Verification of greenhouse gas emission reductions: the prospect of atmospheric monitoring in polluted areas

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Independent verification of greenhouse gas emissions reporting is a legal requirement of the Kyoto Protocol, which has not yet been fully accomplished. Here, we show that dedicated long-term atmospheric measurements of greenhouse gases, such as carbon dioxide (CO₂) and methane (CH₄), continuously conducted at polluted sites can provide the necessary tool for this undertaking. From our measurements at the semi-polluted Heidelberg site in the upper Rhine Valley, we find that in the catchment area CH₄ emissions decreased on average by 32 ± 6% from the second half of the 1990s until the first half of the 2000s, but the observed long-term trend of emissions is considerably smaller than that previously reported for southwest Germany. In contrast, regional fossil fuel CO₂ levels, estimated from high-precision ¹⁴CO₂ observations, do not show any significant decreasing trend since 1986, in agreement with the reported emissions for this region. In order to provide accurate verification, these regional measurements would best be accompanied by adequate atmospheric transport modelling as required to precisely determine the relevant catchment area of the measurements. Furthermore, reliable reconciliation of reported emissions will only be possible if these are known at high spatial resolution in the catchment area of the observations. This information should principally be available in all countries that regularly report their greenhouse gas emissions to the United Nations Framework Convention on Climate Change.

Keywords: carbon dioxide observations; radiocarbon; fossil fuel CO₂; methane observations; ²²²Rn; emission inventories

1. Introduction

In order to limit global anthropogenic warming to less than 2°C, industrialized nations committed themselves to reduce their greenhouse gas (GHG) emissions by 80 per cent by the year 2050 compared with 1990. If an international post-Kyoto agreement can be achieved, Europe attempts to reduce its emissions by 30 per cent already within the next decade (by 2020), otherwise a reduction of 21 per cent

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is envisaged for this time span. Presently, Europe (i.e. the EU-27) is responsible for 11–12% of global anthropogenic GHG emissions. These consist mainly of CO₂ emissions from burning of gas, coal and oil, but also of CH₄ emissions associated with waste treatment, animal farming as well as production and distribution of fossil fuels, along with nitrous oxide (N₂O) emissions from agriculture and industrial processes [1].

As a consequence of the Kyoto Protocol, EU-15 GHG emissions in 2008 were approximately 6.2 per cent below those of the reference year 1990, and there is a good chance to reach the reduction target of 8 per cent or even more in the Kyoto commitment period 2008–2012, if all existing and planned additional measures are fully implemented [1]. However, all of these officially reported data on GHG emissions and their apparent reductions are based on statistical information on the sources and source-specific emission factors, both associated with uncertainties that are of the same order of magnitude as the reductions themselves or even larger. For example, differences among the estimates of some national European fossil CO₂ emissions, including those reported to the United Nations Framework Convention on Climate Change (UNFCCC) are as large as 38 per cent [2]. This points towards a strong need for validation of these so-called ‘bottom-up’ estimates; but do we have the tools at hand to verify these reported emissions and respective reductions? The answer is conditionally yes: global atmospheric GHG trends and dedicated regional concentration measurements, if systematically conducted over a sufficiently long time span and accompanied by bottom-up emission inventory assessments, are expected to provide the required independent verification.

Verification of emissions is most simple with very long-lived and purely anthropogenic GHGs such as SF₆. Here, the global mean annual increase rate in the atmosphere directly corresponds to its annual emission figure. Indeed Levin et al. [3] could recently show that UNFCCC-reported SF₆ emissions by industrialized nations in the last 15 years are most probably underestimated by up to a factor of two. For CH₄ over the European region, which is also dominated by anthropogenic emissions, Bergamaschi et al. [4] also report discrepancies between the so-called ‘top-down’ inverse atmospheric transport model estimates based on atmospheric observations and respective national bottom-up reported emissions that are of the order of 40 per cent. When assuming overall uncertainties of ±30 per cent for this comparison, they are, however, still consistent with each other. Not only do the absolute emissions not agree reasonably between bottom-up and top-down estimates but, even more importantly in the context of Kyoto reporting, the emission trends deviate as well. These, however, can be estimated from atmospheric inversions of regional observations with much better confidence than total absolute fluxes (e.g. any possible bias in modelled atmospheric transport causes much more bias in absolute emissions estimates than in relative emissions changes) [5]. In both cases, the discrepancies between bottom-up inventory-based and top-down atmospheric observation-based emission estimates, therefore, point to an urgent need for more accurate bottom-up emissions estimates, i.e. improved and more realistic source statistics and emission factors, but also for the need of a dense network of continuous and precise atmospheric monitoring. Levin & Rödenbeck [6] were able to demonstrate that a reduction of regional fossil fuel CO₂ emissions of less than 10 per cent can be verified within a time period of only 5 years in the catchment area of a semi-polluted
measurement site with moderately high (of the order of 10 ppm) regional fossil fuel CO₂ levels. This attempt, performed in Heidelberg, was based on quasi-continuous high precision ¹⁴CO₂ observations and dedicated modelling, to account for the variability of atmospheric transport.

