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Zondervan, A; Meijer, HAJ

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Isotopic characterisation of CO_2 sources during regional pollution events using isotopic and radiocarbon analysis

By ALBERT ZONDERVAN* AND HARRO A. J. MEIJER[1], *Centrum voor IsotopenOnderzoek, Groningen University, 9747E AG Groningen, The Netherlands*

ABSTRACT

At the station Kollumerwaard (The Netherlands), for monitoring tracers in the troposphere, air is sampled in 16 containers for off-line ^{13}C, ^{18}O and ^{14}C isotopic analysis of CO_2. The timing of the sampling is chosen such that CO_2 variations correlating with pollutants like CO and CH_4 are optimally covered. The ^{14}C measurements enable us to discriminate between biospheric and fossil fuel contributions to atmospheric CO_2. The analysis of one series sampled on 23 November 1994 resolves the increased CO_2 mixing ratio into a purely biospheric component with a $\delta^{13}C$ of (-22.2 ± 1.5)‰, and a fossil component of up to 35 ppm with a $\delta^{13}C$ of (-34.1 ± 1.6)‰. Another series, recorded on 2 and 3 February 1995, shows a nearby emission of fossil CO_2, methane and carbon monoxide, most likely due to the flaring of natural gas. Both events clearly indicate the importance of natural gas consumption in or in the vicinity of Holland. These experimental values can be compared with estimates of CO_2 emissions from combustion of fossil fuels and the corresponding $\delta^{13}C$ values. The results for ^{18}O show the pronounced difference in behaviour between the O and C isotopes in atmospheric CO_2, due to the fast isotopic exchange processes with (plant, soil or ocean) water. As a side result, the method produces the ratio CO: fossil CO_2, a direct measure for combustion quality on a regional scale.

1. Introduction

Isotopic analysis of carbon dioxide in the lower atmosphere has resulted in a better understanding of its exchange with the biosphere and the role of anthropogenic activity. Studies of global carbon fluxes involve models which are strongly constrained by observations of the carbon isotope ratios. Since the pioneering work of Keeling (Keeling, 1958; Keeling, 1961; Keeling et al., 1979), numerous studies have been performed on atmospheric CO_2 and its isotopes on various regional and time scales (Keeling et al., 1989; Francey et al., 1990; Nakazawa et al., 1993; Conway et al., 1994; Levin et al., 1995; Francey et al., 1995; Keeling et al., 1995). Diurnal and seasonal cycles of the CO_2 mixing ratio and the $^{13}C/^{12}C$ ratio give insight in the magnitude of the exchange on a regional and a global scale, largely thanks to the relatively large differences between the isotopic signatures of the reservoirs. In a continuous effort to improve the description of reality with model calculations, grids are sized down and less dominant components are taken into account wherever sensible and possible. This goes hand in hand with geographically more refined observations of more (carbon containing) components.

The most obvious example is that of anthropogenic CO_2, most of which is produced from combustion of fossil fuels. Its role is paramount to "balancing the carbon budget" between present ocean, atmospheric and biospheric reservoirs

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[1]Corresponding author. Meijer@phys.rug.nl.
*Present address: Institute for Geological and Nuclear Sciences Ltd., PO Box 31312, Lower Hutt, New Zealand.

(Ciais et al., 1995). Consumption levels of fossil fuel, both globally and seasonally averaged, can be calculated, e.g., from import and industrial records (Marland and Boden, 1993). However, it is already much more complicated to determine seasonal and regional variations in fossil fuel (type) use (Rotty, 1987). Since the different fossil fuel types have different $^{13}C/^{12}C$ ratios the temporal and seasonal behaviour of the $^{13}C/^{12}C$ ratio of fossil fuel CO_2 can only be estimated (Keeling, 1973, Tans, 1981). In an effort to supply regional fossil fuel data a database containing annual CO_2 emissions, flux and $\delta^{13}C$ by country has been set up (CDIAC, 1991; Andres et al., 1993; Boden et al. 1995).

From an experimental point of view, fossil fuel CO_2 is best detectable by ^{14}C measurements, since fossil fuel contains no ^{14}C. Furthermore, $^{14}CO_2$ has been and still is monitored on many sites on earth (Nydal and Lövseth 1983; Manning et al., 1990; Meijer et al., 1994; Levin et al., 1995), and the so-called Suess-effect has been studied on several of these sites (Levin et al., 1980; Levin et al., 1989). Combining $^{13}C/^{12}C$ and $^{14}C/^{12}C$ analysis of atmospheric CO_2 in principle enables one to validate experimentally the data on fossil fuel emissions based on the production information mentioned above.

A 2nd example is the rôle of land ecosystems in the exchange of CO_2 with the atmosphere. Analysis of $C^{18}OO$ is particularly suitable for this purpose as CO_2 readily exchanges its oxygen isotopes with water in leaf tissues and soils (Friedli et al., 1987; Francey and Tans 1987; Farquhar et al., 1993; Ciais et al., 1996; Ehleringer et al., 1993).

Another possible use of isotopic characterisation of tracers is finger printing regional sources of pollutants. Although the chemistry of ozone formation in the mixing layer is theoretically largely understood, modelling and prediction remains heavily dependent on fine-scale transport observations of pollutants over rural and urban areas. Most important precursors to O_3 are CO, CH_4 and NO_x, of which only methane has important sources besides combustion, such as microbial activity and leakage from natural gas distribution systems. Again, measurement of all three carbon isotopes enables a separation of components derived from fossil fuel. Such information would be valuable for the assessment of anthropogenic activity, such as the quality of combustion by industry and vehicles.

