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A novel approach for independent budgeting of fossil fuel CO_2 over Europe by $^{14}CO_2$ observations

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[1] Long-term atmospheric $^{14}CO_2$ observations are used to quantify fossil fuel-derived CO_2 concentrations at a regional polluted site, and at a continental mountain station in southwest Germany. Fossil fuel CO_2 emission rates for the relevant catchment areas are obtained by applying the Radon-Tracer-Method. They compare well with statistical emissions inventories but reveal a larger seasonality than earlier assumed, thus contributing significantly to the observed CO_2 seasonal cycle over Europe. Based on the present approach, emissions reductions on the order of 5–10% are detectable for catchment areas of several hundred kilometres radius, as anticipated within a five-years commitment period of the Kyoto Protocol. Still, no significant change of fossil fuel CO_2 emissions is observed at the two sites over the last 16 years. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1630 Global Change: Impact phenomena; 3307 Meteorology and Atmospheric Dynamics: Boundary layer processes. **Citation:** Levin, I., B. Kromer, M. Schmidt, and H. Sartorius, A novel approach for independent budgeting of fossil fuel CO_2 over Europe by $^{14}CO_2$ observations, *Geophys. Res. Lett.*, *30*(23), 2194, doi:10.1029/2003GL018477, 2003.

1. Introduction

[2] Anthropogenic carbon dioxide (CO_2) from burning of fossil fuels plays an important role in the European carbon budget. Thus, without a quantitative knowledge of the fossil fuel component, biogenic CO_2 sources and sinks cannot be univocally estimated there from atmospheric CO_2 observations by inverse modelling. In the Kyoto Protocol, all European Union (EU) member states committed themselves to reduce greenhouse gases emissions, particularly CO_2, by 8% relative to 1990. In view of the difficulties to meet this aim, a key issue of the Kyoto Protocol is its verification. Classical emissions estimates of CO_2 and other greenhouse gases are based on bottom-up statistics; however, the accuracy of these estimates is a matter of permanent debate: In the case of fossil fuel CO_2, error claims range from ±2% to more than ±15%, exceeding the reduction target at the higher end. An independent method to estimate trace gas emissions is the top-down approach, using atmospheric measurements, but CO_2 concentration observations alone do not allow source apportionment. In the case of distinguishing continental biogenic from fossil fuel CO_2, radiocarbon (^{14}C) measurements, however, provide the necessary additional information, because, contrary to biogenic CO_2, fossil fuel CO_2 does not contain any ^{14}C.

[3] ^{14}C ($T_{1/2}$ = 5370 a) is produced in the atmosphere by cosmic ray-induced reactions of neutrons with atmospheric nitrogen. Over the last century, the natural level of $^{14}CO_2$ in the atmosphere has been disturbed by human activities via the ongoing input of fossil fuel CO_2 into the atmosphere (^{14}C Suess effect [*Suess*, 1955]) and by nuclear bomb tests primarily in the 1950s and 1960s (Figure 1a; the $^{14}C/^{12}C$ isotope ratio in CO_2 is expressed on the $\Delta^{14}C$ scale as deviation from an internationally accepted standard material (NBS Oxalic Acid) in permil [*Stuiver and Polach*, 1977]). ^{14}C production during the atmospheric bomb tests led to an increase of the $^{14}C/^{12}C$ ratio in the Northern Hemisphere by a factor of two. After the test ban treaty in 1963, atmospheric $^{14}CO_2$ decreased rapidly due to equilibration of this atmospheric spike with the ocean and the biosphere. After the ^{14}C input from the Chinese bomb tests in 1981 levelled out, bomb $^{14}CO_2$ has become almost well mixed in the global atmosphere. Deviations from a pseudo-equilibrium between all carbon reservoirs manifest themselves only in an ongoing small $^{14}CO_2$ decrease (Figure 1a) and north-south differences of a few permil $\Delta^{14}C$ in marine background air [*Levin and Hesshaimer*, 2000]. In polluted continental areas, however, fossil fuel CO_2 emissions cause significant disturbance of atmospheric $^{14}CO_2$ [*Levin et al.*, 1989]. This signal, measured at two sites in Germany, (the remote mountain station Schauinsland in the Black Forest; and the densely populated Heidelberg area in the Upper Rhine valley), is evaluated to estimate the respective fossil fuel CO_2 components. As a free troposphere continental background reference station, we chose the High Altitude site Jungfraujoch in the Swiss Alps where we have carried out continuous $^{14}CO_2$ observations since 1986. In addition to the $^{14}CO_2$ (and CO_2 concentration) observations, continuous ^{222}Radon (Rn) measurements at Schauinsland and Heidelberg are used to estimate the fossil fuel CO_2 emissions within the catchment areas of the two sites.

