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# Greenhouse gas emissions, inventories and validation

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## *Summary*

The emission of greenhouse gases has become a very high priority research and environmental policy issue due to their effects on global climate. The knowledge of changes in global atmospheric concentrations of greenhouse gases since the industrial revolution is well documented, and the global budgets are reasonably well known. However, even at this scale there are important uncertainties in the budgets, for example, in the case of methane while the main sources and sinks have been identified, temporal changes in the global average concentrations since the early 1990s are not understood. In the absence of a quantitative explanation with appropriate experimental support, it is clear that current knowledge of the causes of changes in the global methane budget is inadequate to predict the effect of changes in specific emission sectors.

In developing control strategies to reduce emissions it is necessary to validate national emissions and their spatial disaggregation. The methodology to underpin such a process is at an early stage of development and is not fully implemented in any country, even though target emission reductions have already been announced. Furthermore, the scale of the emission reductions is large (eg of 60% reductions by 2050 relative to 1990 baseline). There is therefore an urgent requirement for measurement based verification processes to support such challenging emission reductions.

In this paper we provide the background in greenhouse gas emissions globally and in the UK followed by examples of approaches to validate emissions at the UK scale and within the regions.

## *Introduction*

The emission of naturally occurring greenhouse gases to the atmosphere as a consequence of human activities has led to large increases in concentrations since the beginning of the industrial revolution. Clearly the sources of these gases are in excess of the sinks and the rates of change in their concentrations in the atmosphere provide a measure of the degree of imbalance of sources and sinks. Carbon dioxide concentrations have increased from about 280 ppm in 1750 to 367 ppm in 1999, and the rate of increase continues to accelerate (Houghton 2004). Methane concentrations grew from around 770 ppb in 1750 to 1891 ppb in 1999, concentrations growing rapidly until the early 1990s, but since then have increased some years and decreased in other years, and the cause of these changes remains unclear. Uncertainties in the

cause of changes in methane reveal major gaps in understanding the atmospheric methane cycle. Nitrous oxide concentrations grew from 270 ppb in 1850 to 410 ppb in 2000, and total global emissions are well known as detailed later, but country specific sources are poorly understood due to the very large spatial and temporal variability in emissions. There is a requirement to quantify country specific greenhouse gas emissions as part of international commitments within the UNFCCC. However, there are too few direct measurements to provide these emissions from country specific measurements directly. Instead, protocols to estimate national emissions based on prescriptive emission factors and activity data have been developed as part of international efforts in support of Kyoto and related protocols.

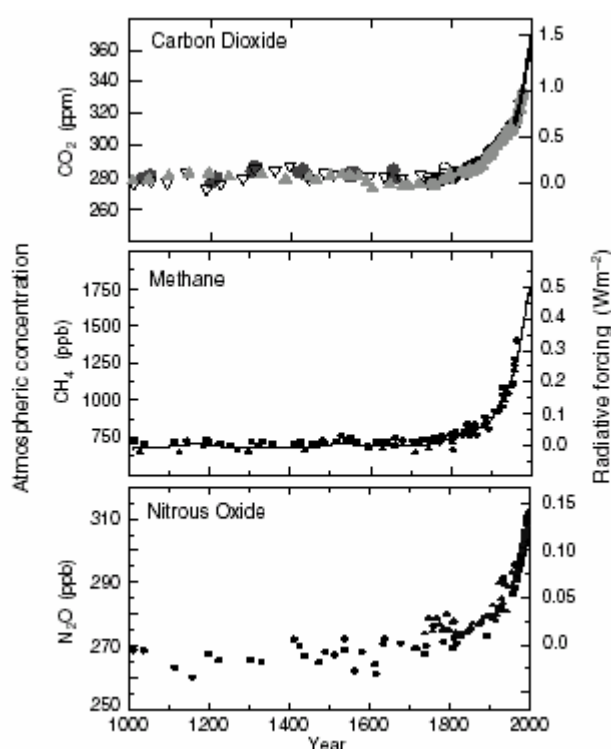


Figure 1. The long term change in greenhouse gas concentrations in the global atmosphere derived from ice cores from Antarctica (IPCC TAR 2001).

Greenhouse gas emissions are provided for the UK (Baggot et al 2005). The energy sector, i.e. fuel combustion, is the largest contributor to the overall emission, and contributes in excess of 80% of UK greenhouse gas emissions. The second largest source of greenhouse gases (7% annual UK emissions) is agriculture, principally as nitrous oxide emissions from fertilised soils and methane emissions from enteric fermentation in ruminants.

Country specific emissions are calculated according to prescribed guidelines, developed by the IPCC (IPCC 1996). The approach ensures a methodology that is consistent between countries to underpin the assessment process. However, the estimates of emission are not directly linked to measurements of the individual gases, or their emission fluxes over the countries specified. Thus uncertainties in the underpinning science or weaknesses in the activity data may lead to errors in estimates of emission within a country.

