Environmental RTDI Programme 2000–2006

CLIMATE CHANGE – Inverse Modelling Assessment of Greenhouse Gas Emissions from Ireland

(2000-LS-5.3.1-M1)

Final Report

Prepared for the Environmental Protection Agency

by

Atmospheric Research Group, Department of Experimental Physics,
National University of Ireland, Galway
and
Laboratoire des Sciences du Climat et de l'Environnement, Bat 709 – Orme des Merisiers,
91191 Gif-sur-Yvette, France

Authors:

S. Gerard Jennings, Philippe Ciais, Sébastien Biraud and Michel Ramonet

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 5391 60600 Fax: +353 5391 60699
E-mail: info@epa.ie Website: www.epa.ie

ACKNOWLEDGEMENTS

This report has been prepared as part of the Environmental Research Technological Development and Innovation Programme (ERTDI) under the productive Sector Operational Programme 2000–2006. The programme is financed by the Irish Government under the National Development Plan 2000–2006. It is administered on behalf of the Department of the Environment, Heritage and Local Government by the Environmental Protection Agency which has the statutory function of co-ordinating and promoting environmental research.

DISCLAIMER

ENVIRONMENTAL RTDI PROGRAMME 2000–2006

Published by the Environmental Protection Agency, Ireland

PRINTED ON RECYCLED PAPER

ISBN: 1-84095-165-6
Price: €7 03/06/300

Details of Project Partners

S. Gerard Jennings
Atmospheric Research Group
Department of Experimental Physics
National University of Ireland
Galway
Ireland

Tel.: +353 91 492490
Fax: +353 91 494584
E-mail: gerard.jennings@nuigalway.ie

Sébastien Biraud
Lawrence Berkeley National Laboratory
1, Cyclotron Road
Berkeley, CA 94720
USA

Tel.: +00 510 4866084
Fax: +00 510 4865686
E-mail: scbiraud@lbl.gov

Philippe Ciais
Laboratoire des Sciences du Climat et de l'Environnement
Bat 709 – Orme des Merisiers
91191 Gif-sur-Yvette
France

Tel.: +33 1 69089506/7121
Fax: +33 1 69087716
E-mail: philippe.ciais@cea.fr

Michel Ramonet
Laboratoire des Sciences du Climat et de l'Environnement
Bat 709 – Orme des Merisiers
91191 Gif-sur-Yvette
France

Tel.:+ 33 1 69084014
Fax: + 33 1 69087716
E-mail: ramonet@lsce.saclay.cea.fr

Table of Contents

Executive Summary

The Kyoto Protocol requires that countries establish a national accounting system and quantification of their sources and sinks of greenhouse gases before the commitment period 2008–2010. Generally, national inventories report greenhouse gas emissions by sectors or activities, using emission factors and statistics. In certain cases, inventories have been shown to be inaccurate due to regional and temporal variations of emissions factors or due to the omission of important sources.

The scope of this work is to analyse the Mace Head atmospheric record to provide an estimate of the fluxes of CO_2, CH_4 and N_2O for Ireland over the period 1995–2000. The method is independent of statistical inventories, and therefore constitutes a 'top–down' verification of Irish greenhouse gas emissions inventories. Radon-222 (Rn-222), a radioactive noble gas emitted by soils is used to infer fluxes of the major European greenhouse species from the Mace Head data. The method uses correlation between synoptic changes in atmospheric Rn-222 taken as a reference tracer of continental (non-oceanic) sources, with changes in other species also measured at the site. The measurements of Lead-212 (Pb-212) provide a fingerprint of regional air masses of recent origin (half a day) while Rn-222 acts as a medium-range continental tracer at synoptic time scales (about 4 days). Therefore, Rn-222 and Pb-212 are used to indicate continental sources in order to restrict source estimates to Ireland and avoid inclusion of remote European emissions.

Regression between gas species x and Rn-222 flux is used to infer the flux of x. Due to the uncertainty of Rn-222 fluxes over Ireland, Rn-222 flux measurements have been made during two intensive campaigns (October 2000 and July 2001) to determine the spatial variability of Rn-222 efflux from Irish soils by carrying out measurements over different soil types. Seasonally averaged emission fluxes for CH_4, N_2O and CO_2 over Ireland were determined for the 1995–2000 period. Mean flux densities are of the order of 220×10^3 kg C km^{-2} year^{-1} and 900×10^3 kg C km^{-2} year^{-1} for CO_2 during wintertime and summertime, respectively. The annual averaged emission flux for CO_2 for the period 1995–2000 is estimated to range between about 560 and 595×10^3 kg C km^{-2} year^{-1}. Using the total area for Ireland of 85,055 km^2, this converts to 4.76–5.06 $\times 10^9$ kg C year^{-1}, which can be compared to the net CO_2 emissions for Ireland (EPA, McGettigan – private communication). The average net emissions of CO_2 for the period 1995–2000, inclusive, are 3.9×10^9 kg CO_2 equivalent. This is within 22–30% of the atmospheric flux derived emission carbon values. This methodology for inferring greenhouse gas emission fluxes is quite promising, but requires further studies of the spatial and seasonal variation of Rn-222 efflux from the Irish soil. The use of air mass back trajectories, which show their origin within selected Irish regions, will be a useful tool in the estimation of greenhouse gas emissions on a regional basis within Ireland.

1 Introduction

The Mace Head station was established in 1987 to monitor the baseline atmospheric composition in the mid-latitudes of the Northern Hemisphere. The station is ideally located to sample air masses from the North Atlantic, an important CO_2 sink (Bousquet *et al.*, 1996). For this reason, the Mace Head CO_2 data are currently being used in atmospheric inverse modelling studies, where the carbon balance of oceans and continents is inferred from CO_2 observations of a global network of stations. In addition, Mace Head also receives air coming from continental Europe, advected by easterly winds. Such air masses generally have a higher concentration of anthropogenic compounds (CFCs, CO_2, CH_4, CO…). Air masses from continental Europe have been analysed by Biraud *et al.* (2000) who estimated the fluxes of CO_2, CH_4, N_2O and CFCs using Radon-222 (Rn-222). Therefore, Mace Head offers a dual constraint on the carbon balance both of the North Atlantic area and of Western Europe, according to which air masses are selected (westerly or easterly). There is a third scale that can potentially be addressed through the Mace Head continuous atmospheric record, which is the region of Ireland.

