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Seasonal variation of N₂O emissions in France inferred from atmospheric N₂O and ²²²Rn measurements

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[1] Nitrous oxide (N₂O) concentrations and ²²²Rn activities are measured semi-continuously at three stations in France: Gif-sur-Yvette (a semi-urban station near Paris), Trainou tower (a rural station) and Puy-de-Dôme (a mountain site). From 2002 to 2011, we have found a mean rate of N₂O increase of 0.7 ppb a⁻¹. The analysis of the mean diurnal N₂O and ²²²Rn cycles shows maximum variabilities at the semi-urban site of Gif-sur-Yvette (0.96 ppb for N₂O and 2 Bq m⁻³ for ²²²Rn) compared to the rural site of Trainou tower (0.32 ppb for N₂O and 1.3 Bq m⁻³ for ²²²Rn). The use of ²²²Rn as a tracer for vertical mixing and atmospheric transport, combined with the semi-continuous N₂O measurements, allows estimation of N₂O emissions by applying the Radon-Tracer-Method. Mean N₂O emissions values between 0.34 ± 0.12 and 0.51 ± 0.18 g(N₂O) m⁻² a⁻¹ and 0.52 ± 0.18 g(N₂O) m⁻² a⁻¹ were estimated in the catchment area of Gif-sur-Yvette and Trainou, respectively. The mean annual N₂O fluxes at Gif-sur-Yvette station correlate well with annual precipitation. A 25% increase in precipitation corresponds to a 32% increase in N₂O flux. The N₂O fluxes calculated with the Radon-Tracer-Method show a seasonal cycle, which indicates a strong contribution from the agricultural source, with the application of fertilizers in the early spring inducing a strong increase in N₂O emissions. Finally, the results of the Radon-Tracer-Method agree well with the national and global emission inventories, accounting for the uncertainties of both methods.

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1. Introduction

[2] Nitrous oxide (N₂O) is an important greenhouse gas with a global warming potential of approximately 300 times that of CO₂ at a 100-year time horizon and an atmospheric lifetime of 114 years [Forster *et al.*, 2007]. Currently, it is also the single most important substance for stratospheric ozone depletion [Ravishankara *et al.*, 2009; Wuebbles, 2009]. Global observations of the N₂O atmospheric concentration from AGAGE (Advanced Global Atmospheric Gases Experiment) and NOAA/ESRL networks indicate a mean surface concentration of approximately 324 ppb in 2010, an atmospheric increase rate of 0.75 ppb per year, and a seasonal variability between 0.32 (Trinidad Head, California) and 0.93 ppb (Barrow, Alaska), depending on the

latitude [Nevison *et al.*, 2011]. Data from background stations located mainly in the marine boundary layer were used in global inverse model studies to constrain the N₂O flux over large regions of the globe [Hirsch *et al.*, 2006], but the sparse network and the unknown bias of transport models provide a weak constraint on the spatial and temporal distribution of regional N₂O emissions.

[3] The largest anthropogenic N₂O source is intensive agriculture [Bouwman *et al.*, 2002; Forster *et al.*, 2007]. N₂O emissions from fertilized arable soils and grassland can be measured by flux chambers at a very local scale (1 m²) or, more recently, by the eddy covariance method with a footprint of less than 1 km² [Laville *et al.*, 2011]. These local measurements show that N₂O surface emissions from fertilized soils are extremely variable in space and time. The measured emissions depend on soil characteristics (pH, organic content, nitrogen availability, texture), on soil temperature and moisture content, on culture type, on the amount and type of fertilizer used, and on the timing of the fertilizer additions, as shown by Bouwman *et al.* [2002]. This complexity makes it extremely difficult to scale up the local flux measurements to regional budgets, and errors associated with regional and national flux estimates are on the order of 100–200% (CITEPA, rapport CCNUCC, Avril 2010).

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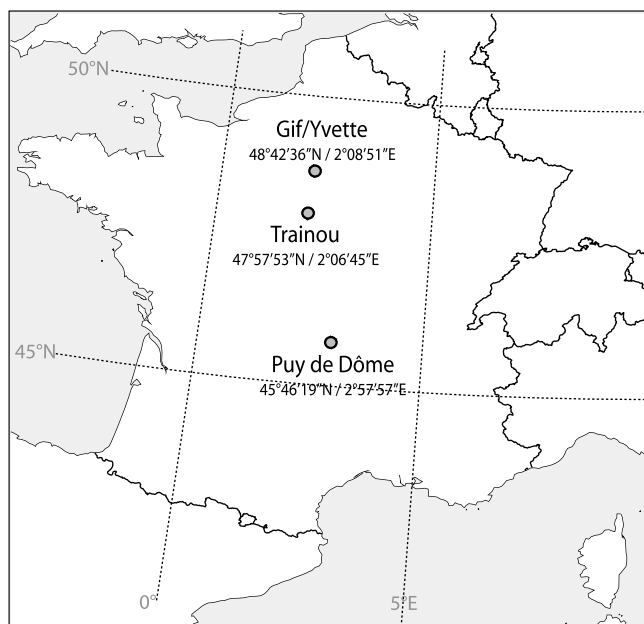


Figure 1. Location of the three stations in France where GCs monitor the N₂O concentration in the atmosphere. They are aligned on a line north-to-south through central France.

[4] In the framework of the Kyoto protocol, N₂O emissions can be very important on a country scale. According to national greenhouse gas inventory reported to the United Nations Framework Convention on Climate Change (UNFCCC, <http://unfccc.int>), France has reduced its greenhouse gas emissions by 7.7% between 1990 and 2009. Approximately 70% of this reduction is attributed to the reduction of N₂O emissions, mainly in industry (production of adipic acid) but also in the agricultural sector. These estimates are based on declarative numbers calculated from bottom-up aggregation of economic statistics. However, no independent method is available for the assessment of the efficacy of N₂O emission policies. Alternative methods are needed to cross-compare regional to national N₂O emissions. N₂O atmospheric measurements integrate local-to-regional emissions of N₂O and can provide a complementary approach to bottom-up inventories. In Europe, several research groups perform continuous measurements of N₂O at rural and semi-urban stations. These measurements have already been used to estimate the regional emissions of N₂O [Biraud *et al.*, 2000; Schmidt *et al.*, 2001; van der Laan *et al.*, 2009]. Schmidt *et al.* [2001] confirmed the consistency of the declared reduction of N₂O emissions by a nearby adipic acid production facility in 1998 using atmospheric measurements at the Heidelberg station.

[5] In this study, we present an analysis of 10 years of N₂O observations at the semi-urban site of Gif-sur-Yvette in France (section 2.1) to estimate regional daily N₂O fluxes. Measurements from Trainou tall tower (Orleans forest, France) and Puy-de-Dôme (center of France), with shorter time series of five and only 1.5 years, respectively, are used as references for more rural stations (section 2.2 and 2.3). The Radon-Tracer-Method, used to estimate the regional N₂O fluxes, and the results obtained are presented in section 3. Finally, in section 4, we discuss our results from the

atmospheric approach, including a comparison with bottom-up inventories.

[6] In this paper, we use the units of ppb (parts per billion) as convenient shorthand for mole fractions in nanomoles of N₂O per mole of dry air.

2. Measurement Stations and Instrumental Setup

2.1. Gif-sur-Yvette Station

[7] Gif-sur-Yvette station (48°42'N, 02°09'E, 160 m above sea level (asl)) is a semi-urban site, located 20 km southwest of Paris (Figure 1). This station is surrounded by agricultural fields (47.4%), forests (25.0%), and urban residential areas (22.2%) (source: INSEE, National Institut of Statistic and Economic Study, 2008, <http://www.insee.fr>). The closest village and small town are Saint-Aubin (673 inhabitants) and Gif-sur-Yvette (21,352 inhabitants), located 500 m north-west and 1 km south of the station, respectively. The station is part of the Laboratory for Climate and Environmental Sciences (LSCE) and belongs to the national Atmospheric Network for Greenhouse Gases Monitoring (RAMCES) [Schmidt *et al.*, 2005]. In 2001, the station was equipped with a gas chromatograph system (GC, Agilent 6890), which measures CO₂, CH₄, N₂O and SF₆ [Pépin *et al.*, 2001; Valant *et al.*, 2005; Messenger, 2007]. In 2006, a second GC (PP1, Peak Performer) was added to measure CO and H₂ [Yver *et al.*, 2009]. This combined GC system is used for flask and high-pressure cylinder measurements, as well as for semi-continuous measurement of ambient air. The ambient air inlet is located on the roof of the laboratory, 7 m above ground level (agl). A ²²²Rn analyzer has been running since 2001, with an air inlet located 3.5 m agl. Meteorological data (temperature, pressure, relative humidity, precipitation, and wind speed and direction) are monitored by Vaisala and Pulsonic probes on a tower (100 m agl) in the CEA research center (Saclay), approximately 1500 m north of the station, over flat terrain with no obstacles. The dominant wind direction is south-west (35% of the time), with a wind speed between 5 and 10 m s⁻¹. Only 14% of the time during most of the year, but 35% of the time in spring, the wind comes from Paris (north-east direction), transporting polluted air masses.