In this paper, we present an experimental method to identify the fossil and biospheric components of the total CO_2 mixing ratio by their unique isotopic signatures in a local/regional atmosphere. In Section 2 the footing of this method is given. Its full implementation in the operation of a station in a rural area of the Netherlands is explained in Section 3. The power and constraints of the method are illustrated in Section 4 with the analysis of the first series of measurements at this station. In Section 5 we discuss possible improvements and the applicability of this method to the three studies mentioned above. Conclusions are drawn in Section 6.

2. Experimental method

The basis for the separation of the measured total-CO_2 mixing ratio into a biospheric, a fossil and a background component are the large differences in carbon isotopic signatures. Fossil CO_2 contains no ^{14}C, whereas the $^{14}C/^{12}C$ ratio in the biosphere remains close to that of the global troposphere due to the continuous and relatively rapid exchange between the two reservoirs. Consequently, a measured $^{14}C/^{12}C$ below the background value directly yields the fraction of fossil CO_2. Finally, the differences between the $^{13}C/^{12}C$ ratios of all three components allow a complete separation of the measured total-CO_2 into the three components if sufficient information is available. A combination with $^{18}O/^{16}O$ measurements may produce additional information on the way atmospheric CO_2 interacts with the biosphere and with the oceans.

Assuming that all background parameters are known, a single measurement (one sample) contains just enough information to assign isotopic ratios to the biospheric and fossil components. However, reliable results can only be obtained by regression analysis of a series of measurements with sufficient variability in the observables. Also, the isotopic signatures of the individual components must remain constant. These conditions require the observation of a changing transport of air from the (polluting) source region during intervals in the order of hours to days.

The variables involved are:

—T the CO_2 volume mixing ratio expressed in ppm and on a WMO mole fraction scale;

—$\delta^{13}C$ the per mille deviation of the $^{13}C/^{12}C$ ratio from the VPDB primary standard and on the Vienna-PDB (VPDB) scale, (Coplen, 1995; Allison et al., 1995);

—$\delta^{14}C$ the per mille deviation of the $^{14}C/^{12}C$ ratio from the standardised value of the pre-bomb atmosphere in 1950 (Stuiver and Pollach, 1977);

—$\delta^{18}O$ the per mille deviation of the $^{18}O/^{16}O$ ratio from the VPDB primary standard and on the VPDB-CO₂ scale without normalisation to SLAP (Coplen, 1995; Allison et al., 1995).

The three reservoirs are distinguished by indices b, f, and a, that stand for Biospheric, Fossil, and background Atmosphere, respectively. For each of the isotopic ratios a budget equation applies:

$$T_i = T_a + T_{b,i} + T_{f,i},\tag{1}$$

$$\delta^{13}C_i \cdot T_i = \delta^{13}C_a \cdot T_a + \delta^{13}C_b \cdot T_{b,i} + \delta^{13}C_f \cdot T_{f,i},\tag{2}$$

$$(1+\delta^{14}C_i) \cdot T_i = (1+\delta^{14}C_a) \cdot T_a + (1+\delta^{14}C_b) \cdot T_{b,i},\tag{3}$$

$$\delta^{18}O_i \cdot T_i = \delta^{18}O_a \cdot T_{b,i} + \delta^{18}O_f \cdot T_{f,i}.\tag{4}$$

where the index i refers to a specific sample in the series. Measured quantities appear only left of the equal signs. Eqs. (2), (3) and (4) are good approximations of the exact budget equations: the linearisation errors are negligible. The absence of ^{14}C in fossil CO_2 has been applied to eq. (3).

Eqs. (1)–(3) reflect two basic assumptions in our method. (i) During the interval of measurement the parameters of the background atmosphere remain constant. This is a reasonable assumption for a time scale of a few days or less, as the seasonal variation and the effect that air masses mix in, originating from different latitudes, are negligible over such intervals. (ii) The regional biosphere is treated as a single reservoir, adding to or taking away CO_2 from the atmosphere with variable amounts, while the carbon isotopic ratios associated with this biospheric CO_2 remain constant. For carbon this assumption is valid thanks to the high temporal resolution used in this work: the diurnal cycle of uptake and release of CO_2 by plants and soils is fully resolved, and can in good approximation be described as exchange of carbon

between two reservoirs (atmosphere and biosphere) with constant isotopic composition over this short time interval. (compare Dirks and Goudriaan, 1995).

Assuming that plant material (B) is only in contact with the background atmosphere (A) and that ^{14}C reservoir effects can be neglected, i.e. no time-lag of carbon isotopic ratios by storage in B, then B is in isotopic equilibrium with A. To account for isotopic fractionation between these two reservoirs the quantity $\Delta^{14}C$ is introduced:

$$\Delta^{14}C_c = \Delta^{14}C_a.\tag{5}$$

These quantities differ from the parameters $\delta^{14}C$, used in equation (3), by a correction term describing the fact that $^{14}C/^{12}C$ fractionation is $2\times$ that of the $^{13}C/^{12}C$ ratio, relative to a general reference value for plant material of $\delta^{13}C = -25‰$ (Stuiver and Pollach, 1977):

$$1+\Delta^{14}C = (1+\delta^{14}C)\left[\frac{0.975}{1+\delta^{13}C}\right]^2.\tag{6}$$

For a series of measurements these eqs. make up an over-determined set, which can be solved by maximum likelihood regression techniques such as minimum least-squares fitting.

