

## Western European N<sub>2</sub>O emissions: A top-down approach based on atmospheric observations

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**Abstract.** We present a 3 year record of continuous gas chromatographic nitrous oxide (N<sub>2</sub>O) observations performed at the urban station Heidelberg (Germany) together with weekly flask data from a remote continental site, Schauinsland (Black Forest, Germany), and two-weekly integrated data from the maritime background station Izaña (Canary Islands). These data are supplemented by continuous atmospheric radon 222 observations. Mean rates of increase of N<sub>2</sub>O of 0.70–0.78 ppb yr<sup>-1</sup> were observed over the continent and in maritime background air (Izaña). The well-mixed continental mixing ratio was found to be higher by only 1.1 ppb (Schauinsland) and 2.4 ppb (Heidelberg) than for maritime background air. Specially tailored data selection of the Heidelberg record allowed the changing influence of a regional N<sub>2</sub>O point source (adipic acid production, BASF AG) to be clearly identified. The radon (<sup>222</sup>Rn) tracer method was applied to nighttime N<sub>2</sub>O observations at Heidelberg to estimate mean regional emissions, which changed from (161 ± 32) μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> in 1996–1997 to (77 ± 10) μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> in 1998 as a consequence of 90% emission reduction from BASF. An estimate of the continental N<sub>2</sub>O flux from southwestern Europe based on further selected Heidelberg data (only well-mixed, late afternoon situations) and observations from the Schauinsland station yielded mean N<sub>2</sub>O fluxes of (43 ± 5) μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> and (42 ± 4) μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>. These results compare well with statistical emissions inventories, when taking into account possible systematic errors of the radon tracer method of 30–35%.

### 1. Introduction

Beginning in 1980, global networks to monitor the atmospheric mixing ratio of N<sub>2</sub>O have been established by the Atmospheric Lifetime Experiment–Global Atmospheric Gases Experiment (ALE-GAGE) [Prinn *et al.*, 1990], the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory NOAA CMDL [Butler *et al.*, 1998], and others. These networks, with stations situated remotely from sources, focus on tracking long-term trends and interhemispheric gradients on the global scale. On the basis of these measurements, global and zonal budgets of N<sub>2</sub>O have been calculated [Prinn *et al.*, 1990; Khalil and Rasmussen, 1992; Bouwman and Taylor, 1996]. The spatial resolution of these observations and of the applied models is, however, not sufficient to calculate emission inventories on a continental scale, to say nothing of individual regions. Increased spatial resolution would be extremely useful, for example, to validate reduction measures within a continent, or even a country, in view of the Kyoto protocol.

On regional and local scales, trace gas fluxes are generally measured directly at the source. For example, chambers have been used to monitor the release of N<sub>2</sub>O into the atmosphere

from fertilized soils in southwestern Germany [Flessa *et al.*, 1995], yielding flux rates that range from 0 to 2700 μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>. These local measurements of source strengths are able to resolve large temporal variations of emission strengths, often accompanied by high spatial variability. However, the inhomogeneity and large temporal variation of many often poorly understood local N<sub>2</sub>O emissions make an upscaling, and thus regional budgeting, very doubtful.

Regional studies that fill the gap between the global and local scales are therefore needed to improve our estimates of emission inventories on the national level. Recently, a few such investigations were undertaken to budget greenhouse gas emissions using atmospheric observations at continental sites, where information about the sources was extracted from concentration changes on timescales of hours and days [Thom *et al.*, 1993; Schmidt *et al.*, 1996; Bakwin *et al.*, 1997; Derwent *et al.*, 1998; Levin *et al.*, 1999]. In this study we use concurrent time series of N<sub>2</sub>O and <sup>222</sup>Rn measurements from two sites in southwestern Germany (Heidelberg, in the Rhine valley, and Schauinsland, a mountain site in the Black Forest adjacent to the Rhine valley) to derive N<sub>2</sub>O emission rates by applying the <sup>222</sup>Rn tracer method [Levin, 1984; Thom *et al.*, 1993; Schmidt *et al.*, 1996; Wilson *et al.*, 1997; Levin *et al.*, 1999; Biraud *et al.*, 2000] to selected data.

Radon 222 is a radioactive noble gas with a half-life  $T_{1/2}$  of 3.8 days, i.e., a lifetime of 5.5 days, that is produced at relatively constant rates in all soils and released to the atmosphere, where it is diluted by (atmospheric) transport and radioactive decay. The <sup>222</sup>Rn flux from ocean surfaces is negligible. The atmospheric <sup>222</sup>Rn activity can thus be used to parameterize continental air mass residence times and also the dilution of ground level emissions in the atmospheric surface layer driven

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by vertical mixing. The <sup>222</sup>Rn tracer method is applied here to two different sets of situations: If nocturnal inversion situations are selected, in Heidelberg, <sup>222</sup>Rn-derived N<sub>2</sub>O emission estimates can be obtained for the local to regional scale. On the other hand, selecting late afternoon (Heidelberg) or early morning (Schauinsland) situations allows estimates of mean fluxes on the continental scale because in these conditions the local concentration measurement is representative of large-scale, well-mixed air over the continent.

## 2. Sampling and Analytical Techniques

### 2.1. Heidelberg Station

Heidelberg (49°24'N, 8°42'E, 116 m above sea level (asl)) is a medium-sized city (139,000 inhabitants) situated in the upper Rhine valley, ~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 there are also frequent easterly winds from the Neckar valley. In contrast to local winds, back-trajectories clearly demonstrate predominance of a westerly air mass influence. Since 1995, when the automated continuous gas chromatographic system (GC) was established in the laboratory of the Institut für Umweltphysik, Heidelberg, values of ambient mixing ratios taken approximately every half hour are available for nitrous oxide, carbon dioxide, methane, and, since May 1998, also sulfur hexafluoride. The air is collected from a permanently flushed stainless steel inlet line located on the roof of the institute, ~20 m above local ground. The Heidelberg institute is located on the university campus on the outskirts of Heidelberg. The use of N<sub>2</sub>O as a narcotic gas in the nearby university hospital influences the ambient N<sub>2</sub>O mixing ratios in Heidelberg on a very local scale. A second point source is a chemical company located 20 km northwest of Heidelberg in the industrial area of Ludwigshafen, which emits N<sub>2</sub>O from adipic acid production. A <sup>222</sup>Rn monitor for continuous atmospheric <sup>222</sup>Rn daughter observations was developed and installed in Heidelberg in 1995.