2.2. Trainou Station

[8] Trainou station (47°58'N, 02°06'E, 131 m asl) is located on a television transmission tower, 200 m high, of TeleDiffusion De France, 15 km north-east of the city of Orléans (116,000 inhabitants) and approximately 100 km south of Paris (Figure 1). According to the national statistics for Orléans county (Loiret), most of the nearby land is agriculture fields (49.7%) and forests (30.1%) (source: INSEE 2008). Since 2007, the station has been equipped with a gas chromatographic system operated by our laboratory [Messenger, 2007; Yver *et al.*, 2011]. We installed three air inlets at 50, 100 and 180 m above ground level at the tower. An additional air inlet was installed in September 2010 on the roof of the laboratory shelter (5 m agl). The tower is equipped with two weather stations: one on the 180 m platform and a second one on the roof of the shelter. The station is mainly influenced by air masses which originate from the south-western direction. In May 2009, a ²²²Rn

Table 1. Summary of Gas Chromatographic Parameters^a

	CO ₂ / CH ₄ (FID)	N ₂ O / SF ₆ (ECD)
Carrier gas	Nitrogen 5.0 50 mL min ⁻¹	Ar/CH ₄ 40 mL min ⁻¹
Injection loop volume	15 mL	10 mL
Oven temperature	80 °C	80 °C
Pre-column		Hayesep-Q column 4' × 3/16"SS, 80/100
Analytical column	Hayesep-Q 12' × 3/16"SS, 80/100	Hayesep-Q 6' × 3/16"SS, 80/100
Detector	FID: 300 °C Catalyst: 390 °C H ₂ flow: 50 mL min ⁻¹ Air flow: 400 mL min ⁻¹	ECD: 395 °C

^aThe setups of the GC-systems at Gif-sur-Yvette, Trainou and Puy-de-Dôme are identical.

gas analyzer was connected to the 180 m air inlet line [Yver *et al.*, 2011].

2.3. Puy-de-Dôme Station

[9] Puy-de-Dôme station (45°46'N, 02°58'E, 1465 m asl) is operated by the Laboratory of Physical Meteorology (LaMP), Clermont-Ferrand, France [Venzac *et al.*, 2009] (Figure 1). This mountain station is situated on an inactive volcano, which is part of Puy's mountain chain in the Massif Central region. The major residential areas are located on the east of Puy-de-Dôme, and the largest town is Clermont-Ferrand (150,000 inhabitants), situated 16 km east of the station at 396 m asl. However, some small villages are also located between Clermont-Ferrand and the station (the nearest is located 3 km from the top of Puy-de-Dôme). The station is surrounded by meadows (36.4%), forest (33.4%), and arable land (17.6%) (source: INSEE 2008). The station is influenced primarily by westerly winds (44% of the time) transporting air masses originating from the Atlantic Ocean but also by polluted air masses from Clermont-Ferrand (22% of the time), equally distributed by season. The only road to access the station has been closed to tourists since May 2010. Since 2001, flasks have been filled by the LaMP team weekly, and are analyzed by the GC at the LSCE laboratory of Gif-sur-Yvette. A ²²²Rn monitor was installed in 2002. Since August 2010, an in-situ GC system for CO₂, CH₄, N₂O and SF₆ measurements has been installed and operated by our laboratory. The two inlet lines are located at 10 m agl. In this study, we will only present the N₂O measurements from weekly flask sampling.

2.4. N₂O Measurement Technique

[10] The three measurement stations are equipped with automated gas chromatograph (GC) systems (HP-6890, Agilent) using the same technical setup and measurement procedure for CO₂, CH₄, N₂O and SF₆ in ambient air. Detailed descriptions of the individual GC systems are given by Pépin *et al.* [2001] and Yver [2006] for the Gif-sur-Yvette station and by Messenger [2007] for the Trainou station. From the inlet system, ambient atmospheric air is pumped through a 0.5 inch Dekabon tube at a rate of 400 mL min⁻¹ before being dried by passing through a glass trap cooled in an ethanol bath maintained at -50 °C by a cryocooler. Each GC is equipped with a flame ionization detector (FID) and a nickel catalyst to determine the CH₄ and CO₂ concentrations

and an electron capture detector (ECD) for N₂O and SF₆ analysis. The injection system separates the sample in two different sample loops (one for each detector) before injection on analytical columns used to separate each species. For CO₂ and CH₄ analysis, we use only one Hayesep-Q column, whereas for N₂O and SF₆, a pre-column and an analytical column (both Hayesep-Q) are used. With this configuration, each analysis takes less than 6 min, allowing two to six ambient air injections every hour. Table 1 summarizes the measurement parameters of the three gas chromatographs.

2.4.1. Characterization of the Electron Capture Detectors

[11] Detection of N₂O is performed by electron capture detectors (ECD) (HP 6890) at Gif-sur-Yvette and by μ ECD (HP 6890N) at Trainou and Puy-de-Dôme. Electron capture detectors are known to have non-linear responses to ambient N₂O concentrations and the possible problem of co-elution of N₂O and CO₂, depending on the column setup. Following Schmidt *et al.* [2001], we determine the non-linear response of the ECD detectors using a reference sample diluted with N₂O and CH₄-free air (CO₂ in synthetic air). Methane is used to determine the dilution factor, as the FID response to CH₄ concentration is linear within the chosen range. For all three ECDs that equip the three GCs systems described above, we found that the ECD underestimates the N₂O concentration with increasing values, but a linear correction can be added to describe the response of the ECDs in the range of 250 to 340 ppb [Yver, 2006; Messenger, 2007; Legrand, 2009]. This matches the results reported by Schmidt *et al.* [2001] for the restricted range of the N₂O concentrations between 250 ppb and 400 ppb, where a simple linear approximation provides an excellent linear correction. Our tests show that for the three ECDs, a linear correction of the ECD response could correct the N₂O concentrations in the atmospheric range of 300 to 350 ppb. We found different slopes for the ECD at Gif-sur-Yvette ($\gamma = -0.161$) and for the μ ECDs at Trainou and Puy-de-Dôme ($\gamma = -0.07$) where:

$$N_2O_{linearity-corr} = \gamma(N_2O_{meas} - N_2O_{reference}) + N_2O_{meas} \quad (1)$$

where $N_2O_{linearity-corr}$ represents the corrected N₂O concentration, N_2O_{meas} corresponds to the calculated N₂O concentration without taking into account the nonlinearity of the detector and $N_2O_{reference}$ is the N₂O concentration of the standard used.

[12] To account also for possible temporal changes in the ECD or μ ECD response, we use two working standards WL (working low) and WH (working high), which span the atmospheric range between 315 and 340 ppb, and we apply a linear interpolation to calculate the ambient air concentrations.