The Kyoto Protocol requires that Annex 1 countries establish a national accounting system of their sources and sinks of greenhouse gases before the commitment period 2008-2010. Generally, national inventories report greenhouse gases emissions by sectors or activities, using emission factors and statistics. In some cases, inventories have been shown to be inaccurate for several reasons (Levin *et al.*, 1999). One source of uncertainty is the use of emissions factors that can vary regionally and temporally. Another source of uncertainty is due to the omission of important sources. This latter point is especially important for the species CH_4 and N_2O that have sources of many distinct origins (livestock, agricultural practices, waste treatment, etc.)

The scope of this project is to analyse the Mace Head atmospheric record to provide a synthesis estimate of the fluxes of CO_2, CH_4 and N_2O for Ireland over the period 1995–2000. Our proposed atmospheric method is entirely independent of statistical inventories, and therefore it constitutes a unique ‘top–down’ verification of Irish greenhouse gas emissions inventories. Rn-222, a radioactive noble gas emitted by soils, is being used to infer fluxes of the major European greenhouse species from the Mace Head record (Biraud *et al.*, 2000). The method uses correlation of synoptic changes in atmospheric Rn-222 taken as a reference tracer of known sources, with changes in other species also measured at the station. The Rn-222 method is a simple and powerful tool to infer regional emissions of greenhouse gases and of long-lived pollutants, without the need of integration of complex atmospheric transport models.

2 The Mace Head Record of Atmospheric Trace Gases

The Mace Head atmospheric research station is located on the western coast of Connemara at 53° 20' N, 9° 54' W, 5 m above sea level (asl), near the village of Carna (about 200 inhabitants) in County Galway. The station is situated 90 m from the shore, and is surrounded by peat lands and wetlands. The closest urban area, Galway (about 65,000 inhabitants) is 88 km to the east of the station. A study by Bousquet *et al.* (1996) showed that according to 5-day back-trajectories analysis over the period 1992–1994, regional air masses (Ireland), formed within a circle of radius 400 km centred on Mace Head station, comprised around 5% of the overall CO_2 events.

2.1 Sampling and Analysis, Procedures and Methods

Atmospheric CO_2 concentration is continuously measured by the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) using non-dispersive infrared analysis (NDIR) since July 1992 (Bousquet *et al*., 1996). CH_4 and N_2O species are measured using a flame ionisation detector (FID) and an electron capture-gas chromatograph (Simmonds *et al*., 1996) since 1987. Rn-222 and Lead-212 (Ld-212) are measured by LSCE using an active deposit method with a time step of 2 h. All measurements are largely automated and require maintenance approximately once a week.

2.2 Quality Control

The Mace Head data are carefully scrutinised before they are communicated to international data centres (World Meteorological Organization (WMO), Carbon Dioxide Information Analysis Centre (CDIAC); GLOBALVIEW-CO_2) to be used, for instance, by modellers. A detailed description of the standards, analytical methods and quality control measures can be found in Prinn *et al*. (1992), Gaudry *et al*. (1995) and Ramonet *et al*. (1998).

3 Selection of Events Influenced by Emissions in Ireland

The measurements of Pb-212 provide a fingerprint of the regional air masses of recent origin (half a day) while Rn-222 acts as a medium-range continental tracer at synoptic timescales (about 4 days). The Mace Head continuous measurements were selected to retain events for retrieving emissions over Ireland. For this purpose, Rn-222 and Pb-212 were used to indicate continental sources, together with meteorological records to restrict our source estimates to Ireland and avoid including remote European emissions. The data selection criteria were based on the following three points: (1) Rn-222 concentrations to be greater than 300 mBq m^{-3}, (2) Pb-212 concentrations to be greater than 10 mBq m^{-3}, and (3) that sources which contribute to changes in concentration are located in Ireland.

An example of hourly changes in the concentration of CO_2, CH_4, N_2O and Rn-222 and Pb-212, together with local wind speed and wind direction (0° corresponds to north) between 6 and 15 May 1996 is presented in Fig. 3.1. The horizontal dashed lines in the Rn-222 and Pb-212 panels are the thresholds of event selection (data above the threshold are retained). The shaded grey bands denote the ‘events’ retained to calculate the regional fluxes.

