

Verification of German methane emission inventories and their recent changes based on atmospheric observations

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Abstract. Continuous methane concentration records and stable isotope observations measured in the suburbs of Heidelberg, Germany, are presented. While $\delta^{13}\text{C}-\text{CH}_4$ shows a significant trend of -0.14‰ per year, toward more depleted values, no trend is observed in the concentration data. Comparison of the Heidelberg records with clean air observations in the North Atlantic at Izaña station (Tenerife) allows the determination of the continental methane excess at Heidelberg, decreasing by 20% from 190 ppb in 1992 to 150 ppb in 1997. The isotope ratio which is associated with this continental methane pileup in the Heidelberg catchment area shows a significant trend to more depleted values from $\delta^{13}\text{C}_{\text{source}} = -47.4 \pm 1.2\text{‰}$ in 1992 to $-52.9 \pm 0.4\text{‰}$ in 1995/1996, pointing to a significant change in the methane source mix. Total methane emissions in the Heidelberg catchment area are estimated using the ^{222}Rn (^{222}Rn) tracer method: from the correlations of half-hourly ^{222}Rn and CH_4 mixing ratios from 1995 to 1997, and the mean ^{222}Rn exhalation rate from typical soils in the Rhine valley, a mean methane flux of $0.24 \pm 0.5 \text{ g CH}_4 \text{ km}^{-2} \text{ s}^{-1}$ is derived. For the Heidelberg catchment area with an estimated radius of approximately 150 km, Core Inventories Air 1990 (CORINAIR90) emission estimates yield a flux of $0.47 \text{ g CH}_4 \text{ km}^{-2} \text{ s}^{-1}$, which is about 40% higher than the ^{222}Rn -derived number if extrapolated to 1990. The discrepancy can be explained by overestimated emissions from waste management in the CORINAIR90 statistical assessment. The observed decrease in total emissions can be accounted for by decreasing contributions from fossil sources (mainly coal mining) and from cattle breeding. This finding is also supported by the observed decrease in mean source isotopic signatures.

1. Introduction

Highly populated and industrialized western Europe is a major source of methane to the global atmosphere. With mean flux densities in the same order or even larger than those reported for northern wetlands [Kuhlmann *et al.*, 1998, and references therein], the predominantly anthropogenic European methane emissions provide a significant contribution to the methane burden of the northern hemisphere. However, estimates from different anthropogenic sources have only been deduced from statistical compilations which were not yet validated by observations on a European-wide scale.

In the last 10 years the Heidelberg methane isotope laboratory established methods for high-accuracy concentration and isotope analyses on atmospheric and source methane [Levin *et al.*, 1993; Thom *et al.*, 1993; Greschner, 1995; Marik, 1998]. These methods have been tested carefully through measurements of ambient air at the Heidelberg Institute and were applied in a continuous measurement program established at three worldwide distributed background stations. Particularly, the isotope measurements on atmospheric and source methane provide a powerful tool to investigate global and regional

methane emission budgets. The different source types as thermogenic ones (e.g., emissions from coal mining) and biogenic ones (e.g., emissions from dairy cattle) can be distinguished by their isotope ratio [Levin, 1994]. Isotope observations performed in parallel to concentration measurements therefore allow quantitative source apportionment, at least for these major source classes where the isotope ratios are significantly different.

To derive emission rates from atmospheric concentration observations, we have used here the ^{222}Rn tracer method [Levin, 1984; Thom *et al.*, 1993; Schmidt *et al.*, 1996; Kuhlmann *et al.*, 1998] to parameterize transport and dilution of ground level emissions in the atmospheric surface layer. Radon 222 is a radioactive noble gas (radioactive life time $\tau = 5.52$ days) which is produced by α decay of ^{226}Ra contained in all soils. After production within the soil grains, ^{222}Rn emanates into the soil air and partly diffuses into the atmosphere where it is diluted by turbulent mixing. The ^{226}Ra concentration in different soil types varies by a factor of 2 to 4, and the ^{222}Rn exhalation rate from continental soil surfaces strongly depends on the texture of the soil. However, ^{222}Rn exhalation from soils turned out to be rather homogeneous in a restricted region and more or less constant with time [Dörr and Münnich, 1990]. Only higher soil humidity in winter leads to slightly decreased exhalation rates for fine-grained soils [Schüßler, 1996]. With these characteristics, ^{222}Rn is a very useful tracer to paramete-

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terize vertical mixing conditions in the surface and boundary layer of the atmosphere over the continents.

Here we made an attempt to use continuous records of atmospheric methane concentrations and isotope ratios along with ^{222}Rn measurements to estimate methane emissions in the regional catchment area of the Heidelberg observation site. The results are applied for validation of statistical emission inventories compiled for the same region.

2. Sampling and Analytical Methods

2.1. Heidelberg Station

Heidelberg (49°24'N, 8°42'E, 116 m above sea level (asl)) is a medium-size city situated in the upper Rhine valley, about 20 km east of the industrial area Mannheim/Ludwigshafen. The local wind system in Heidelberg is dominated by alternate north/south flow along the Rhine valley, but also by frequent easterly winds from the Neckar valley. In contrast to local winds, back trajectories clearly demonstrate predominance of a westerly air mass influence. Since establishment of the automated continuous gas chromatographic (GC) system in the Heidelberg laboratory in 1995, approximately half-hourly values of ambient mixing ratios are available for methane, carbon dioxide, and nitrous oxide. The air is collected from a permanently flushed stainless steel inlet line located on the roof of the Heidelberg Institute building, about 20 m above local ground. The Heidelberg Institute itself is located on the University of Heidelberg campus in the suburbs of Heidelberg. No distinct methane sources can be identified in the very local surroundings of the observational site. Moreover, from earlier $^{14}\text{CO}_2$ studies we could demonstrate that the Heidelberg site is representative for well mixed polluted air in the highly populated and industrialized upper Rhine valley [Levin *et al.*, 1980]. Before the continuous automated GC measurements started in 1995, biweekly integrated air samples for isotopic CH_4 analyses have been collected into large polyethylene-coated aluminium bags (~400 L, Tesseraux, Germany) from 1988 to 1996. From these samples, pressurized flask aliquots were taken for concentration measurements. A ^{222}Rn monitor for continuous atmospheric ^{222}Rn daughter observations was installed in 1995.

2.2. Schauinsland Observatory

The continental Global Atmosphere Watch (GAW) station Schauinsland (47°55'N, 7°55'E, 1205 m asl) is run by the German Environment Agency, Berlin. The station is situated on a mountain ridge in the Black Forest, southwest Germany, at an elevation of about 1000 m above the polluted Rhine valley. During night the station is usually above the boundary layer, while at daytime, particularly in summer, Schauinsland station mostly lies within the convective boundary layer. Regular sampling of duplicate weekly 1 L glass flasks started at Schauinsland already in 1988. Samples were taken usually in the morning and with wind velocities above 2.5 m s^{-1} . This sampling criterion was chosen in order to ensure collection of well-mixed continental air mostly representative for a catchment area with a spatial scale of some hundred kilometers.

