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Isotopic Characterisation of Anthropogenic CO_2 Emissions Using Isotopic and Radiocarbon Analysis

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Abstract. At the station Kollumerwaard (Netherlands), for monitoring tracers in the troposphere, air is sampled in sixteen 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 background atmosphere CO_2. Results during the first year of operation show that the $\delta^{13}C$ values for the anthropogenic CO_2 are significantly more negative than generally assumed (values ranging from -30 to -58 ‰ VPDB), which clearly indicates the importance of natural gas consumption in the Netherlands. We compare these experimental values with results from a detailed study of CO_2 emission estimates from combustion of fossil fuels and the corresponding $\delta^{13}C$ values. As an important side result, the method produces reliable values for the regionally averaged ratio CO : fossil CO_2 (results ranging from 0.5 to 1%), a direct measure for combustion quality.
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1 Introduction

Isotopic analysis of carbon dioxide in the lower atmosphere has proven to be extremely useful for achieving 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.

One of the input values for such model calculations is the amount of CO_2 emitted by fossil fuel combustion and its $^{13}C/^{12}C$ ratio. Consumption levels of fossil fuel, both globally and seasonally averaged, can be calculated, e.g., from import and industrial records, although this is a sub-

stantial undertaking (Marland and Boden, 1993). It is even 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 $^{13}C/^{12}C$ ratio of fossil fuel CO_2 can only be estimated (Tans, 1981). In an effort to supply regional fossil fuel data a database containing annual CO_2 emissions, by fossil fuel type and by country has been set up (Boden at al., 1995). In principle this extensive work could also be used to provide world-wide, country-wise estimates for the $^{13}C/^{12}C$ ratios of fossil fuel CO_2, and first results have been produced (Andres et al., 1993; Andres, personal communication). There is a clear temporal trend towards isotopically "lighter" CO_2 over the years, and there are large differences in $^{13}C/^{12}C$ between the different regions in the world. Naturally, it is hard to estimate the reliability of the outcome, certainly this reliability will vary considerably from nation to nation.

To date, modelers have not paid much attention to the regional and seasonal pattern of fossil fuel consumption, and they have merely used one value for $^{13}C/^{12}C$ of fossil fuel (which is probably too high). To our knowledge no one has incorporated yet any of the above described findings, nor is there discussion about the eventual influences on model results.

In order to draw more attention to the subject, and as an attempt to compare the fossil fuel record based calculations with experimental results, the present study aims at the experimental determination of the fossil fuel $^{13}C/^{12}C$ ratio for the Netherlands. This is done by detecting the fraction of fossil fuel CO_2 using ^{14}C measurements. Combining $^{14}C/^{12}C$ analysis with "common" $^{13}C/^{12}C$ measurements of atmospheric CO_2 makes it possible to experimentally determine the $^{13}C/^{12}C$ data on the fossil fuel emission CO_2. In the second part of our study we estimate the fossil fuel $^{13}C/^{12}C$ ratio for the Netherlands by combining statistical data on fossil fuel consumption with their estimated $^{13}C/^{12}C$ ratios.

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2 Experiment

At the Kollumerwaard station (53.3 °N, 6.3 °E) we take part in the operation of an air monitoring station. Details can be found in a previous paper (Zondervan & Meijer, 1996, hereafter referred to as Z&M96). In short, our air sampling system consists of sixteen 10 liter containers, that are sequentially flushed in such a way, that at any given time they contain air of the last 24 hours in 90 minutes intervals. If an isotopic analysis of the last 24 hours is judged useful, the sampling is stopped and the containers are collected. The CO_2 is then extracted in the laboratory, and analysed for ^{13}C and ^{14}C (and ^{18}O). Together with the semi-continuous GC record of CO_2, CH_4 and CO mixing ratios (as well as basic meteorological data) they form our set of measurements.