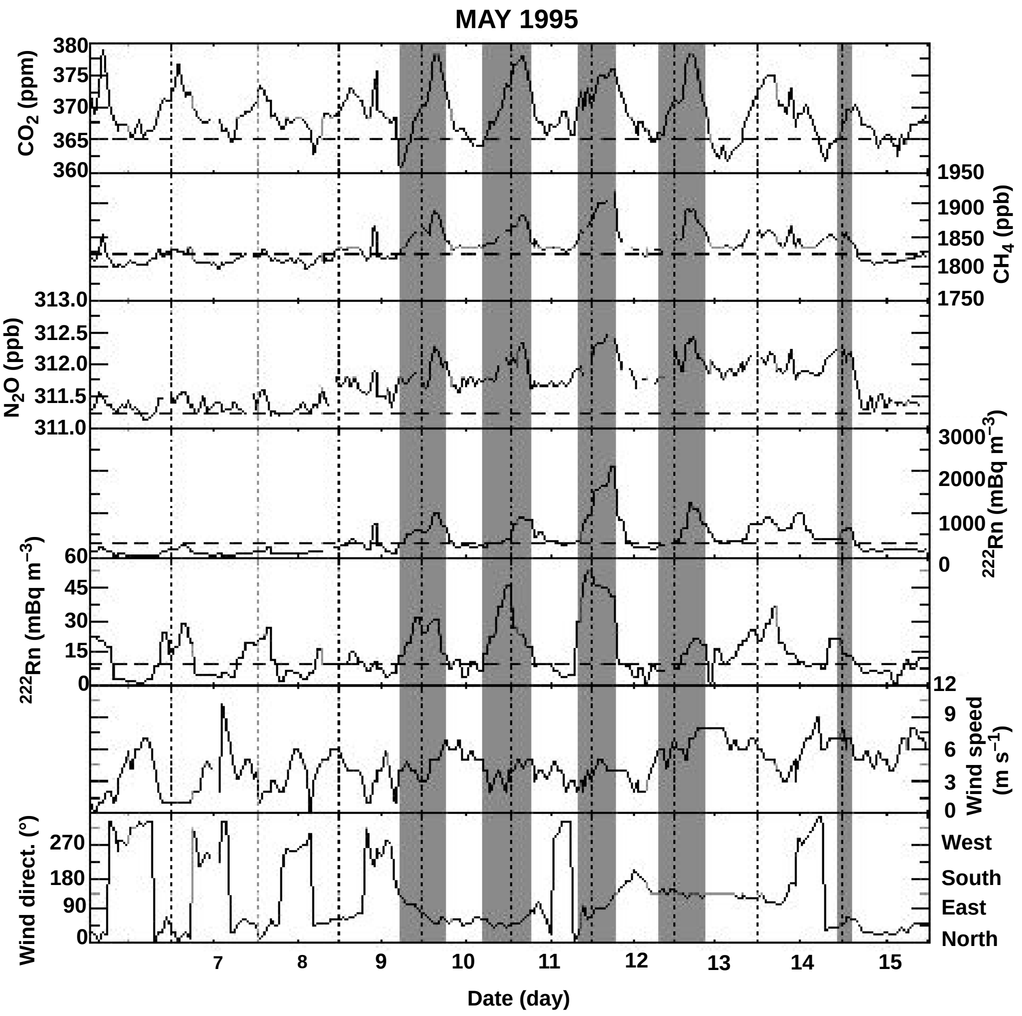

Figure 3.1. Shaded bands correspond to synoptic events influenced by sources located in Ireland. These selected synoptic events are used to infer emission fluxes of CO_2, CH_4 and N_2O over Ireland.

4 Estimation of Fluxes

4.1 Method

The regression between any species x and Rn-222 was used to infer the flux of x using the classical equation (Schmidt et al., 2001)

$$\overline{j_x} = \overline{j_{222}} \frac{\Delta C_x}{\Delta C_{222}} \times \left(1 - \frac{\lambda_{222} \times C_{222}}{\frac{\Delta C_{222}}{\Delta t}} \right) \qquad (1)$$

where $\overline{j_x}$ is the average emission of tracer x over Ireland, $\overline{j_{222}}$ is the flux of Rn-222 over Ireland assumed to be constant and uniform, Δt the time duration of the considered synoptic events and $\lambda 222$ is the Rn-222 radioactive constant value of 0.182 day^{-1}.

Any species with Rn-222 was regressed for each event selected in the local data set using a least-square polynomial fit method. Starting from individual linear regression slopes associated with a temporal correlation between any species and Rn-222 greater than 0.25, an average emission flux was then inferred for each species every season (December to February, March to May, June to August, and September to November) over the period June 1995 to January 2000. Table 4.1 reports the average slope (S) as well as its standard deviation (std).

This method assumes that the Rn-222 flux is well determined. Eckhardt (1990) established an Rn-222 emission flux map over Europe, according to soil texture. He estimated a mean Rn-222 flux over Europe of 0.8 atom $\text{cm}^{-2}\ \text{s}^{-1}$, the value chosen by Biraud et al. (2000) to infer the western European flux of various pollutants. The estimation of the mean Rn-222 flux over Ireland is more uncertain. At the beginning of this project, uncertainty on the Rn-222 emissions by soils was of the order of 40%, which translates into an error of the same magnitude on the inferred fluxes. To reduce the uncertainty on the Rn-222 fluxes, Rn-222 flux measurements over Ireland were made during two intensive campaigns (October 2000 and July 2001) (Fig. 4.1). The objective was to determine the spatial variability of the Rn-222 efflux from Irish soils by carrying out measurements over different types of soils.

4.2 Radon-222 Flux Measurements

The first campaign was carried out in collaboration with the University of Heidelberg (Germany), the University of Galway (Ireland) and the LSCE (France). During this wintertime campaign (9–18 October 2001), 64 air samples in plastic flasks were taken from static chambers and measured within 4 days after sampling using an activation chamber located at the University of Heidelberg (HDG) (Jutzi, 2001). This experimental part of the project used standard technology for the static chamber flux measurements. The major difficulty was to analyse gaseous Rn-222 in plastic flasks as soon as possible after its collection (half-life of 3.8 days). The plastic flasks had to be shipped via express mail to the Rn-222 measurement facility at the University of Heidelberg. The results of these measurements are shown in Appendix A.

After the wintertime campaign, it was decided to use a new technique to measure the Rn-222 fluxes, which allows in-situ measurement of Rn-222 efflux (Ielsch et al., 2001), even if this latter technique is less accurate. This new technique, provided by the IPSN (French Institute for Protection and Nuclear Safety) is also based on the use of the accumulation chamber technique. Prior to using this new measurement technique, an inter-comparison

Table 4.1. Summary of the slope (S) calculated for the period January 1995 through December 1997. Only selected events whose species-^{222}Rn correlation coefficients were greater than 0. 25 were retained in the average (r > 0.5). The slope units are given in ppb/Bq m^{-3} for CH_4 and N_2O, and in ppm/Bq m^{-3} for CO_2.

	Average 1995/2000	Dec–Feb		Mar–May		Jun–Aug		Sept–Nov	
	S	S	std	S	std	S	std	S	std
CH_4	55.1	63.5	9.4	53.9	8.0	58.0	10.1	44.9	12.1
N_2O	1.3	1.7	0.2	1.2	0.3	1.4	0.3	0.9	0.1
CO_2	4.1	2.1	0.3	4.7	0.4	5.1	0.4	4.4	0.3