2.3. Izaña Observatory

The GAW baseline observatory Izaña is located on Tenerife, Canary Islands (28°18'N, 16°29'W), at an altitude of 2367 m asl. The station is operated by the Instituto Nacional de Meteorología, Madrid, Spain. At this high-elevation site of the North Atlantic trade wind system, free midtroposphere condi-

tions of this latitudinal belt prevail. Integrated over 2 weeks, high-volume (1–1.5 m^3) air samples have been collected at Izaña into 400 L aluminium bags. Samples have then been transferred into 10 L aluminium cylinders filled to a pressure of about 150 bar using an air compressor (Bauer, München, Germany). After transfer to the Heidelberg laboratory, samples were analyzed for CH_4 concentration and stable isotope ratios.

2.4. Concentration Measurement

Until 1994, CH_4 and CO_2 mixing ratios at Heidelberg and at the Schauinsland observatory were measured manually on the flask samples by gas chromatography (Sichromat 3, Siemens, Germany) via flame ionization detectors (FID) [Born *et al.*, 1990]. Concentration measurements from Izaña were performed on the same system directly on the pressurized tank samples. Since 1995, an automated gas chromatographic system (HP5890) was used for the flask and tank measurements as well as for semicontinuous measurement of CH_4 , CO_2 , and N_2O mixing ratios in ambient Heidelberg air [Greschner, 1995; Bräunlich, 1996; Glatzel-Mattheier, 1997]. One analysis consists of flushing the two sample loops (3 mL FID, 5 mL electron capture detector (ECD)) simultaneously with 250 mL sample gas followed by pressure and temperature equilibration for 1 min and injection on the GC columns using N_2 as carrier gas for CH_4 and CO_2 and Ar/CH_4 for N_2O . CH_4 and CO_2 are separated on one column (Porapack QS), and the CO_2 effluent is switched to a Ni catalyst where it is reduced to CH_4 prior to FID analysis. The retention times are 3 min for CH_4 and 6 min for CO_2 , N_2O which is separated on a Porapack Q column and analyzed with an ECD has a retention time of 6.5 min. With this configuration it is thus possible to inject and analyze one sample every 10 min. The routine measurement method needs half an hour including one standard and one or two ambient air injections. In the case of automated flask analysis one flask sample replaces one ambient air measurement in a half-hourly interval.

As a long-term stability and quality control check, a so-called "target gas" is analyzed four times every 12 hours. From May 1995 to December 1997 the CH_4 standard deviation of this target gas was ± 2.4 ppb. No significant drift or concentration change after modification of methods and change of system standards is seen. Flask samples (e.g., integrated bag sample aliquots) are collected in 1 L glass flasks pressurized to approximately 1 bar overpressure. Since we need about 250 mL of air for each sample loop flushing, flasks can only be analyzed two to three times. The interpair reproducibility for flask measurements is typically ± 3 ppb (± 0.20 ppm for CO_2 , ± 0.5 ppb for N_2O). All methane (and CO_2) mixing ratios are reported on the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) scale [Dlugokencky *et al.*, 1994].

2.5. Isotope Analyses

The measurement principle for stable isotope analyses on atmospheric methane is based on a two-step enrichment of methane from about 600–800 L of air on activated charcoal by a factor of approximately 10^4 . Gas chromatographic separation of the enriched air sample from carbon- and hydrogen-containing gases other than methane are followed by catalytic conversion of the CH_4 sample on platinum to CO_2 and H_2O . CO_2 is analyzed for $^{13}\text{C}/^{12}\text{C}$ ratio by isotope ratio mass spectrometry (IRMS MAT252, Finnigan, Bremen, Germany) and expressed in the δ notation as per mil deviation from

internationally accepted standard material, Vienna Pee Dee belemnite (VPDB) [Gonfiantini, 1984]. The reproducibility for $\delta^{13}\text{C}-\text{CH}_4$ analyses is typically $\pm 0.05\text{‰}$. The long-term stability of the $\delta^{13}\text{C}-\text{CH}_4$ analyses has been checked via archived air samples from Antarctica [Marik, 1998]. The long-term stability and reproducibility of $\delta^{13}\text{C}-\text{CH}_4$ over the period of 1992 to 1996 was better than $\pm 0.1\text{‰}$.

2.6. ^{222}Rn Measurements

Under most meteorological conditions the short-lived ^{222}Rn daughters are in secular radioactive equilibrium with atmospheric ^{222}Rn , hence the atmospheric ^{222}Rn (gas) activity can be determined via its short-lived daughter activity. At the Heidelberg site, ^{222}Rn is measured with the so-called static filter method (I. Levin et al., manuscript in preparation, 1998): ambient air is continuously pumped through a quartz fibre filter, where the ^{222}Rn daughters which are attached to aerosols are quantitatively collected. The flow rate is measured with a mass flowmeter (MKS Instruments, Type 258C, München, Germany). The α decay of the ^{222}Rn daughters ^{218}Po ($\alpha_E = 6.0$ MeV) and ^{214}Po ($\alpha_E = 7.7$ MeV) is counted in situ, and the net atmospheric ^{214}Po activity is then calculated from the ^{214}Po activity on the filter. The maximum time resolution of atmospheric ^{214}Po (and ^{222}Rn) measurements with the filter method is 0.5 to 1 hour, due to the time lag between changes in the radon daughter activity and ^{222}Rn , respectively. The mean atmospheric disequilibrium, that is, the mean ratio between ^{214}Po and ^{222}Rn activity, has been determined for the Heidelberg observation site through parallel direct ^{222}Rn measurements with a slow-pulse ionization chamber [Roether and Kromer, 1978]. A mean disequilibrium of 0.704 ± 0.081 was found for different seasons and various meteorological conditions at 20 m height aboveground [Cuntz, 1998]. This mean value was used here to calculate the atmospheric ^{222}Rn activity (in Bq m^{-3} STP of wet air) from the atmospheric ^{214}Po activity.

3. Observational Data

3.1. Short-Term Variability of Trace Gas Concentrations

Nighttime inversion situations followed by strong daytime mixing frequently occur in the Rhine valley during the summer season. These situations lead to characteristic diurnal concentration variations of trace substances emitted at ground level. Concentration increases to more than 2200 ppb for CH_4 and 30 Bq m^{-3} for ^{222}Rn during strong surface inversions are observed during the night. Solar radiation-induced strong vertical mixing then leads to efficient dilution of the accumulated trace gases in the morning after sunrise. Figure 1 shows the typical trace gas pattern observed in Heidelberg in summer (August 12–17, 1996). A change of air mass origin from a situation with strong southerly winds during August 12–14 to a situation with moderate and low wind speeds of changing directions happened on August 14. As a consequence, the trace gas levels of CH_4 , CO_2 , and ^{222}Rn change from close to continental background (i.e., Schauinsland concentrations) on August 12–13 to strong diurnal variations with large concentration increases during the calm nights of August 16 and 17.