In the following discussion, we extend this earlier study on fossil fuel CO₂ by Levin & Rödenbeck [6], adding measurements of the second most important anthropogenic GHG, methane. Emissions reductions for CH₄ since 1990 of up to 50 per cent have been reported for a number of countries in Europe, including Germany. Contrary to CO₂ where emissions changes since 1990 occurred mainly in the eastern region owing to the close-down of large industries, CH₄ emission reductions are also reported for the southwestern region of Germany, namely the catchment area of Heidelberg where our long-term measurements have been conducted. Therefore, CH₄ can act as a test case for our proposed observation-based approach to verify emissions reductions. As with CO₂, CH₄ measurements in Heidelberg are strongly influenced by regional anthropogenic emissions. Comparison of observed trends with the trends of respective background mixing ratios will allow calculation of regional concentration offsets. Concurrent measurements of atmospheric ²²²Rn are used to separate source-driven changes from those associated with changes in atmospheric boundary layer mixing: owing to its rather homogeneous continental source with negligible marine emissions, ²²²Rn is an excellent tracer of continental air masses. Thus, continuous ²²²Rn monitoring allows estimating absolute regional trace gas fluxes, if the soil exhalation rate of ²²²Rn in the catchment area is adequately known (cf. [7–11]). The observation-based GHG trends in Heidelberg can then be compared with respective source estimates from emissions inventories in the catchment area. This attempt is critically addressed here, as providing a quantitative assessment of the proposed approach for an observations-based GHG emissions verification protocol.

2. Methods

(a) The Heidelberg sampling site

Heidelberg is a medium size city (160000 inhabitants, 49°25′ N, 8°41′ E, 116 m a.s.l.) in the densely populated upper Rhine Valley, located about 20 km southeast of the industrial area of Mannheim/Ludwigshafen. With predominantly southwesterly to southeasterly winds, the larger catchment area of the Heidelberg sampling site is the upper Rhine Valley, southwestern Germany (Baden-Württemberg) and possibly eastern France (figure 1). The topography of the Rhine Valley (approx. north–south) and the Neckar Valley (from the east) strongly influences the regional air flow and sometimes favours atmospheric inversion situations, leading to strong build-up of the trace gases CO₂, CH₄ and ²²²Rn, which are emitted in the surface layer close to the ground. While these trace gases have mainly distributed source emissions, part of the fluxes of CO₂ and also CH₄ can originate from large point sources such as power plants or large waste deposits. Still, in the Heidelberg region, a large share of the CO₂ and CH₄ emissions comes from distributed sources such as road traffic, domestic heating and agriculture.

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14\(^\text{CO}_2\) sampling and analysis in the polluted Heidelberg region started in 1976. Ambient air was taken from the roof of the Institut für Umweltphysik building (INF 366, approx. 20 m above local ground) located on the university campus in the western outskirts of Heidelberg [12]. Quasi-continuous \(^{222}\text{Rn}\) observations as well as gas chromatographic (GC) measurements of GHGs started at that site in 1995. GC concentration measurements at INF 366 were stopped in December 1998 when the institute moved to a new building (INF 229, sampling inlet at approx. 30 m height above local ground) about 500 m eastward of the old location, now situated closer to the Heidelberg city centre. There is a gap of GC measurements from January 1999 to April 2000 when concentration measurements restarted at INF 229. However \(^{14}\text{CO}_2\) sampling and \(^{222}\text{Rn}\) measurements continued at INF 366 until February 2002, and during the period of November 2000 to February 2002, these measurements were made at both sites. This allowed for an overlap and determination of a small fossil fuel CO\(_2\) difference between the two locations, caused by emissions from traffic and domestic heating in the city of Heidelberg (see below). \(^{222}\text{Rn}\) measurements did not show any systematic difference between the two locations.

Air sampling for GC analysis from the roof of the new Institut für Umweltphysik building (INF 229) was performed via two separate intake lines, one in the southeastern and one in the southwestern corner of the roof. These two lines were installed, and measured consecutively in order to detect very local contamination of GHGs from the building itself (e.g. through the air ventilation system) as well as from very local traffic. During very few occasions, data had to be rejected, i.e. if the two intake lines showed a major deviation from each other. This was based on visual inspection and was applied when the two records showed deviations which approximately corresponded to more than three times the measurement uncertainty persisting over more than 3 h. In all such cases, these deviations could be attributed to a problem with the instrumentation. Half-hourly mean values of both intake lines were then calculated and used for further evaluation.

\(b\) Gas chromatographic measurements of greenhouse gases

The combined Heidelberg GC system (Combi-GC) is designed for the simultaneous analysis of CO\(_2\), CH\(_4\), N\(_2\)O, SF\(_6\), CO and H\(_2\). It has been optimized to measure ambient concentration levels for each trace gas with a temporal resolution of 5 min [13]. It consists of two commercial gas chromatographs aligned in series, a HP5890II (Hewlett-Packard) GC equipped with a flame ionization detector (FID) for the analysis of CO\(_2\) and CH\(_4\) and an electron capture detector (ECD) for the analysis of N\(_2\)O and SF\(_6\) and a reduction gas analyser (RGA-3, Trace Analytics Inc.) for analysis of H\(_2\) and CO. Two ambient air samples, one from the southwestern and one from the southeastern corner of the institute’s roof are collected from permanently flushed intake lines and analysed sequentially, followed by analysis of a known standard gas mixture every 15 min. Ambient air is cryogenically dried to a dew point of \(-40^\circ\text{C}\) before analysis. Mixing ratios of CO\(_2\) are reported on the WMOX2007 mole fraction scale with a measurement uncertainty of better than \(\pm0.2\) ppm (1\(\sigma\)). CH\(_4\) mixing ratios are referenced to the WMO2004 mole fraction scale [14] with a measurement uncertainty of
±3 ppb (1σ). A linear response of the FID is assumed over the whole range of ambient CO₂ and CH₄ mixing ratios. For details of the measurement technique, see Hammer [13].