These introductory comments reveal basic weaknesses in the underpinning science necessary to support policies for reductions in emissions of greenhouse gas emissions. In an ideal world, measurements would test and validate country specific emissions and their spatial disaggregation. The sources and sinks and their response to major controlling variables would all be known at the country and sector level in advance of specific control measures. However, the scale of the global problem of climate change, the very long response time to changes in emissions and the complexity of the interactions has made it necessary to develop policies for large scale emissions reductions in advance of a full understanding of sources and sinks.

In this paper the main sources of greenhouse gases in the UK, Scotland, England, Wales and Northern Ireland, are described. Recent developments in the measurement of greenhouse gas emissions at the landscape and country scale are presented to illustrate possible strategies to validate national and regional emission estimates.

### Nitrous oxide

Soil is the single largest source of nitrous oxide globally (Climate Change 1994, Prinn *et al* 1990). For example, in the UK, soils are responsible for more than 70% of the total annual nitrous oxide emission. Other important sources of nitrous oxide are adipic acid and nitric acid production and fuel combustion (Baggott *et al*, 2006). Vehicle emissions of nitrous oxide have risen sharply since the installation of catalytic converters, but are minor contributors to annual emissions, whereas industrial emissions have declined as processes to regulate the release of N<sub>2</sub>O have been introduced.

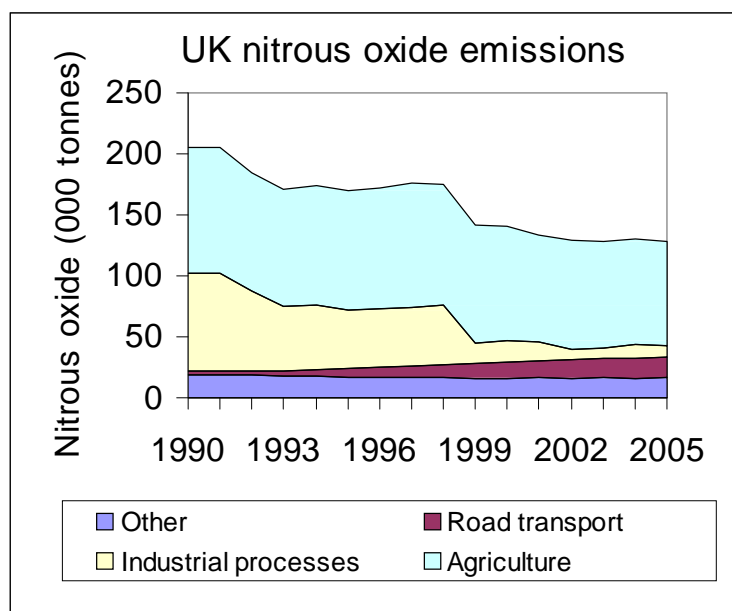


Figure 2 UK emissions of Nitrous oxide between 1990 and 2005 by sector.

In soil nitrous oxide is produced by two microbial processes: nitrification and denitrification (Bremner, 1997). Many experiments in the laboratory and field have shown a linear relationship between nitrogen additions and nitrous oxide emissions.

This relationship has been adopted by the Intergovernmental Panel of Climate Change (IPCC) to provide a simple methodology to calculate country scale annual nitrous oxide emissions. For example, it is assumed that 1.25% of the mineral nitrogen fertiliser applied to agricultural soils and 1% of the atmospheric nitrogen deposition is emitted as nitrous oxide (IPCC 1996). This approach provides a simple methodology for widespread application and a broad picture of the contribution of soils to total emissions. The uncertainties in this estimate, however, are very large, partly because other important environmental variables including rainfall, temperature and land management are not taken into account. This leads to large uncertainties in the emission inventory. In the UK, grasslands are the largest soil source of nitrous oxide and together with manure from housed and grazed animals returned to grassland, this source contributes 74 kt nitrous oxide (>80% of total soil emissions) annually (Figure 1). Grassland emissions of N<sub>2</sub>O are larger than those from fertilised arable land when expressed per unit area because a) grasslands receive larger rates of mineral fertiliser and manure application, b) grasslands occur in high rainfall regions, promoting the anaerobic soil conditions necessary for N<sub>2</sub>O production, c) grazed grasslands have compacted soils. Such conditions are all favourable for nitrous oxide production (Smith et al 1994). The location of intensively managed grasslands is mainly in the wetter, Western parts of Great Britain, these areas are responsible for larger annual rates of nitrous oxide emissions than eastern areas, (Sozanska *et al*, 2002). The contribution of arable land to the total nitrous oxide emission (8%) is of similar importance as nitrogen deposition derived nitrous oxide emission rate (6%). In Scotland, the high nitrogen input grasslands in the west are important N<sub>2</sub>O sources while the fertile soils in Fife and East Lothian, capable of producing a wide variety of arable crops contribute significantly to the local nitrous oxide emission. Forests, heath and moorlands, while large in area, contribute less than 5% to the total soil emissions.