An example of a Heidelberg trace gas record for autumn 1996 is presented in Figure 2 where the regular diurnal pattern as observed in summer is less dominant. Instead, typical high-pressure systems with easterly flow often persist over several days during that season. If in such situations wind speed decreases, as on October 25, surface inversion situations build up

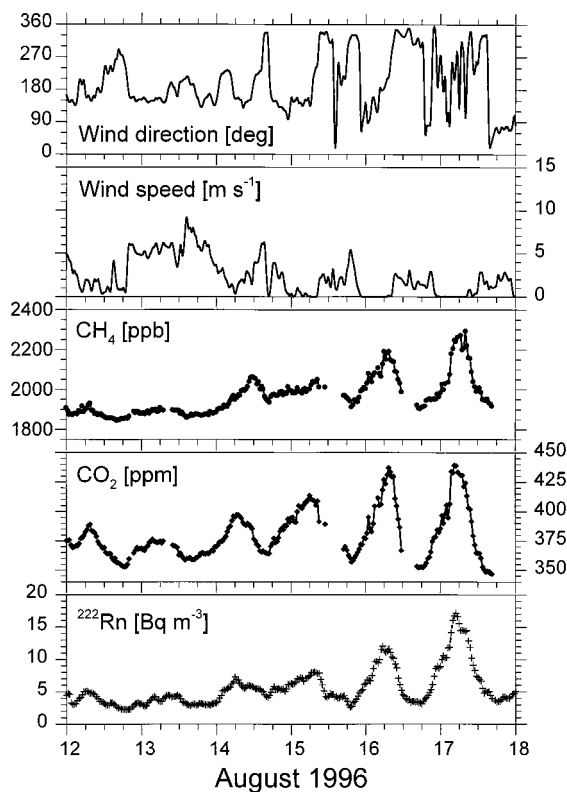


Figure 1. Trace gas concentration records at Heidelberg in summer with the typical diurnal pattern caused by nighttime inversion situations (time axis: local time).

in the Rhine valley (e.g., from October 24 to 26, 1996), with concurrent increases of CH_4 , ^{222}Rn , and also CO_2 . The strong covariance of ^{222}Rn , CO_2 , and CH_4 in summer as well as in autumn (and winter, not shown here) indicates that most of the variability in CH_4 and ^{222}Rn , but also in CO_2 , is caused by changing atmospheric mixing conditions rather than by short-term variations of the respective emissions. The good correlation between ^{222}Rn and CH_4 in summer as well as in autumn is illustrated in the scatterplots in Figures 3a and 3b, showing half-hourly values of the time series in Figures 1 and 2. The slopes of the respective regression lines are, however, different by about 30% for these two examples from August and October 1996, pointing to a seasonal change of the relative emissions of CH_4 and ^{222}Rn . For a detailed discussion and evaluation of the $\text{CH}_4/^{222}\text{Rn}$ correlations, see section 4.3.

For the period of July 1995 to December 1996 a wind sector analysis was made in order to detect possible distinct CH_4 sources in the vicinity of the Heidelberg sampling site [Glatzel-Mattheier, 1997]. No significant correlation of the $\text{CH}_4/^{222}\text{Rn}$ ratio with wind direction was found. The relevant methane emissions are obviously rather homogeneously distributed in the catchment area and may therefore be handled as a homogeneous area source.

3.2. Diurnal Cycle of the Isotopic Signature $\delta^{13}\text{C}-\text{CH}_4$

Under strong nighttime inversion situations, not only the trace gas concentration increases but also $\delta^{13}\text{C}-\text{CH}_4$ changes if the ground level source(s) are characterized by a different isotope ratio compared to atmospheric methane. Such a diurnal cycle experiment from June 1995 is shown in Figure 4. The

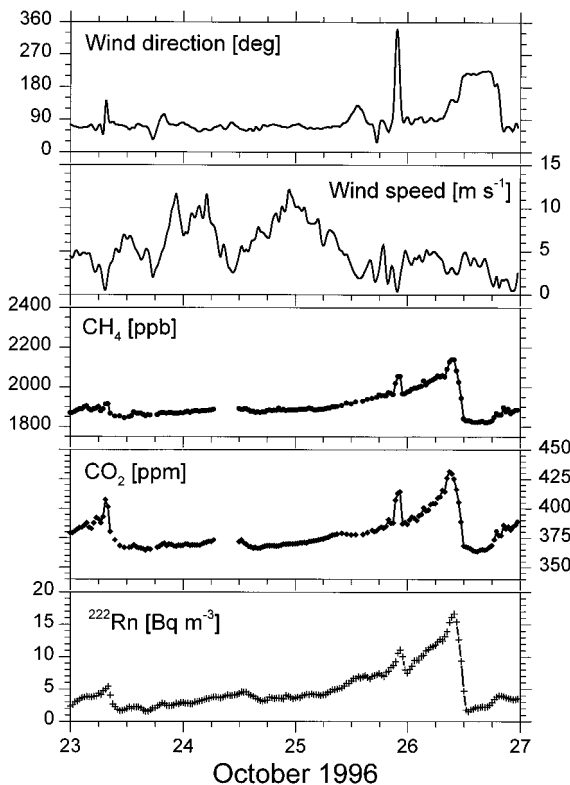


Figure 2. Typical concentration records observed at Heidelberg in autumn when inversion situations last over several days in the Rhine valley (time axis: local time).

increase in methane mixing ratio to nearly 2200 ppb during the night of June 29–30, 1995, is associated with a significant depletion by -0.8‰ in $\delta^{13}\text{C-CH}_4$. Using equation (1) (see section 4.2), the signature of the source is thus determined to $\delta^{13}\text{C} = -53.0 \pm 0.7\text{‰}$.

3.3. Long-Term Trends and Seasonality of Methane Concentration and $\delta^{13}\text{C-CH}_4$ in Heidelberg Compared to Continental and Maritime Background

High-volume air sampling for methane isotope analysis started in Heidelberg already in 1988. Since many changes

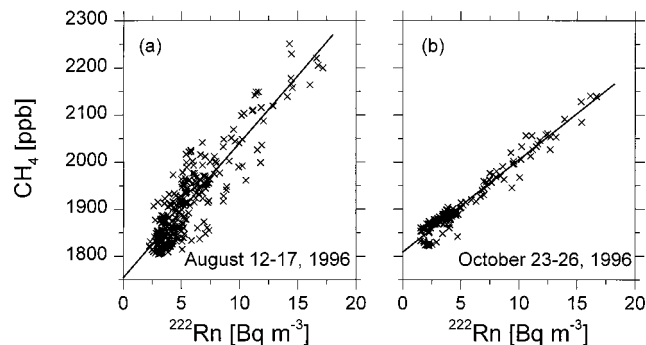


Figure 3. Correlation of half-hourly CH_4 mixing ratios with the respective ^{222}Rn activity in Heidelberg for the periods of (a) August 12–17, 1996, yielding a slope of $28.6 \text{ ppb}/(\text{Bq m}^{-3})$ and (b) October 23–26, 1996, with a slope of $19.6 \text{ ppb}/(\text{Bq m}^{-3})$ (compare Figures 1 and 2).

