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Ten years of CO_2, CH_4, CO and N_2O fluxes over Western Europe inferred from atmospheric measurements at Mace Head, Ireland

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Abstract

We estimated CO_2, CH_4, CO and N_2O emission fluxes over the British Isles and Western Europe using atmospheric radon observations and concentrations recorded at the Mace Head Atmospheric Research Station between 1996 and 2005. We classified hourly concentration data into either long-range European or regional sources from Ireland and UK, by using local wind speed data in conjunction with ^{222}Rn and ^{212}Pb threshold criteria. This leads to the selection of about 7% of the total data for both sectors. We then used continuous ^{222}Rn measurements and assumptions on the surface emissions of ^{222}Rn to deduce the unknown fluxes of CO_2, CH_4, CO and N_2O. Our results have been compared to the UNFCCC, EMEP and EDGAR statistical inventories and to inversion results for CH_4. For Western Europe, we found yearly mean fluxes of $4.1\pm1.5\,10^6\,kg\,CO_2\,km^{-2}\,yr^{-1}$, $11.9\pm2.0\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$, $12.8\pm4.2\,10^3\,kg\,CO\,km^{-2}\,yr^{-1}$ and $520.2\pm129.2\,kg\,N_2O\,km^{-2}\,yr^{-1}$, respectively, for CO_2, CH_4, CO and N_2O over the period 1996–2005. The method based upon ^{222}Rn to infer emissions has many sources of systematic errors, in particular its poorly known and variable footprint, uncertainties in ^{222}Rn soil fluxes and in atmospheric mixing of air masses with background air. However, these biases are likely to remain constant in the long-term, which makes the method quite efficient to detect trends in fluxes. Over the last ten years period, the decrease of the anthropogenic CH_4, CO and N_2O emissions in Europe estimated by inventories (respectively −30%, −35% and −23%) is confirmed by the Mace Head data within 2%. Therefore, the ^{222}Rn method provides an independent way of verification of changes in national emissions derived from inventories. Using European-wide estimates of the CO/CO_2 emission ratio, we also found that it is possible to separate the fossil fuel CO_2 emissions contribution from the one of total CO_2 fluxes. The fossil fuel CO_2 emissions and their trends derived in that manner agree very well with inventories.

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1 Introduction

Global networks to monitor the atmospheric mixing ratio of greenhouse gases (GHG) have been established by the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory NOAA CMDL (Conway et al., 1988;Dlugokencky et al., 1994;Butler et al., 1998), the Atmospheric Lifetime Experiment–Global Atmospheric Gases Experiment (ALE-GAGE) (Prinn et al., 1990; 2000), and others. Traditionally these networks, with stations situated remotely from sources, focused on tracking long-term trends and large-scale gradients on the global scale. On the basis of these measurements, coarse-scale (large ocean basins, continents) budgets of greenhouse gases have been calculated using inverse models. Nowadays, the global budgets of most GHGs are relatively well quantified and their major sources and sinks identified. However, on the regional scale, large uncertainties still remain. At this scale, the information available for GHG emissions is generally limited to statistical inventories (UNFCCC, 2007; EMEP, 2007; EDGAR, 2007). There are several limitations in the inventory based regional GHG budgets: natural sources are generally not taken into account; uncertainties are only based upon errors in input statistics, and information about temporal and spatial variability is not provided. Independent verifications of the national emissions derived from inventories are thus crucial.

On local scales, trace gas fluxes of GHG can be measured directly. However, the spatially heterogeneous and temporally variable distribution of these fluxes requires significant upscaling, using models and datasets with extensive coverage. Regional studies that fill the gap between the global and local scales are therefore needed to improve our estimates of emission inventories. During the last years, the networks of atmospheric measurements have become denser in Europe and also in North America (CARBOEUROPE-IP, http://www.carboeurope.org/, North American Carbon Plan, http://www.isse.ucar.edu/nacp/). Several studies attempted to regionalize greenhouse gas budgets using atmospheric observations at continental sites, where information about the sources was extracted from concentration changes on timescales of hours

and days (Bakwin et al., 1997; Derwent et al., 1998; Levin et al., 1999; Schmidt et al., 2003; Biraud et al., 2000; Manning et al., 2003). All this studies used quasi-continuous GHG concentration measurements, and in most cases combining together the records of different species. Recent inverse modelling work also attempted to make use of these continuous GHGs observations (Bergamaschi et al., 2005; Peylin et al., 2005).

Western European and Irish greenhouse gas emission fluxes for the years 1996 and 1997 (Biraud et al., 2000, 2002) were estimated in two previous studies using the continuous GHG data from the Mace Head station in Ireland. The approach was to scale synoptic variations of GHGs by those of ^{222}Rn, a tracer emitted rather uniformly by soils (Levin et al., 1999; Biraud et al., 2002; Schmidt et al., 2001a). In this study, we re-analyze ten years of atmospheric CO_2, CH_4, CO and N_2O data and use ^{222}Rn to better quantify their fluxes. In this approach, we developed and applied a new data selection procedure to better discriminate between air masses of western European and Irish origin. The fluxes scaled over Europe and Ireland have been analysed for seasonal cycles and trends, and compared to emission inventory estimates.

2 The Mace Head GHG atmospheric records and measurement techniques

Mace Head atmospheric research station (Carna, County Galway) is located on the west coast of Ireland (53°20′ N, 9°54′ W). This station is one of the most important sites for atmospheric research in the northern hemisphere. Its location facilitates the investigation of trace constituents changes in marine and continental air masses. The station is dominated by maritime air masses most of the time, but there are some modified continental air masses coming from Europe, which represents about 10% of the total data.

Mace Head is a part of a number of international research networks and is operated by the Department of Physics of the National University of Ireland, Galway (NUI-Galway). Since 1992, a collaborative CO_2 measurement program has been implemented between LSCE and the University of Bristol (Bousquet et al., 1997). The work

was extended in 1995 to add a ^{222}Rn monitor at the station (Biraud et al., 2000). Atmospheric CO_2 concentration has been continuously measured using non-dispersive infrared analysers (NDIR). A Siemens Ultramat 5F was used from July 1992 to August 2002, and since August 2002 a Li-Cor 6252 has been deployed. The instruments data flow rate is 1 Hz and an hourly mean is automatically computed. The instruments are calibrated against the Scripps Institution of Oceanography (SIO) X93 mol fraction scale and the precision of the CO_2 concentration is better than 0.1 ppm (Bousquet et al., 1997). ^{222}Rn and ^{212}Pb, two natural radioactive compounds, are also measured at Mace Head by an active deposit method, with a time step of 2 h. The absolute error is estimated to be in the order of 20% (Polian et al., 1986; Biraud et al., 2000).

The University of Bristol has been measuring GHG and Montreal species as part of the ALE/GAGE/AGAGE network using a gas chromatograph with multi-detectors (Simmonds et al., 1996; Cunnold et al., 1997; Prinn et al., 2000). CH_4 and N_2O have been measured since January 1987, and CO since 1990 with a time step of 40 min. All the ALE/GAGE/AGAGE data are now recalibrated to the SIO-2005 scale (see Prinn et al., 2000). The data used in the present study can be obtained on the CarboEurope Atmosphere Database (http://www.ce-atmosphere.cnrs-gif.fr/database/index_database.html for CO_2, ^{222}Rn and meteorological parameters) and on the AGAGE web site (http://agage.eas.gatech.edu/data_archive/ for CO, CH_4 and N_2O).

Figure 1 presents the CO_2, ^{222}Rn, CO, CH_4 and N_2O in-situ measurements at Mace Head between 1992 and 2005. In these long-term series, we can see a trend in baselines, as well as in seasonal cycles. For example in the CO_2 time series, we observe a long-term concentration increase (at a mean rate of 2 ppm per yr) and a seasonal cycle with minimum summertime value in August and a broad wintertime maximum from December. Superimposed on this signal are synoptic peaks generally associated with pollution events from Europe, and even from North America.

3 Data selection of the Mace Head record

3.1 Data partitioning into marine, long-range european and regional origins

Different methods have already been tested to classify the Mace Head hourly data (Bousquet et al., 1997; Ryall et al., 1998; Biraud et al., 2000). A baseline selection has been first defined to detect marine air masses from the north Atlantic (clean air sector) using winds and hourly CO_2 concentration stability (Bousquet et al., 1997). Then, data selection protocols based upon winds and variability have also been developed to identify polluted air from Europe (Biraud et al., 2000), and air masses influenced by local sources in Ireland (Biraud et al., 2002). We aim here to classify the data into marine, European and regional (Ireland+UK) categories, based upon local wind speed and direction, CO_2 concentration stability, and ^{222}Rn and ^{212}Pb values criteria. The data selection criteria are summarized in Table 1.

1. To select oceanic air masses, we retain according to Bousquet et al. (1997), wind velocity values $>4\,m\,s^{-1}$ within the (marine) sector 210–290°, and winds $>8\,m\,s^{-1}$ within the tangential to the coast sectors 200–210° and 290–300°. In addition, hourly CO_2 standard deviation must be <0.4 ppm, and a marine "event" must last at least 4 h.