The data analysis is based on the following equations:

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

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

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

$$\Delta^{14}C_b = \Delta^{14}C_a \tag{4}$$

where subscripts a, b, f stand for the background atmosphere, biospheric and fossil reservoirs, respectively. T is the CO_2 volume mixing ratio, $\delta^{13}C$ is the (N_2O-corrected) $^{13}C/^{12}C$ ratio, as usual expressed in per mille deviations on the VPDB-scale (Coplen 1995; Allison et al., 1995). The $\delta^{14}C$ is the $^{14}C/^{12}C$ ratio expressed as per mille deviations from the standard pre-bomb atmosphere, and $\Delta^{14}C$ is the $\delta^{14}C$ corrected for fractionation effects (Stuiver and Pollach, 1977). Parameters that have an index i are considered to be variable from point to point, whereas parameters lacking this index are assumed to be constant during the whole measurement.

Our measurements provide us with 3 measured quantities for each measurement point : the total CO_2 mixing ratio T_i, as well as isotope ratios $\delta^{13}C_i$ and $\delta^{14}C_i$. Since there are 4 equations with 11 unknown, 4 variables have to be provided from elsewhere in order to solve the equations for each measurement point separately. The background air quantities T_a, $\delta^{13}C_a$ and $\delta^{14}C_a$ were taken from measurements of several background air stations (Wahlen and Keeling, personal communication, Conway et al., 1995, Levin et al., 1995). In addition, the $\delta^{13}C_b$ was assumed to be -(25 ± 1.5) ‰. From this set of data, the partial mixing ratios $T_{b,i}$ and $T_{f,i}$ are calculated for each measurement point, as well as the isotope ratio $\delta^{13}C_{f,i}$. Of course care is taken that the propagation of errors is dealt with correctly. The present approach is somewhat different from that followed in Z&M96. There, $\delta^{13}C_f$ was assumed to be

constant for the whole set of measurements, and a complex least squares fit was performed for the full set. The present approach simplifies the data analysis significantly, gives more insight in the general quality of the data and the validity of our assumptions, and makes the results more robust, i.e. less vulnerable for eventual preparation or analytical errors influencing a single point in the set of 16. Furthermore, the progression of errors, which is crucial in our analysis, is better visible. The price paid is that it is now no longer possible, as in Z&M96, to determine both $\delta^{13}C_b$ and $\delta^{13}C_f$ as outcome of the measurements. Of course both analyses are equivalent in the sense that if we use the $\delta^{13}C_b$ of our previous analysis as input we get values for $\delta^{13}C_{f,i}$ that have minimized spread around the $\delta^{13}C_f$ value of the previous analysis method.

3 Results

3.1 The $^{13}C/^{12}C$ ratio of fossil fuel CO_2

The analysis takes place in two steps: First we determine the components $T_{b,i}$ and $T_{f,i}$ using the measured values for $\delta^{14}C_i$ and T_i, the background values T_a and $\delta^{14}C_a$ and by combining (3), (4) and (1). The use of (4) implies the use of the assumed value $\delta^{13}C_b$ too (since the fractionation correction is dependent on this value), but its influence on the result is very small. Figure 1 shows an example of this outcome for a measurements series on November 28, 1995. Significant contributions of both fossil and biospheric origin are clearly distinguished.

Next we get the results for $\delta^{13}C_{f,i}$, using the measured $\delta^{13}C_i$, the assumed $\delta^{13}C_b$ and (2). In most measurement series these results were only significant during part of the time. Since our method essentially determines small differences between large numbers, reliable results were only achieved at points where the $T_{f,i}$ exceeded 10-15 ppm. In cases where the biospheric contribution was significant as well, it needed to be even higher. Yet almost all of our registered measurements had some period in which $\delta^{13}C_{f,i}$ could be determined, sometimes (as in the series showed in fig. 1) this was possible during the whole series. In all cases $\delta^{13}C_{f,i}$ values remained constant within the error bars during a series. Therefore averaging of the values was justified.