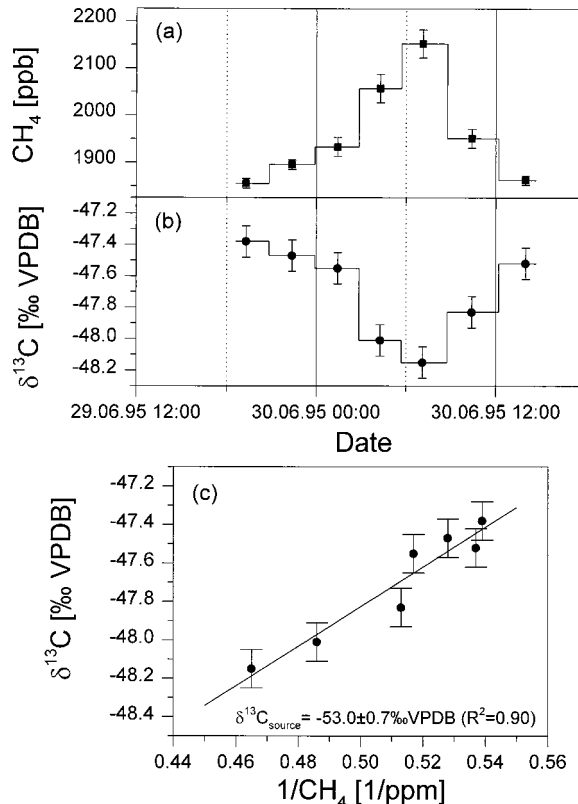


Figure 4. Diurnal cycle of (a) CH_4 mixing ratio and (b) $\delta^{13}\text{C-CH}_4$ in Heidelberg. (c) From a two-component mixing model (see section 4.2) and correlation of $\delta^{13}\text{C-CH}_4$ with inverse mixing ratio, the isotopic signature of the mean source generating the nighttime concentration increase is calculated to $\delta^{13}\text{C}_{\text{source}} = -53.0 \pm 0.7\text{‰}$ (time axis: local time).

have been made in our laboratory procedure for methane isotope analyses, the earlier isotope data from Heidelberg are not as accurate as those from 1992 onward (therefore the 1988–1991 isotope data are not discussed here). However, our record of methane mixing ratios is continuous and reliable since 1988. They have been checked in addition since 1995 against our continuous high-resolution GC measurements and showed a mean difference from this record for the monthly means of $2.6 \pm 5.1 \text{ ppb}$, which is excellent for a site with extremely variable concentrations, such as Heidelberg.

The Heidelberg CH_4 record from 1988 to 1997 is shown in Figure 5a together with the Schauinsland and Izaña measurements. For 1992 to 1997 we observe a mean offset of 170 ppb between Heidelberg and Izaña (see also Figure 6a) which is mainly caused by local and regional methane emissions in the Heidelberg catchment area. At the maritime background station Izaña the seasonal concentration variation is governed by seasonal changes in the major hemispheric sources as well as in the oxidation capacity of the atmosphere. The Izaña mixing ratio shows a slightly increasing trend of $4.4 \pm 0.6 \text{ ppb yr}^{-1}$. In contrast, at the Heidelberg site, much larger and more variable seasonal changes in the methane mixing ratio are observed. These variations are not primarily caused by changes in sources and sinks, but the particularly high mixing ratios in winter are mainly due to long lasting surface inversions in the Rhine valley as most frequently observed during this part of the year (compare Figure 2). Moreover, in autumn and winter the

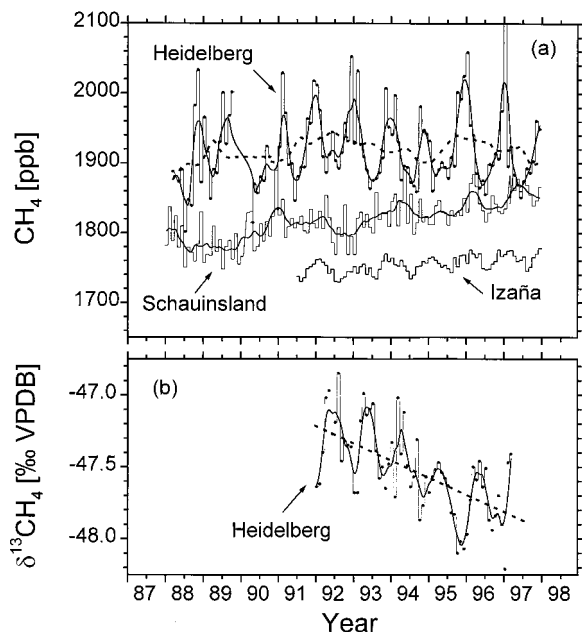


Figure 5. Monthly mean (a) concentration (1988–1997) and (b) $\delta^{13}\text{C}-\text{CH}_4$ (1992–1996) observations in atmospheric methane from ambient air in Heidelberg together with concentration data at the continental background station Schauinsland and the maritime clean air station Izaña (Tenerife). The smooth lines in the Heidelberg and Schauinsland records are spline fits of different stiffness shown as help for the eye.

boundary layer height is much lower than in summer (less than 500 m versus 1000 m or more in summer), and high-pressure systems often lead to increased continental residence times of air masses arriving in Heidelberg. Consequently, mean winter time (December to February) methane mixing ratios are more than 100 ppb higher than the summer values (June to August). Owing to this strong influence of atmospheric mixing conditions on the Heidelberg methane record, interpretation of any long-term concentration change in Heidelberg in terms of changing surface emissions can be misleading without parameterizing this climatological variability. Radon 222 would be the ideal tracer for this purpose; however, our ²²²Rn record in Heidelberg started in 1995 and covers only about half of the relevant time span (see section 4.3).

Similar to the Heidelberg methane mixing ratio, in most years large seasonal variations are observed here in $\delta^{13}\text{C}-\text{CH}_4$ with a mean amplitude of $\pm 0.2\text{‰}$ (Figure 5b) and more depleted values in winter associated with concentration maxima. The most striking feature in the Heidelberg record is the decreasing trend in $\delta^{13}\text{C}-\text{CH}_4$ of -0.14‰ yr^{-1} pointing to a significant change in the regional methane source mix. Samples from Izaña and from the high Arctic measurement site Alert in northern Canada ($82^{\circ}31'\text{N}$, $62^{\circ}18'\text{W}$, 142 m asl) of the same time period both show only $\delta^{13}\text{C}$ trends of $0.04 \pm 0.01\text{‰ yr}^{-1}$ for the period of 1992 to 1996 which is more than a factor of 3 smaller than that observed in Heidelberg [Marik, 1998].

Methane mixing ratio at Schauinsland is generally elevated by about 40–100 ppb compared to the maritime background at Izaña. No seasonality is visible here, indicating that the OH-induced summer minima as observed at Izaña are fortuitously compensated by a relatively larger influence of polluted valley air uplifted by strong convection during this part of the year.

