

# ATMOSPHERIC O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> AND δ<sup>13</sup>C MEASUREMENTS FROM FLASK SAMPLING AT THREE DIFFERENT SITES IN EUROPE

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## ABSTRACT

First atmospheric δO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> and δ<sup>13</sup>C flask measurements from vertical aircraft sampling in the lower troposphere above Griffin Forest (GRI), Perthshire, UK, (56°37'N, 3°47'W) and from ground based flask sampling at the high altitude site Jungfrauoch (JFJ), Switzerland (3580m above sea level (a.s.l.), 46°33'N, 7°59'E), and the mountain site Puy de Dôme (PUY), France (1480m a.s.l., 45°46'N, 2°58'E) are presented.

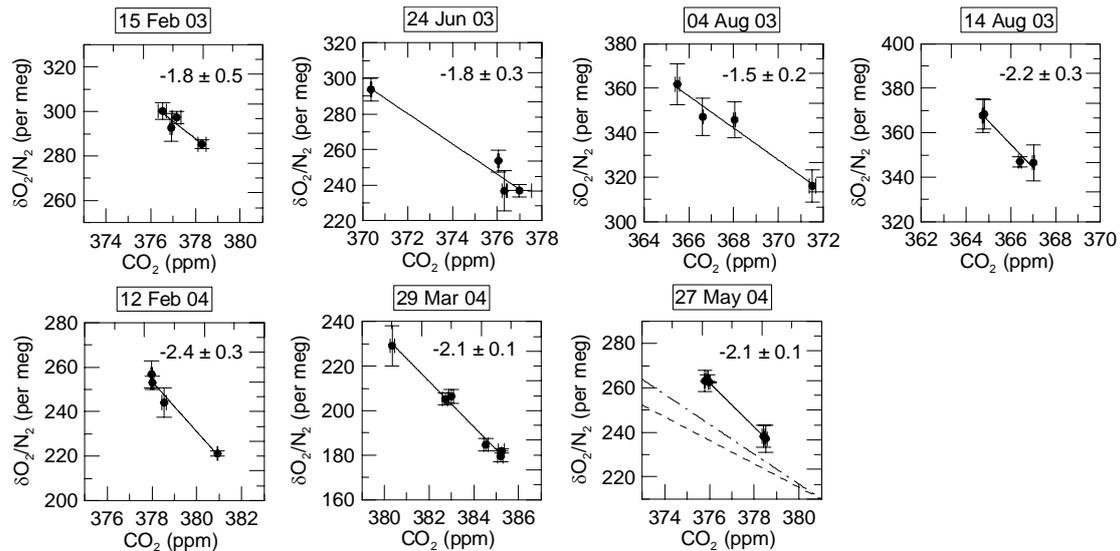
## RESULTS AND DISCUSSIONS

Regular vertical aircraft sampling is performed near the western boundary of the European continent at GRI since February 2003 for analysis of δO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> and δ<sup>13</sup>C of CO<sub>2</sub>. We sampled flasks between 800m and 3100m above sea level. The peak-to-peak amplitude of the seasonal cycle of δO<sub>2</sub>/N<sub>2</sub> decreases from 171per meg at 800m to 113per meg at 3100m. Furthermore the seasonal cycle is shifted from low to high altitudes with a lag of about 1 month between 800m and 3100m. The same features are observed for CO<sub>2</sub> with a decrease in the peak-to-peak amplitude of the seasonal cycle from 17.6ppm at 800m to 11.4ppm at 3100m. This is qualitatively consistent with the seasonal cycle being forced mainly by oceanic and land biotic surface exchange and damping of the amplitude as it is propagated vertically into the troposphere.

The atmospheric potential oxygen (APO), which is invariant to land biotic exchanges [Stephens *et al.*, 1998], shows a peak-to-peak amplitude of the seasonal cycle from 73per meg at 800m to 58per meg at 3100m. Based on this calculation about half of the seasonal cycle of δO<sub>2</sub>/N<sub>2</sub> can be attributed to land biogenic exchange (δO<sub>2</sub>/N<sub>2</sub> minus APO).