(c) $^{14}$CO₂ sampling and analysis

Bi-weekly, and after April 2006 weekly integrated CO₂ samples were collected in Heidelberg by chemical absorption in basic solution (NaOH) [15] and analysed for $^{14}$C activity by conventional radioactive counting [16]. Samples are only collected (from the southwestern intake line for GHG) during night-time (19.00–7.00) to avoid influence from very local CO₂ sources on the university campus. The measurement uncertainty of individual samples (1σ) was generally ±(3–5)% for all samples analysed before 2000 and ±2‰ later on.

For the overlapping period of November 2000 to February 2002, samples were collected at both Heidelberg sites to allow for adjustment of the two records and establishment of one consistent long-term sequence. A small difference between $^{14}$CO₂ at INF 366 and INF 229 was found, and an adjustment of the regional fossil fuel CO₂ offset of +6.4 per cent for the measurements at INF 366 was made as described in detail by Levin et al. [17]. A small correction of 4 to 8‰ (depending on season) for the influence of a nearby nuclear power plant (Philippsburg) was made as described by Levin et al. [12].

(d) $^{14}$C-based fossil fuel CO₂ estimation

The measured CO₂ mixing ratio CO₂meas at a polluted continental site consists of three major components, a background component CO₂bg (i.e. the mixing ratio in the free troposphere), a regional biospheric component CO₂bio and a regional...
fossil fuel component CO$_{2\text{foss}}$. The $^{14}$C/C ratios of these components in the $\Delta$-notation are respectively $\Delta^{14}$C$_{\text{meas}}$, $\Delta^{14}$C$_{\text{bg}}$, $\Delta^{14}$C$_{\text{bio}}$ and $\Delta^{14}$C$_{\text{foss}}$, where $\Delta^{14}$C is the deviation in per mil ($\%$e) of the $^{14}$C/C ratio of a sample from an internationally accepted standard activity, corrected for fractionation and decay [18]. To calculate the regional fossil fuel CO$_2$ component, we can formulate two balance equations, one for the CO$_2$ mixing ratio and one for $\Delta^{14}$C [17]:

$$CO_{2\text{meas}} = CO_{2\text{bg}} + CO_{2\text{bio}} + CO_{2\text{foss}} \quad (2.1)$$

and

$$CO_{2\text{meas}} (\Delta^{14}C_{\text{meas}} + 1000\%e) = CO_{2\text{bg}} (\Delta^{14}C_{\text{bg}} + 1000\%e) + CO_{2\text{bio}} (\Delta^{14}C_{\text{bio}} + 1000\%e) + CO_{2\text{foss}} (\Delta^{14}C_{\text{foss}} + 1000\%e). \quad (2.2)$$

We solve equations (2.1) and (2.2) to assess the fossil fuel CO$_2$ component CO$_{2\text{foss}}$ (the fossil fuel term in equation (2.2) is zero as $\Delta^{14}$C$_{\text{foss}} = -1000\%e$) yielding

$$CO_{2\text{foss}} = \frac{CO_{2\text{bg}} (\Delta^{14}C_{\text{bg}} - \Delta^{14}C_{\text{bio}}) - CO_{2\text{meas}} (\Delta^{14}C_{\text{meas}} - \Delta^{14}C_{\text{bio}})}{\Delta^{14}C_{\text{bio}} + 1000\%e}. \quad (2.3)$$

To estimate CO$_{2\text{foss}}$ from equation (2.3), we use the measured CO$_2$ mixing ratio and $\Delta^{14}$C at the polluted site (i.e. Heidelberg), and, as described in Levin et al. [17] use for $\Delta^{14}$C$_{\text{bg}}$ the measurements from the Jungfraujoch high-altitude research station in the Swiss Alps. CO$_{2\text{bg}}$ is taken from GLOBALVIEW-CO$_2$ [19]. For the time span of 1986 to 1995 where no continuous CO$_2$ measurements exist in Heidelberg, we estimated monthly CO$_{2\text{meas}}$ from the mean difference between CO$_{2\text{bg}}$ and CO$_{2\text{meas}}$ in 1996–2008 for each month, and added this mean difference to the monthly values of CO$_{2\text{bg}}$. The additional uncertainty introduced by this extrapolation on CO$_{2\text{foss}}$ is less than $\pm 0.3$ ppm, much smaller than the uncertainty caused by the $\Delta^{14}$C measurement error. $\Delta^{14}$C$_{\text{bio}}$ is estimated with the GRACE model [20] as being higher by ca. 50\% in 1986 and ca. 20\% in 2008 than the $\Delta^{14}$C value of background air. Assuming $\Delta^{14}$C$_{\text{bio}} = \Delta^{14}$C$_{\text{bg}}$ would thus systematically underestimate CO$_{2\text{foss}}$ in Heidelberg by up to 0.4 ppm (on average by 0.16 ppm).

(c) Quasi-continuous $^{222}$Rn observations and the $^{222}$Rn-Tracer-Method

Atmospheric $^{222}$Rn activity concentration is determined via its measured daughter activity using the static filter method [21]. Air intake for $^{222}$Rn daughter measurements is via a 0.5 m (8 mm inner diameter) Teflon tubing going through a window ca. 5 m below the southeastern air intake for GHGs. A constant disequilibrium factor of 0.704 between atmospheric $^{222}$Rn and its daughter $^{214}$Po was assumed for all Heidelberg measurements.

