

Atmospheric O₂, CO₂ and δ¹³C observations from the remote sites Jungfraujoch, Switzerland, and Puy de Dôme, France

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[1] First atmospheric O₂, CO₂ and δ¹³C flask measurements from the high altitude site Jungfraujoch (JFJ), Switzerland, as well as from the mountain site Puy de Dôme (PUY), France are presented. The four-year records of JFJ and the three-year records of 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 79 per meg for O₂/N₂, 11 ppm for CO₂, and 0.45 ‰ for δ¹³C. At PUY the seasonal variations are about two times larger than at JFJ. The spring time CO₂ maximum at PUY appears in early march, whereas at JFJ it shows up 1 to 2 months later. The O₂:CO₂ correlation gives at both sites slopes of about −2 mol O₂/mol CO₂. Stable carbon isotope ratios of source CO₂ show depleted values in wintertime and isotopically enriched values in summer. **Citation:** Sturm, P., M. Leuenberger, and M. Schmidt (2005), Atmospheric O₂, CO₂ and δ¹³C observations from the remote sites Jungfraujoch, Switzerland, and Puy de Dôme, France, *Geophys. Res. Lett.*, 32, L17811, doi:10.1029/2005GL023304.

1. Introduction

[2] The atmospheric carbon dioxide (CO₂) increase is a result of anthropogenic emissions from fossil fuel combustion and land use changes. However, only about half of the CO₂ emitted by burning of fossil fuel accumulates in the atmosphere. The remaining amount of the CO₂ is taken up by the oceans and the land biosphere. Determining this ocean-land partition and its temporal variation is essential for understanding ecosystem carbon storage and ocean uptake of carbon dioxide. Different methods have been used to experimentally constrain this partition. One approach involves measuring the rate of change of the oxygen (O₂) concentration in air [Keeling *et al.*, 1998, Bender *et al.*, 1994, Battle *et al.*, 2000], another independent approach makes use of the isotopic composition of atmospheric CO₂ [Battle *et al.*, 2000, and references therein].

[3] A large number of globally distributed monitoring station are measuring atmospheric CO₂ and other greenhouse gases, but to reduce uncertainties in net terrestrial carbon fluxes a denser observational network, including more continental sites [Gloor *et al.*, 2000], and additional tracers for source apportionment are needed. Atmospheric O₂ measurements are still very sparse, especially over the

European continent. In the framework of the EU project Aerocarb flask samples have been analyzed for O₂/N₂, CO₂ and δ¹³C taken at the high altitude site Jungfraujoch (JFJ), Switzerland during a four-year measurement period and at the mountain site Puy de Dôme (PUY), France during three years. Our flask sampling and analysis methods are described and preliminary conclusions are discussed regarding the source apportionment in view of remoteness of the high altitude site JFJ.

2. Methods

[4] The high alpine research station JFJ (3580 m a.s.l., 46°33'N, 7°59'E) is located on a mountain crest on the northern edge of the Swiss Alps. The station, which is surrounded by rocks and glaciers, is prevalently situated in the free troposphere, but can be influenced by convection of polluted air from the nearby valleys during the afternoon in the warmer months [Lugauer *et al.*, 1998]. The annual mean temperature is about −8°C, and the mean pressure is 653 hPa. Air sampling was also conducted west of the Alps at PUY station (1480 m a.s.l., 45°46'N, 2°58'E), located at the summit of PUY in the center of France. The nearest larger town Clermont-Ferrand (254,000 inhabitants) is about 15 km away. The site lies in winter mainly in the free troposphere, despite its relatively low elevation [Sellegrri *et al.*, 2003].