2. To select air masses with European long-range transport, we retain periods with ^{222}Rn>1000 mBq m^{-3} and ^{212}Pb<40 mBq m^{-3}. ^{212}Pb is a regional tracer of continental exposure with a radioactive decay time of 10.6 h. Therefore, placing an upper limit on the ^{212}Pb concentration ensures little contamination of the selected European events by proximate Irish emissions. In addition, the mean wind speed during such European long range transport events must be greater than $5\,ms^{-1}$ for at least 4 h.

3. To select regional air masses from Ireland and UK, we retain period with ^{222}Rn>400 mBq m^{-3}, and ^{212}Pb>10 mBq m^{-3}. In addition, the mean wind speed

must remain lower than 5 m s^{-1} for at least 4 h.

The criteria that we have defined are exclusive so that a given synoptic event can only be attributed to a single classification.

3.2 Choice of triple selection criteria using ^{222}Rn, ^{212}Pb and wind speed

^{222}Rn and ^{212}Pb are continuously emitted by soils and can be used as continental tracers (the ^{222}Rn oceanic sources are 100 to 1000 times less than continental sources (Wilkening and Clements, 1975). ^{222}Rn is used as a medium range continental tracer on synoptic transport time scales (radioactive decay time of 3.8 d) while ^{212}Pb provides a fingerprint of air freshly formed over land (radioactive decay time of 10.6 h). Using these two tracers, it is possible to separate local from long-range transported events. High ^{222}Rn coincident with high ^{212}Pb levels relate to local air masses, while high ^{222}Rn and low ^{212}Pb levels are representative of European air masses (Lambert et al., 1982; Polian et al., 1986; Biraud et al., 2000; 2002). One has to determine appropriate dual criteria values for these two tracers. The oceanic data set over 1996–2005 indicates a mean background of 200 mBq m^{-3} for ^{222}Rn and of 5 mBq m^{-3} for ^{212}Pb. Further, 90% of the hourly ^{222}Rn and ^{212}Pb values in the marine selection are below 10 mBq m^{-3} for ^{212}Pb and 400 mBq m^{-3} for ^{222}Rn (Fig. 2). We hence set up our minimum threshold values equal to these upper marine limits to define the Ireland+UK regional selection. A wind velocity maximum of 5 m s^{-1} further ensures that long-range transported air masses from the European continent are filtered out (under such low wind speeds, the air has resided at least 24 h over Ireland or over the UK). To select long-range European air masses, we used the same robust criteria as in Biraud et al. (2000).

In order to increase the data selection performance, ECMWF (European Center for Medium Range Weather Forecasts) wind data have been used in the selection algorithm whenever no in situ wind speed was available. The ECMWF data have been extracted from the ECMWF 45-year re-analysis (Uppala et al., 2005) for the period before 1 September 2002 and from the operational archive since then. Comparison

between ECMWF and in situ wind speed values over 2000–2005 gives a high correlation (R^2=0.86) and a linear regression slope of 0.97. The absolute difference between in situ and ECMWF hourly wind speed is 2 m s^{-1} (it represents 10% of the maximum observed wind speed and less than 1% of the selected data).

Using the above defined criteria we find on average that 30% of the air masses measured at Mace Head are entirely from the Atlantic marine sector, 6% from Ireland+UK and 7% from long-range European origin (Table 2). The average duration of the selected events is 25 h for the Ireland+UK, and 28 h (range 4 to 120 h) for the European long-range selections.

3.3 Occurrence of continental air masses

Figure 3 shows the averaged seasonal and diurnal histograms of selected events for the two continental sectors. European events are predominantly selected during wintertime, while Ireland+UK events occur during summer time. This is due to different meteorological regimes. We distinguish two main types of transport regimes bringing air from the continent to Mace Head. The first regime (regional) corresponds to an anticyclonic circulation over Ireland due to a high pressure system over the United Kingdom or over northern France. The second regime (long range) is characterized by an easterly flow chanelled by a depression situated either over Ireland or over the United Kingdom (Biraud, 2000). It is also clear in Fig. 3 that the air masses classified as being from Ireland+UK are sampled mostly during night-time. A rise in ^{222}Rn, CO_2, CH_4, CO and N_2O concentrations at Mace Head is associated with nocturnal accumulation in the stable boundary layer, coupled to advection by land breeze. As the land cools off at night, air pressure increases, and a land breeze systematically develops which transports air from the interior to Mace Head.

3.4 Independent verification of tracer-based data selection

It is difficult to find an alternative method to independently validate our data selection protocol based upon tracers and meteorology. Back trajectories estimated by the HYSPLIT-4 model, were used for that purpose. HYSPLIT-4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model (Version 4) is a complete system for computing simple trajectories, using the NCEP meteorological data (Draxler and Rolph, 2003; Rolph, 2003). Figure 4 shows the center of mass of air masses backtrajectories selected for a European, and for a Ireland+UK origin. One can see that our long-range European selection corresponds to air masses coming from northern France, Germany, UK and Benelux countries, whereas our Ireland+UK selection corresponds to air masses that spend at least 12 to 24 h over Ireland. Yet, according to the backtrajectory analysis results (Fig. 4), our selection method is ineffective to accurately separate United Kingdom.

We also verified our data selection using the Numerical Atmospheric dispersion Modelling Environment (NAME) transport model results. The NAME dispersion model has been used to determine the fraction of air arriving at Mace Head, from different European regions (Manning et al., 2003). With this methodology, they selected 11% of the total air masses reaching the Mace Head station as long-range European and 16% as regional to local (Table 3). We have compared their selection with our in situ criteria and found a good agreement between the two approaches. At least 60% of agreement was found for Europe and 50% for Ireland+UK (that is more than 50% of the ^{222}Rn and ^{212}Pb based selected events agree with the NAME model classification). The NAME model selection is more effective than ours because it determines an origin for each hour continuously, while we depend on data availability.

In the following, we will use both the in-situ ^{222}Rn and the NAME selection methods to determine the European and Ireland+UK trace gas emissions. We also make a combination of these two techniques in order to derive an error range on the inferred fluxes.

4 Case study of typical irish and european events

4.1 Events influenced by long-range european emissions and transport

Figure 5 shows a three and a half day typical European wintertime synoptic event occurring during the period 21–24 December 2000. During the whole event, the wind velocity is continuously greater than 7 m s^{-1} and the wind direction rotates from 125 to 90° (from the south east). This particular meteorological situation corresponds to a low-pressure system over the Atlantic Ocean, combined with high pressure over Scandinavia. It leads to a European easterly flow with winds coming from western Europe (in this case from France and Spain). From 20 to 21 December, the ^{222}Rn concentration increases rapidly up to values higher than 4000 mBq m^{-3}, about 15 times the oceanic background. The Radon concentration then stays between 2000 and 4000 mBq m^{-3} until 24 December at 10:00 UTC, the end of the event. Such high and persistent ^{222}Rn concentrations denote a clear signature of recent continental air. At the same time, ^{212}Pb is maintained at a relatively low level (<15 mBq m^{-3}), which indicates no recent near-field continental exposure. Within this period, one can observe an increase of CO_2, CH_4 and CO. CO_2 is increasing slowly from 380 ppm up to 390 ppm with a small diurnal cycle (higher concentrations during the night). When the event terminates, ^{222}Rn and ^{212}Pb both drop down to their marine baseline level. This event tail is however not classified as an oceanic one because the wind direction is not from the marine sector.

4.2 Event influenced by ireland and UK emissions

Figure 6 shows an example of CO_2, ^{222}Rn, ^{212}Pb, CH_4 and CO variations together with wind velocity and wind direction at Mace Head from 21–26 May 2001. On 19 May, the station was influenced by strong westerly winds, resulting in low values of all trace gases and CO_2 hourly standard deviations lower than 0.07 ppm. From 21 May, strong diurnal cycles develop in most of the analysed compounds. In the night of 21–22 May,

an Irish event is selected (filled in grey), which fullfills our triple regional selection criteria of low wind speed and high radionuclide concentrations. The situation is similar for the two following nights. Each day, between 00:00 and 12:00 UTC, an increase in ^{222}Rn, ^{212}Pb, CO_2, CH_4 occurs, reflecting accumulation in the shallow stable nocturnal PBL and land breeze. Without a land breeze, one would rather expect a linear progressive increase of all tracers during the night, stopping in the morning when convection gets established (Gibert et al., 2007). Here, the sharper observed increase and its duration until mid-day, coincident to the sharp wind direction shift (Fig. 6) rather suggests that land breeze plays a dominant role. During each regional "event", the ^{212}Pb concentration changes repeatedly from a low level ($\approx$0 mBq m^{-3} i.e. the oceanic background) to an extremely high level (up to 100 mBq m^{-3} on 22 May which is typical of a recent continental exposure). The ^{212}Pb maxima are also related to the low wind speed (<5 m s^{-1}) and local land breeze circulation. This situation is typical of a blocking over Ireland due to a high-pressure system located over the British Isles.