2. Experimental

[4] Two weekly integrated atmospheric $^{14}CO_2$ samples have been collected since the 1980s at three continental European sites: the High Alpine Research station Jungfraujoch (Swiss Alps, 46°33′N, 7°42′E, 3450 m a. s. l.), the continental mountain station Schauinsland (Black Forest, Germany, 47°55′N, 7°55′E, 1205 m a. s. l., ca. 1000 m above the Rhine valley, [*Levin and Kromer*, 1997]), and the polluted Rhine valley at the Institut für Umweltphysik former building in the outskirts of Heidelberg (49°24′N,

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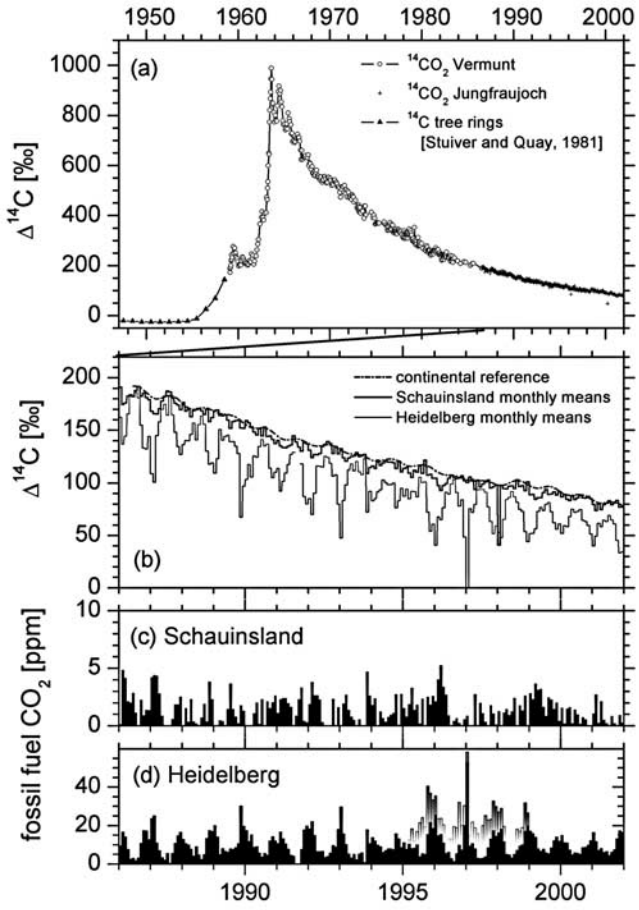

Figure 1. (a) Long-term trend of $\Delta^{14}CO_2$ in background air over Europe, and in tree rings from the northern hemisphere [*Stuiver and Quay*, 1981]. (b) Monthly mean $\Delta^{14}CO_2$ at Heidelberg and at Schauinsland in comparison with the harmonic fit curve through the Jungfraujoch data (continental reference level). (Two negative outliers from Jungfraujoch and one from Schauinsland have been excluded from further evaluation) (c) Fossil fuel CO_2 component at Schauinsland calculated from equation (3). (d) Same as (c) for Heidelberg; the grey values show the total measured CO_2 offset compared to background air [*GLOBALVIEW-CO_2*, 2002]. Note that the biospheric contribution in summer exceeds that of fossil fuels but even in winter it is still as large as the fossil fuel component.

8°42′E, 116 m a. s. l., INF 366, 20 m above local ground). $^{14}CO_2$ sampling and analysis techniques are described by *Levin et al.* [1980] and *Schoch et al.* [1980]. Internal measurement precision of individual samples was generally about $\Delta^{14}C = \pm(2-5)$‰ with the better precision on the continental background samples from Jungfraujoch. For most of the observational period (i.e., since August 1988), Heidelberg samples were collected only at night (19:00–7:00 local time) when local emissions from traffic on the Univ. campus are not significant. All Heidelberg $^{14}CO_2$ data have been corrected for a small contribution from continuous $^{14}CO_2$ emissions by the boiling water reactor Philippsburg 1 (KKP1), situated about 25 km southwest of Heidelberg. To do so, we used the extrapolated [*Turner*, 1970] mean dispersion factor of KKP1 emissions for the Heidelberg site we obtained from dedicated continuous $^{14}CO_2$ measurements in the main wind direction of the reactor at 1.75 km and at 3.25 km distance [*Levin et al.*, 1988]. Monthly mean $^{14}CO_2$ emission rates measured at the reactor stack (H. Auerbach, KKP1, personal communication), and the mean dispersion factor (1.5×10^{-8} s m^{-3}) were then used to derive monthly mean reactor $\Delta^{14}CO_2$ concentrations at Heidelberg. These varied between 0.2‰ and 10‰ with a mean value of $\Delta^{14}C = (4.8 \pm 2.0)$‰ and showed no significant seasonal variation. The reactor signal is on the order of our measurement uncertainty, but amounts to about 25% of the fossil fuel effect in summer and about 10% in winter; therefore, respective correction was required. In addition, a few (10 out of 500) Heidelberg samples have been rejected because they showed $^{14}CO_2$ activities significantly above background which are most probably caused by extended short-term ^{14}C emissions from KKP1 during revision periods.