[5] Flask sampling at JFJ commenced in October 2000 on a biweekly basis. The sampling procedure had to be adapted several times up to July 2002 because the air analysis revealed some deficiencies for precise O₂/N₂ measurements. Initially duplicate whole-air samples were collected into 0.5 L glass flasks, equipped with two Viton O-ring high-vacuum valves at both ends (Louwers Hapert, Netherlands). The sample pressure was equal to ambient pressure at JFJ (about 650 hPa). From July 2002 the sample air was pressurized to about 950 hPa. The sampling took place between 0630 and 0730 in the morning in order to guarantee that the samples are free of polluted uplifted air from the nearby valleys and therefore represent clean air with a wide footprint (background air). Duplicate flasks were sampled at PUY on a weekly basis from July 2001. However, only one flask was sent back to the Physics Institute, University of Bern (PIUB) for O₂/N₂ analysis. The second flask was analyzed by the Laboratoire des Sciences du Climat et de l'Environnement, CE Saclay (LSCE) for CO₂ and other trace gases [Pépin *et al.*, 2001]. At PUY, 0.5L flasks with two Viton O-ring valves

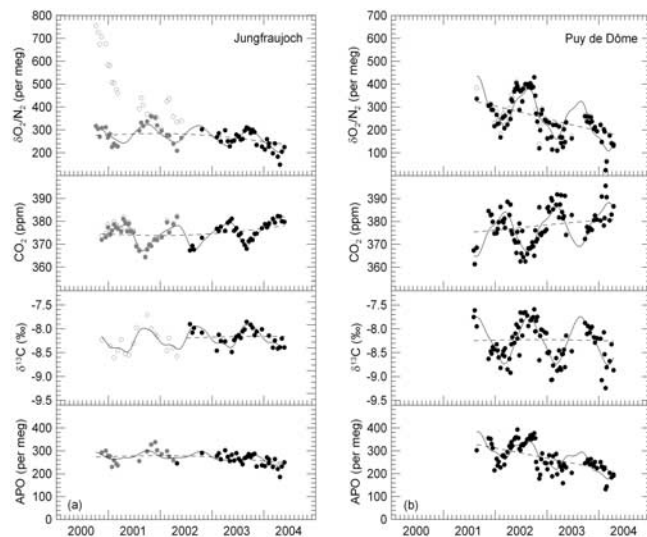


Figure 1. (a) O₂/N₂ ratio, CO₂ mixing ratio, δ¹³C of CO₂, and atmospheric potential oxygen (APO) from JFJ. Air samples were influenced by storage drift (open circles) up to July 2002. Grey closed circles show the corrected values. Since July 2002 a new sampling procedure is used, see text (black circles). Solid lines are least squares fits to a three harmonic seasonal cycle. Dashed lines represent long term trends (cubic smoothing spline). δO₂/N₂ results are reported on the local PIUB scale. (b) Same as Figure 1a but for PUY.

were flushed at ambient pressure without pressurizing the sample air. Mean sample pressure is about 900 hPa. The time of sampling varied between 0730 and 1600.

[6] We use an isotope ratio mass spectrometer (IRMS) for determining the oxygen content in an air sample, following the method described by *Bender et al.* [1994]. To achieve the precision required in global carbon cycle studies for O₂/N₂ measurements (<5 per meg), the conventional dual inlet system of the IRMS with metal bellows was modified as described by *Leuenberger et al.* [2000a]. All results are reported on the local PIUB scale, based on cylinder “LK560962”. The CO₂ mixing ratio was inferred from δCO₂/N₂ measured by mass spectrometry, simultaneously with δO₂/N₂. The background signal originating from the production of N₂O from excited N₂ and O₂ molecules or fragments of those in the ion source [*Leuenberger et al.*, 2000b] was determined at the end of each measurement day using zero CO₂ air. CO₂ mixing ratios are reported in the WMO CO₂ mole fraction scale. Primary standards from NOAA/CCGG, Boulder, CO, USA, are used to calibrate the working and secondary standards. The accuracy of the CO₂ mixing ratio data is estimated to be better than ±0.5 ppm. The δ¹³C of CO₂ was determined by GC/MS using a method, which is adapted from δ¹³C analysis of very small air amounts extracted from ice as it was developed at PIUB [*Leuenberger et al.*, 2003]. The precision is about ±0.1 ‰, compared to ±0.02 ‰ using a conventional CO₂ extraction. However, our principle is fast and we can do several replicates. A N₂O correction of +0.23 ‰ with an associated uncertainty of <±0.02 is applied to the data. Carbon isotopic compositions are expressed on VPDB-CO₂ scale.