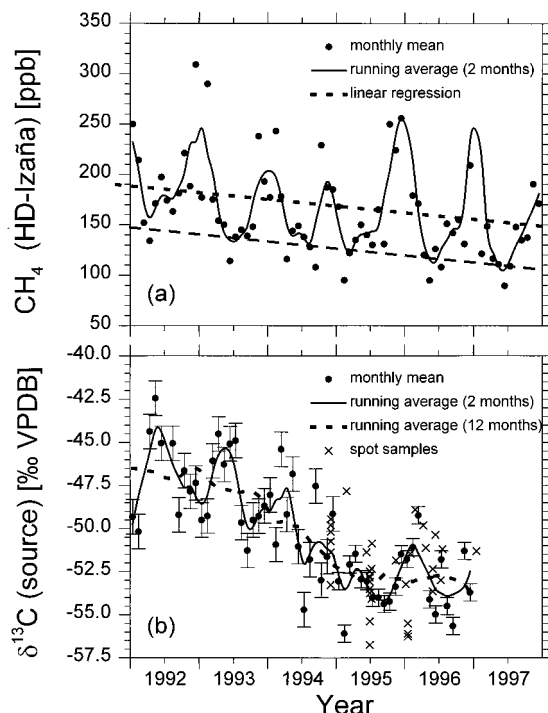


Figure 6. (a) Continental concentration excess at Heidelberg relative to the Izaña background level. The dotted line is the linear trend through all data, and the dashed line gives the trend of only the minimum concentrations. (b) Isotopic composition of the concentration excess, that is, the source methane at Heidelberg derived from a two-component mixing model with Izaña as background level; also shown is the source signature calculated from spot samples collected in 1994–1996 (compare Figure 4).

The long-term methane increase at Schauinsland from 1988 to 1997 is $6.7 \pm 1.0 \text{ ppb yr}^{-1}$, slightly higher than at Izaña for the latter part of the record. Thus there seems to be a slight increase in the CH₄ excess relative to Izaña which has to be confirmed, however, by future observations.

4. Results and Discussion

4.1. Continental CH₄ Excess at Heidelberg

Figure 6a shows the Heidelberg continental methane excess from 1992 to 1997 using Izaña as reference. Izaña, a high-elevation site at about 28°N , is, however, not the ideal reference station to calculate the regional CH₄ excess at Heidelberg. Certainly, a station like Mace Head (53°N) at the Irish coast would be better suited. However, as Izaña is the only site in mid northern latitudes of the Atlantic realm where we have measured $\delta^{13}\text{C}-\text{CH}_4$ continuously [Marik, 1998], we use here Izaña as our background reference.

The long-term trend of the mean Heidelberg excess shows a significant decrease from 1992 to 1997. Also, the yearly minima, which occur during late spring/early summer when the typical diurnal summer pattern with strong nighttime concentration increases is not well established yet, show a similar trend as the mean excess which changes from about 140 ppb in 1992 to about 110 ppb in 1997. To assess this excess trend in terms of changing sources, detailed meteorological information is needed as no ²²²Rn observations were available for the

first half of the observation period. Therefore we analyzed the continental residence time of air masses which arrived in Heidelberg [Glatzel-Mattheier, 1997] using trajectories. No significant trend between 1992 and 1996 was detectable in the mean continental residence time of air masses, and only a slight shift of trajectory paths toward more northerly directions could be observed. The second climatological variable to explain the concentration change is the boundary layer mixing height. This parameter was investigated by analyzing temperature profiles provided by the Deutscher Wetterdienst at the Wetterwarte Mannheim (~20 km to the west of Heidelberg). Here a slight trend toward lower mixing heights between 1992 and 1996 was observed [Glatzel-Mattheier, 1997]. Assuming a constant methane emission rate, this trend of the mixing height would lead to a positive trend in the concentration excess, being in contradiction to the observation. Therefore, from the analysis of meteorological parameters, we conclude that it is most likely that methane emission rates in the Heidelberg catchment area have decreased by about 20–30% in the last 6 years.

4.2. Isotope Ratio of the Mean Source in the Heidelberg Catchment Area

The isotope ratio of the mean methane source in the Heidelberg catchment area can be calculated with a simple two-component mixing model also using the Izaña observations as background reference. The mean isotope ratio of the sources causing the Heidelberg methane concentration offset ($\Delta c = c_{\text{HD}} - c_{\text{Izaña}}$) is approximated by

$$\delta^{13}\text{C}_{\text{source}} = \frac{(\delta^{13}\text{C}_{\text{HD}}c_{\text{HD}} - \delta^{13}\text{C}_{\text{Izaña}}c_{\text{Izaña}})}{\Delta c}. \quad (1)$$

The mean isotope ratio of the sources derived from this calculation is shown in Figure 6b. There is indeed a strong change in $\delta^{13}\text{C}$ of the methane source mix from $-47.4 \pm 1.2\text{‰}$ in 1992/1993 to $-52.9 \pm 0.4\text{‰}$ in 1995/1996, pointing to a significant change of the methane emissions in the catchment area of Heidelberg. It seems worth mentioning that the estimated possible bias in the Heidelberg source signature inferred from choosing Izaña as a reference site instead of a hypothetical reference site at about 50°N is less than $\delta^{13}\text{C}_{\text{source}} \approx +0.5\text{‰}$. This is due to the fact that the mean mid northern hemispheric source which is mainly responsible for the concentration and isotopic gradient between 28°N and 50°N has an isotopic signature close to that derived for Heidelberg, namely, around $\delta^{13}\text{C}_{\text{source}} \approx -53\text{‰}$ [Nisbet *et al.*, 1997].

4.3. Determination of the Large-Scale Methane Emission Rate Using ^{222}Rn as Tracer

From the covariance of the trace gas variations of CH_4 and CO_2 with ^{222}Rn in Heidelberg (section 3.1) we conclude that the short-term CH_4 variability is governed by (diurnal) changes of atmospheric mixing conditions in the surface layer. The most simple way to parameterize these changing mixing conditions is by assuming a diurnal change of the surface layer mixing height, for example, from less than 100 m during night to several hundred and up to 2000 m during the day in summer. Assuming well mixed concentrations within the surface layer, the short-term change in concentration $\Delta c_i(t)$ of any trace substance released at the surface with flux density j_i is then derived from (2):

$$\frac{\Delta c_i(t)}{\Delta t} = \frac{j_i}{H(t)}. \quad (2)$$

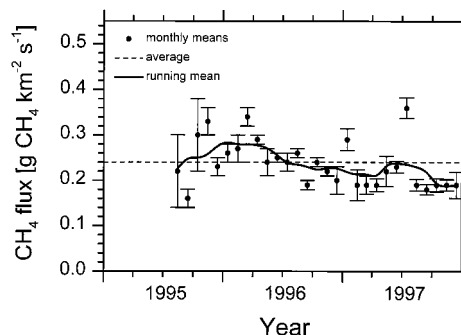


Figure 7. The ^{222}Rn -derived methane flux record for the catchment area of Heidelberg.

