res. B, 172, 530–536, 2000.
Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., and Harris, G. W.: Carbon kinetic isotope effect in the reaction of CH_4 with Cl atoms, Geophys. Res. Lett., 22, 1225–1228, 1995.
Saueressig, G., Crowley, J. N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C. A. M., and Fischer, H.: Carbon 13 and D kinetic isotope effects in the reactions of CH_4 with $O(^1D)$ and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane, J. Geophys. Res., 106, 23 127–23 138, 2001.
Schütze, M.: 1949, Ein neues Oxidationsmittel für die quantitative Überführung von Kohlenmonoxyd in Kohlendioxyd. Ein Beitrag zur Chemie des Jodpentoxids, Ber. Dtsch. Chem. Ges, 77b, 484–487, 1949.

© EGS 2002

Smiley, W.G.: Note on a reagent for oxidation of carbon monoxide, Nucl. Sci. Abstr, 3, 391, 1965.

Smit, H. G. J., Volz, A., Ehhalt, D. H., and Knappe, H.: The isotopic fractionation during the oxidation of carbon monoxide by hydroxyl radicals and its implications for the atmospheric CO-cycle, in: Stable Isotopes, (Eds) Schmidt, H.-L., Förstel, H., and Heinzinger, K., pp. 147–152, Elsevier Scientific Publishing Company, Amsterdam, 1982.

Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., Foreman-Fowler, M., Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Three-dimensional climatological distribution of tropospheric OH: update and evaluation, J. Geophys. Res.,105, 8931–8980, 2000.

Stevens, C. M., Kaplan, L., Gorse, R., Durkee, S., Compton, M., Cohen, S., and Bielling, K.: The kinetic isotope effect for carbon and oxygen in the reaction CO + OH, Int. J. Chem. Kinet., 12, 935–948, 1980.

Stuiver, M. and Polach, H. A.: Reporting of ^{14}C data, Radiocarbon, 19, 355–363, 1977.

Waibel, A. E., Fischer, H., Wienhold, F. G., Siegmind, P. C., Lee, B., Ström, J., Lelieveld, J., and Crutzen, P. J.: Highly elevated carbon monoxide concentrations in the upper troposphere and lowermost stratosphere at northern midlatitudes during the STREAM II summer campaign in 1994, Glob. Change Sci., 1, 233–248, 1999.

Wotawa, G., Novelli, P. C., Trainer, M., and Granier, C.: Inter-annual variability of summer-time CO concentrations in the Northern Hemisphere explained by boreal forest fires in North America and Russia, Geophys. Res. Lett., 28, 4575–4578, 2001.

Wotawa, G. and Trainer, M.: The influence of Canadian forest fires on pollutant concentrations in the United States, Science, 288, 324–328, 2000.

Yurganov, L. N., Grechko, E.I., and Dzhola, A. V.: Variations of carbon monoxide density in the total atmospheric column over Russia between 1970 and 1995: upward trend and disturbances, attributed to the influence of volcanic aerosols and forest fires, Geophys. Res. Lett., 24, 1231–1234, 1997.

Yurganov, L. N., Jaffe, D. A., Pullman, E., and Novelli, P. C.: Total column and surface densities of atmospheric carbon monoxide in Alaska, 1995, J. Geophys. Res., 103, 19 337–19 347, 1998.

© EGS 2002

Table 1. The four major sources of atmospheric CO and their isotopic source signatures (see Brenninkmeijer et al., 1999 for references)

	δ^{13}C (‰)	^{14}CO (pMC)[1]	δ^{18}O (‰)	Δ^{17}O (‰)
Fossil fuel combustion	-27.5	0	23.5	0
Biomass burning	-22.9	$\sim$115	17.2	0
CH_4 oxidation	-51.1[2]	$\sim$125	0	0?
NMHC oxidation	-32.2	$\sim$110	0	$0?$[3]

[1] percent Modern Carbon (Stuiver and Polach, 1977)
[2] updated value taking into account the new determination of the fractionation in CH_4 oxidation by OH (Saueressig et al., 2001)
[3] pathway via ozonolysis of unsaturated hydrocarbons: 25–50‰, see (Röckmann et al., 1998a)

ACPD
2, 213–248, 2002

© EGS 2002

Table 2. k_{CH_4+OH} and the equilibrium CO mixing ratio from oxidation of CH_4 calculated from Eq. (1) assuming 80% CO yield and disregarding transport. The temperatures selected are typical summer and winter values for Spitsbergen (S. Debatin, pers. comm.)