5 Fluxes estimation method

We infer the surface fluxes of CO_2, CH_4, CO, N_2O using ^{222}Rn as a reference species. This method has been used before by (Biraud et al., 2000, 2002; Schmidt et al., 2001b; Schmidt et al., 2003) and is briefly summarized here after. The surface flux $\overline{J_x}$ of species x over the source region influencing the measurement station during a synoptic event, assumed to be vertically diluted in a well-mixed PBL, can be expressed by:

$$\overline{J_x} = \overline{J_{Rn}} \frac{\Delta C_x}{\Delta C_{Rn}} e^{-\lambda_{Rn}\tau} \quad (1)$$

where $\overline{J_{Rn}}$ is the mean ^{222}Rn emission rate in the region of influence (assumed to be constant and uniform), and $\frac{\Delta C_x}{\Delta C_{Rn}}$ is the slope of the linear regression between hourly observations of x and ^{222}Rn. For each event including more than 3 data points we

calculate a linear regression slope between ^{222}Rn and the variation of each other trace gas by minimizing the chi-square error. Then events with a Pearson correlation coefficient less than 0.5 were rejected. The term $e^{-\lambda_{Rn}\tau}$ is a correction factor for the ^{222}Rn radioactive decay, which has to be considered if the air is not in contact with the land surface. We used the ^{222}Rn radioactive constant value λ_{Rn} of 0.182 d^{-1}. For each event classified as long-range European, the transit time τ is computed using the HYSPLIT-4 back-trajectory output and a gridded European country map at 0.5°×0.5° resolution. The transit time is defined as the number of hours when the air mass has not been in recent contact with the land surface (i.e. over the ocean). Given the maximum event duration of 120 hours, a corresponding 120 hours back-trajectory is used to calculate the value of τ for each event, defined as cumulated number of hours spent over the ocean before reaching Mace Head. During the period 1996-2005, the average transit time is 28 h. This value is used by default in case of missing back trajectory data, which reduces the estimated flux by 20%. For events classified as originating from Ireland+UK, the radioactive decay correction factor is neglected and air masses are considered to be in permanent contact with the land surface. Schmidt et al. (2003) showed that during a typical night time inversion, the changes in ^{222}Rn activity as a result of radioactive decay, was offset by emissions from soil, and lowered ^{222}Rn values by only 3–4%.

The ^{222}Rn flux is not constant in time because higher soil humidity decreases the exhalation rate (Eckhardt, 1990). However, due to the few measurements available, it is difficult to estimate the temporal variability of the fluxes (Szegvary et al., 2007; Szegvary, 2007). We have estimated a seasonal cycle for the European ^{222}Rn flux using a yearly mean exhalation rate of 57 Bq m^{-2} h^{-1} (Eckhardt, 1990) and a seasonal variation of 20% higher in summer and 20% lower in winter (Schmidt et al., 2003; Biraud et al., 2002). For the ^{222}Rn flux emitted by Ireland, we used a yearly mean exhalation rate of 54 Bq m^{-2} h^{-1} and a seasonal variation of 65% higher in summer and 43% lower in

winter, based on the field campaigns of Biraud et al. (2008[1]). We did not take into account any spatial or synoptic variability. There are two main sources of uncertainty: the ^{222}Rn emission flux used and the regression slope error. The uncertainty of the ^{222}Rn exhalation rate is estimated to be on the order of 20% (Eckhardt, 1990). We computed a mean uncertainty on the slopes of 10%. Propagating these errors implies an overall uncertainty of the inferred flux $\overline{J_x}$ on the order of 30% (Biraud et al., 2000).

6 Results and discussion

The emissions of CO_2, CH_4, CO and N_2O deduced from the ^{222}Rn method for the events selected as European or Ireland+UK are shown in Fig. 7 and reported in Table 4-11. Three data selection methods were used based upon (1) ^{222}Rn and ^{212}Pb, (2) the NAME transport model results (Manning et al., 2003), and (3) a combination of both where the events common to (1) and (2) are used. We compared the results obtained from these three selection methods with national emission inventories. The UNFCCC inventory data for CO_2, CH_4 and N_2O (http://unfccc.int/ghg_emissions_data/items/3800.php) anthropogenic emissions and the EMEP expert emission data (UNECE, 2003) for CO anthropogenic emissions (sector SNAP national, http://webdab.emep.int) were used. Fluxes deduced from European long-range events were compared to the sum of emissions from France, Germany, Netherlands, Belgium, Luxembourg and United Kingdom. Regional fluxes deduced from UK+Ireland were compared to the sum of emissions from these two countries.

The major shortcoming of the radon flux estimation method is the lack of information on the emission footprint associated with each event. In order to separate the contribution of each European countries emissions to the events recorded at Mace Head,

[1]Biraud, S., Ielsch, G., Ramonet, M., Jutzi, S., Cuntz, M., Ciais, P., Levin, I., and Jennings, S. G.: Direct measurements of the 222-radon exhalation rate from soils in ireland., in preparation, 2008.

we used back trajectories. For each hourly data classified with a European long-range origin, we calculated the residence time over each 1°×1° degree pixel in western Europe. We found that the four countries which contribute dominantly to the Mace Head synoptic events are: France, Germany, Netherlands and United Kingdom. However, each country contribution varies from year to year. For example, the contribution of Germany and Netherlands was found to be four times higher between 1999 and 2002 than during the other years. In addition, the percentage of European long range events is at least two times higher between 1999 and 2002 than for other years (Table 2). We can also see stronger peaks in the CH_4 and CO time series (Fig. 1).

6.1 CH_4 emissions

We determined a mean CH_4 flux of $11.9\pm2.0\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$ and $16.5\pm2.3\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$, respectively, for Western Europe and Ireland+UK over the period 1996–2004. The flux variability within one year, calculated from individual synoptic events, is 5 and $9\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$, respectively, for Europe and Ireland+UK. This variability relates to the different footprint of each event, and also to the period of the year and the day at which the air mass is enriched by surface emissions. For the same period, the mean CH_4 flux of the UNFCCC inventory is $8.3\pm1.0\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$ and $12.5\pm2.0\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$, respectively, for Western Europe and Ireland+UK. The EDGAR inventory provides an emission estimate for 2000 which is in good agreement with the UNFCCC data, with a reported uncertainty of 50% (Olivier et al., 1999). Over the same countries used in our radon and back-trajectory approach (Sect. 5), the NAME model inversion (Manning et al., 2003) gives a mean CH_4 emission of $10.4\pm0.7\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$ and $11.5\pm0.6\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$, respectively, for Europe and Ireland+UK over 1995–2000 (Figs. 8 and 9).

Our flux estimates are greater than the UNFCCC values by about 33% and 24% for Europe and Ireland+UK, respectively. The Manning et al. (2003) results lies in-between

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(Figs. 8 and 9). Unlike the atmospheric estimates, the inventories are not reporting the total emissions, but only account for anthropogenic sources. This explains why they give lower emissions than the atmospheric approach. At the European level or at national scale, there is little information about the relative contribution of natural sources. The CORINAIR inventory indicates 28% of natural sources in 1990 for EU-15 (Grösslinger et al., 1996) which is comparable to the discrepancy observed between our estimates and the inventories.

Another difference between our results and the UNFCCC inventories is the interannual variability. The radon-derived annual fluxes differ from UNFCCC by 25% to 80% depending on the year considered. Between 1996 and 2004, the UNFCCC data indicate a total decrease of CH_4 emissions of 30%. This decrease is attributed to reduced CH_4 emissions from fugitive emissions (−41%) mainly due to the decline of coal mining, followed by waste (−49%) mainly due to reducing the amount of untreated biodegradable waste in landfills and installing landfill gas recovery (EEA, 2005). Over 2002–2004, the CH_4 flux computed using the Mace Head data decrease of 30%, which is comparable to the trend in UNFCCC data. No significant trend was obtained by our method for Ireland+UK emissions, whereas the UNFCCC indicates a 35% decrease of the sum of anthropogenic sources. The main reason for this discrepancy is probably due to the role of the natural sources (wetlands mainly) whose intensities co-vary with the climate (Bousquet et al., 2006). We compared our results to the CH_4 European estimated from the global network of stations in the synthesis inversion of Bousquet et al. (2006). This study solved for monthly fluxes over large regions (Europe being one of them) with a fixed a priori geographic emission pattern within each region. The Mace Head station data were assimilated in the inversion of Bousquet et al. (2006), but monthly concentrations were used. So their flux estimates are rather constrained by spatial-temporal monthly gradients among different stations within and around Europe, than by synoptic scale variations as in this study. We averaged the Bousquet et al. (2006) flux estimate over Europe only for the grid-points belonging to the 4 countries dominantly influencing the Mace Head synoptic variability (Sect. 5). The results are shown in Figs. 8 and 9.