## **Methane**

At the global scale the main sources of methane are natural wetlands in the northern latitudes and the tropics, enteric fermentation, rice paddies, landfills and natural gas and coal mining industries (Prather et al, 2001). Natural wetlands, enteric fermentation of farmed livestock and rice paddies contribute to 29%, 15% and 11% of the global annual emission, respectively. The uncertainty in these estimates unfortunately is high, especially for the wetlands. Natural wetlands are estimated to emit 115 to 237 Mt / year and rice paddies 25 to 100 Mt/year.

Figure 3 illustrates global methane sources both natural and anthropogenic.

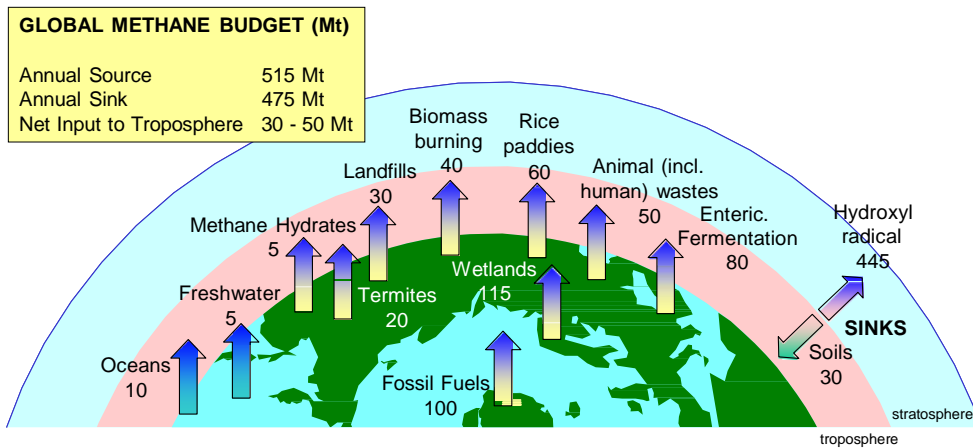


Figure 3. Global sources and sinks of atmospheric methane

Methane is produced by strictly anaerobic microorganisms (methanogens). Production is therefore restricted to micro-habitats where oxygen diffusion is inhibited, for example by high water content in rice paddies or inside the rumen of ruminant livestock. The primary factors controlling the rate of methane production in wetlands and rice paddies are water table height and temperature. Plants play a significant role in the transport of methane from the zones of production to the atmosphere. For example, surface water on a blanket bog in Caithness emitted 10 times more methane when vegetated with *Menyanthes trifoliata* (Bog-bean) compared to adjacent non vegetated parts of the same surface water (MacDonald *et al*, 1998).

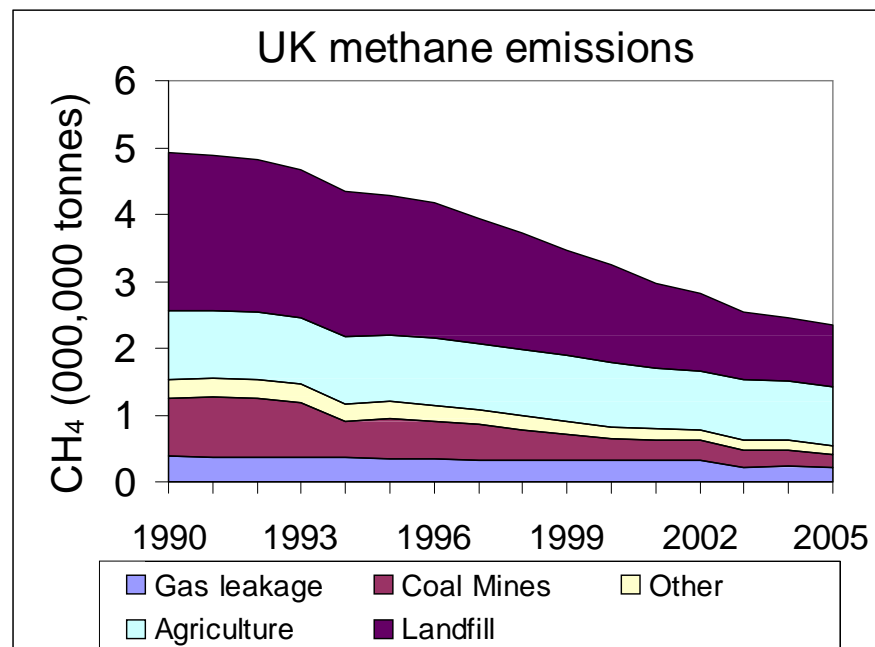


Figure 4. UK sources of methane since 1990, by sector, showing a marked decrease in the coal mining and landfill sectors.