[7] Atmospheric flasks at JFJ were filled to ambient pressure (~650 hPa) during the first year but were stored in the laboratory at Bern (~950 hPa). Those samples showed a strong dependence of the measured O₂/N₂ ratio on storage time. This correlation was attributed to permeation of gases through the Viton O-rings of the flasks’ valves [*Sturm et al.*, 2004]. The O₂/N₂ storage drift was estimated to be 1.19 ± 0.04 per meg/day and an average correction of 158 per meg (ranging from 2 to 455 per meg), corresponding to an average storage time of 130 days, was applied to the data up to July 2002. The effect of permeation and thus the applied correction clearly exceeded any real atmospheric O₂/N₂ variations (see Figure 1). This large and simplified correction gives O₂/N₂ data of somewhat minor value compared to the pressurized samples (filled to 950 hPa), which have been taken afterwards to prevent this problem. For CO₂ an estimated storage drift of 0.0053 ppm/day was applied to the CO₂ flask data up to July 2002, which resulted in an average correction of 0.69 ppm (ranging from 0.01 to 2.02 ppm). CO₂ measurements on duplicate flasks were rejected if the pair difference was >1 ppm (11 values up to July 2002 and 3 values from July 2002 to January 2003). Because it is difficult to accurately quantify the permeation fractionation for δ¹³C, no storage correction could be applied and the δ¹³C data up to July 2002 are rejected from further analysis. The mean pair difference of the remaining samples after July 2002 is 3.9 per meg for O₂/N₂, 0.18 ppm for CO₂ and 0.07 ‰ for δ¹³C. These pair reproducibilities are compatible with the precision of the individual measurements.

[8] The quality of the flask samples from PUY was on some occasions affected by insufficient drying of the sample air. Therefore 12 wet samples had to be rejected. Comparison of the PIUB CO₂ measurements with the LSCE measurements showed in 10 cases a difference of >1 ppm. These samples together with 3 contaminated samples, which could be detected by highly elevated CO₂ mixing ratios, were considered as outliers. The mean difference between the remaining CO₂ measurements of PIUB and LSCE is -0.15 ± 0.50 ppm. Considering the measurement precision of the mass spectrometric method, the agreement of the CO₂ data is regarded as satisfactory. Storage drift corrections of 0.18 per meg/day and 0.0025 ppm/day were applied to all O₂/N₂ and CO₂ flask data, respectively, resulting in average corrections of 6.8 per meg (ranging from 0.2 to 47.3 per meg) for O₂/N₂ and 0.11 ppm (ranging from 0.00 to 0.42 ppm) for CO₂.

3. Results and Discussions

[9] Figure 1 shows the O₂/N₂ ratios, CO₂ mixing ratios, δ¹³C of CO₂, and atmospheric potential oxygen (APO, defined by *Manning* [2001]) together with the harmonic curve fits through the data for JFJ from mid-2000 to mid-2004 and for PUY from mid-2001 to mid-2004. Regular seasonal cycles are observed at both sites and in all measured components. Fossil fuel combustion results at both sites in decreasing trends observed in O₂/N₂ ratios, and increasing trends in CO₂ (dashed lines in Figure 1).

[10] The mean peak-to-peak amplitudes derived from the fit at JFJ were 79 per meg for δO₂/N₂ and 11.0 ppm for CO₂. The annual mean CO₂ mixing ratio in 2003 was 375.0 ppm. The average seasonal cycle of δO₂/N₂ reached a