### 2.2. Schauinsland Station

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, in southwestern Germany, at an elevation of ~1000 m above the polluted Rhine valley. At night the station is usually above the boundary layer, while during the day, particularly in summer, the Schauinsland station mostly lies within the convective boundary layer. Duplicate 1 L samples for CH<sub>4</sub> and CO<sub>2</sub> mixing ratio analysis have been collected regularly once a week in glass flasks at Schauinsland since 1988 [Levin *et al.*, 1999]. Since September 1995 these samples have also been analyzed for N<sub>2</sub>O mixing ratio in the Heidelberg laboratory. Samples were usually taken in the morning and with wind velocities above 2.5 m s<sup>-1</sup>. This sampling criterion was chosen in order to ensure collection of well-mixed continental air that would be most representative for a catchment area with a spatial scale of several hundred kilometers [Schmidt *et al.*, 1996].

### 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 Me-

teorologia, Madrid. At this high elevation site in the North Atlantic trade wind zone, free midtroposphere conditions of this latitudinal belt prevail. Large-volume (1–1.5 m<sup>3</sup>) air samples, integrated over two weeks, were collected at Izaña in 400 L aluminum bags. Samples were then transferred into 10 L aluminum cylinders, filled to a pressure of ~150 bar using an air compressor (Bauer, Munich, Germany). After transfer to the Heidelberg laboratory, samples were analyzed for N<sub>2</sub>O and CH<sub>4</sub> mixing ratios as well as stable isotope ratios of CH<sub>4</sub> [Levin *et al.*, 1999].

### 2.4. N<sub>2</sub>O Measurement Technique

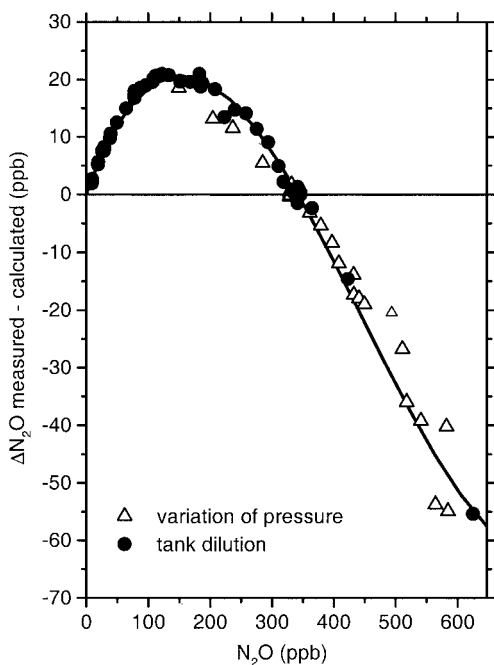
Since 1995 an automated gas chromatographic system (HP5890, Hewlett Packard) has been used for the flask and gas cylinder measurements as well as for semicontinuous measurements of N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> mixing ratios in ambient Heidelberg air [Greschner, 1995; Bräunlich, 1996; Glatzel-Mattheier, 1997; Levin *et al.*, 1999]. The GC is equipped with an electron capture detector (ECD) to determine N<sub>2</sub>O and SF<sub>6</sub>, and with a flame ionization detector (FID) and a nickel catalyst for analysis of CH<sub>4</sub> and CO<sub>2</sub>. Until March 1998, N<sub>2</sub>O was separated on two Porapak Q columns using Ar/CH<sub>4</sub> carrier gas and analyzed with the ECD with a retention time of 6.5 min. Compounds that eluted from the first column (precolumn) slower than N<sub>2</sub>O were back-flushed after 3.5 min. With this configuration it was thus possible to inject and analyze one sample every 10 min. In April 1998 the Porapak Q columns were replaced by HayeSep Q columns. This shortened the retention time to 2.9 min for N<sub>2</sub>O. In addition, analysis of SF<sub>6</sub> became possible. Since April 1998 the samples have been injected and analyzed every 5 min. The routine measurement method takes half an hour and includes two standards and 1–4 ambient air injections. In the case of automated flask analysis, three flask samples replace three ambient air measurements in a half-hourly interval.

### 2.5. Nonlinearity Correction and Calibration

Two concerns in the gas chromatographic measurement of N<sub>2</sub>O are nonlinearity of the ECD response and coelution of CO<sub>2</sub>. To determine the nonlinear response of the ECD, we applied two different procedures. First, a reference gas was injected several times at different pressures in the sample loops. Second, this reference gas was diluted with air free of N<sub>2</sub>O and CH<sub>4</sub>. As the FID response is linear within the chosen range, the CH<sub>4</sub> signal could be used to determine either the pressure or the dilution factor in the respective experiment. Figure 1 compares the expected N<sub>2</sub>O mixing ratio of the two experiments with the difference between measured (i.e., nonlinear) and expected N<sub>2</sub>O mixing ratio. The two experiments agree very well. As displayed in Figure 1, deviations from a linear response curve are very large. For example, an ambient air sample with 10 ppb more N<sub>2</sub>O than the applied reference gas would yield roughly 2.5 ppb lower N<sub>2</sub>O mixing ratios than expected. Over the range of 0–500 ppb N<sub>2</sub>O the nonlinear response of the ECD can be fit with the third-order polynomial given in (1)

$$\Delta N_2O_{\text{calcul-meas}}^{\text{lin}} = 0.78 + 0.282(N_2O_{\text{meas}}) - 0.00112(N_2O_{\text{meas}})^2 + 8.35 \times 10^{-7}(N_2O_{\text{meas}})^3. \quad (1)$$

For the restricted range of N<sub>2</sub>O mixing ratios between 250 ppb and 400 ppb a simple linear approximation provides an excellent fit (equation (2))



**Figure 1.** Nonlinear response of the ECD for N<sub>2</sub>O measurements. The difference between calculated (from dilution experiments (circles) and from variation of pressure in the sample loop (triangles)) and measured (nonlinear) N<sub>2</sub>O mixing ratios is plotted against the calculated values.

$$\Delta N_2O_{\text{calcul-meas}}^{\text{lin}} = -0.213(N_2O_{\text{meas}} - N_2O_{\text{standard}}). \quad (2)$$

Coelution of CO<sub>2</sub> is a concern because CO<sub>2</sub>, which has the same molecular weight as N<sub>2</sub>O, reacts with intermediates of N<sub>2</sub>O ionization in the ECD, thus enhancing the N<sub>2</sub>O signal. To test the interference of CO<sub>2</sub> in our system, we removed CO<sub>2</sub> with ascarite. If only a small amount of ascarite is used, the efficiency of CO<sub>2</sub> removal decreases after several injections of a reference sample. This process was used to measure the N<sub>2</sub>O signal while the CO<sub>2</sub> mixing ratios were continuously increased. The latter was simultaneously analyzed by the FID. From this experiment we determined the following correction term for CO<sub>2</sub> interference:

$$\Delta N_2O^{\text{coelution}} = (CO_2^{\text{standard}} - CO_2^{\text{sample}}) \cdot (0.12 + 0.0016N_2O^{\text{sample}})/100. \quad (3)$$