T(K)	k_{CH_4+OH} (10^{-15} cm^{3}molec.$^{-1}$ s^{-1})	$[CO]_{eq}$ (ppb)
278 (summer)	4.1	23.4
258 (winter)	2.5	14.3

ACPD

2, 213–248, 2002

Isotope variations of high northern latitude surface CO

T. Röckmann et al.

© EGS 2002

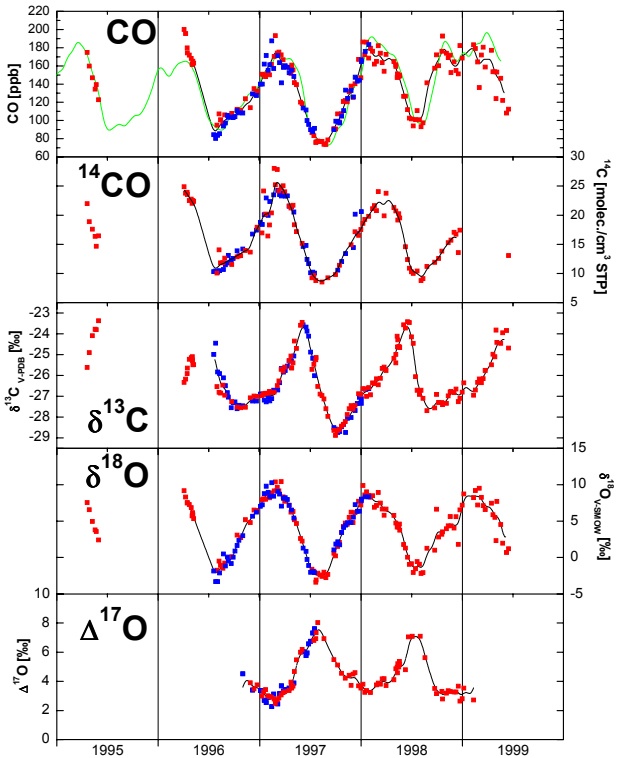

Fig. 1. The complete CO concentration and isotope record for the two high northern latitude stations Spitsbergen (Norway, 79° N) and Alert (Canada, 81° N). The data have been smoothed using a low pass Fourier Transform convolution filter excluding variability on a time scale of less than two weeks (Jöckel, 2000). In the top panel the green line is a similar fit applied to data from Spitsbergen determined by the NOAA/CMDL carbon cycle group (P. Novelli, pers. comm.).