For estimates of mean GHG fluxes $j_{\text{GHG}}$ in the catchment area of Heidelberg with the Radon-Tracer-Method, we apply the following equation (for details see [11]):

$$j_{\text{GHG}} = j_{\text{Rn}} \frac{\Delta c_{\text{GHG}}}{\Delta c_{\text{Rn}}} \cdot \left(1 - \frac{j_{\text{Rn}} \cdot c_{\text{Rn}}}{\Delta c_{\text{Rn}}/\Delta t}\right). \quad (2.4)$$

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Here $j_{\text{Rn}}$ is the mean $^{222}\text{Rn}$ exhalation rate from soils, while $c_{\text{Rn}}$ is the $^{222}\text{Rn}$ activity concentration and $\Delta c_{\text{Rn}}$ its increase overnight. $\Delta c_{\text{GHG}}$ is the corresponding GHG mole fraction increase over the same time span. $\lambda_{\text{Rn}}$ is the decay constant of $^{222}\text{Rn}$ ($\lambda_{\text{Rn}} = 0.182 \text{d}^{-1}$). As we are only evaluating short-term night-time increases of $^{222}\text{Rn}$ and the respective trace gas during the period of a few hours at night (from 22.00 to 6.00), we omit the term in brackets and therewith neglect $^{222}\text{Rn}$ decay during this correlation interval. In the Heidelberg catchment area, $j_{\text{Rn}}$ has been measured to $56.7 \text{ Bq m}^{-2} \text{ h}^{-1}$ with a seasonal deviation of $-25$ per cent in winter and $+25$ per cent in summer [22].

3. Results

(a) The Heidelberg long-term trace gas records

Trace gas mixing ratios in the continental boundary layer which are released (or taken up) close to the ground generally show a large variability owing to strong source influences coupled with large diurnal and synoptic changes of atmospheric mixing. This is illustrated in figure 2 presenting the half-hourly values of $\text{CO}_2$, $\text{CH}_4$ and $^{222}\text{Rn}$ measurements performed in Heidelberg during night (from 19.00 to 7.00 local time). We are evaluating here only the nighttime values because (i) $^{14}\text{CO}_2$ sampling was only during night, (ii) $\text{CO}_2$ has also regional sinks (plant photosynthesis) during day and we want to investigate here only the source signals, and (iii) the Radon-Tracer-Method can only be applied to night-time concentration increases, i.e. during nocturnal inversion situations. While all three gases normally show large positive deviations from the marine background level (as measured at the coastal station Mace Head, Ireland [19,23]), only for $\text{CO}_2$ do we observe mixing ratios lower than in marine air (figure 2a). These concentration depletions only show up in summer and are caused by large-scale net uptake of $\text{CO}_2$ by the terrestrial biosphere while the air mass is travelling over the continent to the measurement site. For $\text{CH}_4$ that has only a very weak soil sink but various sources over the European continent, as in the Heidelberg catchment area, mixing ratios are almost always higher than the marine background level (figure 2b). The same is true for $^{222}\text{Rn}$ which has a marine background level close to zero (not shown in figure 2c).

From figure 2, it is also obvious that highest continental concentration offsets of all three gases are measured during autumn and winter when vertical mixing (convection) over the continent is weak, particularly during nights, and soil-borne trace gases accumulate in a shallow boundary layer in winter, often lasting for several days. Higher $\text{CO}_2$ emissions during winter, caused by enhanced residential heating, are thus of secondary importance, as can be deduced from the strong similarity to $^{222}\text{Rn}$ which has in fact a smaller exhalation rate during winter compared with the summer months (reduced permeability of the unsaturated soil zone caused by increased soil moisture in winter inhibits the flux into the atmosphere [22]).

Visual inspection of the regional $^{222}\text{Rn}$ and $\text{CO}_2$ offsets relative to baseline air does not suggest any long-term trend. This is, however, not the case for the $\text{CH}_4$ offset, which shows slightly larger regional concentration deviations in the first years (1996–1998) compared with the rest of the measurement period.
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Figure 2. Quasi-continuous (a) half-hourly CO$_2$, (b) CH$_4$ mole fractions and (c) $^{222}$Rn activity concentrations measured in Heidelberg (black circles, only night-time data from 19.00 to 7.00 are shown) together with marine background data from Mace Head (grey lines, taken from [19] and [23]). Note that marine background $^{222}$Rn activities are smaller than 1 Bq m$^{-3}$ and not shown here. (The gap from January 1999 until March 2000 occurred when the institute moved from INF 366 to INF 229 and GHG measurements could only be re-started after some delay.)