Compared to the nonlinearity correction (equation (2)), the correction for CO<sub>2</sub> interference is only small. A correction of  $\Delta N_2O^{\text{coelution}} \cong 0.2$  ppb has to be applied for an air sample containing 20 ppm–higher CO<sub>2</sub> mixing ratios than the standard gas. For the N<sub>2</sub>O mixing ratios presented here, solely the linear approximation of the ECD response curve (equation (2)) and the CO<sub>2</sub> correction have been applied, as in (4)

$$N_2O_{\text{corrected}} = N_2O_{\text{meas}} - \Delta N_2O_{\text{calcul-meas}}^{\text{lin}} - \Delta N_2O^{\text{coelution}}. \quad (4)$$

As a long-term stability and quality-control check, a so-called “target gas” is analyzed 4 times every 12 hours. The N<sub>2</sub>O mixing ratio of this target gas is 331.9 ppb, ~18 ppb higher than the standards used. From May 1996 to July 1999 the standard deviation for N<sub>2</sub>O of this target gas was  $\pm 0.4$  ppb. No significant drift or concentration change was seen after modification of the method or change of the system standard gases. We

found that only one working standard is needed for the routine measurements, as long as the ECD response curve is checked periodically over the whole range and on a daily basis with the target gas.

Calibration of our standards is based on the SIO93 scale maintained at the Scripps Institution of Oceanography [Weiss *et al.*, 1981]. We have related our standards to a gas cylinder that was kindly calibrated by R. Weiss. Furthermore, during 1995–1998, N<sub>2</sub>O measurements of compressed air cylinders from the German Antarctic Station Neumayer were performed and compared to ALE-GAGE data from Cape Grim [Prinn *et al.*, 1990], which are also related to the SIO93 scale. This comparison yielded an average difference in mixing ratio between the two southern hemispheric sites of  $0.07 \pm 0.22$  ppb over the whole 4 year period, nicely confirming our calibration scale.

## 2.6. <sup>222</sup>Rn Measurements

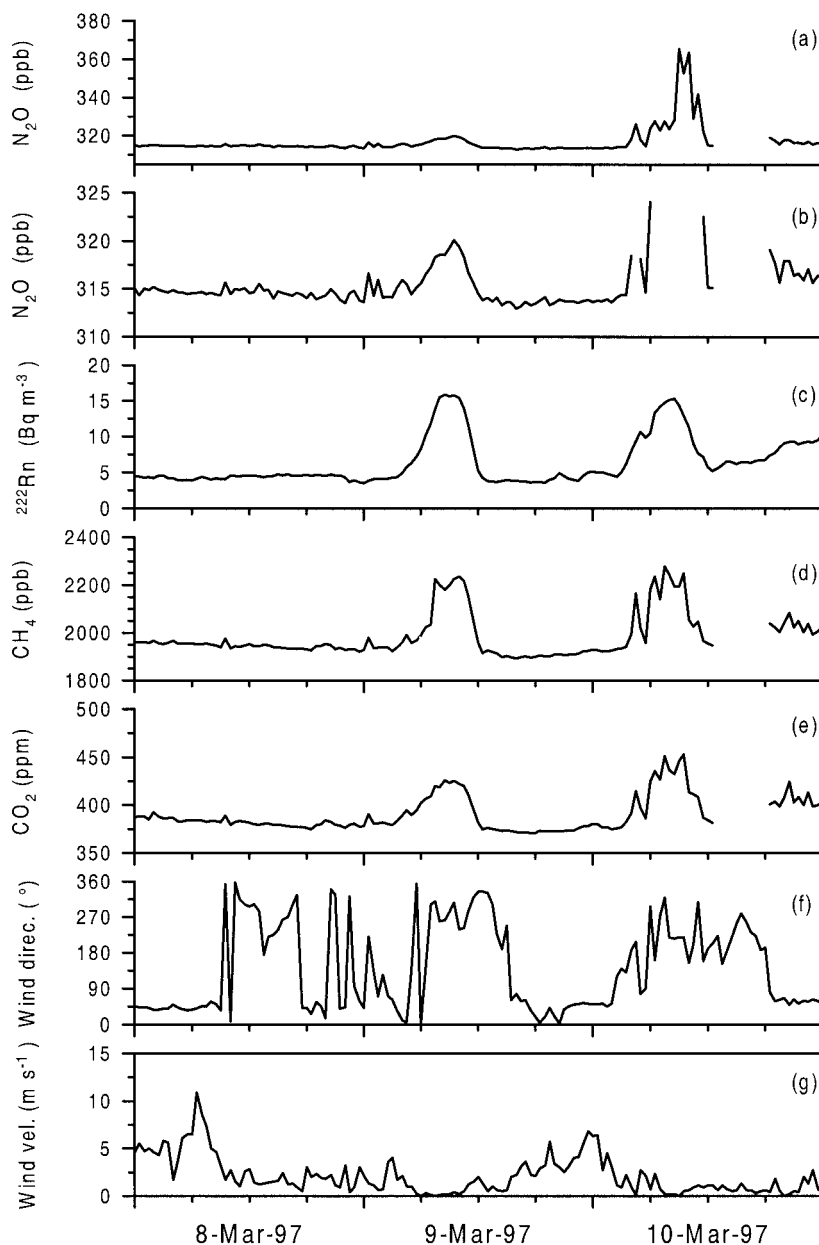
At the Heidelberg site, <sup>222</sup>Rn is measured with the so-called static filter method [Levin *et al.*, 1999]: Ambient air is continuously pumped through a quartz fiber filter, where the <sup>222</sup>Rn daughters that are attached to aerosol particles are quantitatively retained. The  $\alpha$ -decay of the <sup>222</sup>Rn daughters <sup>218</sup>Po and <sup>214</sup>Po is counted in situ, and the net atmospheric <sup>214</sup>Po activity concentration is then calculated from the <sup>214</sup>Po activity on the filter. A mean disequilibrium (mean ratio between <sup>214</sup>Po and <sup>222</sup>Rn activity) of  $0.704 \pm 0.081$  was determined for different seasons and various meteorological conditions at 20 m above ground level for Heidelberg [Cuntz, 1997]. This mean value was used here to calculate the atmospheric <sup>222</sup>Rn activity from the atmospheric <sup>214</sup>Po activity measured in Heidelberg. At the Schauinsland station, <sup>222</sup>Rn is also measured via its daughter activity. The measurement technique is described by Stockburger and Sittkus [1966]. We estimated a mean disequilibrium for Schauinsland of  $0.847 \pm 0.14$  [Schmidt, 1999].