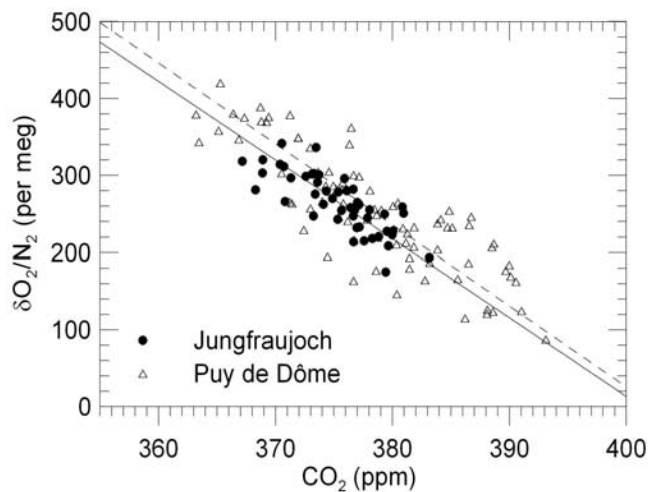


Figure 2. Detrended O₂/N₂ versus CO₂ mixing ratio at JFJ (solid line) and PUY (dashed line). The geometric mean regression slopes for O₂ changes expressed in units equivalent to CO₂ yield -2.1 ± 0.2 mol O₂/mol CO₂ for JFJ and -2.2 ± 0.2 mol O₂/mol CO₂ for PUY.

minimum in April and a maximum in September. The CO₂ mixing ratio varies in opposite phase with the maxima at the end of April, followed by a fast decrease towards the minimum at the beginning of September. These amplitudes are comparable to flask measurements from aircraft sampling above Griffin Forest, UK, where the seasonal cycle at 3100 m a.s.l. reveals a peak-to-peak amplitude of 113 per meg for δO₂/N₂ and 11.4 ppm for CO₂ [Sturm *et al.*, 2005].

[11] At PUY the mean peak-to-peak amplitudes were 190 per meg for δO₂/N₂ and 18.2 ppm for CO₂. The average seasonal cycle of O₂/N₂ reached a minimum in early March and a maximum in late August, again with the CO₂ mixing ratio varying seasonally in opposite phase with O₂/N₂. The annual mean CO₂ mixing ratio derived from these data was 377.3 ppm in 2002 and 379.5 ppm in 2003. The spring time CO₂ maximum and δO₂/N₂ minimum seem to occur 1 to 2 months earlier at PUY than at JFJ. Both findings, the amplitude dampening as well as the time shift of the maximum/minimum of CO₂ and O₂ signal, respectively, indicate mixing phenomena during the uplift of earth boundary layer air. Applying the equilibrium boundary layer concept as described by Helliker *et al.* [2004] may be helpful here.

[12] To distinguish between land and ocean processes affecting the air masses at the sampling sites, we computed the atmospheric potential oxygen (APO). Variations in APO on seasonal time-scales can be caused either by air-sea exchange of CO₂, O₂ and N₂ or by combustion of fossil fuel. The curve fits through the APO records, consisting of two annual harmonics for the seasonal variation, 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 δO₂/N₂ can be attributed to air-sea exchange fluxes.

[13] A comparison of the two sites shows that the remoteness and the higher altitude of the JFJ compared to PUY results in smaller seasonal amplitudes. However, a part of the larger amplitude at PUY is also due to the fact that the

time of flask sampling was not restricted to the early morning hours. Hence diurnal exchange variations with terrestrial biosphere and fossil fuel emissions are important. For example, in winter months, the advection of air from the planetary boundary layer with large amounts of fossil fuel CO₂ can lead to diurnal variations. Air sampling during the day can therefore increase the apparent seasonal amplitude, compared to air samples only taken in the early morning. A selection of the data according to sampling time, wind direction and wind speed is not applicable, because of the limited seasonal data coverage of the current records.

[14] In Figure 2 the detrended O₂/N₂ ratios are plotted against the detrended CO₂ mixing ratios. The slopes calculated by geometric mean regression and expressed in units of mol O₂/mol CO₂ are -2.1 ± 0.2 ($R^2 = 0.62$) for JFJ and -2.2 ± 0.2 ($R^2 = 0.71$) for PUY. These values are rather large compared to the land biota O₂:CO₂ exchange ratio of -1.1 [Severinghaus, 1995] and the globally averaged fossil fuel O₂:CO₂ combustion ratio of -1.4 [Manning, 2001] that should be independent on heights. This points again to a strong oceanic component contributing to the seasonal cycle of the δO₂/N₂ even at the continental sites JFJ and PUY.