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Both for Europe and Ireland+UK, the interannual variability of the CH_4 emissions are comparable between the radon method ($\pm 2.0\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$) and the Bousquet et al. (2006) global inversion data ($\pm 1.4\,10^3\,kg\,CH_4\,km^{-2}\,yr^{-1}$). The mean value of the inversion is lower than the radon based estimates. However, according to Bousquet et al. (2006) the year-to-year CH_4 regional flux changes can be more robustly inverted than their mean values. The inversion mean flux is very close to the EDGAR value, which is used as the a priori flux. Our abnormally high CH_4 European emission in 2001 is very close to the results of Bergamashi et al. (2005) who used a regional inversion and assimilated the synoptic CH_4 variability, but it is significantly higher than the Bousquet et al. (2006) who used a global inversion and assimilated only monthly smoothed gradients.

6.2 N_2O emissions

Fertilizer use in agriculture is the main contributor to the european-scale N_2O flux (39% (Grösslinger et al., 1996). Other natural sources (forest soils, estuaries and wetlands) are estimated to be roughly equivalent to the agricultural source (Grösslinger et al., 1996). The other anthropogenic sources (from industrial processes) represent 30% of the total emission (Grösslinger et al., 1996). The level of uncertainty of inventories for fertilizer induced emissions (based upon emission factors) are very high for N_2O, on the order of 100% (Olivier et al., 1999;Bouwman et al., 2000). According to inventory data, there has been a large decrease of N_2O emissions of 23% during the past decade in the 4 western European countries investigated by the ^{222}Rn method. This decrease is primarily due to reduced anthropogenic emissions via the implementation of cleaner industrial processes (58%) in adipic acid production plants in UK, Germany and France (EEA, 2005). In addition, N_2O emissions from agricultural soils are reported to have decreased by 8% between 1990 and 2002, due to a decline in fertilizer and manure use (EEA, 2005).

We determined a mean N_2O flux of $520.2 \pm 129.2\,kg\,N_2O\,km^{-2}\,yr^{-1}$ and

644.7±171.9 kg N_2O km^{-2} yr^{-1}, respectively, for Europe and Ireland+UK over the period 1996–2004. As shown in Fig. 8 the European emissions are very comparable to the average estimate of Manning et al. (2003) with the NAME model for 1996–2000 (603.6±104.4 kg N_2O km^{-2} yr^{-1}). Our flux estimate for Ireland+UK is however greater than their calculation (488.5±79.8 kg N_2O km^{-2} yr^{-1}). The N_2O source estimation of Schmidt et al. (2001a), based upon the Schauinsland atmospheric record (Germany), is 578±55 kg N_2O km^{-2} yr^{-1} for year 1998, which lies within our error bar for Europe (Fig. 8). Note that the region of influence of the Schmidt et al. (2001a) study corresponds more to south-western Europe.

Our mean European N_2O emission estimate is very close to the UNFCCC inventory data (difference of +7.4%). It is greater than the UNFCCC for Ireland+UK (difference of +30%). Considering that the inventory accounts only for anthropogenic sources, such a relatively small difference would suggest that either anthropogenic sources are overestimated, or that the natural sources are very small in Europe. The EDGAR database gives a total anthropogenic N_2O emission for year 2000 which is 50% higher than the UNFCCC. The EDGAR value is very close to the emission rate we are estimating for year 2000 both for Western Europe and Ireland+UK (Figs. 8 and 9). Regarding the trend over the period 1996–2004, our estimates suggest a decrease of N_2O emissions by 21 and 29% respectively for Western Europe and Ireland+UK. These values are compatible with the trends given by UNFCCC (23% and 28% for the same regions). This good agreement of the trends indicates that the natural sources which are included in the atmospheric method do not have any significant trend for this period.

6.3 CO_2 fluxes

We determined a CO_2 flux for the period 1996–2004 equal to 4.1±1.5 10^6 kg CO_2 km^{-2} yr^{-1} and 6.6±2.9 10^6 kg CO_2 km^{-2} yr^{-1}, respectively, for Western Europe and Ireland+UK. This value is 1.4 times the one of Europe and 2.5 times the one of Ireland+UK compared to UNFCCC data. It is likely that this difference

can be explained by natural fluxes, which are not counted by inventories. Moreover, anthropogenic emissions are spatially heterogeneous, ranging for instance from 0.7 (France) to 4.3 (Netherlands) $10^6\,kg\,CO_2\,km^{-2}\,yr^{-1}$. Depending on the influencing source region, the CO_2 vs. ^{222}Rn slopes differ greatly at Mace Head, resulting in variable inferred fluxes between events. An improvement of our method in the future should be to use footprint calculations (Hirsch, 2006) to provide explicit information about the source region, and allow quantitative comparison with geo-referenced emission inventory data.

The terrestrial CO_2 fluxes are also strongly variable in both space and time. The CO_2 sources from soil and plant respiration estimated by the ORCHIDEE model (Krinner et al., 2005) over western Europe during 1996–2004 range from 2.9 to $3.4\,10^6\,kg\,CO_2\,km^{-2}\,yr^{-1}$, with an average value of $3.2\,10^6\,kg\,CO_2\,km^{-2}\,yr^{-1}$ (Vetter et al., 2007). CO_2 uptake by photosynthesis is of the same order of magnitude, but occurs only in daytime, and during the growing season. Our data selection is strongly biased towards respiratory fluxes. Indeed, the selection of European long-range events picks up more events in autumn and winter. The selection of Ireland+UK events picks up almost always night-time data (Fig. 3). Another process (called rectifier effect) is making the detection of biospheric CO_2 uptake more difficult than the one of respiration. The diurnal and seasonal rectifier effect (Denning et al., 1995) correspond to a covariance between the PBL height and CO_2 biospheric fluxes. Due to a greater dilution of sinks, the surface CO_2 concentration changes caused by photosynthesis is much smaller than the ones caused by respiration. Consequently the correlation between ^{222}Rn and CO_2 variability is not very high in summer and in daytime (Hirsch, 2006). We have also to consider that the combined influence of regional sources and sinks in a given air mass, may degrade the correlation between CO_2 and ^{222}Rn variations. One can expect to find a better correlation for an air mass which is only influenced by a positive flux to the atmosphere.

We have compared in Fig. 10 the ^{222}Rn derived European CO_2 flux with the "bottom up" sum of UNFCCC anthropogenic emissions and total ecosystem respiration of the

ORCHIDEE model (Vetter et al., 2007). On average, the bottom-up estimate is only 9% higher than the ^{222}Rn based value (4.5 versus 4.1 10^6 kg CO_2 km^{-2} yr^{-1}). Our estimate displays a stronger interannual variability than the bottom-up one. This difference could results from a change in the footprint of synoptic events recorded at Mace Head.

6.4 CO emissions

We inferred a mean CO flux of 12.8±4.2 10^3 kg CO km^{-2} yr^{-1} and 11.9±1.9 10^3 kg CO km^{-2} yr^{-1} respectively for Europe and Ireland+UK during 1996-2004. There is practically no natural CO source over Europe (Olivier et al., 2003; Pfister et al., 2004) and secondary emissions by VOC oxidation are in the order of 5% (Granier et al., 2000) which may not influence our estimates. Consequently we expect a closer agreement between inventories and the radon based flux estimates. Our CO source estimate is lower than the EMEP inventory by 14% and 21% respectively for Europe and Ireland+UK. Both EMEP and EDGAR inventory data agree well with each other for CO. The EDGAR uncertainty is estimated to 50%. The EMEP data show a significant quasi-linear decrease of CO emissions, by 35% in Europe and 51% in Ireland+UK over the last ten years. Our radon based fluxes display a strong interannual variability, with a negative trend of about 35% (0.85 significance level) for Europe and 32% for Ireland+UK (0.98 significance level).

6.5 Separating fossil and natural CO_2 sources using CO

The combustion sources of CO are proportional to those of fossil fuel CO_2, which makes CO a good candidate as a proxy tracer of fossil fuel CO_2 (Levin and Karstens, 2007; Gamnitzer et al., 2006). Assuming that the total CO_2 flux is the sum of a fossil fuel and a land biospheric component, and that the fossil CO_2 flux is equal to the CO flux inferred using ^{222}Rn, and divided by the CO/CO_2 emission ratio (R_{CO/CO_2}), it is

possible to estimate the natural CO_2 flux (F_{BIO}) as a residual from the total flux (F_{TOTAL}):

$$F_{BIO}(CO_2) = F_{TOTAL}(CO_2) - \frac{F_{TOTAL}(CO)}{R_{CO/CO_2}} \quad (2)$$

The value of F_{BIO} is strongly dependent of the assumed ratio CO/CO_2 ratio of emissions. A main difficulty being that the CO/CO_2 emission ratio of different fossil fuel combustion sources, such as domestic heating or emissions from traffic, is highly variable. The ratio is also variable from one European country to the other, depending on primary energy sources, on car fleets. Computing and using the mean CO/CO_2 emission ratio (EMEP/UNFCCC) of the four European countries which were found to contribute dominantly to the Mace Head events (Sect. 5), we obtain a relatively good agreement (the averaged absolute difference is 39%) between the ORCHIDEE total respiration CO_2 emission and the value derived from the above equation (Fig. 10).