## 3. Results and Discussion

### 3.1. Data Selection of N<sub>2</sub>O Mixing Ratios for Regional-Scale Results

As mentioned in section 2.1, in the catchment area of Heidelberg, two major sources influence atmospheric N<sub>2</sub>O mixing ratios. On a very local scale the (continuous) measurements are significantly influenced by the nearby university hospital, which uses 10.8 t N<sub>2</sub>O per year as a narcotic gas (B. Graf, personal communication, 1998). Three hospital departments are located within a radius of only 500 m of our sampling site. An even larger point source is the chemical company BASF AG in Ludwigshafen, located 20 km northwest of our sampling site. BASF emits N<sub>2</sub>O 24 hours a day as a waste product of adipic acid production. In 1990, BASF emitted 154 kt N<sub>2</sub>O, corresponding to 75% of the total German N<sub>2</sub>O emissions from adipic acid production [Stein and Strobel, 1997].

Figure 2 gives an example of the complex information hidden in the Heidelberg raw data. Nighttime inversion situations followed by strong daytime mixing lead to characteristic diurnal concentration variations of trace substances emitted at ground level. Figure 2 shows data for a change of air mass origin from a situation with strong northeasterly winds on March 8 to one with moderate and low wind speeds on March 9 and 10. As a consequence, the trace gas levels of N<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub>, and <sup>222</sup>Rn change from close to continental background on March 8 to strong diurnal variations with large concentra-

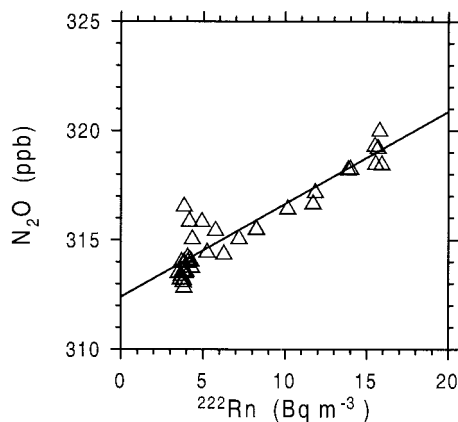


**Figure 2.** Typical record of (a and b) N<sub>2</sub>O, (c) <sup>222</sup>Rn, (d) CH<sub>4</sub>, and (e) CO<sub>2</sub> mixing ratios, along with (f) wind direction and (g) wind velocity, observed in Heidelberg during March 8–10, 1997. On Monday, March 10, the N<sub>2</sub>O mixing ratio increases very quickly because of N<sub>2</sub>O emissions from the nearby university hospital departments, which use N<sub>2</sub>O as a narcotic gas.

tion increases during the early morning on March 9 and 10. CH<sub>4</sub>, CO<sub>2</sub>, and <sup>222</sup>Rn vary strictly in parallel, with similar amplitudes on March 9 and March 10. At the same time, diurnal N<sub>2</sub>O amplitudes differ by almost 1 order of magnitude from March 9 to March 10. On March 10 (Monday morning) the N<sub>2</sub>O mixing ratio increases most dramatically around 0800 LT. The sharp form of the peak clearly indicates a point source in the immediate neighborhood of our sampling site. It turned out that this N<sub>2</sub>O spike was caused by emissions from the nearby university hospital departments, where operations typically start early Monday morning. In Figure 2b the N<sub>2</sub>O scale is expanded to resolve the less pronounced, broader N<sub>2</sub>O peak on the preceding Sunday (fewer or no operations). The whole diurnal pattern here turns out to be very similar in shape to

that of the other trace gases. The good correlation between <sup>222</sup>Rn and N<sub>2</sub>O on Sunday, March 9, as illustrated in the scatterplot of Figure 3, which shows all half-hourly measurements of that day, supports the assumption that the peak on Sunday is caused by diffuse emissions from an area source comparable to <sup>222</sup>Rn emissions originating from soil. The university campus is surrounded by intensively farmed areas, which are also typical for the whole of the upper Rhine valley. Agricultural soils and small combustion sources are the major “area-type” N<sub>2</sub>O emitters in the Heidelberg region (see Table 1).

From the example given above, it is clear that in order to extract the area source signal from the continuous record an individually designed data selection method has to be applied.



**Figure 3.** Correlation of half-hourly N<sub>2</sub>O mixing ratios with the simultaneous <sup>222</sup>Rn activity in Heidelberg for March 9, 1997, yielding a slope of 0.42 ppb Bq<sup>-1</sup> m<sup>3</sup>.

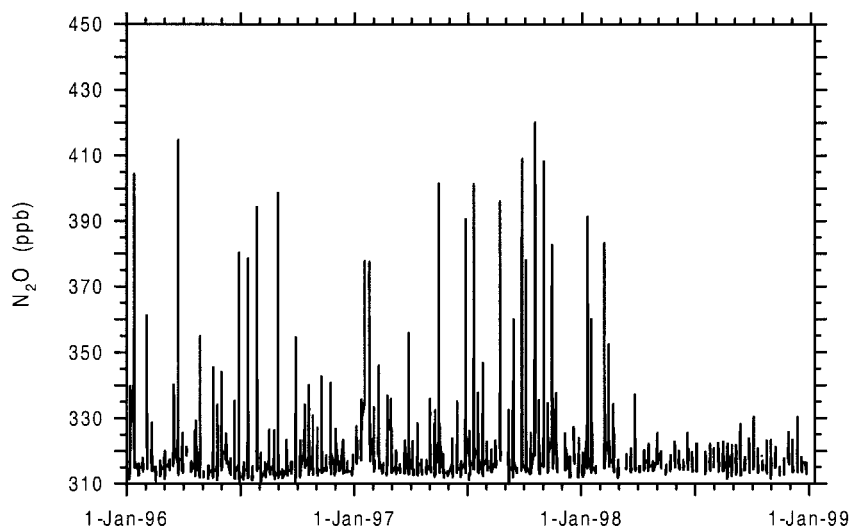
The most important step toward this aim is to remove the very local N<sub>2</sub>O spikes. As our sampling site is surrounded by hospital sources, data selection based on wind parameters is not applicable. Therefore we used a criterion based on the time of day: N<sub>2</sub>O data were only accepted for further interpretation if collected in a restricted period (2200–0600 LT) at night, when only very few, emergency operations are performed. In the following, only these selected data will be processed to derive the N<sub>2</sub>O flux estimate for the regional Heidelberg catchment area.

Besides the very local N<sub>2</sub>O emissions from hospital departments on the university campus, the extremely large N<sub>2</sub>O point source of BASF is present in the regional catchment area of the Heidelberg sampling site, and its direct influence has also to be excluded from the data set. In order to detect the effect of this source we inspected all half-hourly N<sub>2</sub>O mixing ratios measured on Saturdays and Sundays from 1996 to 1998 in Heidelberg. As illustrated in the example of Figure 2, the effect of local hospital departments should be lowest on weekends.