Eq. (4) for $\delta^{18}O$ is deliberately chosen analogous to $\delta^{13}C$. However, while assumption (i) and (ii) are justified for carbon isotopes for time scales of a few days or less, these assumptions will not hold for oxygen. The equilibration process between oxygen isotopes of atmospheric carbon dioxide and of (ocean) water is rapid, can proceed without any net flux of CO_2 and depends on many meteorological variables (Keeling, 1958; Keeling, 1961; Bottinga and Craig, 1969; Francey and Tans, 1987, Farquhar et al., 1993; Ciais et al., 1996). The rapid equilibration process for $\delta^{18}O$ with either ocean surface water or plant and soil water makes it impossible to define a "background air" composition. Large differences in $\delta^{18}O$ will exist between oceanic and land air mass parcels, even in the case that neither of them has experienced any anthropogenic influence. A change of influence of this process on the sampled air immediately modifies in eq. (4) the background parameter $\delta^{18}O_a$ during the time-series. Similarly, assumption (ii) cannot readily be used for exchange of oxygen isotopes between a terrestrial ecosystem and the atmosphere because it does not take the influence of regional humidity on evapotranspiration and

thereby on the $\delta^{18}O$ of the leaf water into account (Francey and Tans, 1987). Therefore, it is expected that analysis of $\delta^{18}O$ information according to eq. (4) does not add any significance to the separation of the fossil and biospheric components from the total-CO_2 signal. On the other hand, the technique presented here is potentially very powerful for research into atmosphere-biosphere interaction using $\delta^{18}O$, since the parallel analysis of the carbon and oxygen isotopes enables one to observe the specific differences in the way they exchange between the reservoirs.

3. Experimental procedure

The monitoring station is jointly operated by three Dutch research institutes: the Electricity Companies joint Research Institute KEMA, the national Institute of Public Health and Environmental Research (RIVM), and the Netherlands Organisation for Applied Scientific Research (TNO). It has been set up in 1991 to monitor radioactivity and several tracers associated with air pollution and ozone production. It is located in the Kollumerwaard polder at 53.3°N 6.3°E, a rural area close to the Waddensea. The city of Groningen, which has circa 200,000 inhabitants, is located 30 km to the SE, and forms the largest industrialised area within a 130 km radius. Station Kollumerwaard is surrounded by farmland and some woodland. There is hardly any cattle nearby.

We have installed an air sampler system utilising the station's existing infrastructure. From a height of 8 m air is sucked down through a central duct, to which each system has a connection. In the sampler system the undried air is delivered to a series of 16 containers which are sequentially flushed. A 10 litre volume of the glass containers corresponds to 0.15 mmol CO_2 at STP, which is more than sufficient for an accurate isotopic analysis. A 1.5 h flushing period for each volume results in a coverage of the past 24 h. The flow of 5 l/min is maintained by an oil-free membrane pump on the exit side. Tubes are made of either stainless steel or Pyrex glassware. Valves are modified versions of Louwers Hapert stopcocks with Viton O-rings. A dust filter on the entrance side removes large dust particles. The operation of the sampler is controlled by a PC. Apart from system diagnostics and operation of the containers' valves, the PC continuously receives the latest CO_2, CH_4, CO mixing ratios and basic meteo data via a local network. The gas concentrations are measured by a Chrompack FID gas chromatograph optimally tuned for methane. The GC is calibrated by measurement of four reference gas mixtures, one by one at 3-h intervals (Van den Beld and Veldkamp, 1995). For CO_2 the calibration error is 2 ppm, while the noise is below 0.5 ppm.

Sequential filling of the air containers can be interrupted or stopped in two ways: by remote control via a modem or by a user-defined trigger in the PC control program. In the frame of the present work, a time series of CO_2 is considered to be of special interest for isotopic analysis only if it contains sizeable variations (>10%) that correlate with carbon monoxide and, less importantly, with methane. Such an event is likely to correspond with air downwind from industrialised or urbanised areas and not solely with the diurnal cycle of photosynthesis and respiration of plant material. Data from an anemometer can be used for a crude selection of the origin of the air and to reject slow-mixing conditions. Because of the combination of a simple sampler with real-time diagnostics of data, we call this mode of operation "event trapping".

Once the sequencing has been stopped, the containers are taken to the laboratory where carbon dioxide is extracted cryogenically. While the air is recirculated (≈ 2 l/min), the bulk of the water vapour is removed by a H_2O trap (dry ice alcohol slush, $-75°C$) during the 1st 15 min. Then, the CO_2 trap is immersed in liquid air ($-180°C$) during one h. Finally the trapped CO_2 is collected in a sample flask immersed in liquid air, while the trap (after thawing) is kept at dry ice temperature to prevent possible water traces to be collected in the flask along with the CO_2. This procedure results in a high extraction efficiency and a negligible fractionation. Testing with artificial N_2-CO_2 mixtures showed a CO_2 extraction yield of >99.9% and no change in its isotopic compositions relative to the original mixture. No special precautions are taken to exclude atmospheric N_2O, O_2, CH_4 and Ar from the extracted fraction. The $\delta^{13}C$ and $\delta^{18}O$ of the CO_2 are measured with a VG-Sira 9 Mass Spectrometer (MS). The accuracy (1-σ) of a single stable-isotope determination, including the MS calibration error, is estim-

ated to be $\leq 0.04‰$ for $\delta^{13}C$ and $\leq 0.08‰$ for $\delta^{18}O$. After retrieval the CO$_2$ is graphitised by a standardised reduction method (Vogel et al., 1984; Lowe and Judd, 1987) and pressed into an aluminium sample holder. The ^{14}C content is measured with the Groningen HVEE Accelerator Mass Spectrometer (AMS) (Mous et al., 1995). Currently, the uncertainty in $\delta^{14}C$ is $\pm 7‰$ (mainly caused by variability in the standards). The counting statistics is regularly as good or better than 2‰ for milligram samples close to "modern".