[5] Radon 222 was measured at Schauinsland and at Heidelberg with the static filter technique via its atmospheric daughter activity [*Stockburger and Sittkus*, 1966; *Levin et al.*, 2002]. For Heidelberg, continuous Rn measurements exist only from mid 1995 onwards. However, comparison of continuous Rn observations in Freiburg (carried out at the Institut für Atmosphärische Radioaktivität since 1981), also located in the upper Rhine valley about 170 km south of Heidelberg, compared very well with Heidelberg's monthly observations (mean ratio of Rn-Heidelberg/Rn-Freiburg = 0.84 ± 0.15) because both sites are generally influenced by the same synoptic weather systems. Therefore, we used Freiburg Rn activities corrected by a factor of 0.84 as a proxy for Heidelberg Rn concentrations to estimate Rn-derived fossil fuel emission rates in the Heidelberg catchment area for 1986–1995. The additional error associated with this approximation on annual mean emission rates is about 6%.

3. Results and Discussion

[6] The Jungfraujoch observations provide the temporal trend of $^{14}CO_2$ in the free troposphere over Europe after 1986 (Figure 1a). There is a small seasonal variation of background $^{14}CO_2$ observed which, to a large extent, is caused by the input from the stratosphere but also by $^{14}CO_2$ disequilibrium fluxes of the biosphere, and by a seasonal variation of the fossil fuel CO_2 component in background air at mid northern latitudes [*Hesshaimer*, 1997; *Randerson et al.*, 2002]. The harmonic fit curve [*Nakazawa et al.*, 1997] calculated through the Jungfraujoch observations will be assumed as the reference level over Europe.

[7] Compared to this reference level, $\Delta^{14}CO_2$ at Schauinsland and Heidelberg are always lower due to dilution with ^{14}C-free fossil fuel CO_2. In Heidelberg mean negative departures of $\Delta^{14}C$ values from the background are about 30–60‰ in winter and 10–30‰ in summer. At the mountain site Schauinsland, the corresponding departures are only 2–6‰, while in winter the fossil fuel effect is 10–15‰. The measured CO_2 mixing ratio c_{meas} at the sites consists of three components, a background component c_{BG}, a biospheric component c_{bio}, and a fossil fuel component c_{foss}. The $\Delta^{14}C$ of these components are resp.

$\Delta^{14}C_{meas}$, $\Delta^{14}C_{BG}$, $\Delta^{14}C_{bio}$ and $\Delta^{14}C_{foss}$. To calculate the fossil fuel CO_2 component, we formulate two balance equations for CO_2 mixing ratio and $^{14}C/^{12}C$ ratios (proportional to $(\Delta^{14}C_i + 1000)$ [*Levin et al.*, 1989]):

$$c_{meas} = c_{BG} + c_{bio} + c_{foss} \quad (1)$$

$$c_{meas}\left(\Delta^{14}C_{meas} + 1000\right) = c_{BG}\left(\Delta^{14}C_{BG} + 1000\right) + c_{bio}\left(\Delta^{14}C_{bio} + 1000\right) + c_{foss}\left(\Delta^{14}C_{foss} + 1000\right). \quad (2)$$

[8] The fossil fuel term in equation (2) is zero as $\Delta^{14}C_{foss} = -1000‰$. We set $\Delta^{14}C_{bio}$ equal to $\Delta^{14}C_{BG}$ as the major flux from the biosphere comes from autotrophic respiration, a young reservoir in very close ^{14}C equilibrium with atmospheric CO_2. Combining both equations leads to the fossil fuel CO_2 component:

$$c_{foss} = c_{meas}\frac{\Delta^{14}C_{BG} - \Delta^{14}C_{meas}}{\Delta^{14}C_{BG} + 1000}. \quad (3)$$