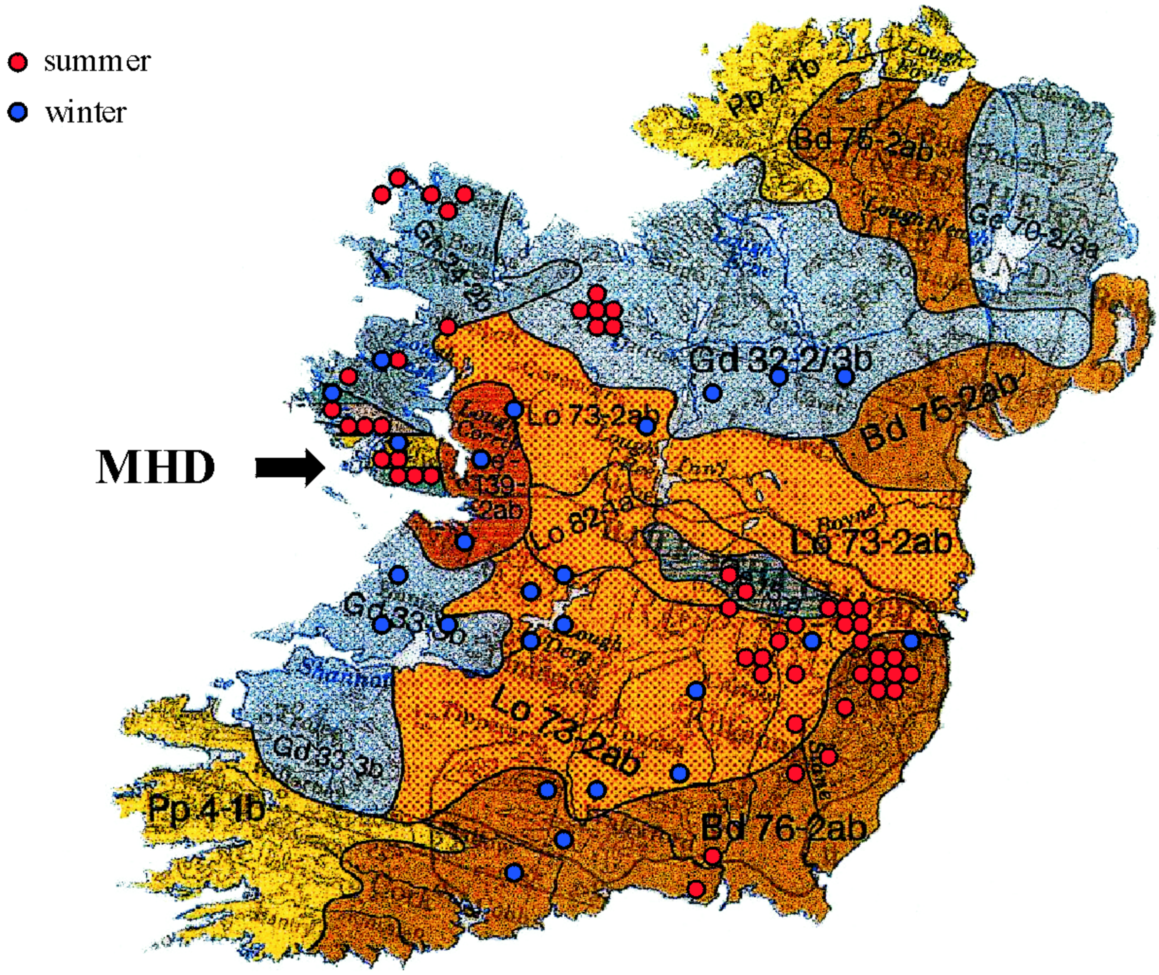

Figure 4.1. Location of the sampling points for Rn-222 efflux measurements during the wintertime (October 2000 – blue dots) and summertime (July 2001 – red dots).

campaign of the two methods was performed in Heidelberg, Germany (15–18 May 2001).

i. Firstly, one particular type of soil was chosen and the ^{222}Rn exhalation was measured using the associated protocol. The Rn-222 exhalation rates measured using both methods are comparable, according to the uncertainties associated with each technique (Table 4.2).

ii. Secondly, in order to compare the activity measurements over a large range of activity an Rn-222 source is used to determine possible linearity problems associated with the instruments. Eight different samples were analysed, each of these filled with 700 ml of outdoors air and various amounts of Rn-222 gas (Fig. 4.2).

Results using ionisation chambers (Heidelberg) and the activity (IPSN) measurements are comparable (Fig. 4.2). The difference between the two methods is larger for activities greater than about 1500 Bq m^{-3}. This does not have much impact on our second measurement campaign, considering that only natural Rn-222 activities are measured.

In July 2001, the second Rn-222 flux measurements campaign was performed. During this campaign, 210 air samples were taken from accumulation chambers and measured using an alpha scintillator. The results of these measurements are shown in Appendix A.

To characterise the flux of ^{222}Rn from the soil on a regional scale (Ireland) we refer to parameters, which are responsible for the variation in flux. Although the source of Rn-222 is Radium-226 (Ra-226), the variability in the radon source is governed mainly by the physical

Table 4.2. Measurements of Rn-222 efflux (atom cm^{-2} s^{-1}) from one particular soil using two different techniques (University Heidelberg and IPSN techniques).

Sample	Heidelberg		IPSN	
	Flux	Uncertainty	Flux	Uncertainty
	atom cm^{-2} s^{-1}		atom cm^{-2} s^{-1}	
1	0.61	0.01	0.56	0.14
2	0.54	0.01	0.43	0.13
3	0.44	0.03	0.37	0.11
4	0.58	0.01	0.44	0.13
5	0.87	0.01	0.72	0.17
6	0.55	0.01	0.42	0.12
7	0.50	0.02	0.37	0.11
8	0.72	0.01	0.56	0.14

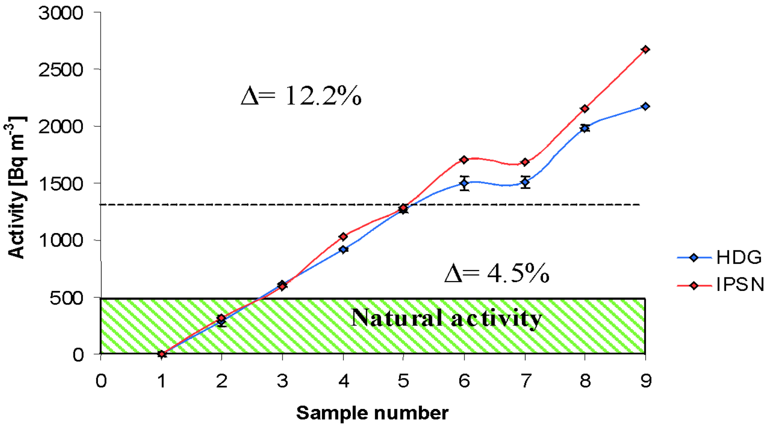

Figure 4.2. Plot of the Rn-222 activities measured using both techniques. Differences between Rn-222 activities measured are of the order of 12.2% and 4.5%, respectively, over all range of activities investigated and over the natural activity range.

constraints on the radon escaping from the land surface (Schery *et al*., 1989). A first approach is to estimate radon flux according to soil texture (Jutzi, 2001). In order to do this, a textural triangle, which refers to the texture of the upper 30 cm of the soil, is used. Textural classes reflect the relative proportion of clay, silt, and sand in soil. Seven textural classes are recognised by the FAO soil map of the world.