7 Conclusions

A ten years continuous record of long-lived atmospheric trace gases at the Mace Head observatory have been analysed. We selected synoptic events influenced either by long-range European or by regional Ireland+UK sources, by using local wind speed data in conjunction with ^{222}Rn and ^{212}Pb threshold criteria. Back-trajectories and Lagrangian transport model simulations further show that the air masses classified as long-range European originate mostly from France, Germany, Belgium, Netherlands, Luxembourg and the United Kingdom.

Continuous ^{222}Rn measurements were used to deduce the unknown fluxes of CO_2, CH_4, CO and N_2O using a tracer approach. In this approach, transport is not explicitly calculated, except for an average residence time for continental air masses to reach Mace Head. The value of the ^{222}Rn approach lies in the fact that it is model free, but its shortcomings are (1) the unknown footprint source region influencing the concentrations, (2) the covariance between ^{222}Rn emissions and each of the other species,

(3) spatial and temporal uncertainties in the ^{222}Rn emissions from soils. These shortcomings cause mostly systematic errors of the inferred mean fluxes. However, these biases are unlikely to be interannual if a large number of events are analysed each year. Therefore, the ^{222}Rn based method is robust to detect trends in fluxes.

Our inferred fluxes have been compared to emission inventory data, with the caveat that inventories often ignore natural emissions. Our estimated CH_4 fluxes are 33% to 24% higher than the inventory data for Europe and Ireland+UK, respectively. This indicates that natural sources of CH_4 (mainly wetlands) contribute up to $3.9\,10^3$ kg CH_4 km^{-2} yr^{-1} in both Europe and Ireland+UK. The decreasing trend of anthropogenic CH_4 emissions over continental Europe (−30% over 1996–2004) reported by the UNFCCC inventory is independently confirmed by our analysis. For N_2O, we determined a mean European flux very close to the UNFCCC inventory data over western Europe, and 30% higher than the inventory value for Ireland+UK. The decreasing trend of N_2O emissions detected with the radon method (−21% and −29%, respectively, for Western Europe and Ireland+UK over 1996–2004) are in good agreement with the UNFCCC inventory (−23% and −28%, respectively). The CO_2 fluxes deduced from ^{222}Rn variations are more difficult to compare with inventories given the variability in space and time of biospheric fluxes. Further, the ^{222}Rn based approach has a sampling bias towards respiratory fluxes, since most of our summer time "events" occur during the night. The radon based CO_2 flux are in good agreement with the sum of UNFCCC fossil fuel emissions and respiratory fluxes from the ORCHIDEE ecosystem model. We have combined the CO_2 and CO fluxes derived from the ^{222}Rn method, with the mean CO/CO_2 emission ratio of inventories, in a rough attempt to separate the contribution of fossil fuel emissions. The fossil CO_2 emissions estimated in that manner agree well with the UNFCCC inventory data (within 23%). This work suggests that ^{222}Rn data can be used to constrain unknown emissions of other compounds. Long time series are useful for independent verification of emission trends. To overcome the present limitations of the ^{222}Rn method, we plan in the future to use a newly available soil emission map (Szegvary, 2007; Szegvary et al., 2007) and to estimate the footprint of

each concentration measurement using transport model simulations (run in backward mode). Furthermore, correcting for the covariance between ^{222}Rn and other species emissions will reduce the biases in the tracer approach.

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Table 1. Parameters used to select air masses from the ocean, Ireland+UK and Europe.

Air mass	initials	^{222}Rn (mBq m^{-3})	^{212}Pb (mBq m^{-3})	wind direction (°)	wind velocity (m s^{-1})	CO_2 hourly SD (ppm)	event duration (h)
				210–290	>4	<0.4	>4
Ocean	RBC	–	–	200–210 & 290–300	> 8	<0.4	>8
Ireland+UK	IRL	>400	>10	–	<5	–	>4
Europe	EUR	>1000	<40	–	>5	–	>4

Table 2. Dual tracer approach selection statistics.

	Ireland+UK		Europe	
year	number of events	% of available data	number of events	% of available data
1996	28	7	24	8
1997	39	11	32	9
1998	22	5	11	3
1999	48	9	19	3
2000	49	8	17	3
2001	38	7	31	5
2002	26	4	36	12
2003	45	5	63	14
2004	21	2	31	5
2005	23	3	21	5
average		6		7

Table 3. NAME model selection statistics.

	Local		Europe	
year	number of events	% of total data	number of events	% of total data
1996	81	19	46	19
1997	90	23	48	15
1998	66	16	28	9
1999	65	16	26	7
2000	67	19	22	6
2001	77	19	38	12
2002	55	14	32	13
2003	52	12	47	17
2004	59	12	34	8
2005	55	14	33	8
average		16		11

Table 4. CO_2 fluxes for Europe region computed using two data selections (units are 10^3 kg CO_2 km^{-2} yr^{-1}).

year	Tracers selection 10^3 kg CO_2 km^{-2} yr^{-1}	NAME model selection 10^3 kg CO_2 km^{-2} yr^{-1}	Combination 10^3 kg CO_2 km^{-2} yr^{-1}	Inventories (UNFCCC) 10^3 kg CO_2 km^{-2} yr^{-1}
1996	2738–3705	4634–6021	3307–5015	1668
1997	2334–5064	3659–6569	4555–6669	1612
1998		557–2796		1629
1999	5009–6814	5513–7139		1585
2000	4974–7564	3610–5718		1591
2001	2130–4984	3786–5504	3255–7720	1614
2002	4440–5807	4103–5597	4251–5989	1582
2003	2067–3072	3271–4547	1926–2640	1604
2004	1089–3547	2993–4644	4053–7217	1606
2005	763–5773	3570–5988	3644–7051	
average	2838–5148	3570–5452	3570–6043	

Table 5. CH_4 fluxes for Europe region computed using two data selections (units are 10^3 kg CH_4 km^{-2} yr^{-1}).

year	Tracers selection 10^3 kg CO_4 km^{-}2 yr^{-}1	NAME model selection 10^3 kg CO_4 km^{-}2 yr^{-}1	Combination 10^3 kg CO_4 km^{-}2 yr^{-}1	Inventories (UNFCCC) 10^3 kg CO_4 km^{-}2 yr^{-}1
1996	11–14	14–18	11–14	10
1997	12–14	10–12	10–12	9
1998		7–14		9
1999	13–15	16–19		9
2000	11–15	17–20	12–18	8
2001	13–16	16–19	13–16	8
2002	8–10	12–16	8–11	8
2003	10–12	10–12	9–11	8
2004	8–10	9–11	7–10	7
2005	14–20			7
average	11–14	12–16	10–13	

Table 6. CO fluxes for Europe region computed using two data selections (units are 10^3 kg CO km^{-2} yr^{-1}).

year	Tracers selection 10^3 kg CO km^{-2} yr^{-1}	NAME model selection 10^3 kg CO km^{-2} yr^{-1}	Combination 10^3 kg CO km^{-2} yr^{-1}	Inventories (UNFCCC) 10^3 kg CO km^{-2} yr^{-1}
1996	14–22	18–26	21–43	18
1997	10–16	13–17	15–24	18
1998	5–10	10–18	4–12	17
1999	17–22	14–20		16
2000	7–13	16–22	7–18	14
2001	13–20	24–29	21–28	14
2002	9–13	13–17	9–14	13
2003	10–13	10–13	9–11	12
2004	7–10	9–12	6–11	12
2005	9–12	11–17	8–11	
average	10–15	14–19	11–19	

Table 7. N_2O fluxes for Europe region computed using two data selections (units are $kg\,N_2O\,km^{-2}\,yr^{-1}$).

year	Tracers selection $10^3\,kg\,N_2O\,km^{-}2\,yr^{-}1$	NAME model selection $10^3\,kg\,N_2O\,km^{-}2\,yr^{-}1$	Combination $10^3\,kg\,N_2O\,km^{-}2\,yr^{-}1$	Inventories (UNFCCC) $10^3\,kg\,N_2O\,km^{-}2\,yr^{-}1$
1996	398–509	954–1300	449–599	662
1997	508–640	702–1205	603–830	660
1998	332–722	352–1137		602
1999	541–659	1081–2037		542
2000	657–888	753–1016		537
2001	498–639	745–890	580–853	525
2002	357–497	790–1127	392–565	511
2003	391–470	396–508	354–426	508
2004	278–379	398–682	289–492	510
2005	556–823	465–495		
average	452–623	663–1040	444–628	

Table 8. Idem Table 4 for Ireland+UK region.