[9] At Schauinsland, CO_2 mixing ratios have been measured since 1972 continuously by the German Environment Agency [*Schmidt et al.*, 2003]. Heidelberg CO_2 mixing ratios have been measured only from 1995 to 1998. For the periods without observations we approximate mixing ratios in Heidelberg using the mean seasonal offset from background air measured for 1995–1998 and adding the actual background mixing ratio from *GLOBALVIEW-CO_2* [2002] for 48°N. The additional uncertainty from this approximation in the fossil fuel CO_2 component is less than 10% for individual monthly mean values since the fossil fuel component is mainly determined by the $\Delta^{14}C$ depletion. Fossil fuel CO_2 is then calculated from equation (3) for Schauinsland and Heidelberg as displayed in Figures 1c and 1d. The long-term mean fossil fuel CO_2 component at Schauinsland is 1.4 ppm and shows generally higher values in the winter half year (1.7 ppm) than in summer (1.0 ppm). In Heidelberg the long-term mean fossil fuel CO_2 component is about seven times larger than at Schauinsland (10.5 ppm). The very pronounced seasonality of fossil fuel CO_2 in Heidelberg (winter: 14 ppm, summer: 6.5 ppm) is caused by a significant seasonality of the emissions, but also by seasonally varying atmospheric dilution. The Rhine valley, particularly during winter, often experiences strong inversion situations causing large pile-ups of ground level emissions in the atmospheric surface layer. It is worthy of note, that even in winter about half of the total CO_2 pile-up is still due to biogenic emissions (Figure 1d).

[10] In order to estimate fossil fuel CO_2 fluxes, we use the Radon-Tracer-Method approach [*Schmidt et al.*, 2003]. The fossil fuel CO_2 flux j_{foss} is calculated from the fossil fuel CO_2 offset c_{foss} at the respective site (Figure 2a), and the concurrent atmospheric Rn activity c_{Rn} (with a seasonally varying background activity at Jungfraujoch between 0.2 and 0.8 Bq m^{-3} [*Lugauer et al.*, 2000] subtracted, Figure 2b), as well as the Rn exhalation rate j_{Rn} according to:

$$j_{foss} = j_{Rn}\frac{c_{foss}}{c_{Rn}} \quad (4)$$

[11] For the respective values of j_{Rn} in the catchment areas, see *Schmidt et al.* [2003] for Schauinsland and *Levin et al.* [1999] for Heidelberg. Figures 2c and 2d show the monthly mean fossil fuel CO_2 emissions calculated from equation (4). The absolute accuracy of our Radon-derived fluxes is determined by the accuracy of (1) the determination of fossil fuel CO_2 (ca. 1.5 ppm or less than 15% for annual means), (2) the atmospheric Rn activity (ca. 20%, including the additional uncertainty from using Freiburg Rn observations as a proxy for Heidelberg), and (3) the accuracy of the determination of the Rn exhalation rate (better than 20%). The accuracy of the top-down fossil fuel CO_2 flux is therefore about 30–35%, and relative year-to-year changes can be determined to better than 20%.