[13] For the co-elution process, N₂O and CO₂ have the same molecular weight and elute, therefore, together from the columns. Ionization of N₂O in the detector produce O⁻ ions, which react with CO₂, thus enhances the N₂O signal. We have tested this interference for all three detectors using a small amount of Ascarite (Fluka, #11133, 5–20 mesh), which removes CO₂ from a reference sample as described by Schmidt *et al.* [2001]. After several injections, the efficiency of Ascarite decreased, and CO₂ concentrations continuously increased. The enhancement of N₂O by CO₂ was determined to be 0.001, 0.0003 and 0.0055 ppb N₂O/ppm CO₂ for the

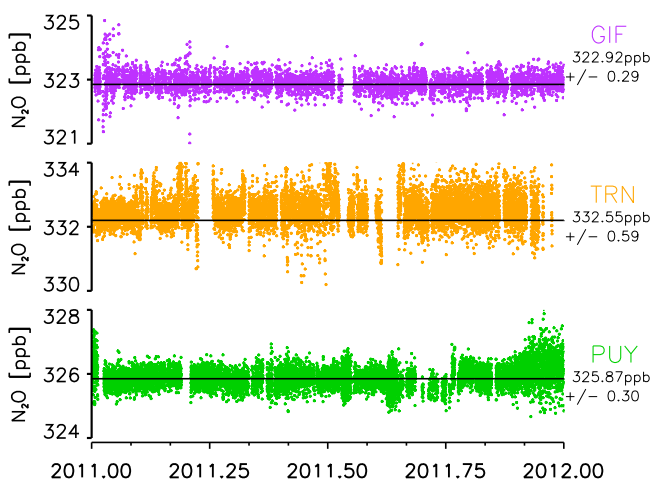


Figure 2. One-year reproducibility of the target gases for N₂O at Gif-sur-Yvette, Trainou and Puy-de-Dôme station for 2011. The horizontal black lines represent the assigned values of the target tanks analyzed in our central laboratory at Gif-sur-Yvette.

detectors at Gif-sur-Yvette, Trainou and Puy-de-Dôme, respectively. For typical annual CO₂ variability of approximately 120 ppm at Gif-sur-Yvette, 80 ppm at Trainou and 60 ppm at Puy-de-Dôme, a possible influence of the CO₂ variations would be in the range of 0.12 ppb N₂O at Gif-sur-Yvette, 0.024 ppb N₂O at Trainou station and 0.33 ppb N₂O at Puy-de-Dôme station. Considering the precision of our N₂O measurements, we conclude that the co-elution correction could be neglected at Gif-sur-Yvette and Trainou. However, at Puy-de-Dôme, a correction will be applied to our measurements.

[14] Moreover, at Gif-sur-Yvette, the mean atmospheric SF₆ concentration was approximately 7.9 ppt in 2010, but we regularly measure SF₆ peaks exceeding 20 ppt (approximately four times per month) and sometimes extreme values of greater than 1000 ppt. We have never observed such elevated SF₆ concentrations at Trainou or Puy-de-Dôme, indicating a local source of SF₆ close to the Gif-sur-Yvette station. We noticed an interference between SF₆ and N₂O measurements: SF₆ concentrations exceeding 15 ppt are associated with N₂O concentrations that are too low. This phenomenon is an artifact of incomplete separation of the N₂O and SF₆ peaks for elevated SF₆ concentration. Therefore, all N₂O measurements at Gif-sur-Yvette station with SF₆ concentrations higher than 15 ppt are flagged as not valid, approximately 2.1% of N₂O measurements. Ongoing tests should help to quantify the cross-interference between SF₆ and N₂O, in a similar way as was done for CO₂ to correct the temporarily rejected data.

2.4.2. Calibration and Quality Control Strategy

[15] As shown above, the ECD detector non-linear correction is a linear function in the atmospheric N₂O concentration range, which varied between 316 and 340 ppb over the past decade. Therefore, the two working standards used for N₂O calibration at our three sites were chosen to span a range between 310 and 340 ppb. The two working standards are injected approximately every 30 min, to correct for short-term variations of the detector response.

[16] All working standards that were used over the last 10 years at the stations Gif-sur-Yvette, Trainou and Puy-de-Dôme were filled by Deuste Steininger (Muehlhausen, Germany) in 40-liter aluminum cylinders (Luxfer) to 180 bar and calibrated regularly against six standards purchased from NOAA/CMDL in 2001 and 2007. Each working standard had a lifetime between 18 and 24 months. The NOAA/CMDL standards purchased in 2001 originally had a quoted accuracy of ± 3 ppb (NOAA-2000 scale), but when the values have been transferred to the NOAA-2006 scale [Hall *et al.*, 2007], the errors were reduced to ± 0.35 ppb. For the cylinders purchased in 2007, N₂O concentrations were directly reported on the NOAA-2006 scale [Hall *et al.*, 2007] with an accuracy of ± 0.3 ppb. Our six NOAA standard gases span a N₂O range between 302 and 340 ppb. All working standards used since 2002 were recalculated on the NOAA-2006 scale. After this step, all N₂O data at Gif-sur-Yvette and Trainou station were reprocessed to be consistent with the NOAA-2006 scale. For quality control and to determine the reproducibility of GCs, a target gas is injected from a cylinder every two hours as an unknown sample. This target gas is used to independently verify the reproducibility of measurements on different timescales and to indicate possible instrumentation problems causing bias or drift. Figure 2 shows the target measurements of each GC for the year 2011, and Table 2 summarizes the standard deviation of the target gases at the three stations for a typical period of 2–3 days, for the year 2011 and over several years. All three GCs show a short-term (2–3 days) variability better than 0.3 ppb and long-term variability (several years) on the order of 0.4 ppb. Because of problems with the ECD at Trainou for the year 2011, we observe better standard deviation for the long term measurements compared with the year 2011. Another way to independently assess the quality of the N₂O measurements at a station is to compare semi-continuous measurements with air sampled in flasks. At the Trainou and Puy-de-Dôme stations, glass flasks of one liter are sampled every week and analyzed in our central laboratory (Gif-sur-Yvette) by GC. The mean difference between the 132 sampled flasks (from 2009 to 2011) and the GC at Trainou is 0.47 ± 0.74 ppb. At Puy-de-Dôme, the results from GC and flask sampling agree very well with a mean difference of 0.03 ± 0.63 ppb for 40 sampled flasks.

[17] The cucumbers intercomparison program (<http://cucumbers.uea.ac.uk>), which started in 2007, aims to analyze twice a year three tanks for intercomparison among five stations, including Gif-sur-Yvette, Trainou and Puy-de-Dôme. We determined mean differences between Gif-sur-Yvette and Trainou and Gif-sur-Yvette and Puy-de-Dôme of 0.30 ± 0.01 ppb and -0.09 ± 0.33 ppb, respectively.

Table 2. Standard Deviation of Target Gas Measurement for N₂O for Different Time Periods Using the GC System at Gif-sur-Yvette, Trainou and Puy-de-Dôme

Station	Short Term (2–3 Days)	Year 2011	Long Term (Years)
Gif	0.20 ppb	0.29 ppb	0.41 ppb (2002–2011)
Trainou	0.30 ppb	0.59 ppb	0.42 ppb (2006–2011)
Puy	0.20 ppb	0.30 ppb	0.30 ppb (2010–2011)

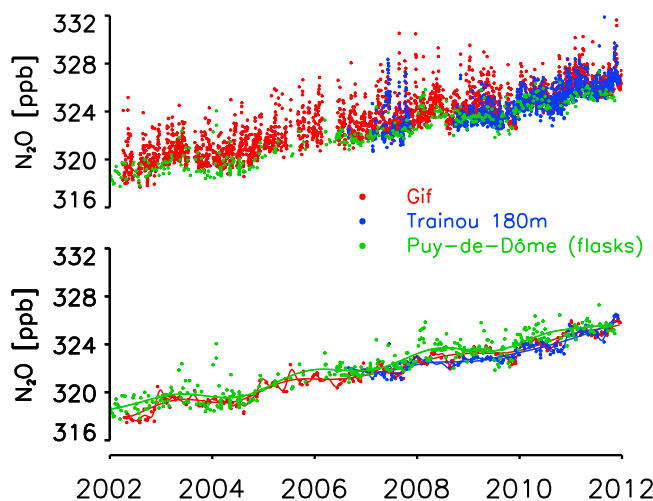


Figure 3. (top) Semi-continuous measurement of the N₂O concentration at Gif-sur-Yvette, Trainou (180 m agl) and weekly flasks measurement at Puy-de-Dôme. (bottom) The colored dots represent the baseline N₂O concentration calculated at Gif-sur-Yvette and Trainou from the first decile (afternoon mean between 1400 and 1600 UTC) of each month. The solid curves fit the baseline and provide an estimate for annual N₂O concentration increase of 0.73 ppb a⁻¹ for Puy-de-Dôme site, which is the closest to tropospheric background air, given the altitude of 1465 m asl.

[18] According to the comparisons from the flasks and cucumber tanks, we observe a very good agreement between measurements at Gif-sur-Yvette and Puy-de-Dôme, whereas an underestimation of approximately 0.35 ppb is detected for the N₂O measurements at Trainou, which must be further investigated.

2.5. ²²²Rn Measurement Systems

[19] ²²²Rn is a natural radioactive gas (half-life $T_{1/2} = 3.8$ days) emitted mainly by soils as a radioactive decay product of uranium-238. Its short half-life, as well as its physical and chemical properties as a noble gas, make radon a good tracer of the planetary boundary layer circulation.