4. Data analysis and results

A rough estimate of the variability of the total-CO$_2$ and its isotopic signals can be made according to the following arguments. Approximate background values for the global troposphere are 350 ppm, $-8‰$ for $\delta^{13}C$ and 100‰ for $\delta^{14}C$. Adding 4 ppm of fossil CO$_2$, for which $\delta^{13}C$ is expected to be around $-28‰$, decreases the measured total $\delta^{13}C$ by 0.2‰. If fossil carbon dioxide variations as small as 4 ppm must be distinguishable, the instrumental error in total $\delta^{14}C$, including counting statistics, should remain well below 10‰. Similar arguments hold if $\delta^{14}C$ and $\delta^{18}O$ measurements are combined.

Obviously, the result of such an analysis highly depends on the assumed background values; e.g., a 10‰ overestimate of the background $\delta^{14}C$ artificially increases the fossil fuel component by about 3 ppm. The fact that there exists no sink of purely fossil CO$_2$ sets a lower limit on the background $\delta^{14}C$. One could take a $\delta^{14}C_a$ equal to the highest value in the event. This is likely to correspond not to a true global background for this latitude but to a more regional or temporary one. The sensitivity of $\delta^{13}C_b$ and $\delta^{13}C_f$ to a background $\delta^{13}C$ is large. Generally, the large dependencies on the background cause the CO$_2$ scale for the biospheric and fossil components to float in a predictable manner, but relative changes of each component during the event remain intact. For the CO$_2$ mixing ratio the NOAA/CMDL network database is used (Conway et al., 1995); station "M" is located at the same latitude and expected to be representative for station Kollumerwaard. The $\delta^{13}C_a$ and $\delta^{18}O_a$ background values are taken from the Scripps records at Pt. Barrow and Alert (Wahlen and Keeling, personal communication).

For $\delta^{14}C_a$, the $\Delta^{14}C$ record from Schauinsland, to our disposal until 1992, was used (Levin et al., 1995). Extrapolation of this record to the date of measurement is assisted by our ^{14}C record from Smilde station (Meijer et al., 1995).

We have chosen to perform the analysis as follows:

(i) *Correct* $\delta^{13}C_i$ and $\delta^{18}O_i$ for the presence of N$_2$O in MS measurements. In the present study no individual N$_2$O corrections were determined by MS measurements at mass 30. Instead, known corrections for the marine background atmosphere are used: $+0.23‰$ for $\delta^{13}C_i$ and $+0.35‰$ for $\delta^{18}O_i$ (Mook and Jongsma, 1987).

(ii) *Estimate* the background values from the above mentioned records.

(iii) *Apply* minimum least-squares fitting of eqs. (1), (2), (3), (5), and (6) to the 16 data points: the fit function $f(T_i, \delta^{14}C_i)$ is fitted to $\delta^{13}C_i$ with fit parameters $\delta^{13}C_a$, $\delta^{13}C_b$ and $\delta^{13}C_f$ while using the estimated background values for T_a and $\delta^{14}C_a$. T_i and $\delta^{14}C_i$ are chosen to be the independent fit function variables whereas $\delta^{13}C_i$ is the dependent variable. This means that the error in $\delta^{14}C_i$ is temporarily ignored. The error in T_i is assumed to be negligible in the whole fit process.

(iv) *Find*, by varying T_a and $\delta^{14}C_a$ around their estimates, a set $(T_a, \delta^{14}C_a, \delta^{13}C_a)$ that is in best accordance with these estimates and with the measurements. Only one background parameter can be varied each time. This is unavoidable due to the nature of the problem: relatively little variability "on top of" a large background. Optionally, one can finalise this step by fixing all background parameters on their values found.

(v) *Shift* data points $\delta^{14}C_i$ by amounts d_i proportional to the deviations of $\delta^{13}C_i$ from their fit values and inversely proportional to the internal errors of $\delta^{14}C_i$.

(vi) *Fit* the function $f(T_i, \delta^{14}C_i + d_i)$.

A shift d_i is in the right direction if X^2 from step (vi) decreases. X^2 is the sum of quadratic, weighted deviations between measured and fitted values, summed over the $\delta^{13}C_i$ and $\delta^{14}C_i$.

(vii) *Iterate* steps (v) and (vi) until all parameters have converged. The shifts d_i must be chosen small, such that convergence is stable. This iterative procedure assures that the instrumental uncertainties from both the $\delta^{13}C_i$ and the $\delta^{14}C_i$ determinations are properly taken into account when searching for the optimum. In the present

analysis, the uncertainty in the mixing ratio T_i is dominated by a calibration error which can, since it is systematic during the event, be corrected for by a small adjustment of the background parameter T_a. The remaining noise in T_i (< 0.5 ppm) is neglected.

(viii) *Calculate* the biospheric and fossil components from the fitted values.