### *Methane and wetlands*

The variables controlling biological methane production, transport, oxidation and emissions are reasonably well researched, especially for northern wetlands (MacDonald et al, 1998, Hargreaves and Fowler, 1998) and tropical rice cultivation (Wassmann et al, 2000). Our understanding of the processes determining methane emissions is sufficient to simulate the temporal variability of methane emissions at small scales. For example, the Denitrification-Decomposition (DNDC) model has been used successfully to predict methane emissions from rice paddies (Pathak et al, 2005). However, applying bottom-up, process-based models to the globe is difficult, especially for heterogeneous systems as natural wetlands. Furthermore, recent findings have demonstrated the importance of labile substrate supply (Christensen et al 2003), vegetation and sulphate deposition via acid rain pollution (Gauci et al., 2002, 2004).

A number of global-scale methane wetland models have been developed, based on water table height, soil temperature and substrate availability (e.g. Walter et al, 2001; Gedney et al, 2004). However, there are important discrepancies between model predictions, even at the coarse scale. Observational data with high resolution in space and time are required to discriminate between these alternatives. High quality observational data for CH<sub>4</sub> are available from a network of remote sites distributed throughout the world provide a time series of ground-based concentrations. These data have been used in models to estimate the source strengths and their global distribution using inversion techniques (Dlugokencky, 2001). At best, this resolves the surface flux for coarse latitudinal bands, ie. northern, tropical & southern latitudes.

Peat bogs are the only significant soil source of methane in the UK and may contribute around 120 kt methane/y. Other ecosystems are only occasional small sources of methane during prolonged wet periods. Soil as a source of methane is not included in the national atmospheric emission inventory. Soils also act as sinks for methane, either from sources located in deeper horizons or from the atmosphere. The soils sink for atmospheric methane is significant at a global scale, but is unimportant in the UK.

### **Carbon dioxide**

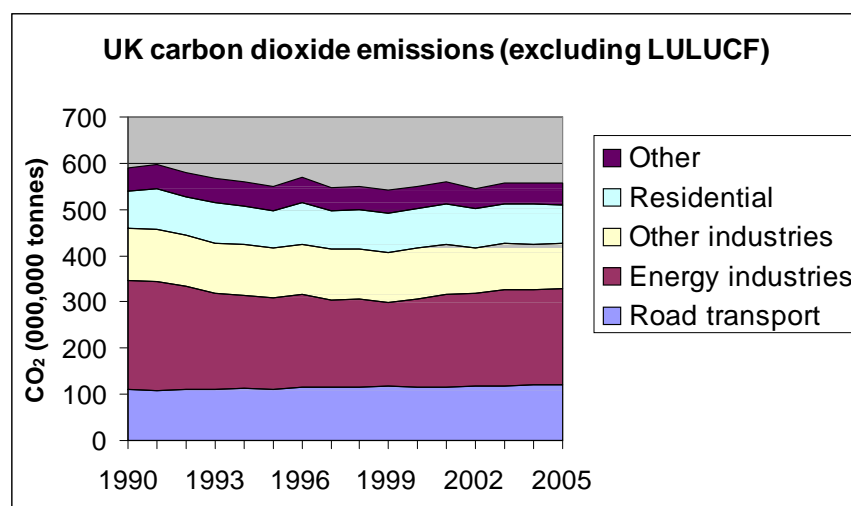


Figure 5 UK emissions of CO<sub>2</sub> since 1990, showing a small decrease in the energy sector and an increase in the transport sector.

Global anthropogenic sources of CO<sub>2</sub> total approx 7 Gt C annually in recent years (IPCC 2007), and are dominated by fossil fuel combustion and cement production, however land use change is also associated with net release of CO<sub>2</sub> to the atmosphere, the amounts being approximately 2 Gt C annually (IPCC 2007). Thus soils are an important reservoir of carbon, and this may accumulate or be depleted depending on land use and climate. Globally, soils hold three times as much carbon as the atmosphere. Table 2 shows that UK soils hold 4562 Tg of carbon, much of which is held in semi-natural vegetation. Soils act as a sink for carbon dioxide if the input from plant litter exceeds the loss from decomposition or a source if this balance is reversed. In cool, wet climates, where decomposition is slow, carbon accumulates in the form of peat, which comprises 60 % of UK soil carbon. If the climate warms and dries, as predicted, this large store of carbon is vulnerable to being released, with a potential positive feedback loop being created as the additional carbon dioxide adds further to the climatic warming. However, the peatland in the UK is located mainly in the north and west of the country, where climate change may increase annual precipitation, favouring increased sequestration of carbon as peat. It is unclear therefore whether climate change will increase or decrease the net soil to atmosphere exchange of carbon.

Recent work has suggested that carbon is generally being lost from UK soils, possibly at high rates (Bellamy *et al.* 2005), though the amount of climatic warming to date cannot account for the reported losses. Land use change is another possible explanation for this trend. Land use change has a major influence on the soil carbon balance, as the soil structure may be disturbed (eg. by ploughing) and different vegetation types produce different quantities and qualities of litter. Globally, it is estimated that around 50 Pg C have been emitted to the atmosphere from soils, following conversion of natural, undisturbed land to cultivated, agricultural land (Paustian *et al.* 2000).