[20] Atmospheric ²²²Rn activity is analyzed at the three stations of this study using two different methods. At Gif-sur-Yvette and Puy-de-Dôme, we use the active deposit method based on the measurement of ²²²Rn's solid short-lived daughters: ²¹⁸Po, ²¹⁴Pb and ²¹⁴Bi [Polian *et al.*, 1986; Biraud *et al.*, 2000; Yver *et al.*, 2009]. These elements are produced in the atmosphere by ²²²Rn decay and then quickly adsorbed onto aerosols. Ambient air is pumped through cellulose filters for a sampling period of one hour, accumulating aerosols on the filter. After the sampling period, the filter is placed under an alpha spectrometer (scintillator and photomultiplier) to measure the radioactive decay of the ²²²Rn daughters over one hour.

[21] With the active deposit method, ²²²Rn is measured only via the radioactive decay of its daughters attached to aerosols. Yver *et al.* [2009] determined a disequilibrium factor between ²²²Rn and its short-lived daughters from January 2007 to December 2008 at Gif-sur-Yvette station. This factor (1.8, with seasonal variations of +15% in summer and -15% in winter) is applied to the whole data set

measured with the active deposit method at Gif-sur-Yvette station.

[22] At Trainou, we use the two-filter method [Whittlestone and Zahorowski, 1998; Zahorowski *et al.*, 2004; Yver *et al.*, 2011], which permits direct determination of ²²²Rn gas atmospheric activity. Ambient air is pumped from the 180 m inlet through a rigid pipe that is 65 mm in diameter, which acts as delay volume. Thoron (²²⁰Rn) decreases during the transit time of at least 600 s in the delay volume, which is 10 times higher than its half-life ($T_{1/2} = 56$ s). This allows ²²²Rn to remain and the removal of only ²²⁰Rn during the analysis. Then air enters into the closed analysis chamber through a first filter that retains the ²²²Rn aerosol daughters but allows ²²²Rn gas to enter. In this chamber, new ²²²Rn daughters are produced and finally collected on the second filter where α decay is counted. The instrument is regularly calibrated (typically each month) with a known quantity of ²²²Rn emitted by a ²²⁶Ra source. A blank measurement performed every three months is used to monitor the increase of the background. The temporal resolution of this instrument is 30 min.

3. Results

3.1. Long-Term Trends and Synoptic Variations of N₂O Concentrations

[23] The daily average of the atmospheric N₂O concentrations for Gif-sur-Yvette (red), Trainou 180 m level (blue) and the weekly flask values at Puy-de-Dôme (green) are plotted together at the top of Figure 3 with their respective baselines, which are calculated from the first decile of the afternoon means (between 1400 and 1700 UTC, when the planetary boundary layer (PBL) is usually well developed, resulting in lower and largely stable N₂O concentrations) of each month (at Gif-sur-Yvette and Trainou) and weekly flask sampling at Puy-de-Dôme. In-situ N₂O measurements began at Puy-de-Dôme in July 2010. From the trends in the baseline of the selected data (the solid curve) at Gif-sur-Yvette and weekly flask sampling at Puy-de-Dôme (Figure 3), we computed a mean annual increase of 0.74 ppb a⁻¹ for Gif-sur-Yvette and 0.73 ppb a⁻¹ for Puy-de-Dôme (which can be considered as a background value) using a linear regression fit (least square method) for the years 2002 to 2010. The Intergovernmental Panel on Climate Change (IPCC) reported a similar global trend of 0.8 ppb a⁻¹ on its fourth assessment Report (AR4) [Forster *et al.*, 2007] for the years 1998 to 2005. The small diurnal N₂O variation at Puy-de-Dôme in 2011 (~0.3 ppb) confirmed that the flask data, filled mostly between 1000 and 1400 UTC, do not introduce a bias based on filling time.

[24] Figure 4 shows the mean diurnal cycle for each season for N₂O and ²²²Rn at Gif-sur-Yvette (Figure 4, left), calculated from 2002 to 2011, and at Trainou at the 180 m inlet (Figure 4, right), computed from 2007 to 2011 for N₂O and from 2009 to 2011 for ²²²Rn. To compute the mean diurnal cycle, we detrended the hourly N₂O values to the reference of January 1, 2012. At Gif-sur-Yvette and Trainou (180 m agl), the diurnal cycles present the same temporal pattern, with maxima during the morning and lower values in the afternoon, but the diurnal amplitudes of both N₂O (ΔN_2O) and ²²²Rn ($\Delta^{222}Rn$) are larger at Gif-sur-Yvette ($\Delta N_2O = 0.96$ ppb and $\Delta^{222}Rn = 2.0$ Bq m⁻³) than at

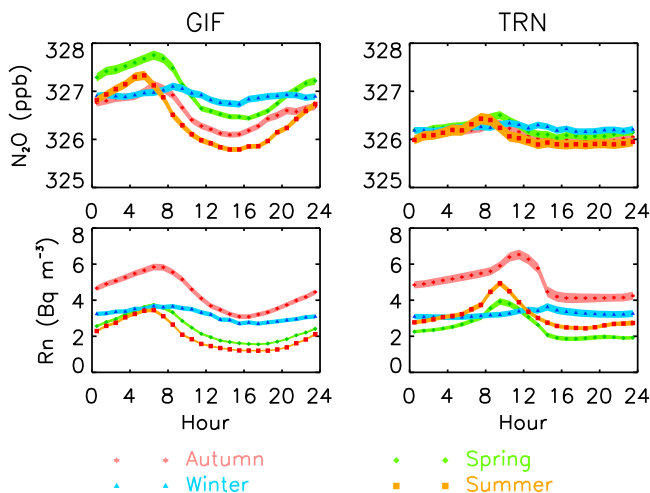


Figure 4. (left) N₂O and ²²²Rn diurnal cycle per season at Gif-sur-Yvette computed from 2002 to 2011 and (right) at Trainou (180 m agl) from 2009 to 2011. N₂O concentration were detrended based on January 1, 2012.

Trainou ($\Delta N_2O = 0.32$ ppb and $\Delta^{222}Rn = 1.3$ Bq m⁻³). Regarding the seasonal variability, maximum N₂O concentrations are systematically measured in spring at Gif-sur-Yvette and Trainou (180 m agl). Concerning ²²²Rn, maximum values are observed in autumn of each year at both sites. The mean diurnal cycles indicate a time shift in the maximum concentration at Gif-sur-Yvette from 0530 UTC in summer to 0830 UTC during winter. This seasonal time shift of the diurnal maxima values is less pronounced at Trainou.

[25] The diurnal cycles are controlled primarily by the dynamic of the boundary layer, which is usually shallow and stable at night, causing an increase of N₂O concentrations

and ²²²Rn activities near the surface. During the day, the boundary layer usually moves upward, causing a decrease in N₂O and ²²²Rn by ‘encroaching’ free tropospheric air with lower concentration values. At Gif-sur-Yvette, the inlet line is located at 7 m agl, and therefore, the variability of N₂O is affected by the local emission at night and by the rise of the boundary layer during the morning. Yver *et al.* [2011] determined for Trainou station that during 50% of the nights, the boundary layer height is below 180 m. This explains why during approximately half of the nights, the 180 m level receives free troposphere air or is within the PBL.

[26] At both sites, Gif-sur-Yvette and Trainou, the maximum activities for ²²²Rn are recorded in autumn. We expected this maxima during the winter when the PBL is lowest (as for N₂O at Trainou), but during the winter, less ²²²Rn exhalation occurs by the soil, as the soil is wet and frozen, slowing and preventing ²²²Rn emission. During autumn months, we also notice several days or even weeks with a strong radiative fog at night, which partly remains during the day. This leads to very high concentrations in all atmospheric samples.

[27] To identify possible N₂O sources from industrial processes in the catchment area of Gif-sur-Yvette and Trainou, we analyzed the N₂O concentrations as a function of wind speed and wind direction using the open-air Polar-Plot script [Carlaw and Ropkins, 2011]. This script plots a bivariate polar plot of concentrations in relation to wind speed and direction, as shown in Figure 5. We applied this function to the detrended N₂O concentration at Gif-sur-Yvette for the years 2002 to 2011 (Figure 5, left) and at Trainou for the years 2007 to 2011 (Figure 5, right). For Gif-sur-Yvette and Trainou stations, we used the analyzed meteorological variables from the data assimilation system of the European Center for Medium-Range Weather Forecasts (ECMWF).