ACPD
2, 213–248, 2002

Isotope variations of high northern latitude surface CO

T. Röckmann et al.

© EGS 2002

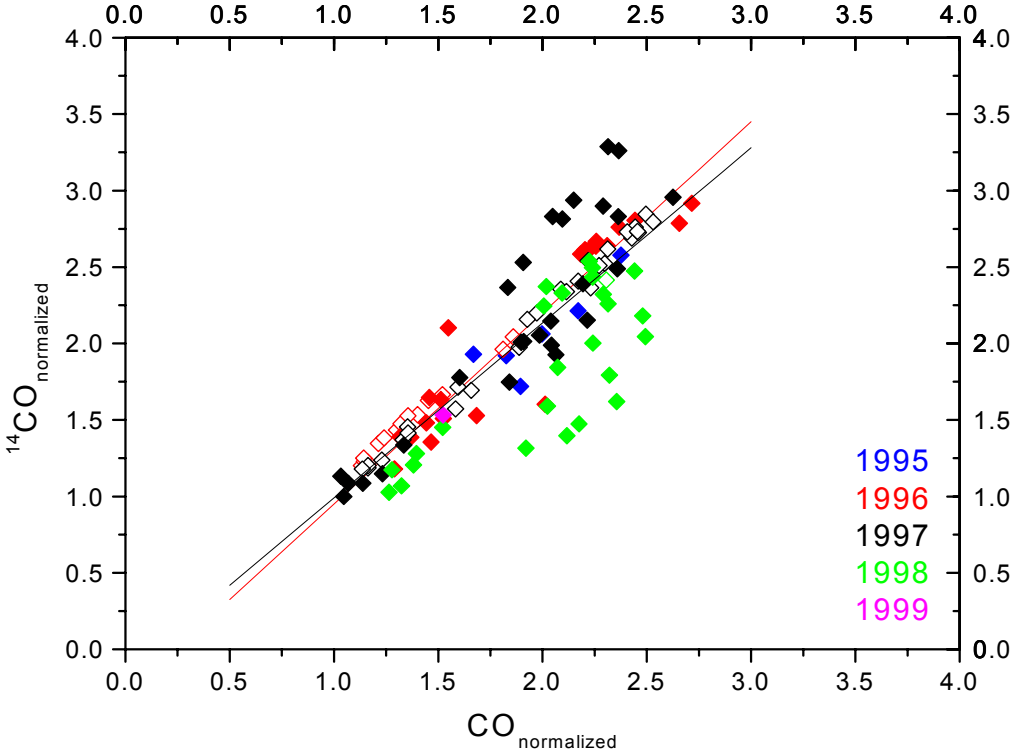

Fig. 2. Normalized ^{14}CO values vs. normalized CO. The original data have been normalized by dividing through the ^{14}CO and CO minimum values. Linear fits are applied to the 1996 data (red line) and to all data (black line).

ACPD

2, 213–248, 2002

Isotope variations of high northern latitude surface CO

T. Röckmann et al.

© EGS 2002

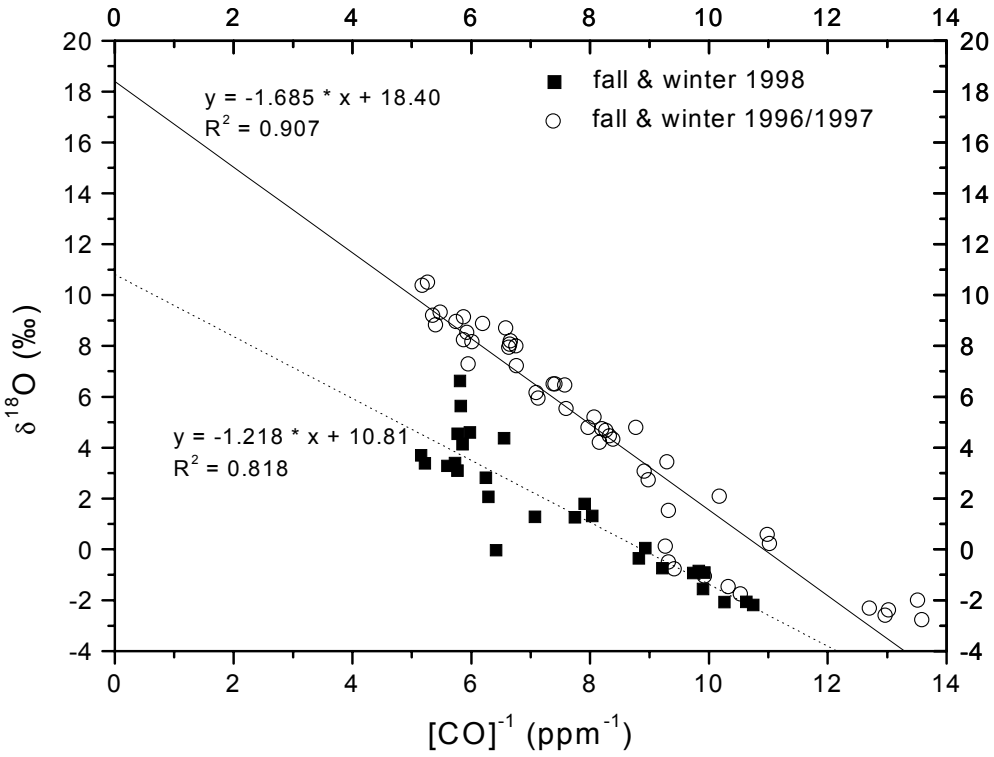

Fig. 3. The correlation plot of fall and winter δ^{18}O data versus inverse CO mixing ratio showing a clear difference between the "normal" years 1996 and 1997, and 1998 with the CO anomaly. The low y-axis intercept has been found to be indicative of CO from biomass burning in boreal forest regions in several recent studies.