year	Tracers selection 10^3 kg CO_2 km^{-}2 yr^{-}1	NAME model selection 10^3 kg CO_2 km^{-}2 yr^{-}1	Combination 10^3 kg CO_2 km^{-}2 yr^{-}1	Inventories (UNFCCC) 10^3 kg CO_2 km^{-}2 yr^{-}1
1996	7268–11126	10663–17187	5958–10764	1944
1997	5696–8941	4424–8123	7298–10635	1878
1998	–992–3145	6516–15460	–4268–3593	1889
1999	3906–7522	5411–9752	-7261–8716	1865
2000	2028–5710	4208–9432	132 - 5237	1890
2001	7977–11077	10887–16713	8422–11916	1946
2002	3591–8430	10191–15423	1731–11506	1889
2003	4234–8841	4863–13541	4103–7639	1922
2004	7351–12778	6881–11412	4176–11634	1934
2005	5883–9416	11584–18778	5934–11383	
average	4694–8699	7563–13582	2623–9302	

Table 9. Idem Table 5 for Ireland+UK region.

year	Tracers selection 10^3 kg CO_4 km^{-}2 yr^{-}1	NAME model selection 10^3 kg CO_4 km^{-}2 yr^{-}1	Combination 10^3 kg CO_4 km^{-}2 yr^{-}1	Inventories (UNFCCC) 10^3 kg CO_4 km^{-}2 yr^{-}1
1996	13–18	25–31	13–26	15
1997	13–17	21–27	13–19	15
1998	10–16	25–38	15–35	14
1999	17–21	27–34		13
2000	19–21	23–29	17–22	12
2001	16–21	28–35	19–24	12
2002	13–18	30–41	16–38	11
2003	13–17	22–29	14–22	10
2004	13–20 7 18–23	12–19	10	
2005		20–31		
average	14–19	24–32	15–26	

Table 10. Idem Table 6 for Ireland+UK region.

year	Tracers selection 10^3 kg CO km^{-2} yr^{-1}	NAME model selection 10^3 kg CO km^{-2} yr^{-1}	Combination 10^3 kg CO km^{-2} yr^{-1}	Inventories (UNFCCC) 10^3 kg CO km^{-2} yr^{-1}
1996	10–16	22–27	12–20	21
1997	11–16	20–25	9–16	19
1998	11–17	15–22		18
1999	8–11	22–29		17
2000	13–16	16–21	11–17	15
2001	9–14	15–22	10–17	14
2002	9–12	15–21		12
2003	8–12	12–20	7–11	11
2004	7–13	8–12	5–8	10
2005	9–18	10–16		
average	10–15	16–22	9–15	

Table 11. Idem Table 7 for Ireland+UK region.

year	Tracers selection 10^3 kg N_2O km^{-2} yr^{-1}	NAME model selection 10^3 kg N_2O km^{-2} yr^{-1}	Combination 10^3 kg N_2O km^{-2} yr^{-1}	Inventories (UNFCCC) 10^3 kg N_2O km^{-2} yr^{-1}
1996	478–656	1148–1459	607–1034	611
1997	625–821	1020–1319	827–1234	629
1998	262–665	1134–1746		599
1999	610–767	1212–1618		463
2000	834–980	902–1112	779–1080	461
2001	791–1028	1165–1497	969–1271	439
2002	413–637	1091–1472	664–2158	421
2003	425–574	605–777	376–548	418
2004	425–615	849–1153	367–669	425
2005		256–372		
average	540–749	1014–1350	656–1142	

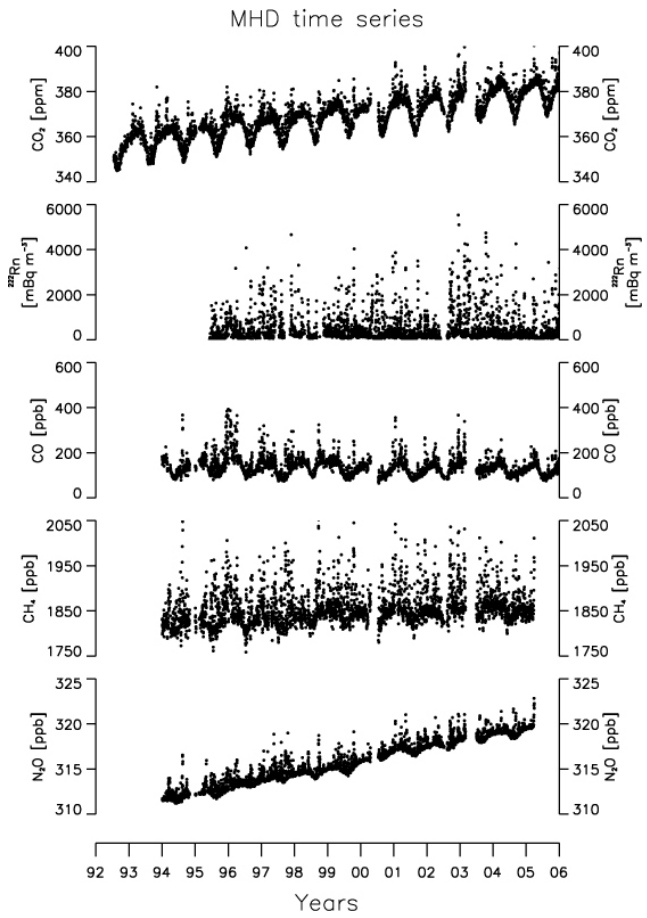

Fig. 1. Daily CO_2, ^{222}Rn (LSCE) and CO, CH_4, N_2O (NUI) concentrations recorded at Mace Head between 1992 and 2005 inclusive.

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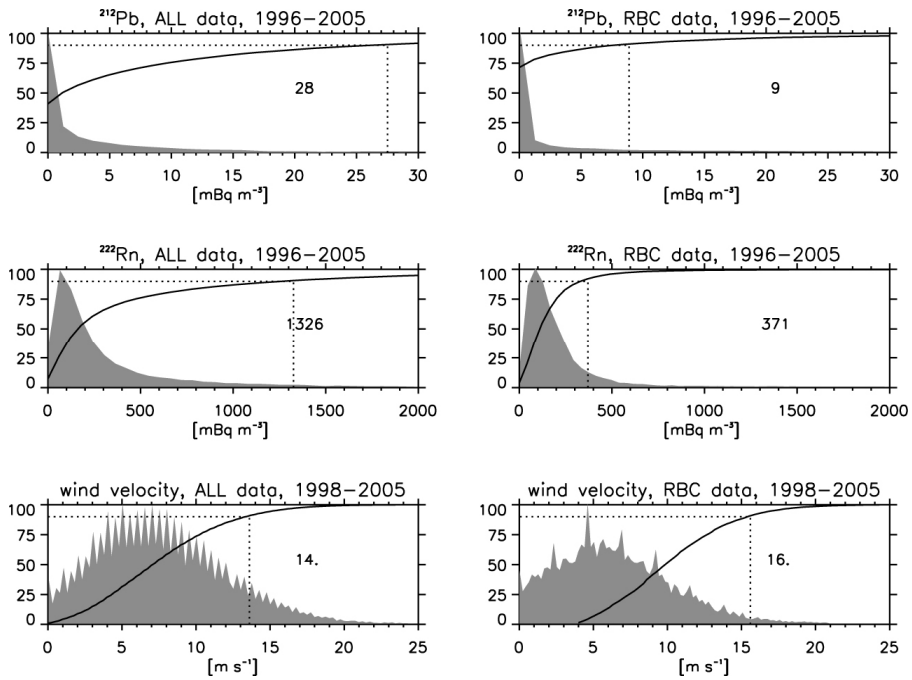

Fig. 2. ^{222}Rn, ^{212}Pb and wind velocity distribution for all data (left panel) and for restricted baseline conditions (RBC) i.e. oceanic data selection (right panel) over the period 1996–2005 for ^{222}Rn and ^{212}Pb. The wind velocity is over the period 1998–2005. The filled grey is the parameter distribution and the solid line is the summed histogram. The dotted line outlines the corresponding parameter value of the 90 percentile and is given in the figure.

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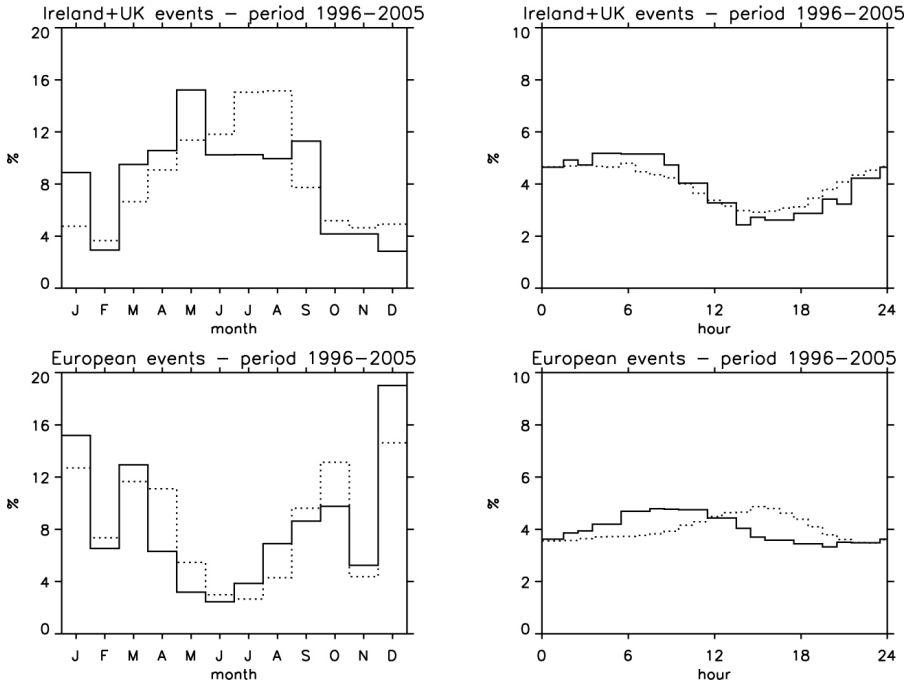

Fig. 3. Seasonal and diurnal distribution of radon based (solid line) and NAME model (dotted lines) selected events over the period 1996–2005 (unit is percentage of available data).