Table 1 shows the results for $\delta^{13}C_f$ for all events analysed up to the present date. The errors incorporate, apart from the measurement errors in the measured values, also uncertainty estimates in the assumed values : ± 1.5 ‰ for $\delta^{13}C_b$, ± 2 ppm in T_a, ± 0.08 ‰ in $\delta^{13}C_a$ and ± 7 ‰ in $\delta^{14}C_a$. Two of the shown results have such large errors that their contribution to the set is negligible. The values range from -30 ‰ to -58 ‰. This is (much) lower than generally
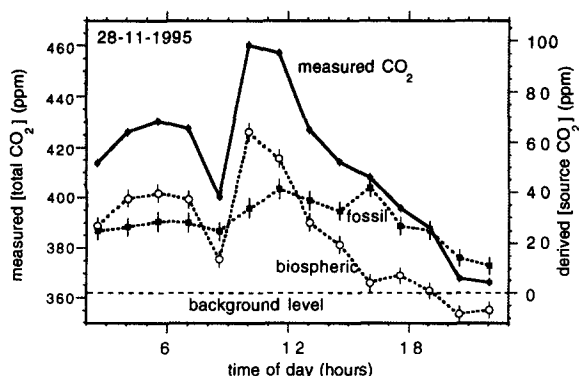
Fig. 1. Separation of the measured total-CO_2 (solid line, left hand scale) into the biospheric and fossil components (circles and squares, respectively, right hand scale) on top of the constant background. The excursion in CO_2 is caused by both fossil and biospheric sources, and both are on the average equally important.

assumed, but this is explainable by the fact that the use of natural gas (known for its low $\delta^{13}C$ values) is widespread in the Netherlands (see below).

Table 1. The results for the $\delta^{13}C$ of the fossil fuel component of atmospheric CO_2 for all measurement days so far. The values range between -30 ‰ VPDB and almost -60 ‰. Whereas the higher values are in the range of what would be expected from a mixture of solid, liquid and gas combustion, the very low values must be caused by combustion of natural gas from very specific origins.

date	$\delta^{13}C_f$ (‰ VPDB)
6-4-1994	-41 ± 13
19-9-1994	-30.3 ± 3.5
5-10-1994	-49 ± 13
23-11-1994	-31.7 ± 1.3
2-2-1995	-49 ± 5
31-10-1995	-58 ± 4
28-11-1995	-42.7 ± 1.4
17-1-1996	-32.7 ± 2.5

3.2 Carbon monoxide

Our method quantifies the amount of CO_2 in the air that is of direct fossil fuel combustion origin. All fossil fuel combustion leads to a certain amount of CO production too, and it is this source that mainly determines the CO mixing ration in W.-Europe. The semi-continuous GC measurement of the CO mixing ratio enables us to relate the CO mixing ratio with the amount of fossil fuel CO_2. In all events CO correlated with the fossil amount of CO_2 to a high degree (and higher than with the CO_2 mixing ratio as a whole). The slope of the linear fit of this relation is the combustion quality, and it is measured here directly on a

regional scale. Table 2 lists the 8 results obtained up to now. Values spread typically between 0.5 an 1 %. On looking more closely to the data of tables 1 and 2, there even seems to be a correlation between the CO:CO_2 ratio and the $\delta^{13}C_f$. This could be explained by the fact that in measurements with higher $\delta^{13}C_f$ the combustion of solids and/or liquids plays a more important role, yielding a higher CO production than natural gas burning. Further measurements must show whether this relation indeed exists.

Table 2. The ratio of CO and fossil CO_2 mixing ratios, for which the measurements of ^{14}C play a crucial role.

date	[CO] : [ff CO_2] (%)
6-4-1994	1.3 ± 0.3
19-9-1994	0.93 ± 0.11
5-10-1994	0.56 ± 0.07
23-11-1994	0.93 ± 0.15
2-2-1995	1.07 ± 0.13
31-10-1995	0.35 ± 0.08
28-11-1995	0.86 ± 0.19
17-1-1996	1.00 ± 0.18

3.3 Fossil fuel consumption in the Netherlands

Connected to the experimental work, we tried to collect data for a full inventory of the actual Dutch combustion of various fossil fuel sorts, from that the amount of CO_2, and finally by assigning $\delta^{13}C$ values to the different fossil fuels, the expected $\delta^{13}C_f$.

Quarterly data on consumption of fossil fuel were obtained from the Statistics Netherlands office (Statistics Netherlands, 1995). Natural gas covers about 2/3 of the energy demand in the Netherlands, which is the highest fraction found anywhere in the world. Figure 2A shows the breakdown of the CO_2 production by the combustion of the three main categories of fossil fuel: solid, liquid and gas. Since natural gas combustion produces considerably less CO_2 / energy unit than petrol or coal, the average contribution of "gas CO_2" is somewhat lower than the energy consumption fraction : 60% on average, varying between 50% in summer and over 65% in winter.