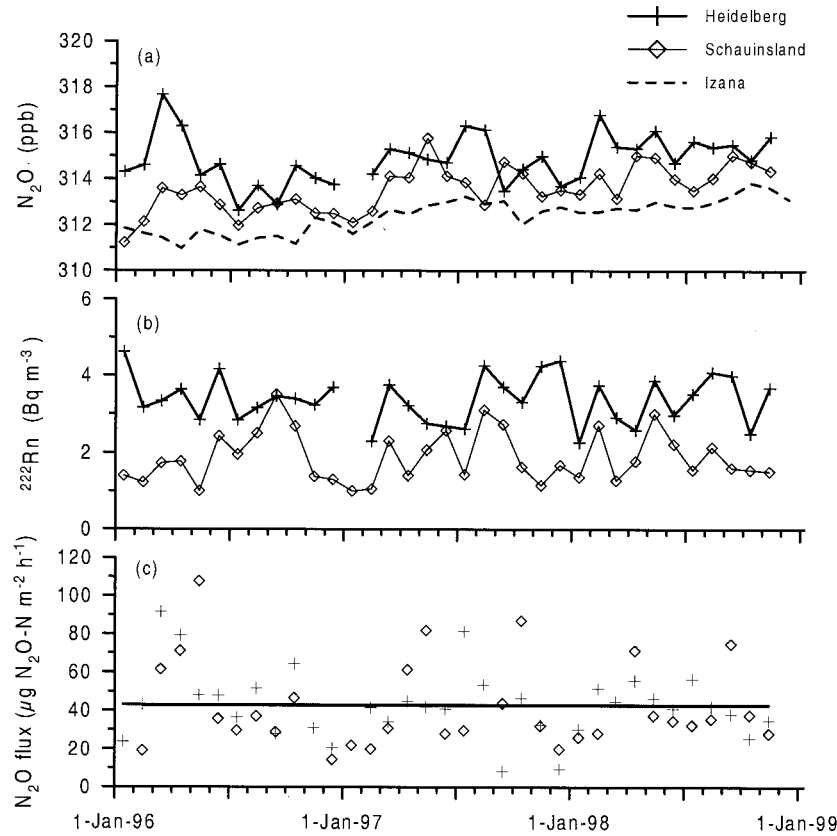
All weekend data from Heidelberg are therefore plotted in Figure 4. In 1996 and 1997, N<sub>2</sub>O spikes with concentration increases up to 100 ppb could be frequently observed. The size of such N<sub>2</sub>O peaks is in good agreement with dispersion estimates for emissions from the point source BASF. Depending on stability and wind velocity, N<sub>2</sub>O concentration increases of 6–70 ppb are predicted from a Gaussian plume model, thus agreeing well with the observed spikes. More obvious, however, is the finding that since February 1998, N<sub>2</sub>O spikes with mixing ratios higher than 20 ppb above the background level are no longer observed in Heidelberg on weekends. This result coincides with the fact that at the end of 1997, BASF implemented a catalytic process to reduce N<sub>2</sub>O emissions from adipic acid production by ~90% [BASF AG, 1996]. This reduction measure is directly visible in the Heidelberg weekend measurements.

### 3.2. Data Selection for Continental-Scale Results

In section 3.1 we exploited the short-term variations to obtain the regional fluxes (catchment area of several tens of kilometers in diameter). In order to derive flux densities that are representative of a larger area than the regional Heidelberg catchment area we performed a different selection of the Heidelberg data: As already shown in Figure 2, the lowest N<sub>2</sub>O and <sup>222</sup>Rn levels occur in Heidelberg generally in the late afternoon or early evening, when vertical mixing is strong, causing polluted air of surface layers to mix with less contaminated, free tropospheric air masses. These well-mixed air masses presumably reflect a far larger catchment area than the local diurnal variations (i.e., a diameter of several hundred kilometers). However, in contrast to records of <sup>222</sup>Rn and other trace gases the N<sub>2</sub>O record in Heidelberg during the early evening can still be affected by N<sub>2</sub>O emissions from surrounding hospital departments and BASF. To determine representative “daily” values of the N<sub>2</sub>O and <sup>222</sup>Rn excess, we therefore selected here the N<sub>2</sub>O and <sup>222</sup>Rn data between 2000 and 2200 LT (shortly before the nighttime increase) but with the additional criterion that these four half-hourly values have a standard deviation of less than 1 ppb N<sub>2</sub>O. Monthly mean



**Figure 4.** Half-hourly N<sub>2</sub>O mixing ratios measured in Heidelberg on Saturdays and Sundays for the period 1996–1998. This “weekend” selection strongly minimizes local influences by hospital departments using N<sub>2</sub>O as a narcotic gas. Strong plumes attributed to emissions from BASF disappeared from the Heidelberg record after introduction of a catalytic N<sub>2</sub>O reduction system at BASF.



**Figure 5.** Monthly mean (a) N<sub>2</sub>O mixing ratios in Heidelberg (fully selected data), at Schauinsland, and at Izaña as well as (b) <sup>222</sup>Rn activity and (c) <sup>222</sup>Rn-derived N<sub>2</sub>O flux densities for Heidelberg and Schauinsland (continental-scale approach).

Heidelberg data selected according to this criterion are shown in Figure 5a.

At the Schauinsland station, flask samples were usually taken in the morning at wind speeds above 2.5 m s<sup>-1</sup>. This sampling criterion ensures collection of well-mixed continental air with almost negligible influence of contaminated air masses from the Rhine valley. The data are shown as monthly averages together with the “background selected” Heidelberg data in Figure 5a.

### 3.3. Model Description for Regional and Continental Flux Estimates

In the present study, we apply two approaches based on the <sup>222</sup>Rn tracer method to estimate N<sub>2</sub>O emissions for (1) a regional catchment area and (2) a continental catchment area.

**3.3.1. Approach for regional-scale results.** When a regional catchment area is being considered, nighttime concentration increases of N<sub>2</sub>O and <sup>222</sup>Rn in Heidelberg are used (see, for example, Figure 2). These short-term mixing ratio variations are caused by (diurnal) changes of atmospheric mixing conditions in the surface layer, as described earlier by *Levin et al.* [1999]. From the slopes of the correlation between nighttime N<sub>2</sub>O and <sup>222</sup>Rn concentrations, as shown in the example of Figure 3, mean nighttime N<sub>2</sub>O emission rates can be estimated by using a simple one-dimensional approach: Assuming that each trace gas is released to the atmosphere at a constant rate  $\bar{j}_i$  and accumulates during the night within a well-mixed ground level inversion layer of height  $\bar{H}$  (assumed to be constant in time), the rate of change of a stable trace gas concen-

tration in this ground level atmospheric box can be described as

$$\Delta c_i(t)/\Delta t = \bar{j}_i/\bar{H}. \quad (5a)$$

It is assumed that there is no mixing of air from the free troposphere into this stable ground level inversion layer. In the case of a radioactive species such as <sup>222</sup>Rn, radioactive decay at a rate of  $\lambda c_i(t)$  has to be considered, leading to

$$\Delta c_i(t)/\Delta t = \bar{j}_i/\bar{H} - \lambda c_i(t). \quad (5b)$$

The unknown inversion layer height  $\bar{H}$ , which is taken to be the same for <sup>222</sup>Rn and N<sub>2</sub>O, is eliminated by combining (5a) and (5b).