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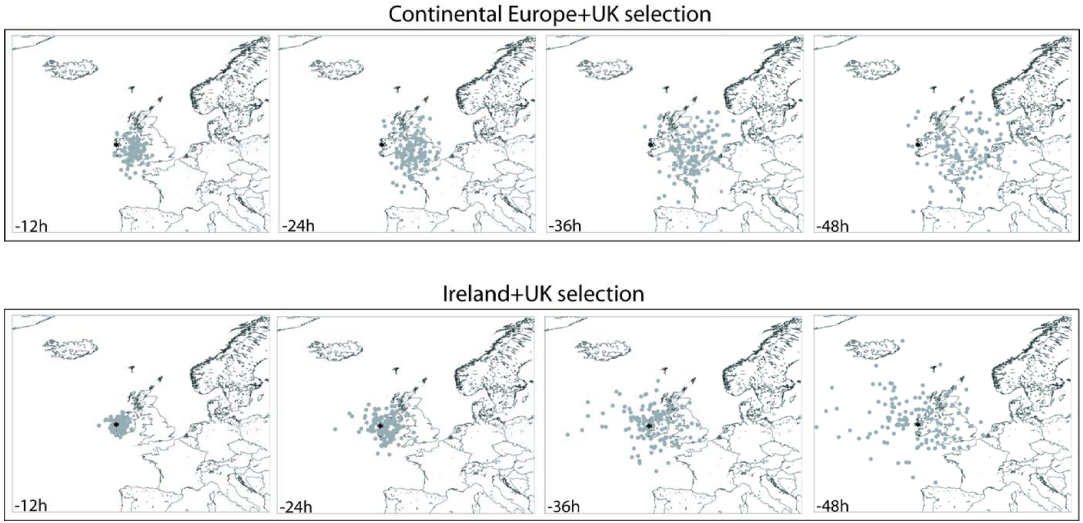

Fig. 4. Center of mass of air masses associated with the European and Ireland+UK selected events according to the Hysplit4 model. The plots show, respectively, air parcel position at 12, 24, 36 and 48 h backward in time for all selected events over the period 1996–2005.

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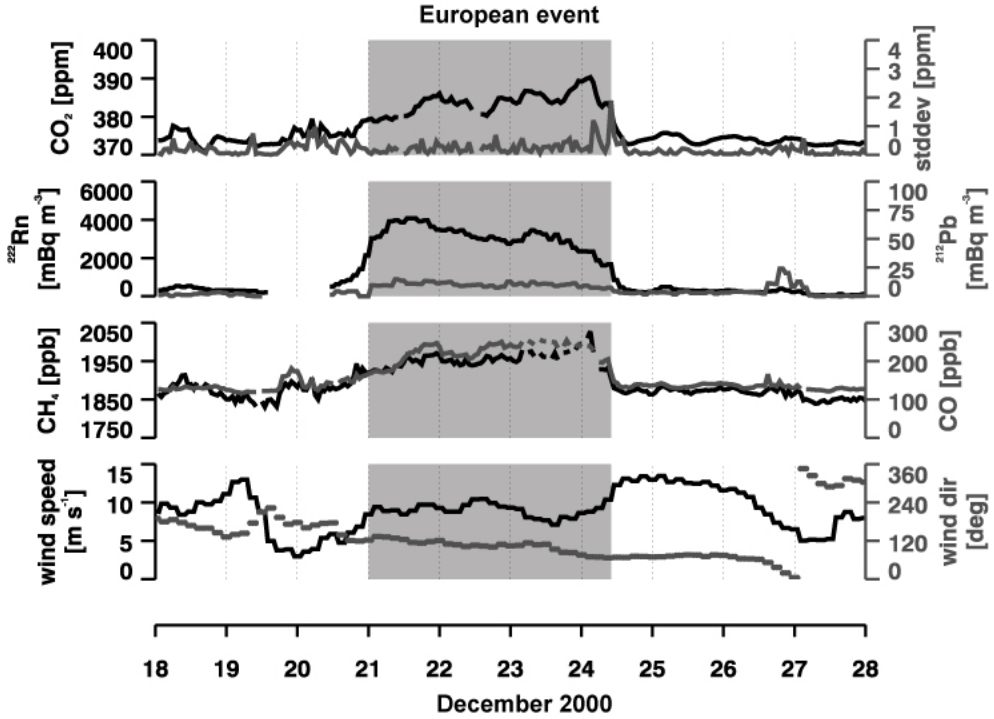

Fig. 5. Example of hourly atmospheric concentrations record of CO_2, ^{222}Rn, ^{212}Pb, CH_4, CO together with wind velocity and wind direction (0° corresponds to north) at Mace Head between 21 December 2000 and 24 December 2000 for a European "event". Time period that has been selected as European has background filled in grey. The vertical dotted lines represents 00:00 UTC each day.

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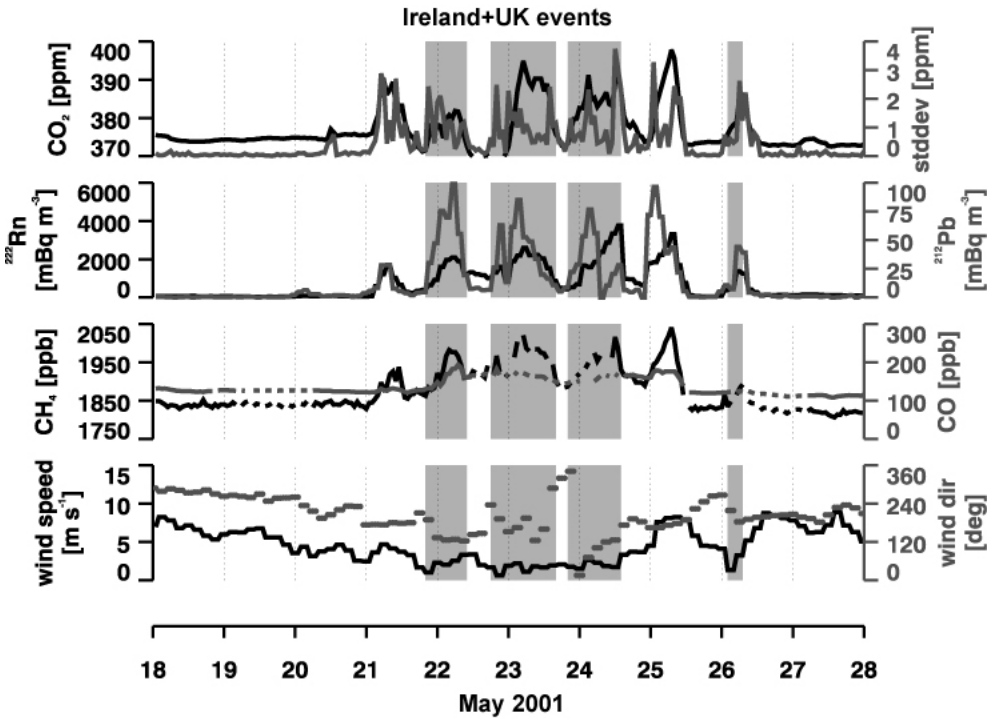

Fig. 6. Example of atmospheric concentrations record of CO_2, ^{222}Rn, ^{212}Pb, CH_4, CO, together with wind velocity and wind direction (0° represents the north) at Mace Head between 21 May 2001 and 26 May 2001 for Irish "events". Time period that has been selected as Ireland+UK has background filled in grey. The vertical dotted lines represents 00:00 UTC each day.