(ix) *Fit* equation (4) to determine the $\delta^{18}O_a$ and $\delta^{18}O_b$ while keeping $\delta^{18}O_f$ fixed at the value for atmospheric oxygen, which is $-17.3‰$ with respect to VPDB-CO_2 (Kroopnick and Craig, 1972). Since eq. (4) is deliberately chosen not to describe additional exchange of oxygen isotopes, this step will result in a poor fit if the history of the sampled air varies during the event. One has the option to vary or simultaneously fit $\delta^{18}O_a$. Its value should be consistent with margins set by the background stations.

As an example an event trapped on 23 November 1994 is discussed. Fig. 1 shows the evolution of the CO_2 and CO mixing ratios during that day (A and B), as well as the corresponding isotopic signatures of the CO_2 (C, D and E). Clearly, the ≈ 70 ppm CO_2 excursion corresponds with significant changes in the isotope ratios with an analogous behaviour in time, indicating increased contributions from biospheric and fossil origin. The strong similarity between the CO_2 and CO signals indicates that a considerable part of this contribution must be due to combustion of fossil fuel. The result from fit procedure steps (i) through (viii) is: $T_a = 363$ ppm, $\Delta^{14}C_a = 106‰$, $\delta^{13}C_a = (-8.06 \pm 0.09)‰$, $\delta^{13}C_b = (-22.2 \pm 1.5)‰$, $\delta^{13}C_f = (-34.1 \pm 1.6)‰$, X^2-reduced (i.e., the X^2 divided by the number of free parameters)$= 1.5$, all errors are 1-σ.

The separation of the total-CO_2 into the three components, step (viii), is shown in Fig. 2. It shows that the excursion in CO_2 is caused by both fossil and biospheric sources, and that both are equally important. Fig. 3A shows the fit results for $\delta^{13}C_i$ for the present method (solid line). Agreement with the measurements is very good, as can be seen in the upper part of the graph where the difference between the measurements and the fit is shown. There is no systematic difference between fit and measurement, and the residual spread of the points is in accordance with their error bars.

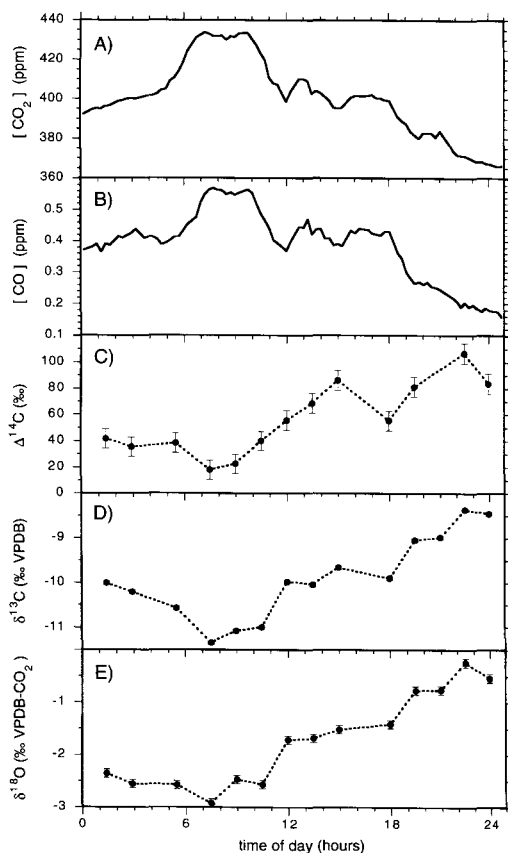When this event is treated as background air with a single source ("the conventional way"), a

Fig. 1. CO_2 (A) and CO (B) mixing ratios continuously measured by the GC at Kollumerwaard station during November 23, 1994. The time scale starts at 00 hrs. AM (MET). Approximate background levels, representing unpolluted marine air, are 361 ppm, and 0.1 ppm, respectively. The curves show that in the second part of that day there is a clear trend towards background conditions. This trend is also observed in the isotopic ratios $\Delta^{14}C$ (C), $\delta^{13}C$ (D) and $\delta^{18}O$ (E) of the CO_2 in the air stored by the 16 containers of the sampling system. Data points that have been rejected from the analysis are not shown. The approximate background values are 106‰ for $\Delta^{14}C$ (cf. Levin et al., 1995 and Meijer et al., 1995), $-8.14‰$ for $\delta^{13}C$ (Keeling and Wahlen, pers. comm.). For $\delta^{18}O$, the situation is more complicated.

regression analysis of this event (being a linear least squares fit of the relation $\delta^{13}C_i$ versus $1/T_i$) results in $\delta^{13}C_{b+f} = (-28.0 \pm 0.8)‰$ and X^2-reduced $= 13$. Fig. 3A also shows the result of this conventional method (dashed line). It shows clearly that accounting for two sources with different isotopic composition gives a better description of
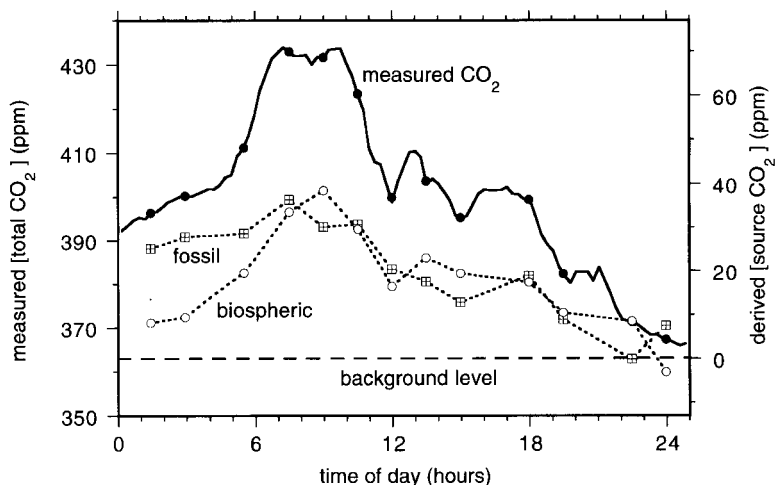
Fig. 2. Separation of the measured total-CO$_2$ (solid line, left hand scale) into the biospheric and fossil components (circles and squares, respectively, right hand scale) on top of the constant background. The excursion in CO$_2$ is caused by both fossil and biospheric sources, and both are equally important.