$$\bar{j}_{\text{N}_2\text{O}} = \bar{j}_{\text{Rn}} \frac{\Delta c_{\text{N}_2\text{O}}/\Delta t}{\Delta c_{\text{Rn}}/\Delta t} \left( 1 + \frac{\lambda_{\text{Rn}} c_{\text{Rn}}}{\Delta c_{\text{Rn}}/\Delta t} \right)^{-1}, \quad (6a)$$

which, for  $\lambda c_{\text{Rn}} \ll \Delta c_{\text{Rn}}/\Delta t$ , simplifies to

$$\bar{j}_{\text{N}_2\text{O}} = \bar{j}_{\text{Rn}} \frac{\Delta c_{\text{N}_2\text{O}}}{\Delta c_{\text{Rn}}} \left( 1 - \frac{\lambda_{\text{Rn}} c_{\text{Rn}}}{\Delta c_{\text{Rn}}/\Delta t} \right). \quad (6b)$$

The N<sub>2</sub>O flux can thus be calculated from the N<sub>2</sub>O/<sup>222</sup>Rn concentration rate of change ratio and the <sup>222</sup>Rn exhalation rate  $\bar{j}_{\text{Rn}}$ , together with a correction term (in brackets) that takes into account the <sup>222</sup>Rn decay. During a typical nighttime inversion situation lasting 8–12 hours, the change in radon activity as a result of radioactive decay, offset by fresh emission from soil, is only 3–4%. Therefore we applied a mean correc-

tion factor of 0.965 when estimating <sup>222</sup>Rn-based N<sub>2</sub>O fluxes for the regional catchment area.

The <sup>222</sup>Rn exhalation rate from continental soil surfaces strongly depends on the texture of the soil, but studies show quite homogeneous behavior in a restricted area with fluxes 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 [Schübler, 1996]. Here we use a yearly mean <sup>222</sup>Rn exhalation rate of 56.7 Bq m<sup>-2</sup> h<sup>-1</sup> for the Heidelberg catchment area with a seasonal deviation of -25% in winter and +25% in summer. This figure was derived from a large number of flux measurements in the surroundings of Heidelberg summarized by Schübler [1996]. The uncertainty of the <sup>222</sup>Rn exhalation rate is estimated as ~25%.

Corresponding to the short integration time of fluxes of several hours (i.e., one night), the catchment area for the emissions estimated with this method can only be regional, namely, several tens of kilometers to 100 km. On the basis of average wind speeds a regional Heidelberg catchment area of roughly 150 km radius was estimated by Levin *et al.* [1999] for a similar methane study; the minimum radius was estimated to be 36 km. For comparison with statistical emission inventories (see section 3.6) we use the same regional catchment area as Levin *et al.* [1999], namely, 150 km.

The <sup>222</sup>Rn tracer method used to estimate N<sub>2</sub>O emissions for the regional catchment area has two major sources of uncertainties, namely, <sup>222</sup>Rn flux and N<sub>2</sub>O/<sup>222</sup>Rn regression. The mean uncertainty of the slopes is ±18%; thus the overall uncertainty of the N<sub>2</sub>O flux estimates amounts to ±30%.

**3.3.2. Approach for continental-scale results.** In order to expand the catchment area for our emission estimates to the continental scale we apply a different variant of the <sup>222</sup>Rn tracer method: Instead of evaluating short-term increases of N<sub>2</sub>O and <sup>222</sup>Rn concentrations during nighttime inversions we now focus on atmospheric concentration changes during the large-scale transport of air masses over the European continent. For this we use the selected early evening situations in Heidelberg (see section 3.2) in which intensive vertical mixing leads to minimum N<sub>2</sub>O and <sup>222</sup>Rn mixing ratios, and thus minimum local and regional source influence in the data set. Then we compare these selected data from Heidelberg and the Schauinsland site with maritime background values. The concentration differences of the two gases between the respective continental level and maritime background (where <sup>222</sup>Rn is assumed to be zero) reflect the emissions of the two gases along the path of the (maritime) air mass moving across the European continent. Assuming constant fluxes, we can again apply (5a) and (5b) to describe the temporal concentration change  $\Delta c_i$  of the respective gas in the air mass during the time  $\Delta t$  it takes to travel over Europe. As both N<sub>2</sub>O and <sup>222</sup>Rn are expected to follow the same transport path and dilution processes, we can calculate the integral emission of N<sub>2</sub>O along the transport path again using (6a) and the covariance of N<sub>2</sub>O and <sup>222</sup>Rn changes from maritime mixing ratios to the observed offset at the respective site. Again, the <sup>222</sup>Rn emanation rate over the continent has to be known, and we use here the same value as was used for the Heidelberg catchment area. For this continental-scale approach the radioactive loss of <sup>222</sup>Rn is important. Trajectory analyses show a mean residence time of  $3 \pm 1$  days for an air mass over the European continent before reaching Heidelberg [Glatzel-Mattheier, 1997]. During a continental residence time of 2–4 days the net effect of radioactive decay, offset by continuous replenishment of the radon in the

air mass by emission from the soil, corresponds to a loss of 16–29% (calculated from (6b)). As a first-order approach, we applied a common constant decay correction factor of 0.77 for both Heidelberg and Schauinsland.

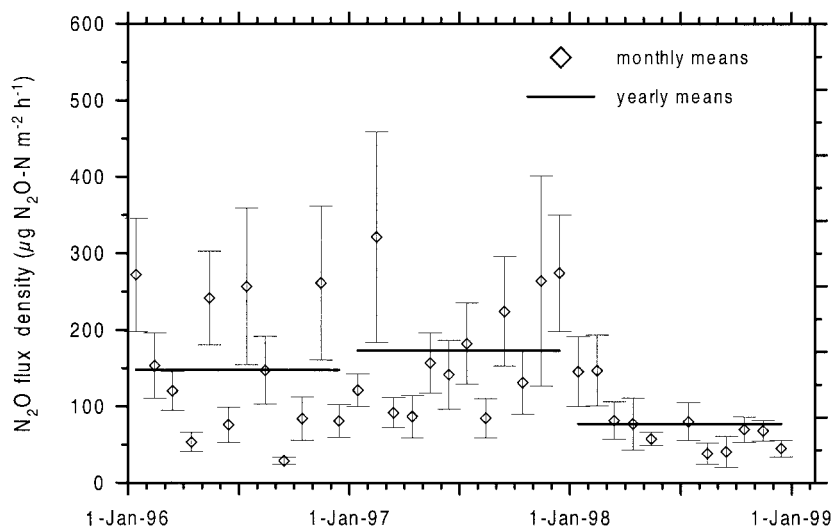
As southwesterly winds in general dominate in Heidelberg as well as at Schauinsland, the large-scale catchment area will be the southwestern part of Europe, i.e., mainly France and western Germany. Trajectories show long-range transport from northern and eastern Europe as well, although less frequently. We therefore assume that the continental catchment area concerns mainly southwestern Germany and France with a radius of the order of the distance to the Atlantic coast, i.e., roughly 500 km. As the Heidelberg and Schauinsland sites are only 180 km apart, they have a similar long-range catchment area. We therefore expect similar N<sub>2</sub>O flux densities when the continental-scale variant of the <sup>222</sup>Rn tracer method is applied to the observations at the two sites.