ACPD

2, 213–248, 2002

Isotope variations of high northern latitude surface CO

T. Röckmann et al.

© EGS 2002

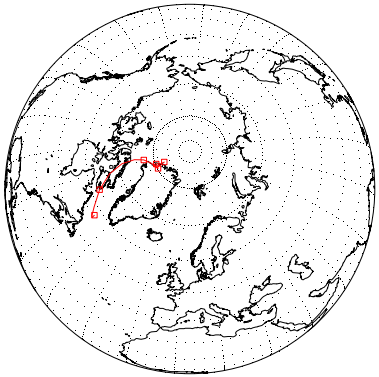

Fig. 4a. A 5-day back trajectory for the air sampled 20 March 1997 in Alert. Clean air is advected from lower latitudes over the North Atlantic.

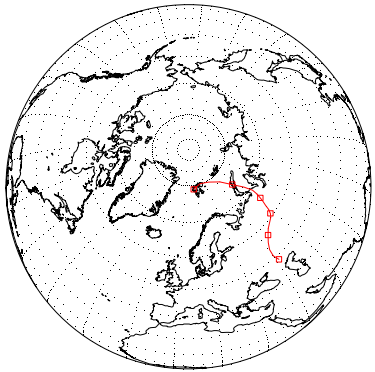

Fig. 4b. A 5-day back trajectory for the air sampled 26 February 1997 in Spitsbergen. Air is transported over the industrial part of Russia within few days, and the high CO and δ^{18}O values imply anthropogenic contamination.

ACPD

2, 213–248, 2002

© EGS 2002

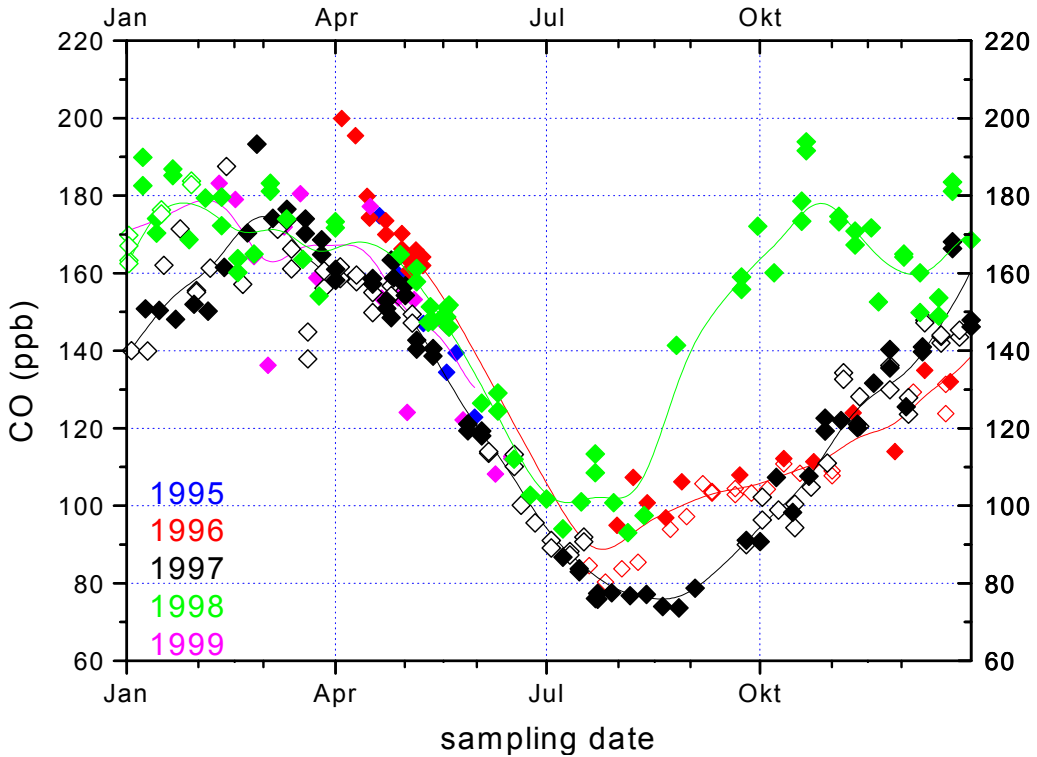

Fig. 5. Seasonal cycles of the CO mixing ratio for each individual year of the study. The anomaly in 1998 is prominent.

ACPD

2, 213–248, 2002

Isotope variations of high northern latitude surface CO

T. Röckmann et al.

© EGS 2002