(b) Long-term trend of $^{14}$CO$_2$ in Heidelberg and estimate of the regional fossil fuel CO$_2$

When comparing monthly mean $\Delta^{14}$CO$_2$ measurements in Heidelberg with those at background stations (here, we use as background our measurements at the Jungfraujoch high-altitude station in the Swiss Alps from [20]), strong negative deviations from the long-term background (smooth line in figure 3a) are very obvious. These deviations are caused by regional CO$_2$ emissions from $^{14}$C-free fossil fuel sources in the catchment area of Heidelberg. Applying equation (2.3) to the Heidelberg measurements allows us to calculate monthly mean regional fossil fuel CO$_2$ offsets compared with background air (i.e. Jungfraujoch). These fossil fuel CO$_2$ offsets (figure 3b; red bars) vary strongly between summer (below 10 ppm) and winter (20 up to 40 ppm). Highest regional fossil fuel CO$_2$ offsets are often observed during January when long-lasting inversions in the Rhine Valley suppress vertical mixing. The larger domestic heating source at very low temperatures also partly contributes to this signal. Figure 3b also shows the monthly mean total CO$_2$ offset (i.e. fossil fuel CO$_2$ and biospheric CO$_2$ shown as green bars) observed in Heidelberg during night (compare figure 2a). This total offset is also largest during autumn and winter with highest values of the non-fossil part in autumn when biogenic fluxes from heterotrophic respiration are large at still relatively high soil temperatures. But also in winter, the biogenic CO$_2$.
Figure 3. (a) Monthly mean long-term night-time atmospheric $^{14}$CO$_2$ measurements in Heidelberg (red histogram) compared with background air at Jungfraujoch (smooth grey line), (b) monthly mean biospheric (green) and fossil fuel (red) CO$_2$ offsets as well as (c) $^{222}$Rn activity concentrations in Heidelberg. The monthly mean night-time total CO$_2$ offset (which is the sum of biospheric (green) and fossil fuel (red) CO$_2$) and $^{222}$Rn data were calculated from the half-hourly values in figure 2a,c. The fossil fuel CO$_2$ component of the total offset was calculated from the $^{14}$C data using equation (2.3).

flux on average contributes about half to the total observed offset, because even in winter, soil temperatures in the first 25 cm, where decomposition of organic material happens, in our region are high enough (above 0°C; U. Wollschläger 2010, personal communication) to allow for substantial soil microbial activity. The total CO$_2$ offset (but also the fossil fuel CO$_2$ part alone) shows strong seasonal variations, which compare well with those of the $^{222}$Rn activity concentration (figure 3c, compare also figure 2c). In particular, the highest values of either total CO$_2$ or of the fossil fuel CO$_2$ component are very well correlated with $^{222}$Rn. This indicates that a large part of the observed seasonality is due to the seasonality of atmospheric mixing rather than of emissions [12].

Inspection of the complete record from 1986 to 2008 does not, however, reveal any long-term change, neither of the fossil fuel nor of the total CO$_2$ offset. Annual mean fossil fuel CO$_2$ offsets will be compared with respective annual emission estimates obtained from inventory data in §3d.

(c) $^{222}$Rn-based regional CH$_4$ flux estimate

Evaluation of the half-hourly CH$_4$ and $^{222}$Rn measurements in Heidelberg reveals a very strong similarity of the diurnal variations between these two trace gases. This was already noted by Levin et al. [9]. In this earlier work we calculated $^{222}$Rn-based CH$_4$ fluxes for the Heidelberg catchment area. The complete CH$_4$
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Figure 4. (a) Individual night-time radon-based CH$_4$ fluxes calculated for the 22.00 to 6.00 correlation time window with 1σ uncertainties and (b) box plot with annual median (horizontal lines) and annual mean (black squares) results (50% of the annual data fall into the range covered by the box, the error bars indicate the standard deviations of the annual means). Night-time fluxes were also calculated for slightly shifted time windows (by ±30 min), and the annual means are plotted in (b) as open triangles.

and $^{222}$Rn records from 1996 onwards were re-evaluated here and CH$_4$/$^{222}$Rn correlations were calculated for every night where sufficient data (more than 80% of the possible half-hourly values) were available. We selected the local time period from 22.00 to 6.00 for this correlation (i.e. only the time period when a strong ground-level inversion layer had been established and concentrations of both gases were increasing), and calculated the slopes of the regression using an error-weighted least-squares algorithm proposed by Krystek & Anton [24]. Only nights with correlation coefficients of $R^2 > 0.7$ were accepted for estimates of $^{222}$Rn-based night-time mean CH$_4$ fluxes calculated using equation (2.4).

All accepted individual night-time flux data are displayed in figure 4a. On average, 10 per cent of all nights met the criteria above and were suitable for estimating $^{222}$Rn-based CH$_4$ fluxes. Note that, as in Hammer & Levin [8], we have set the selection criterion for $^{222}$Rn-based flux estimates rather strict because we need to make sure that only inversion situations with a restricted, mainly regional, source influence are evaluated. We thus had to reject synoptic events that are frequently observed during winter, because their catchment area is normally much larger than only the Rhine-Neckar area. Besides evaluating all data from the 8 h time window of 22.00 to 6.00 local time, we also investigated the effect of a half-hour time shift (both forwards and backwards) of this window. The corresponding annual mean values are plotted in figure 4b as open triangles together with the means and medians for the base time window from 22.00 to 6.00. Differences in the annual mean fluxes can be as large as 10 per cent, and owing to this large sensitivity of the $^{222}$Rn-based flux estimates to the chosen time window, we will
Figure 5. (a) Normalized annual mean regional fossil fuel CO₂ offsets as well as (d) normalized observation-based annual mean (and median) CH₄ emissions in comparison with reported emission inventory data of (b,c) fossil fuel CO₂ and (e,f) anthropogenic CH₄ for Baden-Württemberg and Germany. For Baden-Württemberg two different inventories are available \([25,26]\). For better comparison, all values have been normalized to 1996 = 100%. The uncertainties of the observed annual values in (a) and (d) are standard errors of the means calculated for FFCO₂ from (de-seasonalized) standard deviations of the monthly values and for the CH₄ flux from standard deviations in the individual years as shown in figure 4b.

