REGIONAL MULTI-TRACER CO_2 CHARACTERISATION BY EVENT FLASK SAMPLING

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ABSTRACT

The $^{14}CO_2$ analysis of atmospheric samples enables us to discriminate between biospheric and fossil fuel contributions on top of the atmospheric CO_2 background [e.g. *Meijer et al*, 1996]. Following, the CO vs. fossil CO_2 ratio gives an indication of the combustion quality and also the possibility to regionally and temporarily calibrate the CO concentration measurements as a surrogate for fossil CO_2 determination by means of (the rather expensive) $^{14}CO_2$ measurements.

Once divided into biogenic and fossil contributions, the stable carbon isotopic signature ($\delta^{13}C$) of the fossil fuel derived CO_2 can be computed, given a certain ($\delta^{13}C$ of the biogenic CO_2. In the same way we can also find the oxidative ratio of the fossil fuel mix by supposing a mean biogenic oxidative ratio. The Netherlands are a quite unique country, as the fossil fuel mix consists of an unusually high percentage of natural gas. Indeed, in pollution events we could find back values close to the expected oxidative ratio, ΔO_2: ΔCO_2 = -2, of methane.

The results of all diurnal cycles so far will be presented.

The mean fossil CO_2 component is determined by integrated $^{14}CO_2$-sampling at Lutjewad in threefold: the total monthly mean (24 hours/day) is compared to wind-selected samples from the northern (North Sea clean air) resp. southern (continentally influenced) sectors.

DIURNAL CYCLES

In order to improve the knowledge about the characteristics of different kinds of anthropogenic and biogenic CO_2 emissions, flask samples have been taken in diurnal cycles during pollution as well as clean air events at the stations Lutjewad and Kollumerwaard (Netherlands) during all seasons. Besides the concentrations of CO_2, methane and CO, also the stable isotopes of CO_2 have been measured, and on subsets of the samples also the $^{14}CO_2$ content and the oxygen concentration (mass spectrometric as O_2/N_2 ratio) have been analyzed. In order to sample air with a wide range in CO-concentrations and $\Delta^{14}C$, a computer controlled continuous air drying and flask sampling system was developed by the CIO [*Neubert et al.*, 2004]. The system is set up for taking air samples automatically at remote places. It is capable of drying air continuously without operator intervention, with a flow rate of up to 4 L min^{-1}, to a dew point below -50°C. Twenty glass flasks are connected to the inlet and are flushed with air one by one at pre-set intervals. By following the CO_2 concentrations over the past day/night cycle home in the laboratory it is possible to keep an air sample at certain times within a CO_2 maximum by remote control. One of these event trapping units is operational at Lutjewad, The Netherlands (CIO) since July 2001. Earlier sample series had been taken with simpler devices.

The events were evaluated using the model by Meijer et al. [1996]. A typical example of the separation of the total measured CO_2 concentration into the different sources, as for an event sampled on 09/10/02, shows that during the night the biogenic CO_2 input has its maximum due to high respiratory activity. At noon CO_2 is taken up by plants,

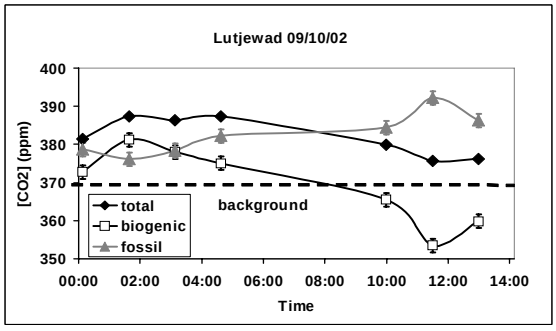

Fig. 1 Separation of the total measured CO_2 concentration into its biogenic and fossil components on top of the constant background CO_2 concentration for the event sampled at Lutjewad at 09/10/02.

which are at the maximum of their photosynthetic activity, while, at the same time, the fossil CO_2 input reaches its maximum due to increased anthropogenic activity.

The fossil $\delta^{13}C$ between -29 and -47 per mil found in two events sampled at 19/10/02 and 17-18/11/02 suggests that their fossil CO_2 input was due to the burning of natural gas. For both events the [CO]/[fossil CO_2] slopes are in the range of the slopes determined by Meijer et al. [1996] over the period from 1994 to 1996 for the same area.

INTEGRATED $^{14}CO_2$-SAMPLING

In the summer of 2000, integrated sampling of CO_2 for analysis of ^{14}C could be started in a threefold way. Besides the continuous sampling ("24h"), at Lutjewad two more samples are taken depending on the wind direction and a minimum wind speed.

As it is not possible for us to compute back air trajectories in real time, we use fixed wind sectors and minimum wind speeds to control the integrated sampling of CO_2 (by absorption in sodium hydroxide solution) for $^{14}CO_2$ analysis. We defined a “Continental Background Sector”, with the main fetch area above the North Sea, and a “Continentally influenced sector”. The minimum windspeed was set to 3 m/s, which excludes very local influences. The main wind direction for strong winds and storms, the southwest with the economic centre of the Netherlands, was excluded, as well-mixed air would dilute the regional signals. ^{14}C analysis was partly done by conventional counting technique, partly by AMS (especially for the Northern Sector, where sample time is scarce, and thus the amount of sample is low).

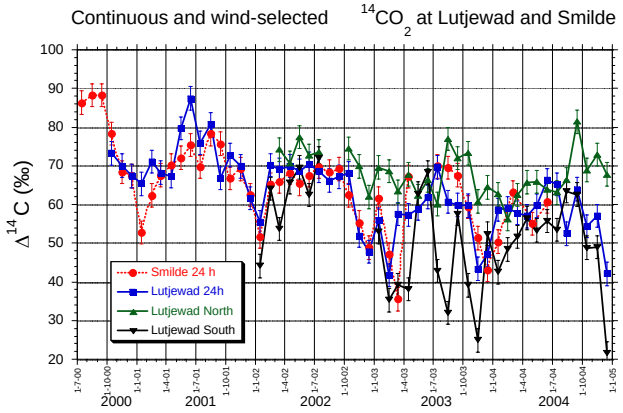

Fig. 2 Integrated $^{14}CO_2$-sampling at Lutjewad: the total monthly mean (24 hours/day), the wind direction-selected samples from the northern (North Sea clean air) and the southern (continentally influenced) sectors, as well as those from Smilde’s station, which is 70 km to the south of Lutjewad.

Figure 2 shows all results (together with station Smilde, which is 70 km to the south of Lutjewad) to date. Clearly, the air from the northern sector contains less fossil fuel derived CO_2 (thus being less depleted in $^{14}CO_2$) than that from the southern sector. In winter, differences can be up to 20 ‰, corresponding to about 8 ppm of fossil fuel CO_2. As winds from the South/West are prevailing, the total (integrated) ^{14}C signal stays closer to that of the southern sector, eventually showing similar pollution patterns, e.g. in February 2003. It keeps following the “expected” decrease with a sinusoidal annual cycle. Especially the annual pattern seems to be much less pronounced in air from the north. However, in certain periods the representativity of the data is rather small, as can be seen e.g. in January and October 2002, February 2003 (little wind from the North) and April 2003 (almost no southerly winds).

REFERENCES

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