### **Validating regional and national emissions**

The provision of greenhouse gas emission estimates is generally at the country and annual time scale, and these data are provided both at the UK and at the devolved countries, as illustrated in Figure 5. These data are subject to uncertainty both in magnitude of the annual values and also in spatial variability. It is not very useful to know that the total is incorrect and by how much, it is necessary to know which sector is responsible.



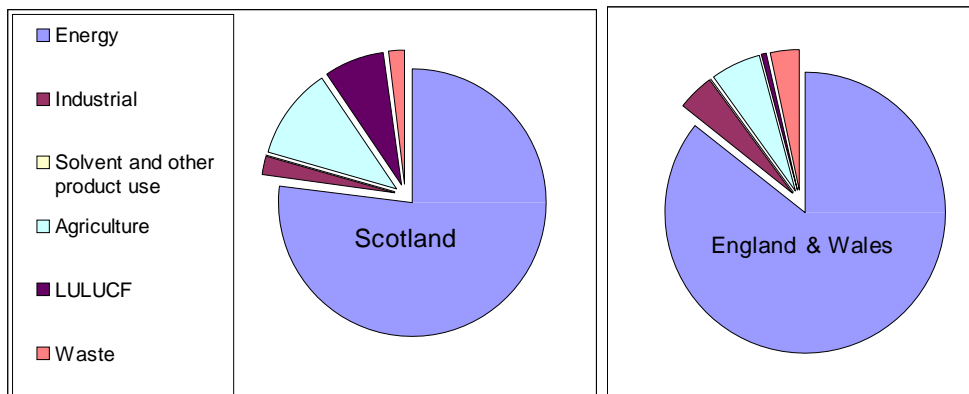


Figure 6. Shows the sector contributions for greenhouse gas emissions, and revealing the dominance of energy related activity overall for Scotland and for England and Wales. LULUCF refers to the contribution of greenhouse gas emissions resulting from land use change.

The development of validation methods is at a relatively early stage. This in part results from the processes leading to our current understanding of greenhouse gas emissions and their effects on the global climate. The individual contributions towards the overall knowledge have been mainly in the process science, measuring and modelling individual trace gases. The political developments leading to control strategies for greenhouse gas emissions, all stem from the synthesis provided within the IPCC and the Framework Convention on Climate Change. These processes are now leading towards clear long term targets at the country scale for emission reductions. For example, in the UK, legislation is currently being developed with a target emission reduction in greenhouse gas emissions of 60% (<http://www.defra.gov.uk/ENVIRONMENT/climatechange/uk/legislation/index.htm>).

*Validation from surface measurements using tall towers* The ‘Keeling Curve’ showing 50 years of observations of carbon dioxide concentration measured in Hawaii is something of an icon for this environmentally-aware age. The observations of CO<sub>2</sub> concentration in the air, the increase in its concentration year-on-year and the variability of the annual increases, provide a greater insight to the interactions between anthropogenic emissions and sequestration of CO<sub>2</sub> by the biosphere than any other data series (Conway et al, 1994). Much more recently, networks of ‘Tall Towers’ have been set up, primarily in Europe and the USA to monitor carbon dioxide and other greenhouse gases on a regular basis and to a very high standard of accuracy.

*Precision and accuracy goals for greenhouse gas observation in the CHIOTTO project and CarboEurope-IP*

| Gas Species      | Intra-laboratory instrumental precision | Inter-laboratory calibration scale accuracy | Precision in % |
|------------------|---|---|----------------|
| CO <sub>2</sub>  | 0.05 ppm                                | 0.10 ppm                                    | 0.01           |
| CH <sub>4</sub>  | 2.0 ppb                                 | 3.0 ppb                                     | 0.1            |
| CO               | 1.0 ppb                                 | 3.0 ppb                                     | 0.3            |
| N <sub>2</sub> O | 0.1 ppb                                 | 0.2 ppb                                     | 0.03           |
| SF <sub>6</sub>  | 0.1 ppt                                 | 0.2 ppt                                     | 1.6            |
| Rn               | 0.2 Bq m <sup>-3</sup> or 10%           | 10%   | 10             |

Table 1. The precision and accuracy in measurement of trace gases in the CHIOTTO and CARBO EUROPE EU projects. This level of accuracy is required for the validation of inventories using dispersion modeling.

By taking samples of air at a few hundred metres above the ground surface, it is possible to determine the local sources and sinks of these gases in addition to monitoring their rates of change on a global basis. The observations are usually combined with atmospheric transport models to calculate the back trajectories of air parcels that brought any particular air sample to the Tall Tower. By combining observations with atmospheric transport and dispersion, it is possible to calculate budgets for the main greenhouse gases (Bergamaschi et al, 2005); it is also possible to model natural and anthropogenic emissions and in combination with the observations and the transport model, to partition the measured concentrations into the relevant source sectors (Bousquet et al 2006, Vermeulen et al, 2006).