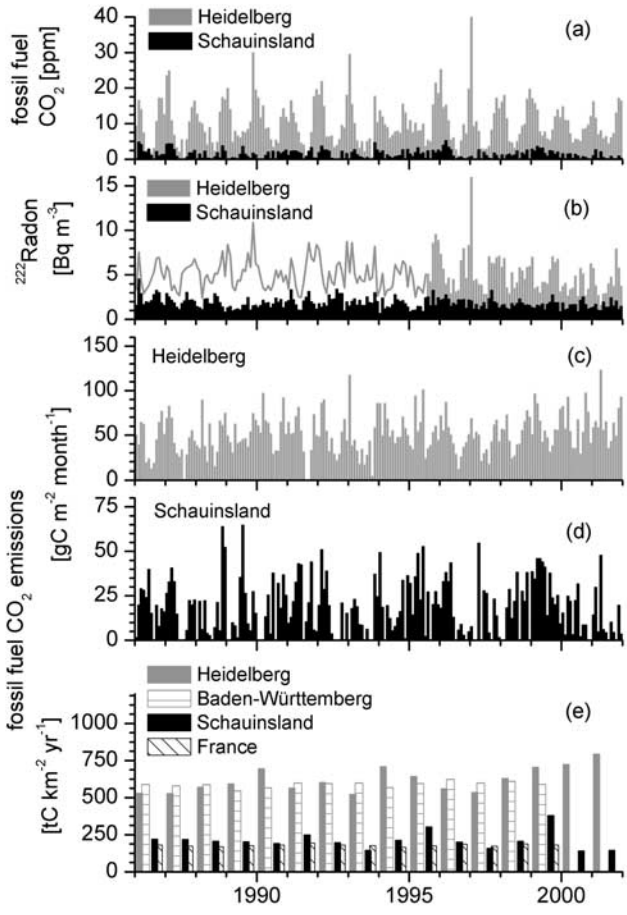

Figure 2. (a) Fossil fuel CO_2 components at Heidelberg and Schauinsland. (b) Monthly mean Rn activity at Heidelberg (data before 1996 were extrapolated from Freiburg observations, see text) and Schauinsland, with Jungfraujoch activities subtracted. (c) Monthly mean fossil fuel CO_2 flux at Heidelberg calculated from equation (4), (d) Same as (c) for Schauinsland. (e) Annual mean fossil fuel CO_2 flux for Heidelberg in comparison with statistical emissions estimates for Baden-Württemberg, and Schauinsland flux estimates in comparison with emissions inventories for France.

[12] There is a significant seasonality observed in the emission rates, but in Heidelberg, the seasonality in the flux is less pronounced than in the concentrations. Mean seasonal cycles of the fluxes for both sites normalised to the

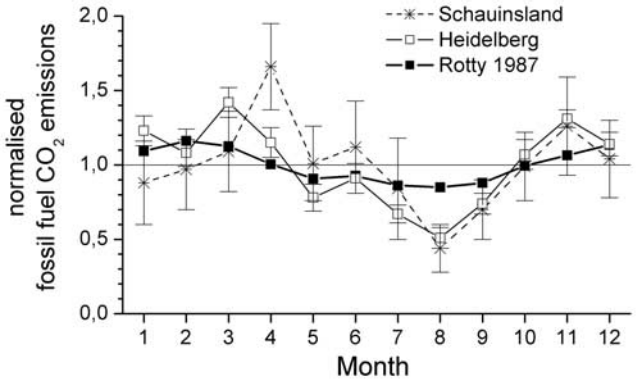

Figure 3. Normalised seasonal variation of the mean fossil fuel CO_2 flux for Schauinsland and Heidelberg in comparison with bottom-up estimates from *Rotty* [1987].

respective annual means are presented in Figure 3 together with estimates reported by *Rotty* [1987] for western European countries. Clearly, the observed seasonality at both sites is significantly larger than the estimate by *Rotty* [1987]. This is an important result of our study because model estimates of the global and continental European CO_2 budgets very often adopt, if any, only the weak seasonality of fossil fuel emissions based on the work of *Rotty* [1987]. The source-driven component of the atmospheric CO_2 seasonal cycle is therefore interpreted as almost exclusively of biogenic origin reflecting net primary productivity (NPP). Instead, from our $^{14}CO_2$ observations at Schauinsland, we calculated a mean seasonal cycle peak-to-peak amplitude of the fossil fuel CO_2 component of 1.4 ppm with the same phasing as total CO_2 which has a mean peak-to-peak amplitude of ca. 13 ppm [*Schmidt et al.*, 2003]. The fossil fuel CO_2 component thus contributed more than 10% to the total annual CO_2 cycle over Europe.

[13] From the monthly mean top-down fossil fuel flux estimates, we calculated annual means and compared them with bottom-up statistical data. Heidelberg emissions are first compared to the 1998 mean value for the rural district around Heidelberg (Rhein-Neckar-Kreis, http://www.umeg.de/ekat). The statistical data report emissions larger by about 40–50% compared to our top-down estimate, i.e., 875 gC m^{-2} yr^{-1} compared to about 600 gC m^{-2} yr^{-1} from our observations. The uncertainty of our atmospheric approach cannot fully explain the difference between the top-down and the bottom-up estimates for the rural district of Heidelberg. One explanation could be that the Heidelberg catchment area is much larger than several tens of kilometres distance around the measurement site, thus including predominant agricultural areas with smaller fossil fuel emissions, comparable to the respective properties of Baden-Württemberg. Here, mean fossil fuel emissions are very similar to our top-down estimate (Figure 2e). Schauinsland emissions compare very well with those from France [*Marland et al.*, 2002] which is assumed as the main catchment area of this site with predominant air mass origin from western and southwestern Europe.

[14] Equally important as the absolute values of our Rn-derived fossil fuel fluxes is their long-term development. Neither in our observations nor in the bottom-up data significant trends are observed until now. When assuming that the catchment area of our observations did not change, averaging annual means over five years obviously leads to uncertainties on the order of 5% for Heidelberg and 10% for Schauinsland. In Heidelberg's case, these five years means would be accurate enough to detect emissions changes on the order of the anticipated Kyoto reductions, i.e., 8% in the first commitment period of 2008–2012 compared to the base year of 1990.

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