In a previous study, Eckhardt (1990) established a ^{222}Rn emission flux map over Europe, according to soil texture. The estimation of the mean ^{222}Rn flux over Ireland is uncertain. Very few ^{222}Rn direct flux measurements have been made. They include one in Ardara, Donegal, and another one in a suburb of Dublin (Eckhardt, 1990). Measurements over Europe and Ireland suggest a ^{222}Rn flux over Ireland of the order of 0.6 atom cm^{-2} s^{-1} (Table 4.3).

The results of the campaigns suggest a mean Rn-222 flux of the order of 0.51 ± 0.1 atom cm^{-2} s^{-1}, with a summertime and wintertime Rn-222 flux of 0.65 ± 0.09 atom cm^{-2} s^{-1} and 0.37 ± 0.1 atom cm^{-2} s^{-1}, respectively. These results will also be published in a scientific journal (*Atmospheric Environment*).

4.3 CO$_2$, CH$_4$, and N$_2$O Emissions over Ireland

After estimating Rn-222 flux over Ireland (Table 4.3) and the regression between any species x and Rn-222 (Table 4.1), emissions of CO$_2$, CH$_4$ and N$_2$O over Ireland were calculated. These results are presented in Table 4.4.

Table 4.3. Rn-222 efflux (atom cm^{-2} s^{-1}) over Ireland estimated by Eckhardt (1990) and from this study.

Class of texture	Mean flux Eckhardt (1990) (atom cm^{-2} s^{-1})	Mean flux this study (atom cm^{-2} s^{-1})	Surface per class of texture (%)
1	0.37 ± 0.12	0.38 ± 0.02	23.6
2	0.60 ± 0.24	0.43 ± 0.02	24.5
2/3	0.90 ± 0.41	0.77 ± 0.02	33.1
3	1.12 ± 0.06	0.75 ± 0.01	8.6

Table 4.4. Seasonal average of emissions of CO_2, CH_4 and N_2O over Ireland. Fluxes expressed in units of 10^3 kg CH_4 km^{-2} year^{-1} for CH_4, in kg N_2O km^{-2} year^{-1} for N_2O, and in 10^3 kg C km^{-2} year^{-1} for CO_2.

	Average 1995/2000	Dec–Feb	Mar–May	Jun–Aug	Sept–Nov
CH_4	10.4	8.7	10.2	14.0	8.5
N_2O	620	590	580	860	430
CO_2	595	220	650	900	610

5 Feasibility Study to Infer Regional-Scale Fluxes over Ireland

The above results suggest that the Rn-222 method is not capable of calculating regional emissions within Ireland using the atmospheric record from Mace Head. However, the method can be applied to potentially deduce emissions from different provinces within Ireland with a better knowledge of air masses trajectories. The feasibility to reanalyse the Mace Head data was tested using a back-trajectory model to infer emissions at the regional level within Ireland. Ireland was divided into four geographically distinct regions (Fig. 5.1) and each selected synoptic event associated with one back trajectory and thus to one sector. Back trajectories were obtained using the HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated Trajectory), a model developed at the Air Resources Laboratory of the National Oceanic and Atmospheric Administration by Roland Draxler of NOAA's Air Resources Laboratory. A brief description of the back trajectory model is given in Appendix B.

For each sector, the percentage of back trajectories was calculated for the complete data set, retaining synoptic events whose origin can clearly be associated with one of the four defined regions. Region 3 (34%) and Region 4 (27%) are the most abundant, while Region 1 is the poorest (13%), indicating that the inferred average greenhouse gas fluxes may not be fully representative of the Irish emissions. CO_2, CH_4 and N_2O emissions were calculated within each of the four regions. No significant difference is evident between emissions inferred in each of these regions and mean Irish emissions.

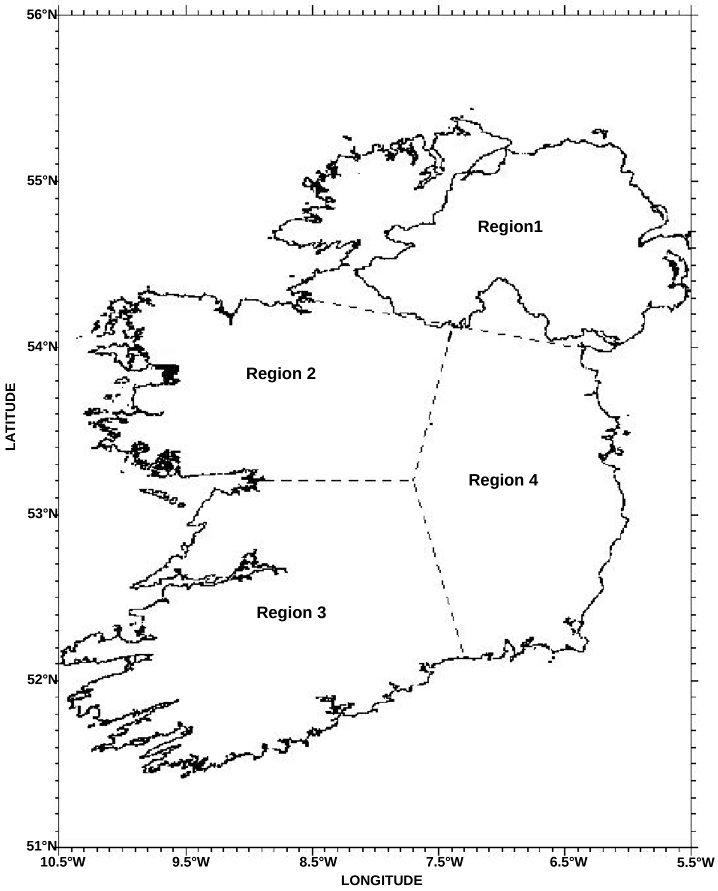

Figure 5.1. Back-trajectory sectors used to infer emissions over Ireland at regional level.

6 Discussion and Conclusions

This project allows us to develop a reliable and innovative methodology to monitor Irish sources of CO_2, CH_4 and N_2O, based on the Mace Head atmospheric record. A synthesis estimate of the fluxes of CO_2, CH_4 and N_2O is provided for Ireland over the period 1995–2000.