The data on solid and liquid fuel consumption are regarded to be reasonably reliable. Moreover, $\delta^{13}C_f$ values for these two types of fuel only show a small spread around their average values of -24.1 ‰ and -26.5 ‰, respectively (Tans, 1981). The natural gas consumption numbers are available on a monthly basis, and are very accurate, since the distribution of natural gas is concentrated at a single company, the Nederlandse Gasunie. However, it is known
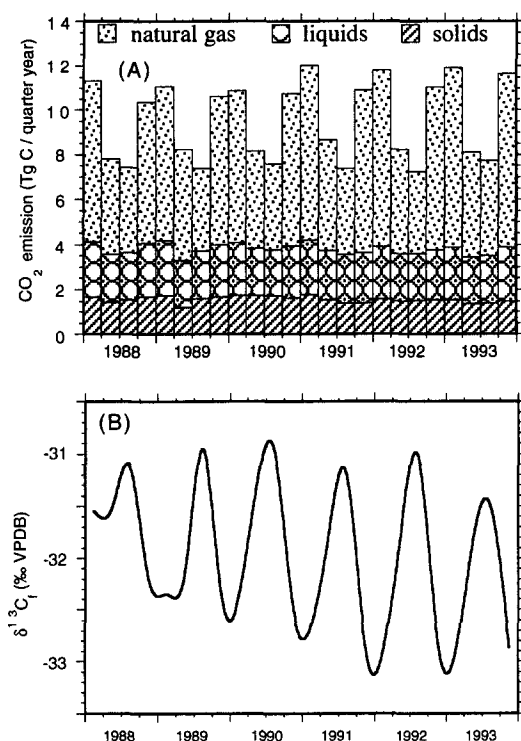
Fig. 2. A) Breakdown for the period 1988-1993 of the CO_2 exhaust by fossil fuel combustion in the Netherlands into the three main categories of fossil fuel: solids, liquids and natural gas. It is clearly visible that gas is by far the most important energy source. The winter-summer differences of $\approx$ 1.5:1 are completely met by natural gas consumption variation. Since natural gas combustion emits less CO_2 per energy unit than liquids or solids, the share of natural gas in the *energy* use is even higher than suggested by this figure.

B) The calculation of the $\delta^{13}C_f$ of the fossil fuel CO_2 in the Netherlands based on the values assumed for solids -24.1 ‰, liquids -26.5 ‰, and natural gas -35 ‰ . The latter is found by assuming that 50% of the natural gas consumption originates from the Groningen gas field (known to have a $\delta^{13}C = -29$ ‰), whereas for the other 50% the "world average" value of -41 ‰ is taken.

that different sources of natural gas can have widely different $\delta^{13}C$ values, ranging from -25 ‰ to lower than -60 ‰. Since the Gasunie does not exploit gas sources itself, but rather trades gases from different sources and guards their quality, it is impossible to compute the breakdown of total consumption by the different sources. However, the main source for the Dutch consumption is the Groningen natural gas field, accounting for 50% of the total trade volume of the Gasunie (of which trade volume again 50% is exported, but not in the same source ratios!). This big source has been determined some time ago (Hut et al., 1984) to have $\delta^{13}C = -29$ ‰. Other fields in the Netherlands as well as off shore fields in the North Sea do presumably have lower $\delta^{13}C$ values.

For computing the total $\delta^{13}C$ values for the Dutch fossil fuel CO_2 exhaust we assumed that 50% of the natural gas was from the Groningen field (having -29‰), whereas the rest was estimated to have -41 ‰ on average. These assumptions, combined with the above-mentioned numbers

for solid and liquid fuels, lead to the data presented in figure 2B. Still, it needs to be stressed that this is no more than an educated guess. To improve the $\delta^{13}C_f$ estimate, we plan to measure $\delta^{13}C$ of natural gas samples from various sources used by the Gasunie (on-shore and off-shore). Where this still will not enable us entirely to compute the average $\delta^{13}C$ for the natural gas, it will at least give us a better idea of what range of values can be expected.