To estimate the overall uncertainty of the continental-scale variant of the <sup>222</sup>Rn tracer method, we have to consider three major error sources. Again, the determination of the Rn flux yields a large uncertainty (±25%). In contrast to the regional approach the radioactive decay correction for the continental-scale approach is not negligible; its uncertainty amounts to ±7%. In addition, the small concentration gradient between the continental sites Heidelberg and Schauinsland, on one hand, and Izaña, on the other, results in a measurement-based uncertainty of ±25%. The three errors add up to an overall uncertainty of ±35%.

### 3.4. Regional N<sub>2</sub>O Flux Densities Derived From Diurnal N<sub>2</sub>O Mixing Ratio Variations

The regional variant of the <sup>222</sup>Rn tracer method was used to calculate N<sub>2</sub>O flux densities on a daily basis. For the period of January 1996 to December 1998 we calculated all correlations between N<sub>2</sub>O and <sup>222</sup>Rn of the concentration changes during the night (2200–0600 LT, see section 3.1). The slopes are determined using the algorithm “fitexy” described by Press *et al.* [1993], which is independent of the value of the correlation coefficient. To derive monthly means, only those days were included which showed a  $\chi^2$  probability >0.01. This criterion also eliminates direct plumes of BASF emissions, because there is no correlation between BASF plumes and radon. On average, 8–10 days per month (25–30%) satisfy this criterion. The record of the <sup>222</sup>Rn-derived monthly mean N<sub>2</sub>O flux densities for the Heidelberg region is shown in Figure 6. The error bars in this graph represent statistical uncertainties (1 $\sigma$ ) of the monthly mean values derived from the variation of N<sub>2</sub>O fluxes from day to day. During the years 1996 and 1997 the monthly mean values of N<sub>2</sub>O fluxes show a large scatter between 50 and 300  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ . In 1998 the scatter of monthly mean N<sub>2</sub>O fluxes is clearly reduced. In addition, the error bars, i.e., the day-to-day flux variations, are on average smaller than in the years before.

In 1998 the yearly mean N<sub>2</sub>O flux in the catchment area of Heidelberg clearly shows a value half that of the previous 2 years,  $(77 \pm 10) \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  in 1998 instead of  $(148 \pm 26) \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  in 1996 and  $(173 \pm 24) \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  in 1997. This observation coincides with the dramatic N<sub>2</sub>O reduction measure of BASF in Ludwigshafen mentioned in section 3.1. Although direct N<sub>2</sub>O plumes from the BASF point source have been excluded from the flux estimate, the N<sub>2</sub>O emissions of BASF, particularly during calm nights, seem to have been dispersed in the whole upper mid-Rhine valley



**Figure 6.** Monthly mean N<sub>2</sub>O fluxes derived from the <sup>222</sup>Rn tracer method (regional approach) in the catchment area of Heidelberg. Solid lines represent the yearly average fluxes for 1996–1998.

air. In fact, from earlier studies of <sup>14</sup>CO<sub>2</sub> to derive fossil fuel emission estimates we were able to show that the atmospheric surface layer in the highly polluted and industrialized Rhine valley is a relatively well mixed one [Levin *et al.*, 1980]. Therefore we conclude that in the years 1996 and 1997 the air masses in the Rhine valley contained major contributions from the BASF N<sub>2</sub>O emissions. Possibly, they were not always perfectly dispersed, which is manifested in the relatively large scatter of the Rn-derived fluxes in these years. In 1998 the emission reductions were clearly detectable, first through missing plumes on weekends (Figure 4) and second through significantly lower <sup>222</sup>Rn-derived flux values with considerably smaller scatter.

### 3.5. N<sub>2</sub>O Fluxes From Continental Offsets

Figure 5a and 5b show the monthly mean selected N<sub>2</sub>O and <sup>222</sup>Rn values from Heidelberg (selection according to section 3.2) and Schauinsland together with maritime background data from Izaña. Compared to Izaña, both continental records (Schauinsland and Heidelberg) show clear influences of the continental N<sub>2</sub>O emissions (i.e., industrial and agricultural sources). From 1996 to 1998 we observed a mean N<sub>2</sub>O offset of (2.4 ± 1.0) ppb between Heidelberg and Izaña and (1.1 ± 0.4) ppb between Schauinsland and Izaña. No clear seasonality in

the N<sub>2</sub>O concentration is visible for any of the three stations over the period of observations. Izaña and Schauinsland mixing ratios show similar increasing trends of (0.71 ± 0.1) ppb yr<sup>-1</sup> and (0.78 ± 0.15) ppb yr<sup>-1</sup>, respectively. This rate of increase also agrees very well with global trends derived from the ALE-GAGE network (0.73 ppb yr<sup>-1</sup>) for this period [Prinn *et al.*, 1990].

Figure 5c shows the large-scale continental N<sub>2</sub>O flux densities for the Heidelberg and Schauinsland catchment areas, determined from (6a). A significant trend of the N<sub>2</sub>O flux densities is not visible in these data for the years 1996–1998. However, N<sub>2</sub>O fluxes seem generally higher during the spring at both stations. This finding corresponds to results from direct N<sub>2</sub>O flux measurements from forests and agricultural soils in southwestern Germany performed by the chamber technique [Flessa *et al.*, 1995; Papen and Butterbach-Bahl, 1999]. The authors found the highest N<sub>2</sub>O fluxes during thawing of the soils because of high microbial nitrogen turnover rates.