The vertical profiles show decreasing δO<sub>2</sub>/N<sub>2</sub> values in summer with increasing sampling height, reflecting O<sub>2</sub> net sources at the ground from photosynthesis and outgassing. In winter, δO<sub>2</sub>/N<sub>2</sub> is observed to increase with altitude due to a net O<sub>2</sub> sink from soil respiration, fossil fuel combustion and a net oceanic O<sub>2</sub> sink. The O<sub>2</sub>:CO<sub>2</sub> exchange ratios for these vertical profiles vary between -1.5 and -2.4mol O<sub>2</sub>/mol CO<sub>2</sub> (Fig. 1). They are all larger than the land biota O<sub>2</sub>:CO<sub>2</sub> exchange ratio of -1.1mol O<sub>2</sub>/mol CO<sub>2</sub> [Severinghaus, 1995] and the globally averaged fossil fuel O<sub>2</sub>:CO<sub>2</sub> combustion ratio of -1.4mol O<sub>2</sub>/mol CO<sub>2</sub> (Manning, 2001). This points to natural gas being the predominant fuel type, with a molar O<sub>2</sub>:CO<sub>2</sub> ratio of about -2.0, or a strong oceanic influence on the vertical δO<sub>2</sub>/N<sub>2</sub> variations. The latter is further supported by trajectory analyses suggesting that the primary origin of air masses is over the North Atlantic.

The four-year records of δO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> and δ<sup>13</sup>C at JFJ and the three year records at PUY show distinct seasonal cycles and superimposed long-term trends in the measured parameters. The mean peak-to-peak amplitudes of the respective seasonal cycles at JFJ are 79per meg for δO<sub>2</sub>/N<sub>2</sub>, 11ppm for CO<sub>2</sub>, and 0.45‰ for δ<sup>13</sup>C, as derived from data fitting. These amplitudes are comparable to the seasonal cycle amplitude at 3100m a.s.l. at GRI. At PUY the seasonal variations are about two times larger than at JFJ. The remoteness and the higher altitude of the JFJ compared to PUY result in smaller seasonal cycle



**Fig. 1:** O<sub>2</sub>:CO<sub>2</sub> ratio for vertical profiles above GRI. The slopes expressed in units of mol O<sub>2</sub>/mol CO<sub>2</sub> are between -1.5 and -2.4. The molar O<sub>2</sub>:CO<sub>2</sub> exchange ratios of -1.1 (dashed line) and -1.4 (dashed-dotted line) are shown for clearness in the last diagram of 27 May 2004.

amplitudes. The spring time CO<sub>2</sub> maximum at PUY appears in early march, whereas at JFJ it shows up 1 to 2 months later. The APO records reveal peak-to-peak amplitudes of 34 and 97 per meg at JFJ and PUY, respectively. Thus, at both sites about half of the seasonal cycle of  $\delta\text{O}_2/\text{N}_2$  can be attributed to air-sea exchange fluxes.

The O<sub>2</sub>:CO<sub>2</sub> correlation from the detrended data gives slopes of  $-2.1 \pm 0.2$  mol O<sub>2</sub>/mol CO<sub>2</sub> at JFJ and  $-2.2 \pm 0.2$  mol O<sub>2</sub>/mol CO<sub>2</sub> at PUY. This points again to a strong oceanic component contributing to the seasonal cycle of the  $\delta\text{O}_2/\text{N}_2$  even at the continental sites JFJ and PUY.

Stable carbon isotope ratios of source CO<sub>2</sub> show depleted values in the wintertime and isotopically enriched values in the summer. The  $\delta^{13}\text{C}$  source signatures obtained from “Keeling plots” showed a seasonal difference with isotopically depleted values in autumn and winter of  $-29.6 \pm 2.4\text{‰}$  and  $-31.4 \pm 1.1\text{‰}$  and enriched values in spring and summer of  $-24.4 \pm 1.9\text{‰}$  and  $-26.0 \pm 0.6\text{‰}$  at JFJ and PUY, respectively. In wintertime, when the CO<sub>2</sub> source is likely dominated by fossil fuel combustion, the isotopic signal of the source is more depleted than in summer, when biological processes dominate.

Together with data from other aircraft and ground based sites within Europe, these measurements will provide important new information on regional and continental CO<sub>2</sub> fluxes. Additionally, recently installed O<sub>2</sub> and CO<sub>2</sub> analyzers at the high-altitude site JFJ will provide continuous records of O<sub>2</sub> and CO<sub>2</sub> and give new insights in source apportionment of atmospheric CO<sub>2</sub>. The combination of O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> and  $\delta^{13}\text{C}$  measurements can then be used to partition CO<sub>2</sub> variations into ocean, biosphere and fossil fuel components.

## REFERENCES

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