Emission fluxes of CO_2, CH_4 and N_2O over Ireland are calculated using Eqn 1 from a knowledge of ^{222}Rn flux data over a reasonably large tract of Ireland (Fig. 4.1), together with regression data between gaseous species and ^{222}Rn (Table 4.1). These results are shown in Table 4.4. Average annual emission fluxes over the period 1995–2000 of 10.4 kg CH_4 km^{-2} $year^{-1}$, 620 kg N_2O km^{-2} $year^{-1}$ and 595 kg C km^{-2} $year^{-1}$ for CH_4, N_2O and CO_2, respectively, are estimated. The atmospheric method used is entirely independent of statistical inventories, and therefore constitutes a unique 'top–down' verification of Irish greenhouse gas emissions inventories.

Using the total area for Ireland of 84,755 km^2, this converts to total CH_4 and N_2O emissions for Ireland of 881 Gg, 52.5 Gg for CH_4 and N_2O, which compares reasonably well to the total inventoried CH_4 and N_2O emissions for Ireland (M. McGettigan, EPA, personal communication, 2002; the data can be accessed at: http://coe.epa.ie/CRF2005/nirdownloads.html) of 638 Gg (within 38%) and 31.7 Gg (within 66%) as shown in Table 6.1. A mean flux density in the order of 220 × 10^3 kg C km^{-2} $year^{-1}$ for CO_2 is estimated during wintertime months. This converts to 68.4 Tg CO_2 equivalent, which is within a factor of 2 of that obtained from the EPA-inventoried fuel combustion and industrial processes sectors. It should be noted that the atmospheric estimate includes both anthropogenic and biogenic emissions and is therefore expected to be greater than that obtained from inventories. It is less straightforward to compare summer emissions because of the diurnal variation of the CO_2 concentration over the summer months (Biraud *et al.*, 2002).

The spatial variability of the Rn-222 efflux from Irish soils was also investigated by carrying out measurements over different types of soils during summertime and wintertime. The results of the campaigns suggest a mean Rn-222 flux of the order of 0.51 ± 0.1 atom cm^{-2} s^{-1}, with a summertime and wintertime Rn-222 flux of 0.65 ± 0.09 atom cm^{-2} s^{-1} and 0.37 ± 0.1 atom cm^{-2} s^{-1}, respectively.

The feasibility of analysing the Mace Head data using a back-trajectory model to infer emissions at regional level within Ireland has been tested. Ireland was divided into four geographically distinct regions (Fig. 5.1) and emissions of CO_2, CH_4 and N_2O were inferred within each of the regions. No significant difference has been shown between individual regions and the average greenhouse gas emissions over Ireland. This study is promising but requires more investigations in term of Rn-222 efflux spatial variability and the use of back-trajectory models.

In conclusion, in this project, the synoptic scale variations observed in the mixing ratios of greenhouse gases and radon were selected to isolate the events representative of trace gases emissions over Ireland. This methodology for inferring greenhouse gas emission fluxes is potentially promising, but requires further studies of the spatial and seasonal variation of Rn-222 efflux from the Irish soils. Radon flux measurements performed within this project show a large variability both in time and space according to the type of soil. The combination of the radon flux map, together with air mass back trajectories will be a useful tool in the estimation of greenhouse gas emissions on a regional basis within Ireland. An atmospheric approach towards the estimation of Irish greenhouse gas emission fluxes will be strengthened through additional measurements of greenhouse gases at other locales in Ireland.

Table 6.1. Comparison of total emissions of CH_4, N_2O and CO_2 for Ireland (EPA, 2002), with estimates from the atmospheric approach.

1995–2000 average	Total emissions (EPA)	Total emissions (Atmospheric Method)
CH_4 (Gg)	638	881
N_20 (Gg)	31.7	52.5
CO_2 equivalent (Gg)	36.7[a]	68.4[b]

[a]Based on the winter months of December, January and February.
[b]Biogenic emissions due to soil respiration are accounted for.

References

Biraud, S., Ciais, P., Ramonet, M., Simmonds, P., Kazan, V., Monfray, P., O'Doherty, S., Spain, T.G. and Jennings, S.G., 2000. European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland. *Journal of Geophysical Research* **105:** 1351–1366.

Biraud, S., Ciais, P., Ramonet, M., Simmonds, P., Kazan, V., Monfray, P., O'Doherty, S., Spain, T.G. and Jennings, S. G., 2002. Quantification of carbon dioxide, methane, nitrous oxide, and chloroform emissions over Ireland from atmospheric observations at Mace Head. *Tellus* **54B:** 41–60.

Bousquet, P., Gaudry, A., Ciais, P., Kazan, V., Monfray, P., Simmonds, P.G., Jennings, S.G. and O'Connor, T. C., 1996. Atmospheric CO_2 concentration variations recorded at Mace Head, Ireland, from 1992 to 1994. *Physics and Chemistry of the Earth* **21:** 477–481.

CDIAC, Carbon Dioxide Information Analysis Center, http://cdiac.esd.ornl.gov/.

Eckhardt, K., 1990. *Messung des Radonflusses und seiner Abhängigkeit von der Bodenbeschaffenheit.* Universität Heidelberg, Heidelberg.

Gaudry, A., Ciais, P., Kazan, V. and Monfray, P., 1995. *Report on the 8th WMO meeting of experts on carbon dioxide concentration and isotopic measurement techniques.* WMO/GAW, Boulder.

GLOBALVIEW-CO2, 2001, *Cooperative Atmospheric Data Integration Project – Carbon Dioxide.* NOAA/CMDL, Boulder, CO.

Ielsch, G., Thieblemont, D., Labed, V., Richon, P., Tymen, G., Ferry, C., Robe, M.C., Baubron, J.C. and Bechennec, F., 2001. Radon (Rn-222) level variations on a regional scale: influence of the basement trace element (U, Th) geochemistry on radon exhalation rates. *Journal of Environmental Radioactivity* **53:** 75–90.

Jutzi, S., 2001. *Verteilung der Boden-222Radon-Exhalation in Europa.* Universität Heidelberg, Heidelberg.

Levin, I., Glatzel Mattheier, H., Marik, T., Cuntz, M., Schmidt, M. and Worthy, D.E., 1999. Verification of German methane inventories and their recent changes based on atmospheric observations. *Journal of Geophysical Research* **104:** 3447–3456.

Prinn, R., Cunnold, D., Simmonds, P., Alyea, F., Boldi, R., Crawford, A., Fraser, P., Gutzler, D., Hartley, D., Rosen, R. and Rasmussen, R., 1992. Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methylchloroform) data for 1978–1990. *Journal of Geophysical Research* **97:** 2445–2461.