the experimental data. To emphasise the advantage of the present method, the average value of and the difference between the $\delta^{13}C$ signatures of the biospheric and fossil components have been calculated: $\frac{1}{2}\{\delta^{13}C_b + \delta^{13}C_f\} = (-28.2 \pm 0.8)$‰ and $\delta^{13}C_b - \delta^{13}C_f = 12$‰ with asymmetric errors $+12$‰ and -5‰ (derived by a full analysis of the X^2 hyper-surface).

Fig. 3B shows the comparison between the measured and fitted $\Delta^{14}C$ values, as well as the difference between the measurements and the fit. Also here, the fit quality is good.

The wind during this event has changed both speed and direction. A high-pressure system above central Europe resulted in calm weather with a high relative humidity. Back trajectories have been calculated by the Dutch meteorological institute KNMI (Reiff et al., 1986). Until noon (on the time scale used in the figures), the sampled air had closely passed industrialised areas in central Belgium and western Germany at altitudes below 2 and 0.5 km, respectively. Once below 0.5 km, the air was transported across 300 km of Dutch territory towards station Kollumerwaard arriving there from the S-SW, whereas, during the second half of that day, air descended from over the North Sea towards Kollumerwaard station from the NW direction.

For oxygen, step (ix) yields only a sensible result if $\delta^{18}O_a$ is kept fixed at its estimate, which is

-0.8‰, and if $\delta^{18}O_f$ is fixed at the value for atmospheric O$_2$, which is -17.3‰ (Kroopnick and Craig, 1972). The latter value is chosen because most combustion of fossil fuel takes place at high temperatures with atmospheric oxygen abundant. The result is: $\delta^{18}O_b = -7.8$‰, X^2-reduced $= 28$. The oxygen of biospheric CO$_2$ is in isotopic equilibrium with that of ground water, so the $\delta^{18}O$ of biospheric CO$_2$ is about -8‰ on the VPDB-CO$_2$ scale (Hesterberg and Siegenthaler 1991, Yakir et al, 1994). Fig. 3C shows the corresponding fitted (solid line) and measured values. The discrepancy, which gradually changes over time, can be explained qualitatively by the gradual change of background air. Air that was sampled during the early half of the day has been in long contact with the regional on-land biosphere. This has "dragged down" the background $\delta^{18}O$ towards precipitation and ground water values. The opposite holds for the second half, during which air flow was more directly from the waters of the Atlantic ocean and the North Sea, thereby "dragging up" the background $\delta^{18}O$ towards $\approx +1$‰.

As an attempt to quantify the $\delta^{18}O$ change of the background air, the measurement series has been divided into three parts. In all three parts the value for $\delta^{18}O_a$ was fitted, while keeping $\delta^{18}O_f$ and $\delta^{18}O_b$ fixed on -17.3‰ and -7.8‰, respectively. The results are $\delta^{18}O_a = -1.0$‰ for the first part, $\delta^{18}O_a = -0.45$‰ for the second, and

$\delta^{18}O_a = -0.1‰$ for the last part. Fitting the biospheric values along does not change the background values by more than $\pm 0.1‰$. The 3 partial fits are also shown in Fig. 3C (dashed lines). Agreement with the measurements is rather good, from which we conclude that variations in $\delta^{18}O$ of CO_2 in background air can be as large as 0.9‰ within just a few hours.

The same procedure, but with a fixed value for $\delta^{18}O_a$, and a fit for $\delta^{18}O_b$ for the three parts, leads to bad fit results and unrealistic values for $\delta^{18}O_b$. From this we conclude that in this event we really observe the variability of the background component $\delta^{18}O_a$. Further study is needed to investigate whether this phenomenon of different ^{18}O signatures of background CO_2 is reproducible. If so, it might complicate the interpretation of background air monitoring series for $\delta^{18}O$ (Francey and Tans, 1987; Ciais et al., 1996). As shown here, the difference between the measurements and the "fit", based on known values for biospheric and fossil $\delta^{18}O$ values, and on the concentrations of the 3 compartments using the present analysis, is in itself a new measurement: it reveals the magnitude and time dependence of the exchange processes with water, that are specific to $C^{18}OO$.

Apart from CO_2 and CO, also methane, ozone and nitric oxides are monitored at the station. During this event CH_4 and NO correlated with CO_2, albeit much less than CO, whereas NO_2 showed no correlation with CO_2 at all. Both NO and NO_2 drop sharply after dawn, at which moment O_3 increases sharply. Fig. 4 is a plot of CO and NO mixing ratios versus fossil CO_2, showing linear correlation between those tracers.