Since $H(t)$ are common for ^{222}Rn and CH_4 , we can eliminate $H(t)$ by combining both tracers

$$j_{\text{CH}_4} = j_{^{222}\text{Rn}} \frac{\Delta c_{\text{CH}_4}}{\Delta c_{^{222}\text{Rn}}} \quad (3)$$

Furthermore, assuming a constant and homogeneous ^{222}Rn exhalation rate from soils $j_{^{222}\text{Rn}}$ (on the seasonal timescale), we can use the atmospheric ^{222}Rn activity and the mean ^{222}Rn exhalation rate to calculate emission rates j_{CH_4} for CH_4 . This method has been used earlier by Thom *et al.* [1993] and Schmidt *et al.* [1996] to estimate methane flux densities in southwest Germany, and by Kuhlmann *et al.* [1998] to derive methane emission rates from wetlands in the Canadian Hudson Bay Lowland. Here we use this method to calculate ^{222}Rn -derived methane flux densities from daily correlations of the concentration changes (compare Figure 3) for the period of continuous CH_4 and ^{222}Rn observations in Heidelberg (July 1995 to December 1997). Only those days were included showing correlation coefficients larger than $R^2 = 0.5$ (about 60% of all observations). The results of the ^{222}Rn -derived monthly mean methane flux densities are shown in Figure 7. In this calculation we used a yearly mean ^{222}Rn exhalation rate of $56.7 \text{ Bq m}^{-2} \text{ h}^{-1}$ with a seasonality of $\pm 25\%$ observed by Schüßler [1996] for the Heidelberg area. From the continuous observations of CH_4 and ^{222}Rn we derive a mean methane flux for the Heidelberg catchment area of $(0.24 \pm 0.05) \text{ g CH}_4 \text{ km}^{-2} \text{ s}^{-1}$ for the June 1995 to December 1997 period and an annual mean of $(0.25 \pm 0.04) \text{ g CH}_4 \text{ km}^{-2} \text{ s}^{-1}$ for 1996.

4.4. Comparison of the CH_4 Flux Estimate Derived From Atmospheric Observations With CORINAIR90 Emission Inventories

The crucial question in this study is how the findings from atmospheric observations compare with CH_4 emission inventories based on statistical assessments. All countries of the European Union have compiled national emission inventories for trace gases such as CO_2 and CH_4 . On the basis of statistical data of the year 1990 a first assessment of emission inventories has been made by the European Union which is summarized in Core Inventories Air 1990 (CORINAIR90) [McInnes, 1996]. Meanwhile, this project has been continued on the basis of 1994 statistical data, and for particular source types, revised emission factors have been used in some of the national inventories. High-resolution emission inventories on the scale of Provinces down to rural districts are, however, yet only available for 1990. Therefore we have to compare our regional scale atmospheric results, starting in 1992, with this older

Table 1. Comparison of CORINAIR90 Emission Inventories of the 36 and the 150 km Catchment Areas With Results From the Atmospheric Approach

	36 km Radius	150 km Radius
Source type		
Waste treatment	54.5 kt yr ⁻¹	477.5 kt yr ⁻¹
Coal mining	2.6 kt yr ⁻¹	178.6 kt yr ⁻¹
Gas distribution	7.9 kt yr ⁻¹	69.4 kt yr ⁻¹
Cattle breeding	11.5 kt yr ⁻¹	211.0 kt yr ⁻¹
Others	3.3 kt yr ⁻¹	35.5 kt yr ⁻¹
Total source	79.8 kt yr ⁻¹	972.0 kt yr ⁻¹
Surface area	4,409 km ²	65,748 km ²
Methane flux		
CORINAIR90	0.57 g km ⁻² s ⁻¹	0.47 g km ⁻² s ⁻¹
Atmospheric approach (1992)	0.30 ± 0.06 g km ⁻² s ⁻¹	0.30 ± 0.06 g km ⁻² s ⁻¹

Numbers are given in kt CH₄ yr⁻¹ and in g CH₄ km⁻² s⁻¹, respectively.

CORINAIR90 data set for the Heidelberg catchment area. As we could calculate ²²²Rn-derived CH₄ fluxes only for the years 1995–1997, we used the yearly mean 1996 emission value of 0.25 g CH₄ km⁻² s⁻¹, the mean observed 1996 concentration excess in Heidelberg of 157 ppb, and its mean trend from 1992–1997 of -9 ppb yr⁻¹ (or approximately 5% yr⁻¹) to extrapolate a ²²²Rn-derived CH₄ flux for 1992, namely, 0.30 ± 0.6 g CH₄ km⁻² s⁻¹. The flux, if linearly extrapolated back to 1990, would be 10% higher than in 1992. However, reliable data of the isotopic signature of this excess are only available from 1992 onward. Therefore, for consistency, we will henceforth compare the 1992 atmospheric results with the 1990 CORINAIR data, thus accepting a possible bias of about 10%.

For the comparison with statistical emission inventories, determination of the regional catchment area of the Heidelberg observational site is needed, which is a nontrivial task. We estimated a lower boundary for the (nighttime) catchment area by using the frequency distribution of nighttime wind velocities. The mean nighttime wind velocity (2200 to 0600 local time) varies between 3.5 m s⁻¹ and 4 m s⁻¹ for different years. On average, more than 90% of the situations have wind speeds higher than 1.25 m s⁻¹. Thus, using this critical velocity of 1.25 m s⁻¹, and a duration of a nighttime inversion situation of 8 hours, we calculate a distance of 36 km for an air mass to travel within this particular situation. This distance of 36 km is therefore assumed as lower limit of the catchment radius. The respective catchment area, as considered in the CORINAIR statistic, covers a real surface area of 4409 km² and includes the following cities and districts: Rhein-Neckar, Bergstrasse, and Neckar-Odenwald as well as the cities of Bad Dürkheim, Frankenthal, Heidelberg, Ludwigshafen, Mannheim, Speyer, and Worms. As an upper limit of the potential catchment area, we simply include all administrative districts surrounding the 36 km catchment area (Südhessen, Mittelhessen, Nordbaden, Nordwürttemberg, Rheinhessen-Pfalz, Saarland, Koblenz, Trier, Unterfranken, and Department Bas Rhin (France)). This larger catchment area has a radius of approximately 150 km around Heidelberg.

Table 1 summarizes the results from CORINAIR90 emission inventories integrated over the two catchment categories. Also included in Table 1 are the total surfaces of the districts in the two catchment areas as well as the individual contributions from the four most important source types accounting for more than 95% of emissions, such as waste treatment (landfills), coal mining, gas distribution networks, and cattle breeding. Obviously, for both catchment areas the CORINAIR90

inventories are significantly higher by a factor of 1.5–1.9 if compared with the results from our atmospheric approach. As the total uncertainty of the atmospheric approach is estimated to be less than 30%, the statistical database as well as the emission factors used in CORINAIR90 for the dominating CH₄ sources had to be critically assessed first. In this context the isotopic signature of the mean source derived from our atmospheric measurements will be used, noting that the respective value ($\delta^{13}\text{C} = -47.4 \pm 1.2\%$ for 1992) and the isotopic signatures of the individual sources provide additional constraints on the actual source apportionment.

4.5. Characterization of CH₄ Sources in Southwest Germany

4.5.1. Waste treatment. One important source type in the Heidelberg catchment areas are landfills. As compiled by Schön *et al.* [1993], methane emissions from landfills can vary by more than 1 order of magnitude depending on the particular waste treatment. In CORINAIR90 for Germany the total CH₄ emission from landfills in 1990 has been estimated to 2200 kt CH₄ yr⁻¹ based on the total deposited waste in preceding years. A range of turnover times of 6–12 years for organic waste to be converted to CH₄ by bacteria was assumed leading to a possible range of emissions of 1800–3100 kt CH₄ yr⁻¹. In CORINAIR90, German CH₄ emissions from landfills on the district level have been assumed to be proportional to the respective population density with the total German emissions to sum up to 2172 kt CH₄ yr⁻¹, not significantly different from the estimate by Schön *et al.* [1993]. The isotopic signature of methane released from landfills has been measured at various sites in Europe and showed very consistent values with a mean $\delta^{13}\text{C}$ of $-55.4 \pm 1.4\%$ [Bergamaschi *et al.*, 1998]. Other non-landfill methane emissions associated to waste treatment are in the order of 1–2% of all sources and will in the further discussion be added to the landfill emissions.