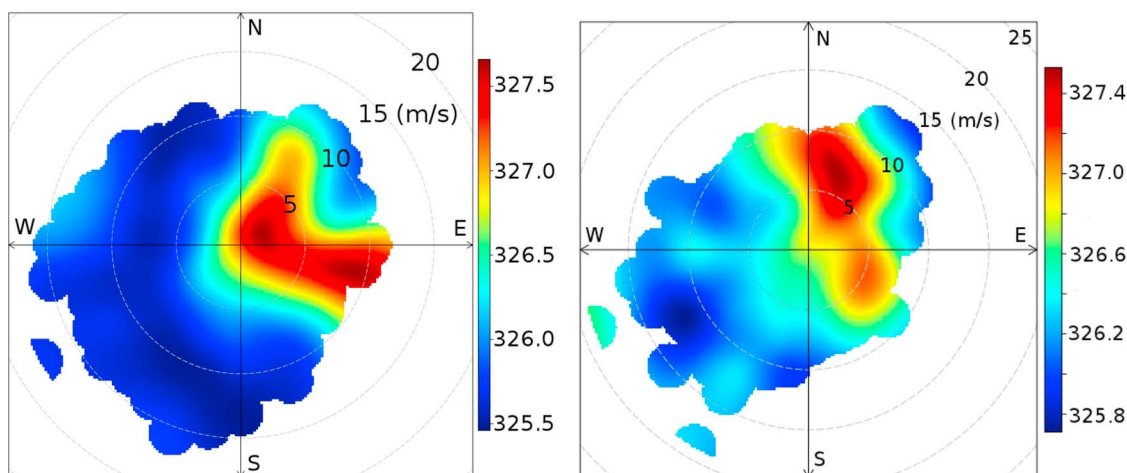


Figure 5. Representation of N₂O concentration at (left) Gif-sur-Yvette and (right) Trainou in polar coordinates showing the concentration by wind speed and wind direction. The N₂O concentration data are detrended based on January 1, 2012. At Gif-sur-Yvette, we observed two hot spots (in red and orange) with strong N₂O concentrations: one in the East with high wind speed and the second on the North-East corresponding to a low wind speed regime. At Trainou, we distinguished two hot spots: the more marked coming from North-East with wind speed between 10 and 15 m s⁻¹ and the second on the South-East with lowest wind speed.

Table 3. Chosen Hour for the Nighttime Inversions

Season	Gif	Trainou (180 m)
Autumn	1700–0600 (13 h)	1800–0700 (13 h)
Winter	1700–0600 (13 h)	1800–0700 (13 h)
Spring	1800–0600 (12 h)	1900–0700 (12 h)
Summer	1900–0500 (10 h)	1900–0700 (12 h)

[28] Concerning Gif-sur-Yvette (Figure 5, left), two different zones with the highest concentrations of N₂O are detected, originating from two different directions: one from north-east sector with a wind speed between 0 and 5 m s⁻¹, indicating a local source, and a second one from easterly direction with a wind speed between 10 and 15 m s⁻¹, showing a more distant source. The first source sector is located in the direction of Paris, which can be a source of N₂O due to traffic or industry. In the region ‘Ile-de-France’, the main industrial source of N₂O is a chemical company (iREP, www.pollutionsindustrielles.ecologie.gouv.fr/IREP/index.php) that emitted 1050 t of N₂O (10.2% of Ile de France emission using CITEPA values) in 2005 and as many as 2040 t in 2009. This chemical company is located approximately 60 km east of our laboratory (Grandpuits-Bailly Carrois), corresponding well to the second observed source.

[29] At Trainou, we identify two zones of high N₂O concentrations: one is detected in the north, with wind speeds between 5 and 10 m s⁻¹, and the second, which is less marked, is in the south-east direction, with a wind speed of approximately 5 m s⁻¹ (Figure 5, right). According to iRep, we expected an industrial source in the westerly direction with an emission of 129 t of N₂O in 2007, but this is not reflected in our atmospheric data.

3.2. The Radon-Tracer-Method

[30] As shown in Figure 4, the N₂O concentrations and ²²²Rn activities are well correlated on a diurnal timescale because they are subject to the same mixing processes in the PBL and because their emissions are rather diffuse in space. The Radon-Tracer-Method (RTM) uses these correlations to estimate N₂O emissions from the concentrations during nighttime inversions or synoptic events [Schmidt *et al.*, 2001; Biraud *et al.*, 2000; Yver *et al.*, 2009; Hammer and Levin, 2009]. Assuming that both species, each with a constant surface flux *J*, are released in a boundary layer of height *H* and that their fluxes are collocated spatially and temporally, we can write the temporal variation of their concentrations as:

$$\frac{\Delta C_{N_2O}}{\Delta t} = \frac{J_{N_2O}}{H} \quad (2)$$

$$\frac{\Delta C_{Rn}}{\Delta t} = \frac{J_{Rn}}{H} - \lambda_{Rn} \cdot C_{Rn} \quad (3)$$

The last term in equation (3) accounts for the radioactive decay of ²²²Rn during the time Δt of the nighttime inversion. Combining the two equations, we can remove the unknown boundary layer height *H* and thus use the first approximation $\lambda_{Rn} \cdot C_{Rn} \ll \Delta C_{Rn} / \Delta t$ to estimate the N₂O flux:

$$J_{N_2O} = J_{Rn} \frac{\Delta C_{N_2O}}{\Delta C_{Rn}} \left(1 - \frac{\lambda_{Rn} \cdot C_{Rn}}{\frac{\Delta C_{Rn}}{\Delta t}} \right) \quad (4)$$

In this equation, J_{N_2O} represents the inferred flux of N₂O during the nighttime period, given the mean ²²²Rn emission rate (J_{Rn}) and the slope of linear regression of hourly mean N₂O and ²²²Rn observations ($\frac{\Delta C_{N_2O}}{\Delta C_{Rn}}$). The term in brackets is a correction term depending on Δt that accounts for the ²²²Rn radioactive decay during the nighttime inversion. Schmidt *et al.* [2001] estimated that during a typical nighttime inversion of 12 hours, this term is equal to 0.96 ± 0.05 .

[31] We calculate N₂O fluxes at Gif-sur-Yvette and Trainou 180 m, applying three different criteria to the N₂O and ²²²Rn data:

[32] 1. We use only nighttime N₂O and ²²²Rn observations to enhance the effect of surface emissions (shallow boundary layer with a smaller influence of the residual layer), showing a joint increase of the N₂O concentration and ²²²Rn activity. Table 3 summarizes the selected start and end times of the peak based on the diurnal cycle observed for each season. Typically, we are selecting data between 1800 and 0600 UTC.

[33] 2. The ²²²Rn nighttime increases must be larger than 0.75 Bq m⁻³, and N₂O increases larger than 0.6 ppb to be considered as significant events. For N₂O, this corresponds to approximately two times the mean standard deviation of the GC measurements. Applying these criteria, we keep 95% of all nights at Gif-sur-Yvette and 82% at Trainou.

[34] 3. The coefficient of determination (R^2) between ΔC_{N_2O} and ΔC_{Rn} should be larger than 0.6 for Gif-sur-Yvette and 0.5 for Trainou. To calculate the coefficient of determination between ΔC_{N_2O} and ΔC_{Rn} , we performed an orthogonal distance regression using a least square fit. For each N₂O value, we applied a weight of 20% (detailed below in the section 3.3), whereas for ²²²Rn, we used a weight of 10% of the value activity corresponding to the errors of measurements.

[35] Applying all of these criteria leads to the selection, on average, of 66 and 43 nocturnal events per year at Gif-sur-Yvette and Trainou, respectively, that are suitable for deducing N₂O fluxes, with a maximum of occurrence in May and a minimum in January/December, with nine and two suitable nights for Gif-sur-Yvette, respectively, and four and two for Trainou.

[36] The ²²²Rn emission rate from soils depends on the type and nature of the soils. Yver *et al.* [2009, 2011] compiled several studies with direct measurements close to the measurement station [Servant, 1964] and other literature values [Szegvary *et al.*, 2009; Jutzi, 2001] to compute a climatology for the radon flux in the catchment area of Gif-sur-Yvette and Trainou. They estimated a mean value for the ²²²Rn flux of 52 ± 13 Bq m⁻² h⁻¹ at Gif-sur-Yvette and 50 ± 12.5 Bq m⁻² h⁻¹ at Trainou. The radon flux is estimated to be +25% larger in summer and -25% lower in winter [Yver *et al.*, 2009, 2011] due to the meteorological conditions: in winter, when the soil is flooded or frozen, the ²²²Rn flux is lower than in summer, when the soil is dry.