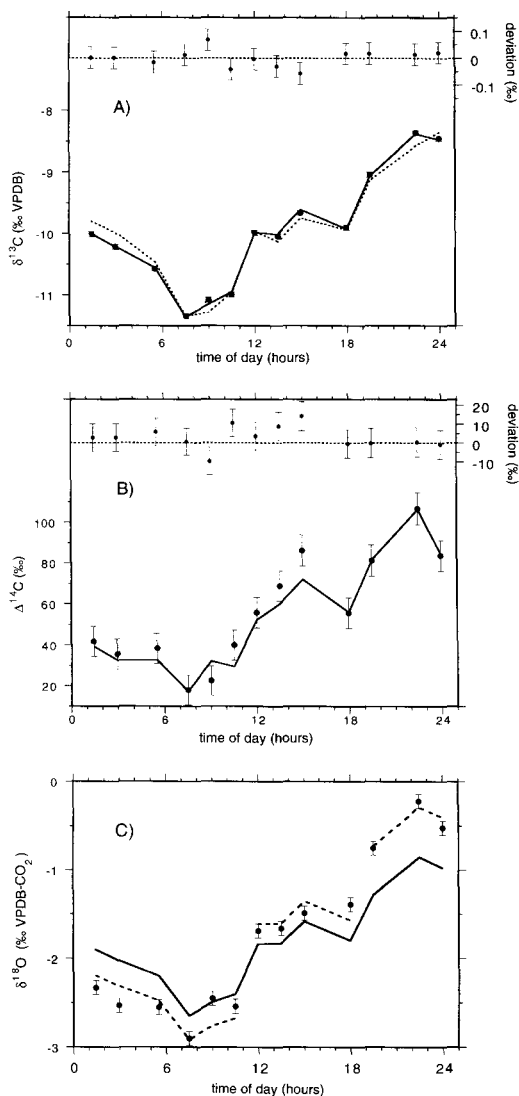*Fig. 3.* (A) Comparison of measured $\delta^{13}C$ values with values resulting from two different fit procedures. The solid line shows the fit results for the present method (solid line). Agreement with the measurements is very good, as can be seen in the upper part of the graph where the difference between the measurements and the fit is shown. There is no systematic difference between fit and measurement, and the residual spread of the points is in accordance with their error bars. The dashed line is the result for the case in which this event is treated as background air with a single source (being a linear least squares fit of the relation $\delta^{13}C_i$ versus $1/T_i$). It shows clearly that accounting for two sources with different isotopic composition gives a better description of the experimental data. (B) The comparison between $\Delta^{14}C$ measured values and the fitted values (solid line). The upper part of the graphs again shows the difference between the measurements and the fit. Also here, the fit quality is good. (C) Comparison of measured $\delta^{18}O$ values with fit values (solid line). The used fit function describes the ^{18}O budget analogous to ^{13}C: a source CO_2 flux from fossil fuel combustion and a net CO_2 flux from interaction with the biosphere on top of a constant background. The mixing ratios are taken from the $^{13,14}CO_2$ analysis. The discrepancy is caused by an increasing $\delta^{18}O$ of the background air as transport becomes more direct from the Atlantic and the North Sea during the 2nd half of the day. Alternatively, the three dashed lines show the division of the measurement series into three parts, each with its own fitted $\delta^{18}O$ value for the background component. Clearly, this leads to a much better fit result.
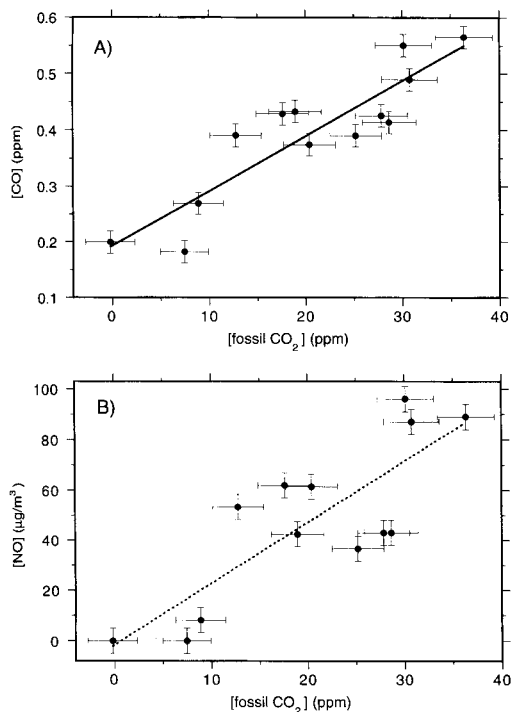
Fig. 4. (A) Correlation between the CO concentration and the concentration of fossil CO$_2$, derived in the present work. There is good correlation. The slope of the regression line corresponds with CO: fossil CO$_2$ = (0.0098 ± 0.0014) : 1. The intercept (0.19 ± 0.03 ppm) agrees with what is to be expected for continental background conditions. (B) Correlation between the NO concentration (in μg/m^3) and the concentration of fossil CO$_2$. Correlation is reasonable.

Since in western Europe the single largest source of tropospheric carbon monoxide is incomplete combustion, it is expected that CO correlates with fossil CO$_2$ in populated/industrialised areas. The strong correlation observed supports the validity of our analysis approach. The slope of the correlation is an average measure for the fossil fuel combustion efficiency in the region. For this present event we measure (0.0098 ± 0.0014) : 1. To our knowledge this is the first time such an average regional CO : CO$_2$ ratio for fossil fuel combustion is measured.