4.5.2. Coal mining. Methane emissions from coal mining in Germany are rather well determined due to safety reasons [Schön *et al.*, 1993]. The emission factor for hard coal has been estimated to 20.8 m³ CH₄/t leading to a total emission of 1170 kt CH₄ yr⁻¹ for Germany. In CORINAIR90 a slightly different number of 1219 kt CH₄ yr⁻¹ was used which includes storage as well as mining of soft coal (1% of the total). The estimated uncertainty of this figure is 40%. The isotopic signature of hard coal associated gas in southwest Germany ranges from $\delta^{13}\text{C} = -50$ to -21% [Teichmüller *et al.*, 1970]. Recent Heidelberg measurements on exhaust gas from coal mining in west Ger-

many (Saarland) showed a mean value of $\delta^{13}\text{C} = -33.9 \pm 1.0\text{‰}$ [Poß, 1998].

4.5.3. Gas distribution networks. Methane emissions from natural gas distribution networks in the CORINAIR90 assessment are assumed proportional to the consumption. For Germany an emission factor corresponding to 1.3% gas loss from distribution and consumption is used, summing up to 309 kt $\text{CH}_4 \text{ yr}^{-1}$ from this source. In the Heidelberg region, gas losses are probably lower than 1% (S. Heidelberg, personal communication, 1997). The isotopic signature of natural gas from the Heidelberg distribution network has been measured at our Institute regularly since 1991. A mean value of $\delta^{13}\text{C} = -40.3 \pm 3.0\text{‰}$ was observed with systematical seasonal variations showing more depleted values of up to -50‰ in summer when supply is mainly from Russian pipelines and more enriched values of up to -30‰ during winter when supply comes mainly from northern Europe.

4.5.4. Traffic. We made a regional screening experiment in the Heidelberg area to determine methane exhaust from traffic within the city, on the highway, and in an underground parking lot [Bönisch, 1997]. When normalizing the specific CH_4 emissions to the CO_2 emissions from car exhaust, and using the CO_2 emission estimates for cars cited in CORINAIR90, our number is only slightly (25%) higher than the CORINAIR90 estimate for Germany (58 kt $\text{CH}_4 \text{ yr}^{-1}$). The isotopic signature of methane from car exhaust has been determined to $\delta^{13}\text{C} = -28.0 \pm 2.4\text{‰}$ [Bönisch, 1997], very close to that of the associated CO_2 or the original fuel, respectively.

4.5.5. Cattle breeding. A very important CH_4 source in southwest Germany are dairy cows. In an earlier study we investigated emissions from dairy cows in a modern cow shed close to Heidelberg [Marik and Levin, 1996]. From this study the best estimate for dairy cow emissions in southwest Germany is $116 \pm 10 \text{ kg CH}_4$ and $21 \pm 4 \text{ kg CH}_4$ per cow and year from enteric fermentation and excretions, respectively. These two numbers are slightly but not significantly higher than the values used in CORINAIR90, namely, 95 kg CH_4 per cow and year from enteric fermentation and 24.4 kg CH_4 per cow and year from excretions. The $\delta^{13}\text{C}$ value of methane from cows depends on their diet. It is common practice in southwest Germany to include $\sim 30\%$ maize silage (i.e., C4 plant) in the diet of cows. Levin *et al.* [1993] could show that the percentage C4 plants in the diet is directly reflected in the $\delta^{13}\text{C}$ value of the produced methane. We can therefore estimate a mean $\delta^{13}\text{C}$ value of $-63 \pm 2\text{‰}$ for methane from enteric fermentation of cows. Marik [1993] measured isotope ratios of methane from animal excretions near Heidelberg throughout a whole year. From these measurements a mean $\delta^{13}\text{C}$ value of $-58 \pm 3\text{‰}$ can be derived. The weighted mean isotopic signature of CH_4 from cows in southwest Germany can thus be estimated to $\delta^{13}\text{C} = -61.5 \pm 2.0\text{‰}$.

4.6. Revised Emission Inventory for the Heidelberg Catchment Area

On the basis of sources which have well-defined emission factors, and using the additional information on isotopic signatures of the major sources in southwest Germany, we have established a revised emission inventory for the Heidelberg catchment area. To close the emission budget, the sum of the contributions j_i from all individual sources must equal the total flux (j_{total}) derived from the observed correlations with ^{222}Rn , hence

$$j_{\text{total}} = \sum_i j_i. \quad (4)$$

Accordingly, the weighted isotope mix of the individual sources must sum up to the isotope ratio of the mean source:

$$\delta^{13}\text{C}_{\text{mean source}} = \frac{\left(\sum_i \delta^{13}\text{C}_i j_i \right)}{j_{\text{total}}}. \quad (5)$$

As we are quite confident about the statistical database and the emission factors used in CORINAIR90 for dairy cows and their excretions, we further on adopt the figures for enteric fermentation of cows and other cattle as well as their excretions from CORINAIR90. The respective isotope ratios are assumed as stated in section 4.5 for cows and their excretions. Contrary, for emissions associated with waste treatments, only the $\delta^{13}\text{C}$ isotope ratio seems well defined, while the absolute emissions generally have large uncertainties. In the fossil source group we also have quite well established isotopic information, while the total emissions are quite uncertain. For the present discussion we therefore dissected all fossil fuel associated methane sources (namely, gas production and distribution networks, coal mining, traffic, and all other combustion processes) due to their restricted range in $\delta^{13}\text{C}$ (-28‰ to -40‰). The mean isotope ratio of the fossil sources is then calculated from the ratios of the individual sources (for all combustion processes a $\delta^{13}\text{C} = -28\text{‰}$ is assumed) weighted according to the CORINAIR90 emission data. For the 36 km catchment area this mean value is $\delta^{13}\text{C}_{\text{fossil}} = -36.7\text{‰}$, for the 150 km catchment area, $\delta^{13}\text{C}_{\text{fossil}} = -35.1\text{‰}$. If we further neglect all minor CH_4 sources in the catchment area (which, according to the CORINAIR90 statistics in total contribute less than 5% to the total emissions), the remaining unknowns in our budget estimate are the absolute emissions from fossil sources and from waste treatment. These two unknowns can now be derived from (4) and (5):

$$j_{\text{total}} = j_{\text{cattle}} + j_{\text{wastes}} + j_{\text{fossil}} \quad (6)$$

$$\delta^{13}\text{C}_{\text{total source}} = \frac{(\delta^{13}\text{C}_{\text{cattle}} j_{\text{cattle}} + \delta^{13}\text{C}_{\text{wastes}} j_{\text{wastes}} + \delta^{13}\text{C}_{\text{fossil}} j_{\text{fossil}})}{j_{\text{total}}}. \quad (7)$$