For 1996–1998 we obtain an average N<sub>2</sub>O flux density of (43 ± 5) µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> for Heidelberg and (42 ± 4) µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> for Schauinsland. As expected, Heidelberg and Schauinsland data reflect similar continental N<sub>2</sub>O emissions, which are only slightly lower than regional N<sub>2</sub>O flux

**Table 1.** Emission Inventories for the 150 km Catchment Area of Heidelberg Derived From CORINAIR 90 (Original) and With the Modifications CORINAIR90mod (Realistic Treatment of the N<sub>2</sub>O Emissions From BASF) and CORINAIRmod98 (Including Reduction Measures at BASF)

	CORINAIR 90	CORINAIR90mod	CORINAIRmod98
Combustion, t	4557	4557	4557
Production of nitric acid, t	4092	4092	4092
Production of adipic acid, t	20,920	50,820	5082
Road transport, t	2519	2519	2519
Wastewater treatment, t	1130	1130	1130
Arable land, t	11,348	11,348	11,348
Animal breeding, t	1051	1051	1051
Total source, t	45,618	75,518	29,780
Surface area, km <sup>2</sup>	61,254	61,254	61,254
N <sub>2</sub> O flux, µg N <sub>2</sub> O-N m <sup>-2</sup> h <sup>-1</sup>	54	90	35



**Table 2.** Summary of N<sub>2</sub>O Flux Densities in  $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$  During the Period 1996–1998

	Heidelberg: Regional Approach	Heidelberg: CORINAIRmod	Heidelberg: Continental Approach	Schauinsland: Continental Approach	Germany: National Inventory	France: National Inventory	Germany: EDGAR	France: EDGAR
1996–1997	161 <sup>a</sup>	90	43 <sup>a</sup>	43 <sup>a</sup>	45	40	26	17
1998	77 <sup>a</sup>	35	42 <sup>a</sup>	40 <sup>a</sup>	35	...		

<sup>a</sup>N<sub>2</sub>O flux densities calculated from atmospheric measurements for the regional and continental catchment areas of Heidelberg and for the continental catchment area of the Schauinsland station. These flux densities are compared to the national emission inventories as well as the global emission database EDGAR.

densities in Heidelberg during 1998, i.e., after the BASF reduction measures for N<sub>2</sub>O (see section 3.1). Obviously, the very strict selection of afternoon-evening situations in Heidelberg effectively eliminated any dominating influence from local and even regional point source emissions.

### 3.6. Comparison of N<sub>2</sub>O Flux Estimates Derived From Atmospheric Measurements With Emission Inventories

We compare our N<sub>2</sub>O flux densities derived from atmospheric measurements with national emission inventories and with the global emission database EDGAR [Olivier *et al.*, 1996]. These emission inventories differ in their temporal and spatial resolution. All countries of the European Union have compiled national emission inventories for trace gases such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, SO<sub>2</sub>, and NO<sub>2</sub> with the spatial resolution of countries for 1990–1998. For the continental-scale approach with an estimated catchment area of around 500 km we can compare our results with these national inventories as well as EDGAR data for Germany and France. However, for comparison of the regional-scale approach, with a catchment area of only 150 km radius, we need an emission inventory with a far higher spatial resolution. On the basis of statistical data of 1990 a first assessment of high-resolution emission inventories has been made on the scale of provinces down to rural districts in Europe (CORINAIR 90) [McInnes, 1996]. This project has been continued on the basis of the 1994 statistical data, but until now CORINAIR 94 is solely available with the spatial resolution of countries.

Therefore we compare our regional N<sub>2</sub>O flux densities from 1996 to 1998 with this older CORINAIR 90 data set for the Heidelberg catchment area. For this purpose, a modification of CORINAIR 90 was necessary. A major problem of CORINAIR 90 is its treatment of industrial point sources. For data protection reasons, point sources of industrial emissions are added up for the whole of Germany and distributed between the provinces and rural districts by area weight. In Germany only two companies contribute to the N<sub>2</sub>O emissions from adipic acid production, which amount to ~15% of the total German N<sub>2</sub>O emission inventory. Especially for the Heidelberg region, located close to BASF, a realistic treatment of their N<sub>2</sub>O emissions is very important. We therefore made two modifications to the CORINAIR 90 database. CORINAIR90mod takes the BASF adipic acid production into account in a realistic way. Furthermore, CORINAIR-mod98 includes the reduction measures in 1998, while reflecting CORINAIR 90 in all other emission sectors. Using the 1990 statistical data in the case of N<sub>2</sub>O is plausible, as the sum of emissions was quite constant between 1990 and 1997.

Table 1 summarizes data of CORINAIR 90 and its modifications for the 150 km catchment area of Heidelberg. The realistic treatment of the N<sub>2</sub>O emissions from adipic acid pro-

duction in CORINAIR90mod leads to values a factor of 2.5 higher than in CORINAIR 90 and results in a mean N<sub>2</sub>O flux of 90  $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ . The reduction measures in 1998 then decrease the N<sub>2</sub>O flux by ~60% to 35  $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ . Table 2 compares N<sub>2</sub>O emissions derived from the atmospheric measurements (footnoted values in table) for Heidelberg and Schauinsland with the statistical ones. On the regional and continental scales both the atmospheric and statistical approaches lead to N<sub>2</sub>O emission values of similar orders of magnitude. The uncertainty of the atmospheric approach is estimated to be less than 30% for the regional-scale approach and 35% for the continental-scale approach (see section 3.3). For the statistical emission inventories no uncertainties are reported, but note that CORINAIR 90 and EDGAR differ by almost a factor of 2!

Moreover, the inventories based on statistical data do not take into account natural sources, whereas our direct measurements include them. On the basis of average values of N<sub>2</sub>O fluxes measured in German forests of various kinds [Seiler and Conrad, 1981; Schmidt *et al.*, 1988; Dong *et al.*, 1998; Papen and Butterbach-Bahl, 1999] we estimate a total natural N<sub>2</sub>O contribution for Germany of (2.1–6.6)  $\mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ . Taking this natural contribution into account leads to the general conclusion that within the estimated uncertainty not only of <sup>222</sup>Rn-derived fluxes but also of statistically derived emission inventories, the measured flux densities are comparable to the statistical ones.

## 4. Conclusions

In this study we have demonstrated that atmospheric trace gas measurements in combination with continuous <sup>222</sup>Rn observations are well suited to deriving top-down emission estimates on both regional and continental scales. In the case of N<sub>2</sub>O studied here, the precision of the concentration measurements, also at the regionally polluted Heidelberg site, was found to be particularly crucial as diurnal signals of the order of only a few ppb N<sub>2</sub>O have been used to estimate regional fluxes. The same is true for spatial N<sub>2</sub>O concentration gradients between the Atlantic Ocean and western Europe, which are even smaller, ~2 ppb or less. Provided that this high measurement precision is achieved, reliable integrated large-scale top-down <sup>222</sup>Rn-derived fluxes can be determined, which is especially important in the case of N<sub>2</sub>O, which is emitted from large-area sources (agricultural land and forests), and, moreover, in an episodic way. Under such conditions the bottom-up approach by means of direct flux chamber measurements would need an enormous effort to catch all emissions.

A particularly important finding from our study is the detection of a significant reduction of N<sub>2</sub>O emissions from adipic acid production at BASF, a chemical plant in the neighbor-

hood of the Heidelberg site. This was only possible through sophisticated data selection of the continuous Heidelberg concentration record. We can conclude, therefore, that atmospheric observations provide very important and totally independent verification of reduction measures in the frame of the post-Kyoto process.

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