For the UK, tall towers have been established very recently and in time will provide the means of validating regional and national emissions. The network is at an early stage will be some time before sufficient data are available for this comparison. However, a long running monitoring station at Mace Head on the west coast of Ireland has provided greenhouse gas measurements as part of an international network since the 1980s (Manning et al 2003, Simmonds et al 1996).

Tall Tower observations can reveal seasonal cycle of photosynthesis/respiration at the country scale. (Observations limited to  $\pm 4$  hours from noon;  $\delta\text{CO}_2$  is the difference between the 8 am and 4 pm measured concentrations.)

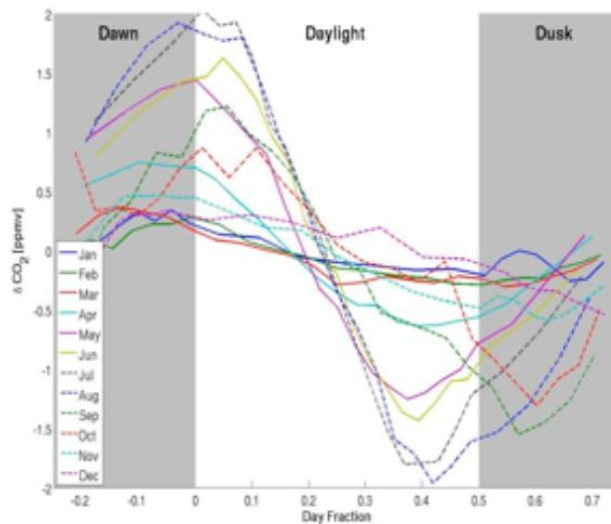


Figure 7. Monthly mean diurnal variations in concentrations of  $\text{CO}_2$  revealing the very large diurnal changes during the growing season as a consequence of photosynthesis during the daylight hours and respiration at night.

The measurements at individual stations may be used in combination with dispersion models to show whether current inventories are consistent with measured concentrations of these long lived gases. The comparison can be achieved in a forward mode, in which the model simply disperses the emissions within a three dimensional field of the airflow and turbulence. In this case, emissions may be increased or decreased to achieve agreement with the model, providing an estimate of the emissions needed to be consistent with surface observations. For the greenhouse gases, this approach using a network of global background stations has been used to evaluate the sources and sinks of methane (Hein et al 1997), and by Kaminski et al (1996) to investigate the annual and seasonal cycles in  $\text{CO}_2$  sources and sinks.

### Sciamachy and methane

New satellite data are now available from the satellite-borne SCIAMACHY instrument, which estimate the atmospheric methane concentration at much higher spatial and temporal resolution than previous ground-based air sampling data. For example, SCIAMACHY can clearly detect spatial and temporal variations in methane concentrations and emissions due to rice cultivation, ruminants and wetlands are visible for China and India and the Po valley in Italy (Buchwitz et al, 2006). Initial comparisons between SCIAMACHY observations of methane concentrations and those derived from simple emission inventories (Frankenberg et al, 2005; Buchwitz et al, 2006) revealed large regional and seasonal differences. Discrepancies were particularly large for the tropical regions, especially the tropical rain forest. These differences can be caused by (1) uncertainty in the interpretation of the satellite data, (2) uncertainty in the models or (3) missing methane sources.

The SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography), added to ENVISAT-1 satellite in 2002, is a spectrometer that measures reflected, scattered and transmitted solar radiation and thereby allows the

characterisation of the composition of the Earth atmosphere from the ground to the mesosphere. The data have been analysed to retrieve atmospheric concentrations of CO<sub>2</sub>, CO and CH<sub>4</sub> for the year 2003 (Buchwitz et al, 2005). Improvements have been made by moving to a different absorption band, located closely to the CO<sub>2</sub> absorption band (Buchwitz et al, 2006) and the data have been validated against FTIR concentration measurements (Dils et al, 2006).

*Validation of regional emissions in the UK using aircraft.*

The use of aircraft, in combination with atmospheric transport and dispersion models, allows, in suitable conditions, the entire UK emissions over a day to be measured and the measurements compared with the official inventory. The UK is ideally suited to these measurements by virtue of being located at the western boundary of Europe, with the Atlantic ocean providing uniform and reasonably clean upwind atmospheric composition. The aircraft samples this clean ‘background’ air during westerly airflow off the west coast. This is followed by a transect of the East coast, again within the boundary layer, at heights over the North sea of 300m to 100m allows the green house gas additions to the background air to be measured directly, as illustrated in figure 7.