In Table 2 the revised budgets, and associated uncertainties from solving (6) and (7) for the 36 and the 150 km catchment area, respectively, are presented in comparison with the CORINAIR90 emission estimates. Two findings are remarkable: (1) for both catchment areas, in the revised budget, CH_4 emissions from waste treatment are by more than a factor of 4 lower than in CORINAIR90, (2) fossil source emissions deviate between CORINAIR90 and the revised budget only by about 40 and 10% in the 36 and the 150 km catchment area, respectively. Important implications of these findings are the following:

1. Most probably, emissions from waste management are largely overestimated in the CORINAIR90 assessment. This conclusion is supported by the fact that the CORINAIR90 emission factor for landfills in Germany is the highest out of all European countries and thus is probably generally too high. In the Rhein-Neckar area, in particular, a population proportional emission factor for waste treatment as used in CORI-

Table 2. Revised 1992 Emission Budget for the 36 and 150 km Catchment Areas Based on Atmospheric Observations and Mean Source Isotopic Signatures

Source Type	36 km Radius			150 km Radius		
	Revised, kt yr ⁻¹	CAir90, kt yr ⁻¹	CAir90/ Revised	Revised, kt yr ⁻¹	CAir90, kt yr ⁻¹	CAir90/ Revised
Total ($\delta^{13}\text{C} = -47.4 \pm 1.2\text{‰}$)	41.7 ± 8.0	79	1.89	622 ± 120	962.2	1.55
Cattle ($\delta^{13}\text{C} = -61.5 \pm 3.0\text{‰}$)	11.5 ± 1.5	11.5	1.00	211 ± 20	211.1	1.00
Waste ($\delta^{13}\text{C} = -55.4 \pm 1.4\text{‰}$)	8.6 ± 5.0	54.5	6.33	102 ± 50	478.1	4.67
Fossil ($\delta^{13}\text{C} = -36.7 \pm 3.0; -35.1 \pm 3.0\text{‰}$)	21.6 ± 4.0	13	0.60	309 ± 60	273	0.88

The total emissions in the atmospheric approach were derived from the CH₄ flux of $0.30 \pm 0.06 \text{ g CH}_4 \text{ km}^{-2} \text{ s}^{-1}$.

NAIR90 seems not applicable, since solid wastes are here incinerated or composted rather than deposited.

2. It is very likely that the Heidelberg catchment area is considerably larger than the assumed lower boundary of 36 km radius, since we have no indication from direct source studies that the CORINAIR90 emission factors for fossil sources as a whole are too low by 40%. It is more likely that, at least for the 36 km catchment area, the emission factor for, for example, gas distribution networks is even lower by 30% than quoted in CORINAIR90 (see section 4.5). Therefore we conclude that the Heidelberg catchment area is probably better defined by the 150 km area.

Altogether, we come to the conclusion that CORINAIR90 emission factors for southwest Germany are probably correct within 20–30% for cattle breeding and fossil fuel associated emissions as a whole. They seem to be much too high, however, for waste treatment emissions, at least in the Heidelberg region but most probably all over Germany. In particular, the assumption that waste emissions correlate with population should be applied with caution as it may cause erroneously high emission inventories, particularly on the district and Province scale.

4.7. Possible Causes for the Observed Decrease of CH₄ Emissions From 1992 to 1997

During the period of our atmospheric observations from 1992 to 1996/1997, a 20% decrease of total methane emissions in the Heidelberg catchment area has been deduced. In addition, the isotope property of the Heidelberg concentration offset (i.e., the isotope ratio of the mean source) has changed significantly from $\delta^{13}\text{C} = -47.4 \pm 1.2\text{‰}$ in 1992/1993 to $-52.9 \pm 0.4\text{‰}$ in 1995/1996. These findings imply that the decreasing source(s) must be isotopically enriched or one or more sources must have changed their signature toward more depleted $\delta^{13}\text{C}$ values.

One important isotopically enriched source in the 150 km catchment area (on which we will henceforth concentrate on) is coal mining and storage, contributing more than 25% to the total emissions. In fact, German CH₄ emissions from coal mining have been reduced by nearly 30% from 1990 to 1994 (Statistik der Kohlewirtschaft, 1996; CORINAIR, 1996, available at <http://www.aeat.co.uk/netcen/CORINAIR>). A minor fossil source, namely, traffic, has also decreased in Germany from 1990 to 1994 by about 30–50% (CORINAIR, 1996) as the percentage of cars with catalyst has largely increased, and these cars have been shown to emit about 50% less CH₄ than cars without catalyst [Bönisch, 1997]. Also, the number of dairy cows in southwest Germany has decreased by about 15% (Statistisches Landesamt Baden-Württemberg, 1997, available at <http://www.statistik.baden-wuerttemberg.de>), and recent numbers of solid waste production in southwest Germany show

a decrease by more than 37% since 1990 (Statistisches Landesamt Baden-Württemberg, 1997).

The total change in methane flux can therewith be well accounted for from known emission changes. It is harder, however, to quantitatively explain the total $\delta^{13}\text{C}$ change in the mean source mix by $(-4.5 \pm 1.4)\text{‰}$. Taking into account the change in isotopic signature of the fossil sources leads to a 1996 value of this source of -37‰ in the 150 km catchment area (1990: $\delta^{13}\text{C} = -35.1\text{‰}$, section 4.6). Considering further the absolute change in emissions, this is still not sufficient to account for the observed change in the atmosphere. Thus other factors, mainly influencing the isotopic signature of the regional CH₄ sources, must have changed in addition. In this context, one candidate is the isotope ratio of natural gas supply to southwest Germany: a large company close to Heidelberg has changed its gas supply since 1995 to pure Russian gas which is by more than 10‰ depleted compared to the public Heidelberg gas supply and may also contribute to the isotopic change observed in the atmosphere. Contrary to 1992, the $\delta^{13}\text{C}$ budget in 1995/1996 could not be quantitatively closed based on our present information about the major regional sources (the largest uncertainty being due to the yet unknown changes in methane emissions from coal mining in our catchment area). In spite of that, the regional source apportionment as well as its change from 1992 to 1996 could be quantified within $\pm(20$ to 30)%.

5. Conclusions

A 6-year record of continuous methane concentrations in Heidelberg combined with $\delta^{13}\text{C}$ -CH₄ and atmospheric ²²²Rn observations was used to estimate methane emissions in the regional catchment area. The results were compared with statistically derived emission inventories from CORINAIR90. The statistical inventory turned out to overestimate total emissions by at least 50%, which is most probably due to an incorrect population-proportional emission factor for solid waste deposits. In contrast, emission factors for fossil fuel sources (coal mining and gas distribution networks) and cattle breeding could be verified within an uncertainty range of 20 to 30%, based on isotopic constraints.

The results from this study clearly demonstrate that national emission inventories, which are based on statistical source compilations and emission factors, can be validated through atmospheric observations if suitable tracers such as ²²²Rn measurements and source markers such as isotope ratios are included in such studies. In particular, changes of emissions of the order of 10% can significantly be detected through atmospheric measurements over a time period of several years even on the regional scale. Thus the method presented here turned

out to provide a very powerful tool to verify national emission reductions such as agreed upon in the Kyoto Protocol to the UN Framework Convention on Climate Change.

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