4 Discussion

The experimental results for $\delta^{13}C$ as presented in table 1 show low, and in part strikingly low values. In order to try and identify source regions (and even couple them to different $\delta^{13}C_f$ values) back trajectories have been calculated by the Royal Dutch Meteorological Institute (KNMI) for 5 of the measurement days.

For three of the five series, namely on Sept 19, 1994, Nov. 23, 1994 and on November 28, 1995, the trajectories show that air has been transported over the Netherlands and in part over Northern Germany at low altitudes prior to arriving at Kollumerwaard. This means that the $\delta^{13}C_f$ value for these days are probably representative for the Netherlands during winter. Furthermore, weather conditions for these days were stable, with moderate to high wind speeds, thereby most likely excluding local effects. Also the error bars in the values for $\delta^{13}C_f$ are small for these events. The values for two of these three events, -31.7 ± 1.3 ‰ and -30.3 ± 3.5 ‰, respectfully, compare favourably with our fossil fuel consumption based calculations, whereas the third, -42.7 ± 1.4 ‰, is significantly lower, but still in the range of values for natural gas. Also the last event from table 1, for which we do not have back trajectories available to date, gives a result in accordance with our calculations.

Neglecting the first and third result in the table because of their very large error bars, two very low values remain. The trajectories for Feb 2, 1995 show that background air directly from the North Sea was transported to the station over the whole period. Yet we observed a significant, though short (6-8 hours) rise of the CO_2 mixing ratio, and were able to calculate the $\delta^{13}C_f$ shown in table 1. Therefore it is likely that we have captured a source with a more local character. The most likely candidate is flaring of natural gas, since only natural gas can exhibit such a low $\delta^{13}C$. The Kollumerwaard station is close to the North Sea off shore activities. In this event the CH_4 mixing ratio correlates very well with the fossil CO_2 mixing ratio. This further supports the possibility of the influence of natural gas flaring.

Finally, the event at October 31, 1995 yields a strikingly low result. During this event, the total CO_2 mixing ratio decreased from over 410 ppm to background values, and the ^{14}C analysis shows this excursion to be totally of fossil

fuel origin. The back trajectories show circulation of the air parcels around (that is within 200 km) Kollumerwaard in the first half of the event, gradually turning into longer distance patterns over the North Sea. So one would expect to measure a reliable regional average value for $\delta^{13}C_f$. We cannot explain the unrealistically low result. A possible error source is the calibration of the CO_2 mixing ratio scale, with which we had some trouble shortly before this event registration. However, one would have to assume an error of over 20 ppm in order to bring the outcome of -58 ‰ to a value around -40 ‰. Another possibility is again the influence of a local source of natural gas combustion (that must have an extremely low $\delta^{13}C_f$!), since also in this event the fossil fuel CO_2 and CH_4 mixing ratios correlate very well.

The rather detailed investigation we performed using the records of fossil fuel consumption in the Netherlands shows that a global approach as performed by Boden et al. (1995) cannot be regarded as very precise. Comparison of even the most straightforward outcome, the yearly averaged fossil fuel CO_2 production shows that Boden et al. (1995) underestimate the CO_2 exhaust by about 10%, although their data are based on the same sources as ours. Differences originate from their use of world-wide averages for combustion heat and CO_2 production per unit energy for the various fossil fuels.

Calculations of more complicated parameters, such as the seasonality in CO_2 production, or even the $\delta^{13}C_f$ are necessarily less precise. In the latter case, we have found that it is principally impossible to calculate the $\delta^{13}C_f$ of natural gas combustion in the Netherlands. Difficulties of this kind, and probably much worse, are expected to hamper calculations based on fossil fuel combustion records for many other countries. Therefore we regard experimental data, as gathered in the present paper, justified and even necessary.

In the light of this work, we recommend that more attention be paid by global carbon cycle modelers to the values and regional differences that occur in the world-wide values for fossil fuel CO_2 exhaust and its $\delta^{13}C_f$, as they are produced in the extensive work by Boden, Marland and Andres on this subject, in spite of the inevitable uncertainties in their results.

Our more detailed case study of fossil fuel consumption data for the Netherlands is in general agreement with their findings, and even gives a feeling for the uncertainties to be expected. Four out of six of the events presented here give results in line with our calculations.

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