Further on discuss only the mean values calculated using all three time windows. Note, however, that the (1σ) error bars reported and plotted in figures 4b and 5d are those for the base time window.

About 50 per cent of the individual flux estimates fall into a range of 0.5–1.0 mg CH₄ m⁻² h⁻¹ (boxes in figure 4b). This range compares very well with the earlier estimate of a mean CH₄ flux of 0.86 ± 0.24 mg CH₄ m⁻² h⁻¹ reported by Levin et al. \([9]\) for the years 1995–1997. For the total period investigated here...
Atmospheric monitoring of GHG emissions (1996–2008), a mean CH$_4$ flux of 0.72 ± 0.43 mg CH$_4$ m$^{-2}$ h$^{-1}$ was obtained. A strong decrease of the annual mean CH$_4$ flux of about 7 ± 2% per year from 1996 until 2001 is visible in figure 4b. It is also visible in figure 4a that the lower envelope of estimated fluxes, i.e. the annual minima of the fluxes in figure 4a, slightly decreased during the last 13 years. This also points to a decrease of CH$_4$ emissions in the Heidelberg catchment area. However, from 2001 onwards, no more decrease is observed. When fitting a linear trend curve through all annual mean data, the average decrease rate is 2.0 ± 0.9% per year, which is significant at a 2σ confidence level.

(d) Comparison of observed fossil fuel CO$_2$ offsets and $^{222}$Rn-based regional CH$_4$ flux estimates with reported emissions and their long-term changes

As shown in §3b,c, we do not observe significant changes of the regional fossil fuel CO$_2$ offset in the catchment area of Heidelberg, while $^{222}$Rn-based CH$_4$ flux estimates strongly decreased in the first half of the observation period but stayed constant or possibly slightly increased in the second half. The annual mean regional fossil fuel CO$_2$ offsets from figure 3b and the annual mean (and median, which are less susceptible to outliers) $^{222}$Rn observation-based CH$_4$ fluxes are displayed in figure 5a,d. For better comparison, we normalized all values displayed in figure 5 to the year 1996 when our continuous GHG observations start.

In order to properly compare our observation-based estimates with emission inventories requires these data at high spatial resolution. Similarly important is a correctly determined catchment area of our measurements. Trajectory analyses for Heidelberg suggest a stronger influence from southwesterly directions than from other wind sectors but they do not provide quantitative estimates of the catchment area. Levin & Rödenbeck [6] have shown with the TM3 adjoint atmospheric transport model that approximately 50 per cent of the offset signal measured in Heidelberg during nights comes from sources about 50–100 km away from the station. This is in accordance with a simple catchment area estimate based on mean local wind speed (ca 1.5–3 m s$^{-1}$) and a travelling time of 8 h from the source region to the measurement site (corresponding to the time span evaluated for the $^{222}$Rn-based CH$_4$ flux estimate). All these rough estimates show that the most relevant regions influencing the Heidelberg measurements would include the city of Heidelberg, occasionally (because this is not the main wind direction) the city of Mannheim with the neighbouring industrial area in Ludwigshafen as well as the Rhein-Neckar County. For illustration, figure 1 shows the state of Baden-Württemberg with Heidelberg city in the northeast and the dashed rectangle indicating the approximate catchment area of our measurements. The inset in the upper left corner indicates the location of Baden-Württemberg in Europe.

Every 2 years since 1994, the Landesamt für Umwelt Baden-Württemberg (LUBW) reports total GHG emissions for the state of Baden-Württemberg and for selected source sectors also on the county scale [25]. Unfortunately, consistent GHG emissions trends over the time span of 1994–2006 are only reported for Baden-Württemberg as a whole, but not at higher spatial resolution, i.e. on the county scale. Another set of emissions data can be obtained from the Statistisches Landesamt Baden-Württemberg (StaLa) [26], in this case data are available
from 1990 onwards on an annual mean basis, but also only for the whole state. Therefore, our observed trends can be compared here only with reported emissions trends of Baden-Württemberg as a whole (figure 5b,e).

As already stated by Levin & Rödenbeck [6], no emissions reductions of fossil fuel CO2 are reported for Baden-Württemberg (figure 5b). This is unique for Germany where fossil fuel CO2 emissions reductions since 1990 of almost 20 per cent have been reported (figure 5c) [27]. These reductions are mainly owing to the shut-down of industries in the 1990s in East Germany and, thus, not visible at our monitoring site in southwest Germany. Note that in the case of fossil fuel CO2 we can only compare observed trends of fossil fuel mole fraction offsets with reported trends in emissions. This is only applicable if we are confident that atmospheric mixing did not change over the period investigated. From the observed 222Rn activity concentration record (figure 2c), a significant long-term trend is not visible from 1996 to 2008, so that this approach is justified. As was shown by Levin & Rödenbeck [6], the short-term inter-annual changes of the fossil fuel CO2 offsets displayed in figure 5a could, however, indeed be partly explained by inter-annual changes of the atmospheric mixing conditions.