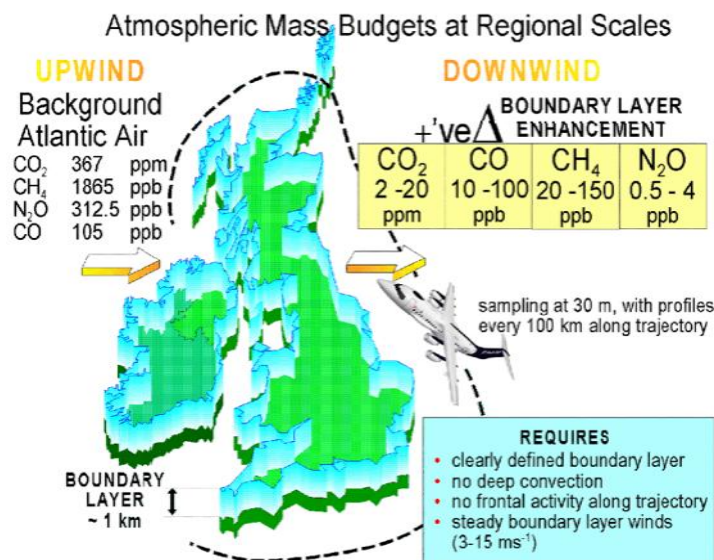


Figure 8 . Illustrating the measurement of greenhouse gas emission from the UK using aircraft, the magnitude of the increases in boundary layer concentrations of the greenhouse gases and atmospheric conditions required for the measurements.

The atmospheric conditions in which these measurements are possible are provided by an anticyclone to the south of the UK and westerly airflow over the country in the absence of frontal activity or deep convection. Clearly these conditions do not occur every day, and the field measurement programme to develop the method provided 16 days during the six months from May to October 2006.

The boundary layer budget measurements have provided a unique set of measurements of UK scale fluxes of CO, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O. The measurements of

CO were included in the work as this gas has a sufficiently long residence time in the atmosphere to be confident that atmospheric chemistry would not greatly influence the concentrations in the boundary layer over 24 hours. Thus the variability in the measured concentrations observed were due to emissions and dispersion processes.

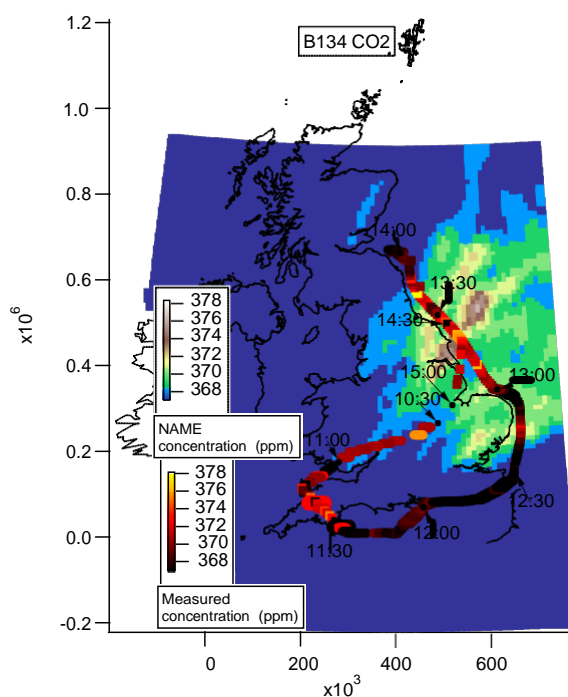


Figure 9 Emissions of CO<sub>2</sub> from the UK modelled in south westerly airflow using the NAME model and compared with measurements upwind and down wind of the UK coastline using the NERC aircraft. (Polson 2008).

The measured concentrations may be compared with modelled values using UK spatially disaggregated emission inventories and an atmospheric transport and dispersion model. In this case the model (NAME) developed and provided by the UK Meteorological Office and described by Manning et al (2003) has been used. The model – measurement comparison may be used to modify the emissions by sector iteratively to seek the statistically ‘best fit’ between measurements and model. Using this method Polson (2008) has deduced emissions of the main greenhouse gases emitted by the UK from 16 days of flying in 2006. An alternative to the dispersion model for analysis of the field data is provided by a simple box model. In this method the upwind and downwind edges of the box are used in a simple mass balance study.

The measured emissions of CO and CO<sub>2</sub> agreed well with the UK national inventory, within approximately 8%. For CH<sub>4</sub> and N<sub>2</sub>O, the measured values substantially exceeded the inventory, by a factor of two in the case of CH<sub>4</sub>, and by a factor of three in the case of N<sub>2</sub>O. A key question in this analysis is the representativity of the 16 days for the annual emissions of these greenhouse gases. In the case of CO<sub>2</sub> and CH<sub>4</sub>, the summer months are not considered to be unrepresentative of the year as a whole, but in the case of N<sub>2</sub>O, the temporal variability in emissions is very large and a substantially larger number of days of measurement spread through the seasons and

the surface conditions would be needed to reduce the uncertainty in the measured estimate of UK emissions.