[37] The amplitudes of the diurnal N₂O variability are, on average, approximately 1–2 ppb at the Gif-sur-Yvette and Trainou stations. The nighttime accumulation may even be smaller and therefore not detectable with our GC system. The method used in this study is based on a few individual nocturnal accumulation episodes selected using relatively stringent criteria. Therefore, a positive bias could be induced

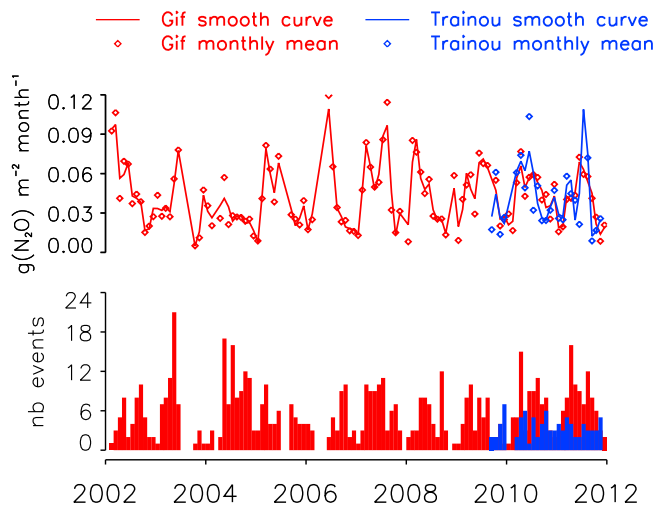


Figure 6. (top) Monthly mean N₂O emissions estimated in the footprint of Gif-sur-Yvette station (red dots) and for Trainou tall tower (blue dots). The lines are smoothed curve fit to monthly data. The estimated emissions are statistically lower during the winter compared to the spring and summer. (bottom) The numbers of selected events per month.

in the calculated N₂O fluxes because only the large peaks are retained. To estimate the magnitude of this potential bias, we compute for each month (at Gif-sur-Yvette and Trainou) the monthly average diurnal cycles of N₂O and ²²²Rn. Then we apply the RTM to these average diurnal cycles, correlating each monthly N₂O and ²²²Rn diurnal cycle to estimate a monthly mean flux. This alternative application of the RTM is expected to result in lower N₂O fluxes than the standard application described above because the averaging process accounts for N₂O and ²²²Rn data during nights where no or weak accumulation occurs, e.g., during the passage of frontal systems. We cannot apply this alternative method on Trainou data, as we have only two complete years, which is not enough to perform statistical analyses.

3.3. Uncertainties of the Radon-Tracer-Method

[38] Several types of uncertainties arise when using the RTM, including the instrumental accuracy of the semi-continuous measurements of ²²²Rn and N₂O, the error on the N₂O/Rn slopes and the uncertainty of radon flux. The two instruments measuring the ²²²Rn concentration, the active deposit and two-filter methods, have random errors of 10% and 5% [Biraud *et al.*, 2000; Zahorowski *et al.*, 2004], respectively, whereas the gas chromatographs used to analyze N₂O yield a systematic random error approximately equal to 0.3 ppb (1-sigma deviation), which is, relative to the amplitude of the mean diurnal cycle (typically 1.5 ppb), an error of approximately 20%. These instrumental errors are accounted for the calculation of the N₂O/²²²Rn slope, and the error on the slope is typically 17% at Gif-sur-Yvette and 10% at Trainou.

[39] Moreover, the precision of hourly mean N₂O measurements (± 0.25 ppb) produces a systematic error in the calculated fluxes. We over-estimate the calculated N₂O emissions, as we are not able to detect N₂O peak lower than 0.3 ppb (description above). This systematic error was calculated in part 3.4 and sums to approximately 15%.

[40] Another source of uncertainty results from the estimation of the ²²²Rn exhalation by soils, which was estimated by different methods [Yver *et al.*, 2009, 2011]. ²²²Rn emissions by soils depend on the atmospheric and soil conditions (temperature, humidity, pressure, etc.). Accounting for the variations induced by all these methods leads to an error of ²²²Rn flux on the order of $\pm 25\%$. Integrating all of these sources of errors, we estimate a total uncertainty of the N₂O flux inferred from the RTM to be close to $\pm 35\%$ [Biraud *et al.*, 2000; Schmidt *et al.*, 2001; van der Laan *et al.*, 2009].

3.4. N₂O Emission Results

[41] The monthly mean nitrous oxide fluxes calculated with the RTM using the selected nighttime episodes are presented in Figure 6 (top). The N₂O emissions estimated from the Gif-sur-Yvette observation are plotted in red from May 2002 to 2011 and in blue for those inferred from the Trainou tall tower data (180 m agl) from October 2009 to 2011. Each point represents a monthly mean value, and the smoothed curves are calculated using the temporal filter and signal decomposition algorithm given by Thoning *et al.* [1989]. In Figure 6 (bottom), the numbers of individual events that are used to calculate the monthly mean flux are shown. We observe similar variations in the inferred N₂O fluxes in the footprint of both stations, with higher fluxes in spring and summer and lower fluxes in winter. The monthly mean N₂O fluxes vary between 0.12 ± 0.04 g(N₂O) m⁻² month⁻¹ (June 2006) and 0 ± 0.01 g(N₂O) m⁻² month⁻¹ during winter at Gif-sur-Yvette and between 0.13 ± 0.05 g(N₂O) m⁻² month⁻¹ (July 2011) and 0 ± 0.01 g(N₂O) m⁻² month⁻¹ during winter at Trainou. The mean annual averaged N₂O fluxes are between 0.34 ± 0.12 and 0.51 ± 0.18 g(N₂O) m⁻² in the catchment area of Gif-sur-Yvette and 0.52 ± 0.18 g(N₂O) m⁻² in the catchment area of Trainou (180 m agl).

[42] The N₂O fluxes are on the same order of magnitude as those in the literature. Biraud *et al.* [2000] found a mean annual N₂O emission between 0.33 and 0.47 g(N₂O) m⁻² at Mace Head (for Western Europe), Schmidt *et al.* [2001] calculated N₂O fluxes of 0.59 g(N₂O) m⁻² a⁻¹ for South-western Europe using selected data from Heidelberg and Schauinsland station (Germany), and van der Laan *et al.* [2009] found an emission of 0.90 g(N₂O) m⁻² a⁻¹ at Ludjewad (Netherlands).

[43] Figure 7 shows the annual cycle of N₂O emissions at Gif-sur-Yvette catchment area computed from the mean of each nighttime event in orange and from the monthly mean diurnal cycle in green. The mean annual N₂O emissions are, respectively, 0.51 ± 0.18 and 0.34 ± 0.12 g(N₂O) m⁻² a⁻¹. These two curves show the range of the N₂O emissions and contribute to the characterization of total uncertainties. As expected, the standard RTM gives higher flux estimates than the alternative method based on monthly average nocturnal accumulation. The mean difference between the two methods is 0.17 g(N₂O) m⁻² a⁻¹. Regarding the green curve, only a few correlations have been computed between N₂O and ²²²Rn during the winter months, due to the particular meteorological conditions around Gif-sur-Yvette during this season. Conditions of fog and mist formation, which remain for several days in the area surrounding the Gif-sur-Yvette stations do not allow the systematic diurnal cycles in N₂O and radon like those we observe during summer. The non-

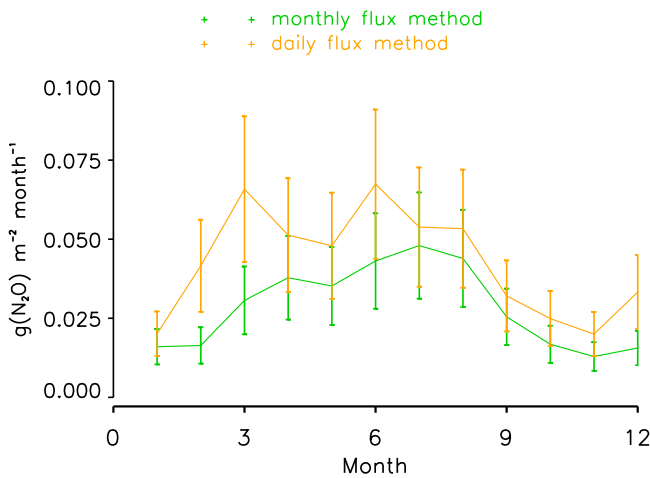


Figure 7. Mean seasonal cycle of N₂O emission in the footprint of Gif-sur-Yvette station computed during the period 2002 to 2011 using two different methods based on collocated ²²²Rn observations: the first method is based on selected nighttime episodes of N₂O accumulation (daily), and second alternative method is based on the monthly average.

correlation observed during winter was expected, as seen from Figure 4, where the diurnal cycles of N₂O and ²²²Rn are very weak in winter. Both calculation methods show the same seasonality trend, with the increase of emissions at the end of winter and early spring to reach a first maxima in March/April. Furthermore, a decrease of emissions is followed by a second peak in summer, with maximum values of 0.067 g(N₂O) m⁻² month⁻¹ for the orange curve and 0.048 g(N₂O) m⁻² month⁻¹ for the green curve. This second maximum is followed by a decreasing N₂O flux until the following spring.