Ramonet, M., Ciais, P., Biraud, S., Bourg, C., Chamaret, P., Kazan, V. and Monfray, P., 1998. *Report on the 9th WMO meeting of experts on carbon dioxide concentration and related tracer measurement technique.* WMO/GAW No. 132, Aspendale, Australia.

Schery, S.D., Whittlestone, S., Hart, K.P. and Hill, S.E., 1989. The flux of radon and thoron from Australian soils. *Journal of Geophysical Research* **94:** 8567–8576.

Schmidt, M., Glazel-Mattheier, H., Sartorius, H., Worthy E.D. and Levin, I. 2001, Western European N_2O emissions – A top–down approach based on atmospheric observations. *Journal of Geophysical Research* **106:** 5507–5516.

Simmonds, P.G., Derwent, R.G., McCulloch, A., O'Doherty, S. and Gaudry, A., 1996. Long-term trends in concentrations of halocarbons and radioactively active trace gases in Atlantic and European air masses monitored at Mace Head, Ireland from 1987–1994. *Atmospheric Environment* **30(23):** 4041–4063.

Appendix A

Table A1. Measurements of Rn-222 efflux from different soil types over Ireland during the wintertime campaign (9–18 October 2000).

Sample name	Longitude	Latitude	Date	Texture class	Measured flux (atom cm^{-2} s^{-1})	Uncertainties (atom cm^{-2} s^{-1})
G01-HDG	53°08'N	8°27'W	10 Oct 2000	1	0.19	0.02
G02-HDG	53°08'N	8°27'W	10 Oct 2000	1	0.27	0.04
G03-HDG	53°10'N	8°22'W	10 Oct 2000	1	1.00	0.13
G04-HDG	53°10'N	8°22'W	10 Oct 2000	1	1.01	0.13
G05-HDG	53°10'N	8°50'W	10 Oct 2000	2	1.09	0.14
G06-HDG	53°10'N	8°50'W	10 Oct 2000	2	0.52	0.07
Ce01-HDG	52°55'N	9°15'W	10 Oct 2000	3	0.07	0.01
Ce02-HDG	52°55'N	9°15'W	10 Oct 2000	3	0.06	0.03
G07-HDG	53°14'N	8°15'W	11 Oct 2000	1	0.79	0.10
G08-HDG	53°14'N	8°15'W	11 Oct 2000	1	0.33	0.04
Rn01-HDG	53°28'N	8°10'W	11 Oct 2000	1	0.15	0.02
Rn02-HDG	53°28'N	8°10'W	11 Oct 2000	1	0.21	0.03
Rn03-HDG	53°46'N	8°05'W	11 Oct 2000	2	0.20	0.03
Rn04-HDG	53°46'N	8°05'W	11 Oct 2000	2	0.37	0.05
Lm01-HDG	53°58'N	7°51'W	12 Oct 2000	2/3	0.22	0.03
Lm02-HDG	53°58'N	7°51'W	12 Oct 2000	2/3	0.25	0.03
Cn01-HDG	53°50'N	7°03'W	12 Oct 2000	2/3	0.03	0.00
Ke01-HDG	53°20'N	6°53'W	13 Oct 2000	2	0.24	0.05
Ke02-HDG	53°20'N	6°53'W	13 Oct 2000	2	0.09	0.01
Oy01-HDG	53°12'N	7°23'W	13 Oct 2000	2	0.43	0.06
Oy02-HDG	53°12'N	7°23'W	13 Oct 2000	2	0.14	0.02
Ty01-HDG	53°04'N	7°58'W	13 Oct 2000	2	0.51	0.07
Ty02-HDG	53°04'N	7°58'W	13 Oct 2000	2	0.47	0.06
G09-HDG	53°8'N	8°27'W	14 Oct 2000	1	0.13	0.02
G10-HDG	53°08'N	8°27'W	14 Oct 2000	1	0.23	0.03
G11-HDG	53°10'N	8°22'W	14 Oct 2000	1	0.18	0.02
G12-HDG	53°10'N	8°22'W	14 Oct 2000	1	0.35	0.05
G13-HDG	53°10'N	8°50'W	14 Oct 2000	2	0.87	0.11
G14-HDG	53°10'N	8°50'W	14 Oct 2000	2	0.06	0.01
G15-HDG	53°14'N	8°22'W	15 Oct 2000	1	0.18	0.02
G16-HDG	53°14'N	8°22'W	15 Oct 2000	1	0.37	0.05
G17-HDG	53°31'N	8°41'W	15 Oct 2000	2	0.13	0.02
G18-HDG	53°31'N	8°41'W	15 Oct 2000	2	0.09	0.01
Rn05-HDG	53°46'N	8°05'W	15 Oct 2000	1	0.45	0.06
Rn06-HDG	53°46'N	8°05'W	15 Oct 2000	1	0.31	0.04
Ce03-HDG	52°50'N	9°02'W	16 Oct 2000	3	0.24	0.03
Ce04-HDG	52°50'N	8°45'W	16 Oct 2000	3	0.09	0.01
Ty03-HDG	52°25'N	8°10'W	17 Oct 2000	2	0.19	0.08
Ty04-HDG	52°25'N	8°10'W	17 Oct 2000	2	0.21	0.03
Ty05-HDG	52°25'N	7°55'W	17 Oct 2000	2	0.08	0.01
Ty06-HDG	52°25'N	7°55'W	17 Oct 2000	2	0.05	0.01
Wd01-HDG	52°05'N	8°02'W	18 Oct 2000	2	0.14	0.02
Wd02-HDG	52°05'N	8°02'W	18 Oct 2000	2	0.12	0.12

Table A2. Measurements of Rn-222 efflux from different soil types over Ireland during the summertime campaign (9–23 July 2001).