Looking at bottom-up CH4 emissions, reductions of more than 50 per cent have been reported for all of Germany since 1990 (figure 5f) [27] and also for the southwestern state of Baden-Württemberg (figure 5e) [26]. An almost linearly decreasing trend of 3.3 ± 0.28% per year is reported by LUBW [25] while StaLa reports a mean decrease of emissions by 4.5 ± 0.15% per year during the period of our observations [26] (figure 5e). These emissions reductions are mainly associated with changes in waste treatment [28]. Both decreasing trends are considerably larger than the mean trend estimated from the observations (i.e. 2.0 ± 0.9% per year).

4. Discussion and prospects

As outlined in §3, we do not see any long-term changes in regional fossil fuel CO2 offsets in Heidelberg compared with background air. This finding is in accordance with the emissions inventories, which also did not report any CO2 reductions for Baden-Württemberg [25,26]. However, for CH4 where relatively large emission reductions of between 3.3 and 4.5 per cent per year have been reported for Baden-Württemberg, our monitoring approach revealed only about half of this trend. However, we could also evaluate the observed and the inventory data in a different way: as we observed a strong decrease of emissions in the first part of the record and no more decrease in the second part, we could simply compare the mean observed and reported emissions of the late 1990s (i.e. 1996–2000) with those from 2001 to 2006. Doing this with the inventory data of figure 5e, we find a change of emissions by 21 ± 9% [25] and 28 ± 7% [26] between the two periods. This is smaller than the observation-based decrease of 32 ± 6%, but in agreement within the uncertainty estimates. The uncertainty values correspond to the respective standard errors of the means of the averaging periods (note that no uncertainty estimates are available for the emission inventory data for Baden-Württemberg).

The differences in the temporal behaviour between top-down atmospheric observation-based and bottom-up inventory-based CH4 results challenge a number of key questions. (i) Are regional atmospheric measurements, as performed in
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Heidelberg and presented here, generally suitable to verify (or falsify) reported bottom-up emissions? (ii) How could such a comparison/verification be made reliable? (iii) What are the limits of this method? (iv) What additional information is required to improve such an observation-based verification approach? In this context, we first address possible reasons for the differences between the bottom-up inventory-based and the top-down observation-based emissions estimates for the Heidelberg region and discuss obvious uncertainties of the two independent approaches (§4a). In the second part, we make suggestions for future requirements which could substantiate our approach of independent emission verification (§4b).

(a) Assessment of the differences between observed and reported CH$_4$ emissions trends and their uncertainties

In 2006, about half of the emissions reported for Baden-Württemberg were from biogenic systems (mainly agriculture) and half from technical devices (including ca 76% from waste deposits, ca 18% from distribution of natural gas and ca 5% from waste water treatment). Since 1994, most of the CH$_4$ emissions reductions in Germany and Baden-Württemberg were reported to be associated with changes in the waste treatment [28]. In the immediate footprint of Heidelberg, i.e. the Rhine-Neckar and Heidelberg counties (figure 1), the distribution of CH$_4$ emissions between the dominant sectors of biogenic systems and technical devices is different compared with Baden-Württemberg as a whole: in 2006, only about 33 per cent were associated with biogenic systems while about 56 per cent came from technical devices [25]. From this setting, we can conclude that CH$_4$ emission trends in the Heidelberg catchment area should not exactly follow those reported on average for Baden-Württemberg, but we would expect a larger reduction in the Heidelberg catchment area than in Baden-Württemberg. It also seems surprising that the temporal behaviour of the change is significantly different between reporting (almost linearly decreasing trend) and observation (strong decrease from 1996 until 2001, and no more changes thereafter).

There are several reasons that could explain the differences between reported Baden-Württemberg and observed Heidelberg CH$_4$ emissions trends.

— Time series of annual emission estimates. In March 2001, a new waste deposition law (Abfallablagerungsverordnung) for the deposition of domestic waste went into force in Germany. For a transition period of 5 years it was, however, still possible to deposit domestic waste as was done in the decades before, but from mid 2005 onwards, deposition of organic waste that could produce CH$_4$ was forbidden by law [29]. In view of this new waste deposition law, which had been under negotiation since the early 1990s, one can assume that transfer to new technologies (i.e. waste incineration) and associated CH$_4$ emissions reductions in a large state like Baden-Württemberg would not happen as a step change, because not all facilities in a state could be upgraded at the same time. This would explain, for example, a linear trend of state aggregated CH$_4$ emissions until 2006, as reported by LUBW [25] and StaLa [26]. However, in a smaller area with only a few waste deposit sources (e.g. the Heidelberg catchment area) one may rather expect stronger changes over shorter time intervals (or even
step changes) of aggregated emissions, i.e. when new facilities for waste treatment get into operation or old ones are upgraded. Therefore, at a site such as Heidelberg, one should not expect smooth trends of CH₄ emissions. Comparing estimated linear trends from 1996 to 2008 of observed and reported emissions thus seems to be inappropriate; a more reliable method, also in view of the uncertainty of the top-down approach, is expected to be the comparison of changes of mean values over several years.

— *Determination of the catchment area.* Estimate of the catchment area of our measurements is indeed very uncertain, but essential for a proper comparison with bottom-up emissions; it could be determined much more accurately using an adequate atmospheric transport model, run at high spatial resolution (less than 10 km) which was, unfortunately, not available for the present study. An appropriate regional transport model would also be able to provide the correct weighting function of emissions from the different sources at various distances from the measurement site.