[44] In France, the major source of N₂O emissions is agriculture, 83.6% in 2009 (CITEPA), with the application of fertilizer in soil [Mosier, 1994; Bouwman et al., 2002]. The first peak we observe on Figure 7 is coincident with the timing of the first spreading of fertilizer after January. For most of the arable land in France, the application of fertilizers is forbidden before January (http://www.marne.chambagri.fr/index/action/page/id/93/title/Calendrier_d_epandage). The second peak may result from a second spreading of fertilizer, when plants have grown, or it may be the result of the harvest of a crop followed by an application of fertilizer for the next plantation. At Gif-sur-Yvette and Trainou, local N₂O emissions from nearby fields could also be a large contributor to the observed signals, as described in sections 2.1 and 2.2.

4. Discussion

4.1. Soil Humidity and Rain Events

[45] Two mechanisms are mainly responsible for N₂O emissions from soils: nitrification and denitrification. Laville et al. [1999, 2009] showed that soil moisture content strongly increases N₂O emissions due to an intensification of soil microbial activity. We correlated soil moisture and rainfall with the annual N₂O flux, and we obtained a positive correlation between the annual precipitations at Gif-sur-

Yvette and the annual N₂O flux calculated in the footprint of the station, with an R^2 equal to 0.6 from 2003 to 2010. For years with high precipitation, statistically larger N₂O fluxes are inferred than for years with lower precipitation. For example, an increase of 25% of in annual precipitation results in an increase of 32% in N₂O emission around Gif-sur-Yvette station. This finding illustrates that the N₂O fluxes calculated from atmospheric measurements at Gif-sur-Yvette must be largely influenced by emissions from soils. At Trainou station, we have only two years of data, which do not indicate a statistically significant correlation with precipitation. Figure 8 represents the mean seasonal cycle of N₂O fluxes at Gif-sur-Yvette from 2002–2010 (in yellow) and the N₂O flux at Gif-sur-Yvette for the year 2011 (in blue). The N₂O fluxes in spring 2011 show significantly lower values, with no pronounced peak in March or April. It is recognized that in winter and spring 2011, Northern France had an exceptionally low number of days with precipitation. In April and May 2011, we monitored only 9 mm of rain (with just 1 mm in May). The precipitation from February to May 2011 sums to only 89 mm, which is much lower than the mean seasonal precipitation of 196 mm computed for the same period for the years 2002–2010. This especially dry April and May has affected the N₂O flux insofar as we observe N₂O fluxes approximately two times lower in the winter and spring of 2011 compared with the mean seasonal cycles of the past decade.

4.2. Comparison With Emission Inventories

[46] We compared the N₂O fluxes calculated with the RTM with two emission inventories: EDGAR 4.2 [Olivier and Berdowsky, 2001; Olivier et al., 2001] and CITEPA (<http://www.citepa.org>), which have different spatial and temporal resolutions. CITEPA is the Interprofessional Technical Center for the Study of Air Pollution, which reports the

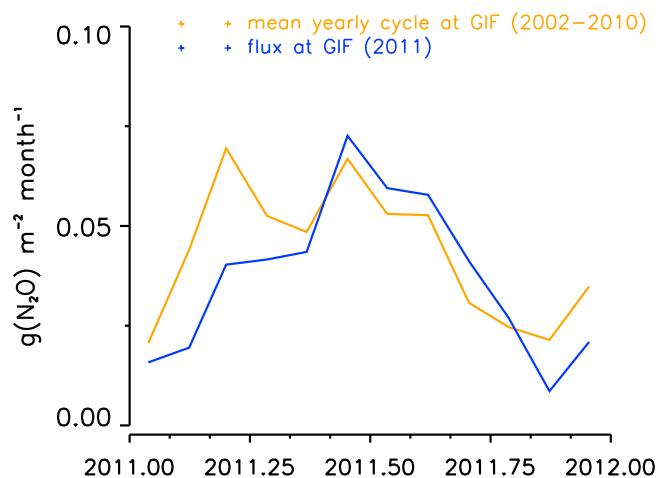


Figure 8. Comparison between mean seasonal cycle of N₂O flux at Gif-sur-Yvette computed for the period 2002 to 2010 (in yellow) and the N₂O flux at Gif-sur-Yvette for the year 2011 (in blue). We observe significant low N₂O fluxes in spring 2011, which result from the dry condition in Northern France during this period.

Table 4. N₂O Flux Densities in the Surroundings of the Stations Gif-sur-Yvette and Trainou Calculated by RTM and the Inventories EDGAR 4.2 and CITEPA for Essonne and Loiret Counties^a

	Gif (Essonne) (g(N ₂ O) m ⁻² a ⁻¹)	Trainou (Loiret) (g(N ₂ O) m ⁻² a ⁻¹)
RTM	0.34 ± 0.12 / 0.51 ± 0.18	0.52 ± 0.18
EDGAR 4.2 grid cell of station	0.57	0.25
EDGAR 4.2 grid cells average	1.02 ± 1.12	0.28 ± 0.16
EDGAR 4.2 for county	0.34	0.24
CITEPA for county	0.32	0.20

^aWe added the variabilities of grid cells around the station given by EDGAR 4.2.

French GHG inventory to UNFCCC. CITEPA reports N₂O emissions for five anthropogenic source categories: agriculture/forestry, industry, road transport, energy conversion and residential/service. The national anthropogenic N₂O emission inventories of France, as reported by CITEPA, between 1990 and 2010, indicate a decrease of 33.2% (from 298 kt to 199 kt of N₂O). This reduction is due mainly to the reported decline in the industrial N₂O source (77%, -67 kt) and in the agriculture/forestry sector (16.4%, -33 kt of N₂O). In 1998, a strong reduction in N₂O emissions from chemical production facilities was reported due to the implementation of catalysts in adipic acid production. From CITEPA, the decreasing trend in reported emissions in the agriculture sector is explained by the reported reduction and optimization of nitrogen fertilizer application. Over the measurement period at Gif-sur-Yvette (2002–2010), the CITEPA inventory gives a reduction of 15.7% for French N₂O emissions (-28 kt from agriculture/forestry and -19 kt from industry). At a regional scale (county), N₂O emissions for the five anthropogenic source categories described above are only available for the year 2000. The regional emission inventories for Essonne County and Loiret County were used to compare to Gif-sur-Yvette and Trainou stations, respectively, as these stations are part of each county. The N₂O emissions given by the CITEPA for the reference year 2000 are, respectively, 0.32 and 0.20 g(N₂O) m⁻² a⁻¹ for Essonne and Loiret counties (Table 4).

[47] EDGAR 4.2 is a global anthropogenic emission database with a spatial resolution of 0.1 × 0.1 degree for N₂O and other trace gases for the reference year 2008 [Olivier and Berdowsky, 2001; Olivier et al., 2001]. EDGAR 4.2 also provides annual emission data for the period 1970–2008 at a country scale. EDGAR 4.2 shows that the N₂O emissions in France decreased by 37% (233 kt to 146 kt of N₂O) for the period 1990–2008. As for CITEPA, this reduction mainly comes from the reported reduction in chemical production (80% reduction, -69 kt of N₂O) and from agricultural sources (10% reduction, -11 kt of N₂O). The decreasing trend in N₂O emissions of approximately -10% from 2002 to 2008 is close to the value reported by the CITEPA. Extracting the corresponding grid cells for Essonne and Loiret Counties, EDGAR 4.2 gives emissions of 0.34 and 0.24 g(N₂O) m⁻² a⁻¹, respectively, for 2008 (Table 4). This result agrees well with the county emission reported by CITEPA for 2000. Using the EDGAR 4.2 gridded emissions, it is possible to extract a more refined scale than the county scale. The nearest grid cells of gridded EDGAR

4.2 emissions were extracted for each station (Gif-sur-Yvette and Trainou). The number of extracted grid cells was chosen using the mean of nighttime wind speed (when we captured a flux event) and considering that we are more sensitive to the emissions from the grid cells closest to the station. For Gif-sur-Yvette, we extracted the four nearest grid cells, and we extracted the nine nearest grid cells at Trainou station. The N₂O emissions of the grid cells around Trainou station show fluxes ranging from 0.15 g(N₂O) m⁻² a⁻¹ (grid cell containing approximately 70% of forests and fields) and 0.75 g(N₂O) m⁻² a⁻¹ (grid cell containing the city of Orleans). For Gif-sur-Yvette, the EDGAR 4.2 emission map gives an even less uniform spatial repartition of N₂O emissions, with fluxes ranging from 0.26 g(N₂O) m⁻² a⁻¹ (grid cell including mostly fields, with 69% of total emission coming from agricultural sources) and 3.85 g(N₂O) m⁻² a⁻¹ (grid cell close to the city of Paris, with 75% of total N₂O emissions coming from road transportation and industrial processes). The EDGAR 4.2 averages of the extracted grid cells for each station are, respectively, 1.02 and 0.28 g(N₂O) m⁻² a⁻¹ for Gif-sur-Yvette and Trainou (Table 4).