Sample name	Longitude	Latitude	Date	Texture class	Measured flux (atom cm^{-2} s^{-1})	Uncertainties (atom cm^{-2} s^{-1})
G01-IPSN	9°54.045′ W	53°19.573′ N	11 July 2001	1	0.12	0.05
G02-IPSN	9°54.066′ W	53°19.567′ N	11 July 2001	1	0.07	0.04
G03-IPSN	9°54.066′ W	53°19.567′ N	11 July 2001	1	0.06	0.03
G04-IPSN	9°51.666′ W	53°22.035′ N	11 July 2001	1	0.03	0.02
G05-IPSN	9°46.106′ W	53°19.371′ N	11 July 2001	1	2.25	0.53
G06-IPSN	9°32.656′ W	53°15.587′ N	12 July 2001	1	0.57	0.15
G07-IPSN	9°32.315′ W	53°14.904′ N	12 July 2001	1	1.63	0.39
G08-IPSN	9°35.765′ W	53°16.735′ N	12 July 2001	1	0.41	0.12
G09-IPSN	9°37.070′ W	53°19.224′ N	12 July 2001	1	0.20	0.07
G10-IPSN	9°30.456′ W	53°17.507′ N	12 July 2001	1	2.34	0.55
G11-IPSN	9°29.749′ W	53°17.755′ N	12 July 2001	1	0.24	0.08
G12-IPSN	9°47.375′ W	53°24.968′ N	13 July 2001	1	0.02	0.03
G13-IPSN	9°50.415′ W	53°25.204′ N	13 July 2001	1	0.07	0.03
G14-IPSN	9°56.103′ W	53°23.786′ N	13 July 2001	1	0.29	0.09
Mo01-IPSN	9°11.835′ W	53°56.556′ N	14 July 2001	2	1.01	0.25
Mo02-IPSN	9°14.944′ W	53°57.748′ N	14 July 2001	2	0.10	0.05
Mo03-IPSN	9°14.500′ W	53°59.238′ N	14 July 2001	2	0.54	0.15
Mo04-IPSN	9°16.587′ W	54°00.692′ N	14 July 2001	2	0.34	0.10
Mo05-IPSN	9°20.992′ W	54°03.342′ N	14 July 2001	2	0.82	0.22
Mo06-IPSN	10°04.212′ W	54°10.715′ N	15 July 2001	2	0.07	0.03
Mo07-IPSN	10°03.761′ W	54°11.586′ N	15 July 2001	2	0.15	0.06
Mo08-IPSN	9°54.967′ W	54°10.337′ N	15 July 2001	2	0.23	0.07
Mo09-IPSN	9°51.720′ W	54°15.330′ N	15 July 2001	2	0.85	0.22
Mo10-IPSN	9°45.121′ W	54°16.805′ N	15 July 2001	2	0.10	0.04
Mo11-IPSN	9°44.875′ W	54°12.886′ N	15 July 2001	2	0.02	0.02
Ww01-IPSN	6°26.631′ W	53°11.771′ N	17 July 2001	2	1.31	0.32
Ww02-IPSN	6°25.608′ W	53°10.913′ N	17 July 2001	2	1.29	0.32
Ww03-IPSN	6°19.742′ W	53°02.941′ N	17 July 2001	2	0.92	0.23
Ww04-IPSN	6°19.703′ W	53°01.700′ N	17 July 2001	2	1.42	0.35
Ww06-IPSN	6°33.761′ W	53°05.503′ N	17 July 2001	2	2.10	0.50
Ww07-IPSN	6°36.855′ W	53°00.768′ N	18 July 2001	2	0.63	0.17
Ww08-IPSN	6°38.836′ W	52°59.342′ N	18 July 2001	2	0.31	0.09
Ww09-IPSN	6°38.758′ W	52°57.750′ N	18 July 2001	2	3.69	0.86
Ww10-IPSN	6°38.694′ W	52°57.985′ N	18 July 2001	2	0.91	0.23
Ww11-IPSN	6°37.872′ W	52°55.469′ N	18 July 2001	2	0.40	0.12
Ww12-IPSN	6°35.648′ W	52°54.892′ N	18 July 2001	2	0.29	0.09
Ww13-IPSN	6°36.036′ W	52°54.476′ N	18 July 2001	2	0.39	0.11
Ww14-IPSN	6°36.449′ W	52°56.310′ N	18 July 2001	2	1.64	0.40
Ww15-IPSN	6°36.064′ W	52°56.793′ N	18 July 2001	2	0.23	0.08
Ww16-IPSN	6°33.279′ W	52°58.250′ N	18 July 2001	2	0.79	0.21
Cw01-IPSN	6°53.235′ W	52°28.995′ N	19 July 2001	2	5.12	1.19
Cw02-IPSN	6°53.622′ W	52°30.534′ N	19 July 2001	2	1.73	0.42
Cw03-IPSN	6°52.702′ W	52°31.938′ N	19 July 2001	2	2.07	0.50
Cw04-IPSN	6°54.225′ W	52°34.431′ N	19 July 2001	2	2.87	0.68
Cw05-IPSN	6°54.228′ W	52°35.509′ N	19 July 2001	2	3.64	0.85
Cw06-IPSN	6°56.535′ W	52°37.902′ N	19 July 2001	2	3.42	0.80
Cw07-IPSN	6°52.835′ W	52°40.393′ N	19 July 2001	2	1.63	0.39
Cw08-IPSN	6°51.677′ W	52°41.008′ N	19 July 2001	2	3.18	0.74
Kk01-IPSN	6°59.758′ W	52°39.116′ N	19 July 2001	2	2.92	0.69
Kk02-IPSN	7°00.994′ W	52°38.225′ N	19 July 2001	2	1.86	0.45
W01-IPSN	7°10.425′ W	52°08.531′ N	20 July 2001	2	1.35	0.34
W02-IPSN	7°11.894′ W	52°11.191′ N	20 July 2001	2	0.68	0.18

Appendix B

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is the newest version of a complete system for computing simple air parcel trajectories for complex dispersion and deposition simulations. HYSPLIT computes the advection of a single pollutant particle, or simply its trajectory. The dispersion of a pollutant is calculated by assuming either a puff or particle dispersion. In the puff model, puffs expand until they exceed the size of the meteorological grid cell (either horizontally or vertically) and then split into several new puffs, each with its share of the pollutant mass. In the particle model, a fixed number of initial particles are advected about the model domain by the mean wind field and a turbulent component. The model's default configuration assumes a puff distribution in the horizontal and particle dispersion in the vertical direction. In this way, the greater accuracy of the vertical dispersion parameterisation of the particle model is combined with the advantage of having an ever-expanding number of particles represent the pollutant distribution.

Model features:

- Multiple simultaneous trajectories
- Computations forward or backward in time
- Default vertical motion using an omega field
- Other options: isentropic, isosigma, isobaric, isopycnic