[15] The seasonal variations of δ¹³C are in opposite phase with CO₂, with enriched values in summer and autumn and depleted values in winter and spring. The mean peak-to-peak amplitudes are 0.45 ‰ at JFJ and 1.00 ‰ at PUY. No significant long-term trends can be seen in these records. From the two-component mixing approach according to Keeling [1958] we calculated the δ¹³C signature of the source CO₂. In Figure 3 the correlation of detrended δ¹³C and the detrended inverse CO₂ mixing ratio is shown. The mean carbon isotope ratios of source CO₂ are -25.2 ± 1.5 ‰ ($R^2 = 0.81$) at JFJ and -28.8 ± 0.8 ‰ ($R^2 = 0.90$) at PUY. The larger standard error of the intercept at JFJ is due to the smaller CO₂ range compared to PUY. The mean value at JFJ of -25.2 ‰ is comparable with the source signature of -24.8 ± 1.4 ‰ observed for free tropospheric air from aircraft sampling over Orléans, France, by Levin *et al.* [2002]. The δ¹³C source signatures also showed a seasonal difference with isotopically depleted values in

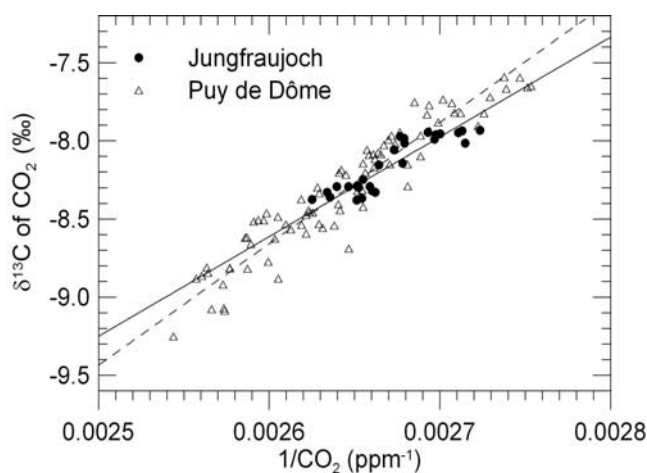


Figure 3. Keeling plot from the detrended data of the δ¹³C of CO₂ and the inverse CO₂ mixing ratio. The mean δ¹³C source signatures are -25.2 ± 1.5 ‰ at JFJ (solid line) and -28.8 ± 0.8 ‰ at PUY (dashed line).

autumn and winter of -29.6 ± 2.4 ‰ and -31.4 ± 1.1 ‰ and enriched values in spring and summer of -24.4 ± 1.9 ‰ and -26.0 ± 0.6 ‰ at JFJ and PUY, respectively. In wintertime, when the CO₂ source is likely dominated by fossil fuel combustion, the isotopic signal of the source is more depleted than in summer, when biological processes dominate. Similar seasonal differences in the order of 4–6 ‰ have also been found at other continental mid-northern latitude sites [Levin *et al.*, 2002, and references therein].

[16] Carbon flux estimates based on O₂ measurements are most robust when averaged over many years, because of inter-annual variations of oceanic fluxes. Longer observational records of δO₂/N₂ are therefore needed to provide reliable constraints on the European carbon budgets. Flask sampling at JFJ and PUY will continue within the framework of the succeeding EU project CarboEurope-IP. Additionally, recently installed O₂ and CO₂ analyzers at the high-altitude site JFJ will provide continuous records of O₂ and CO₂ and give new insights in source apportionment of atmospheric CO₂. The combination of O₂/N₂, CO₂ and δ¹³C measurements can then be used to partition CO₂ variations into ocean, biosphere and fossil fuel components.

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