— *Spatial resolution of bottom-up emission inventories.* Even if the catchment area of a measurement site has been accurately determined by dedicated regional modelling, we would need emission inventories at a spatial resolution high enough to be adequately compared with our top-down estimate. In the present study, these high-resolution data (in space and time) were not available. However, if the CH₄ source apportionment in the Heidelberg catchment area as well as the average trends were at least approximately comparable to those in Baden-Württemberg as a whole, comparison of inventory data averaged over the periods suggested by observed emissions changes may be justified. Therefore, although the calculated long-term trends of bottom-up and top-down estimates differ by almost a factor of two, our top-down estimates do not falsify the reported average changes (i.e. about 25% reduction between the second half of the 1990s (1996–2000) and the first half of the 2000s (2001–2006)).

— *Uncertainties of bottom-up inventories.* While reported emissions for Germany and Baden-Württemberg continue to decrease also after 2005, we do not observe any significant decreasing trend after 2001 (but perhaps even a slight increase). It is indeed very difficult to accurately determine CH₄ emissions from waste deposits, as fluxes in particular from old landfills may vary by many orders of magnitude ([30] and references therein). Even soil-covered landfills may have large undetected CH₄ leakages and emit CH₄ at much higher rates than assumed. Only direct field measurements and screening of the whole landfill area would allow for estimating reliable CH₄ emission rates from individual deposits. Continuation of our observations will be the only reliable way to tell about any future development of emissions in our catchment area.

— *Uncertainties of the top-down Radon-Tracer-Method.* Our ²²²Rn observation-based CH₄ emission estimates may be biased owing to different reasons. (i) They take into account only night-time data and exclude CH₄ spikes from point sources that are not correlated with ²²²Rn. This is indeed a valid point for criticism of our method; however, in the case of landfills, emissions are from extended ground-level distributed sources and are thus more rigorously mixed within the boundary layer than emissions from elevated point sources. Still we cannot exclude the possibility of a bias
in our $^{222}$Rn-based estimates, also because only a small fraction (ca 10%) of the observations (only those during strong inversions) could be used in the flux estimates. Again, a high-resolution regional model combined with geographical information about the relevant sources would be an adequate way to overcome this problem and largely improve observation-based emission verification. (ii) Also the time window chosen for the night-time flux estimates may bias the results. (iii) Besides that, there may be inter-annual changes of the $^{222}$Rn exhalation rate in the catchment area of our measurement site: the exhalation rate from fine-grained soils depends on soil moisture (with wet soils having less $^{222}$Rn flux [22]). As we use the same exhalation rate for every year, this may contribute to the relatively large inter-annual variation of the $^{222}$Rn observation-based flux estimates. It may even introduce a trend in our estimates, if long-term trends of soil moisture had occurred in our catchment area.

Also in the case of other GHGs there may be shortcomings of the proposed observation-based regional verification approach; but, most importantly, a reliable verification would need not only a reliable determination of the catchment area by dedicated regional modelling, but also detailed expert knowledge about the relevant sources in this catchment area, disaggregated to scales of the order of a few square kilometres.

(b) Setting the agenda to 2030

Besides mandatory reporting of GHG emissions, the Kyoto Protocol also requires independent verification of this reporting. It is accepted that globally distributed atmospheric GHG measurements are the key to understanding their sources and sinks as well as climate- and/or anthropogenically induced changes of their global budgets. In a similar way, atmospheric observations on the continental, regional and local scale can provide the necessary information to monitor changes of sources and sinks on the respective scales: making measurements in areas where actual emissions and their changes are expected to happen is the logical way to go forward.

A suitable Kyoto or post-Kyoto verification network should, therefore, use an approach based on long-term atmospheric observations nested on different complementary scales: starting on the local scale with observations close to critical emitters such as waste deposits, power plants, traffic junctions, large factories, etc. will allow estimating more reliable emission factors for these anthropogenic activities, which could then be transferred to other regions with a similar source structure. The next larger scale would include monitoring of the plume of large cities or industrial areas with catchments on the scale of 20–50 km, while on the subsequent scale, one would monitor parts of individual countries with catchment areas of several thousand square kilometres (e.g. from tall towers). Expected atmospheric signals and their variability will decrease when the monitored scale increases and modelling atmospheric mixing conditions with correspondingly nested atmospheric tracer transport models will correspondingly decrease in their complexity. On all scales transport tracers such as $^{222}$Rn with well-defined sources and sinks will be essential for model validation.
However, a critical prerequisite will also be detailed knowledge on the source distributions which are to be monitored. For UNFCCC reporting, a tremendous amount of high-resolution information has already been gathered on scales down to a few kilometres, i.e. of single towns and cities, large facilities and individual motorways, to be eventually buried in the one single number every year to be reported per country or large region. This small-scale accounting information needs to be made transparent and available as input for the regional-scale transport models. These model results could then be compared with atmospheric observations. Likewise, emission fluxes can be estimated from atmospheric observations in an inverse modelling approach, and then be compared with the inventory data. Both ways will allow for optimization of the inventory compilation on the regional scale. This information from key representative areas may then be used to improve the bottom-up inventories of the whole country concerned.

Besides a reliable modelling framework, including comparison of different transport models to reduce uncertainties in this part, the suggested top-down verification approach also requires harmonization and excellent comparability of the atmospheric observations in order not to introduce bias owing to measurement errors. Such a joint effort involving specialists from the different disciplines would have tremendous value to eventually come up with more accurate and trustable numbers, finally turning emission trading into a reliable and less volatile business.

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