An event recorded on 2 and 3 February 1995 shows a 15 ppm increase of fossil CO$_2$ within a 5-h period, strongly correlating with total-CO$_2$, CH$_4$ and CO and with a 1.5‰ decrease of $\delta^{13}C$. The rapid excursions and trajectory analysis sug-

gest a flaring of natural gas*, supported by the result of the isotopic analysis: $\delta^{13}C_f = (-44 \pm 8)$‰.

To test the overall accuracy of the method one "non-event", i.e., all 3 gases showed little variability in their mixing ratio above clean air background, has been measured. Analysis of the scatter in the isotopic data confirms our earlier error estimates of 0.04‰ for $\delta^{13}C$ and 7‰ for $\delta^{14}C$. Up to now, 6 events have been measured in 1994 and 1995. The first three were hampered by instrumental problems or by too little variability in the observables, giving rise to results which are unrealistic or which have large error bars. They are therefore not discussed.

5. Discussion

The intrinsic limitations of the new method are related to "the background" in two ways. Obviously, numerical results are only reliable if marine background values are available. Secondly, ambiguity may arise and "the background" may no longer be uniquely defined if two or more anthropogenic (or biospheric) signals of different duration, strength and isotopic signature superpose. Multiple sources contributing to one certain component cannot be resolved individually by this method. Furthermore, soil respiration is not accounted for in the sense that it may restrict the validity of eq. (5). Soils may contain components with more ^{14}C than living plants if the corresponding carbon turnover times are large relative to the decaying bomb-peak of atmospheric $^{14}CO_2$. On the other hand, local vegetation experiences on average $\delta^{14}C$ values that are lower than that of marine air, although the difference is small in the growing season (Meijer et al., 1995).

Experimentally, a number of improvements are possible. First of all, sampling at larger heights will decrease the influence of local biospheric (and fossil) effects in favour of more regional processes. Secondly, early removal of the bulk of water vapour from the air prevents possible water condensation during sampling and CO$_2$ extraction, thus avoiding possible ambiguity in $^{18}O/^{16}O$ determinations. Further improvements could be realised by duplicate sampling (substantially

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*There is intensive natural gas production in the North Sea, and in the nothern part of The Netherlands.

increasing costs of measurements however), a more accurate CO_2 concentration determination, and by individual determination of the N_2O correction during stable isotope analysis, or alternatively by implementing on-line N_2O concentration measurements. Finally, it is expected that, with increasing experience in AMS target preparation, a total accuracy of below 5‰ for the ^{14}C measurements is feasible.

The reliability of the method can be tested by analysing simulated events that are composed of several hypothetical biospheric and fossil sources, or by performing "Jack-knife" tests on the data.

The $\delta^{13}C$ of industrial CO_2 has been estimated from a number of data sources; average values for coal and natural gas are $-24‰$ and $-41‰$, respectively (Tans, 1981). The $\delta^{13}C_f$ of the event discussed, $-34.1‰ \pm 1.6‰$, reflects the fact that more than 50% of the fossil fuel CO_2 exhaust produced in the Netherlands comes from natural gas (Boden et al., 1995). In winter, this percentage is even higher (Statistics Netherlands, 1995).

Our result can be compared with the outcome of a calculation of $\delta^{13}C_f$ via reconstruction from production figures of fossil fuels (Andres, personal communication; Boden et al., 1995). This model shows the Netherlands to release carbon dioxide with significantly lower $\delta^{13}C$ than the nearby countries Belgium, France and Germany. Our experiments corroborate this outcome.

In order to make a more robust comparison more events with different trajectories must be analysed. Furthermore, identification of source locations along these trajectories is warranted. Expansion with atmospheric ^{222}Rn measurements would facilitate the interpretation of experimental data since it gives independent information about the "contact time" of air with land and sea surfaces (Levin, 1987). It is planned that the presented method will be applied in Poland, North Carolina (USA) and New Zealand to further test the validity of the calculations based on fossil fuel production and consumption statistics.

6. Conclusions

In this paper a sampling method for the isotopic analysis of tropospheric carbon dioxide has been presented. The filling of the 16 sample containers is cycling continuously until an interesting event has occurred, in which case a user-definable trigger or a (remote) user interrupts the sampling. Increased values of CO_2 and carbon monoxide mixing ratios, measured by some other device, indicate that polluted air or exhaust from fossil fuel combustion is passing by. Complete $^{13,14}C/^{12}C$ analysis of the sampled CO_2, in addition to its mixing ratio, allow a complete separation of its biospheric and fossil fractions from the background, including the determination of the associated $\delta^{13}C$ values.

Due to sampling and measurement errors and too small signals, we have not been successful in a consistent determination of both the $\delta^{13}C$ and $\delta^{18}O$ signatures of all measured events. The first event successfully measured indicates that presently natural gas is a major source for energy conversion in the Netherlands and surrounding regions. Also, strong correlations between CO and fossil CO_2 have been observed, and quantitative numbers for the quality of combustion could be produced. The variation of these numbers (between 1 and 2%) probably reflects different quality levels of fuel combustion. So far, it remains unclear whether such correlations yield specific information about pollution sources, such as fuel type and combustion technique.

The $^{18}O/^{16}O$ analysis has shown a high degree of sensitivity to isotopic exchange between the oxygen isotopes of atmospheric CO_2 and water (in plants, soils and ocean), an interesting feature by itself. The background value for $\delta^{18}O$ changed from $-0.9‰$ to $-0.1‰$ within 10 h, due to this exchange. This shows that the present method potentially offers a new way to produce and test on a regional scale the description of the exchange of oxygen isotopes in atmospheric CO_2 with oceans and the biosphere.

7. Acknowledgements

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