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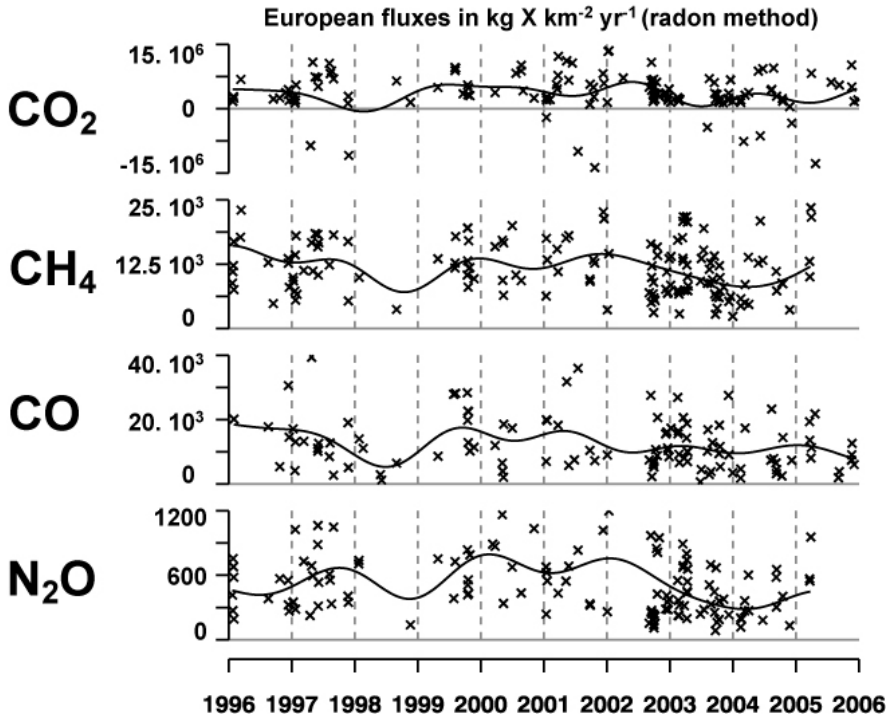

Fig. 7. European fluxes computed with the radon based selection method between 1996 and 2005 for CO_2, CH_4, CO, N_2O. The crosses represent the individual event fluxes and the black line show the smoothed trends of fluxes. Note that only events with a good correlation coefficient (i.e. greater than 0.5) are plotted.

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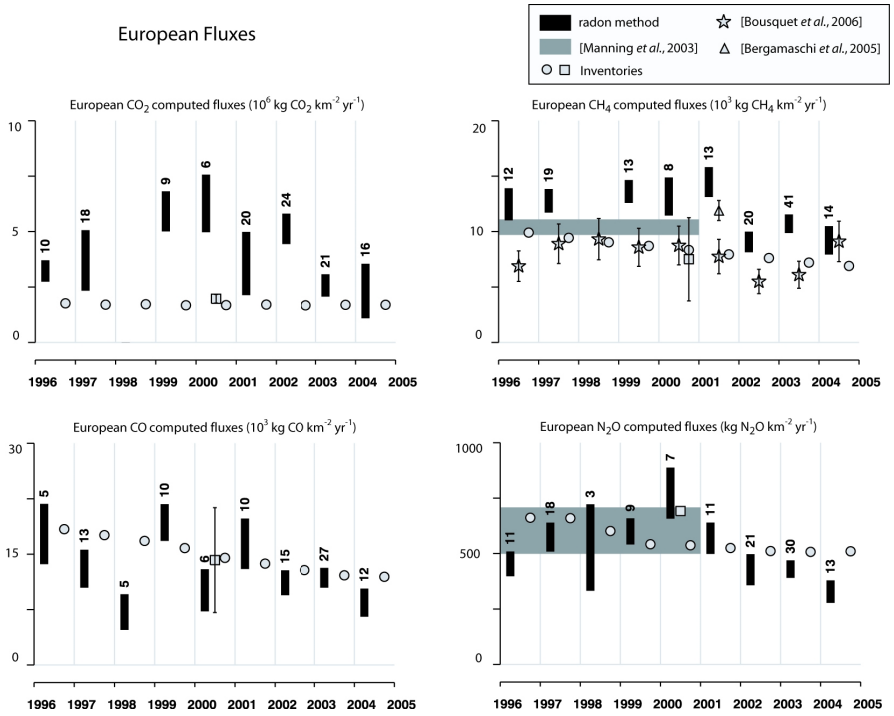

Fig. 8. Fluxes for the European region computed using the radon tracer method between 1996 and 2004 inclusive. Radon based results are plotted in black and the NAME transport model results in grey [Manning et al., 2003]. The heights of the bars give an idea of the associated uncertainties, the top and bottom of the bars are respectively equal to the yearly average flux plus and minus the standard deviation divided by the square root of number of events (the number of events are shown by the number on top of each bar). For CO_2, CH_4 and N_2O the circles represent the UNFCCC emissions. For CO, they are the EMEP emissions. The squares are EDGAR3.2 inventory results. Note that for N_2O the EDGAR3.2 uncertainty (100%) is too large to be shown. For CH_4, we also plotted [Bergamaschi et al., 2005] (triangle) and [Bousquet et al., 2006] (stars).

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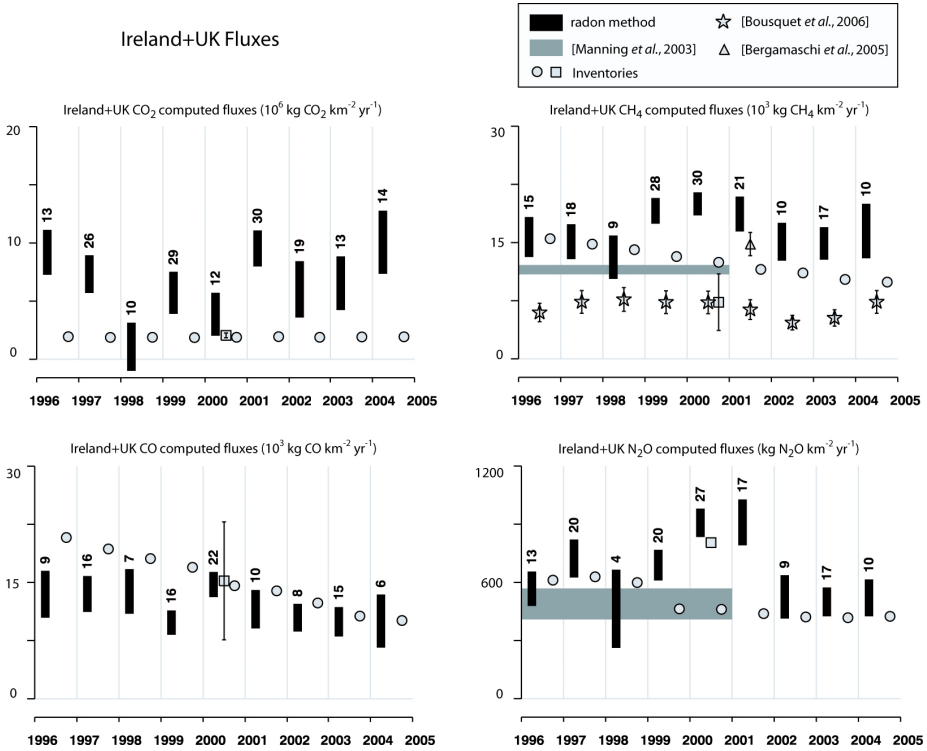

Fig. 9. Idem Figure 8 for Ireland+UK fluxes.

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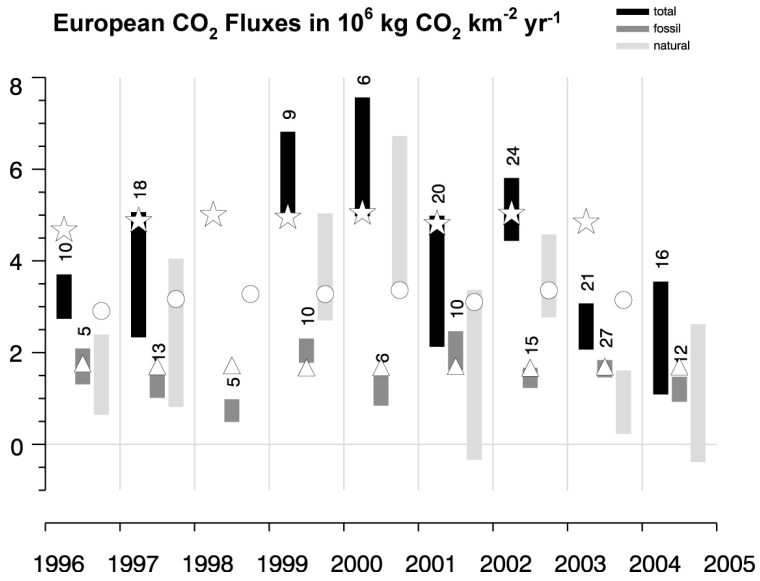

Fig. 10. European CO_2 fluxes by emission sources between 1996 and 2005. Total CO_2 (black) is our radon based emission estimates, fossil fuel CO_2 (dark grey) is deduced from CO/CO_2 emission ratio from EMEP/UNFCCC, and natural CO_2 (light grey) is the difference between total and fossil. The triangles represent the UNFCCC emissions, circles are total respiration fluxes from ORCHIDEE model [Vetter et al., 2007], and stars are the sum of the inventories and respiration.

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