[48] The mean annual flux density for Gif-sur-Yvette (2002–2011) between 0.34 and 0.51 g(N₂O) m⁻² a⁻¹ calculated from atmospheric measurements compares reasonably well (Table 4) with both EDGAR 4.2 and CITEPA inventories, considering the large uncertainties of inventories on emission factors (from 10% for industrial sources up to 200% for agricultural source, following CITEPA and chapter 6 of IPCC good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, http://agrienvarchive.ca/bioenergy/download/ipcc_ghg_inv.pdf), the errors of the RTM and the unknown catchment area. The value of the four extracted grid cells from EDGAR 4.2 is strongly influenced by the closest grid cell to Paris, which has an N₂O flux approximately four times higher than the average of the nine grid cells. The grid cell containing Gif-sur-Yvette shows a N₂O emission of 0.57 g(N₂O) m⁻² a⁻¹, very close to the RTM value.

[49] At Trainou, the N₂O emissions estimated by EDGAR 4.2 and CITEPA are in good agreement (Table 4) with a more homogenous repartition of the flux densities around the station (mix of fields, forests and urban area). The N₂O flux density computed with RTM is more than two times greater (0.52 ± 0.16 g(N₂O) m⁻² a⁻¹) than both inventories. This difference can be partly explained by the presence of an industrial point source in the vicinity of the station. The database for industrial emissions from iREP, the French department of Ecology (www.pollutionsindustrielles.ecologie.gouv.fr/IREP/index.php), reports N₂O emissions of industrial plants located in France. According to this database, a manufacturer of household appliances, located 20 km south-west from Trainou station, emitted 129 t of N₂O in 2007 (iREP). This is not accounted for by EDGAR 4.2, which reports only a total emission of 38 t of N₂O for this grid cell. Our measurements are most likely influenced by this extreme point source of N₂O, located in the direction of dominant winds at Trainou station.

[50] N₂O fluxes calculated from atmospheric measurements by the RTM are the sum of emissions from agriculture, forest, industry, road transport and waste management in the catchment area of the station. We now use a simple

Table 5. N₂O Flux Densities From Agricultural Soils and Forests Calculated by RTM and Bottom Up Approach^a

	Gif-sur-Yvette (Essonne)		Trainou (Loiret)	
	(g(N ₂ O) m ⁻² a ⁻¹)	(%)	(g(N ₂ O) m ⁻² a ⁻¹)	(%)
RTM	0.19 / 0.28	54.7 / 53.8	0.23	44.6
EDGAR 4.2 grid cell of station	0.10	18.1	0.19	74.9
EDGAR 4.2 grid cells average	0.10	9.3	0.17	61.7
EDGAR 4.2 for county (2000/2008)	0.17 / 0.17	53.2 / 49.4	0.19 / 0.18	77.4 / 75.9
CITEPA for county (2000)	0.07	21.9	0.15	76.2

^aThe values in g(N₂O) m⁻² a⁻¹ are standardized to the total surface of the county or grid cell.

approach to partition the total emissions into two source categories, based on the analysis of the seasonal cycle. Assuming that industrial, traffic and waste treatment sources do not show a seasonal variation in the source strengths, one can attribute the seasonal cycle purely to the emission of agricultural and forest soils. *Stanford and Vander Pol* [1975] and *Smith et al.* [1998] have shown that N₂O emissions from soils during winter months are very low or close to zero. The low temperatures inhibit nitrification and denitrification, so we can assume that no N₂O emissions occur from the agricultural soils during winter. Therefore, we can consider the lowest N₂O flux density in winter as the sum of industrial processes, traffic and waste treatment without any contribution from soils. The seasonal cycle on top of the background is attributed to emissions from soils. Consequently, it is estimated that the repartition of N₂O emissions between soils and other sources (industry, traffic, waste treatment) is 54%/46% for the catchment area of Gif-sur-Yvette and 45%/55% for Trainou station (Table 5).

[51] Compared to the bottom-up inventories from CITEPA and EDGAR 4.2, the RTM infers a stronger contribution from the soil source at Gif-sur-Yvette. The proximity of fields (less than 500 m to the north) from the Gif-sur-Yvette station measurement implies a larger contribution of N₂O emissions by fields. On the contrary, regarding the ratio of agricultural sources at Trainou, we found a smaller contribution of N₂O emissions from soils compared to the inventories. As explain above, the inventories do not account for the industrial source, which emitted 129 t of N₂O in 2007. The RTM results are affected by the emissions of this industry, which increase our background estimation, inducing a decrease in the percentage from the agricultural source.

[52] Furthermore, the EDGAR 4.2 inventory does not account for the N₂O emissions of natural soils such as forests, whereas CIPETA considers agricultural and forest sources as a single source. A study by *Pilegaard et al.* [2006] shows that the emissions of N₂O by forests (mainly due nitrogen deposition) can be significant, and they attribute to forests a mean N₂O emission of 0.09 g(N₂O) m⁻² a⁻¹. This emission value of N₂O by forests is considered by IPCC as a maximum (IPCC Good Practice Guidance for LULUCF, Appendix 3a.2). Normalizing the forest emissions to the surface of Essonne and Loiret Counties, we compute a respective contribution by forests of 0.02 and 0.03 g(N₂O) m⁻² a⁻¹ to the total N₂O surface emission, which represents a net emission of 40.6 t in Essonne and 182.9 t in Loiret County. Accounting for the estimated uncertainties of the inventories and the RTM, the flux densities (bottom up) and the statistical ones (top-down) agree fairly well. The repartition of emissions from soils and the other sources shows a

more heterogenic picture between the two inventories themselves, the extracted grid cells, and the results of the RTM.

5. Conclusions

[53] In this study, we have demonstrated that atmospheric trace gas measurements in combination with semi-continuous ²²²Rn observations are well suited to derive top-down estimates of emissions for gases with very large spatial and temporal variable emission sources, such as N₂O. Analyzing the diurnal variation of the small N₂O peaks on the order of only 1–3 ppb, we calculate the flux densities, revealing clear seasonality due to emissions from arable soils and forests. Especially in spring and summer, we found large N₂O emissions, whereas the determined N₂O fluxes during winter months are close to zero. Here, we were able to integrate larger regions, suggesting good integration over individual, temporal and quantitative applications of fertilizer on different land parcels. Resolving these processes by direct chamber measurements or eddy covariance measurement would require a more extensive effort. The very good agreement in the N₂O flux densities for the monthly average value around Trainou and Gif-sur-Yvette station, within a distance of approximately 80 km, shows clearly that the RTM method is valuable on a regional scale.

[54] On the country scale in France, the EDGAR 4.2 and CITEPA emission inventories reported decreasing N₂O emissions of approximately 10% during 2002 and 2008. This decreasing trend could not be constrained by the N₂O flux densities inferred from atmospheric measurement at Gif-sur-Yvette during this period. However, the N₂O flux density derived by the atmospheric approach shows a slightly increasing tendency over the last years. In general, N₂O fluxes from soils, as shown for the catchment area of Gif-sur-Yvette station, are strongly dependent on soil humidity and precipitation. The results deduced here reflect the meteorological conditions during various years. Therefore, it is difficult to directly compare the inventory-based decreasing trend, which does not account for the actual meteorological observations, as does our study. A longer time series would be required to minimize the meteorological influences.

[55] This study shows how useful top-down estimates can be to provide independent verification of bottom-up inventories. In the case of N₂O, where meteorological conditions play an important role, long term measurements are necessary to determine reduction efforts.

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