However, the data obtained to date demonstrates the applicability of the method.

|                          | CO          | CO2              | N2O       | CH4           |
|--------------------------|-------------|------------------|-----------|---------------|
| <b>UK Inventory</b>      | 2,757       | 572,196          | 130       | 1,933         |
| <b>Ireland Inventory</b> | 239         | 43,469           | 31        | 607           |
| <b>NAME</b>              | 2,400 ± 226 | 560,000 ±        | 350 ± 208 | 4,000 ±       |
| <b>Box Approach</b>      | 2,700 ± 898 | 670,000 ± 94,000 | 310 ± 217 | 4,200 ± 2,130 |

Table 2 UK emissions of CO, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O (kt) estimated from aircraft sampling in the boundary layer over the UK combined with either a dispersion model (NAME) or a box model and compared with the UK national inventory of greenhouse gases.

#### *Inverse modelling*

Simulating regional concentration fields and budgets using of greenhouse gas emissions using a dispersion model has so far been described using a forwards modelling approach, working from given emissions to the concentrations. An alternative procedure is to work backwards with the model from the measured concentrations to calculate the likely emission footprint on the surface responsible for the observed concentrations. Inverse modelling at a regional scale has been used as a part of the validation process, but as yet is not widely applied. Taking the measurements from the aircraft described above, Polson (2008) has used an inverse modelling approach to estimate the regional distribution of UK sources of the gases measured.

The example presented is for carbon monoxide (CO) simply because emissions of CO and their spatial distribution in the UK are well known. The high quality aircraft measurements allow the technique to be tested before applying it to the other, more challenging trace gases.

An example of inverse modelling is presented in Figure 10, showing the footprint for the enhanced concentration measured in westerly airflow measured over the North Sea a few km from the Norfolk coastline. The method builds a picture of the footprint of all samples along the East coast. This potentially powerful technique allows the geographical location of discrepancies in the inventory to be located.

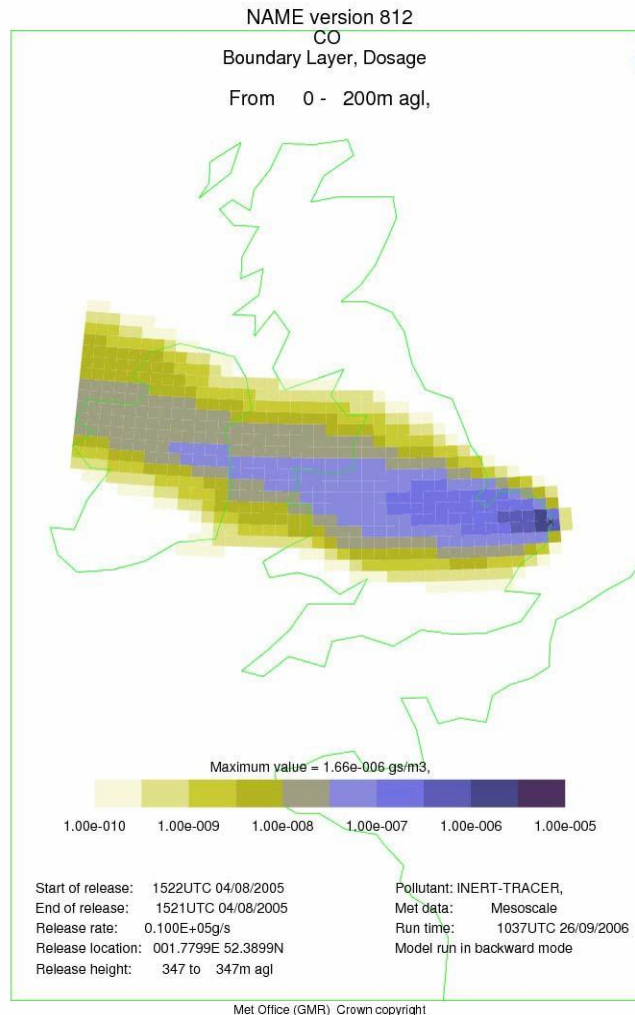


Figure 10. Inverse modelling of trace gas emissions over the UK using NAME.

### *Conclusions*

The high priority given to science underpinning climate change and the political processes in train leading to the delivery of the large scale reductions in emissions of greenhouse gases make this an important area of science. It is surprising given the time that we have been observing the growth in greenhouse gas emissions and concentrations that the methodology to validate national emissions is not fully developed and both accurate and precise. The reality is that there are some very powerful methods in development, to provide the necessary validation, but these are not fully developed. For atmospheric trace gases which have been subjected to international controls for a few decades, the monitoring and assessment is reasonably mature (EMEP 2007). There are therefore lessons from other control strategies. However, in the case of greenhouse gases, the issues are fully global, they involve all



nations and the monitoring and assessment has been focussed to date on identifying the problem and attributing the cause to the different contributors to the radiative forcing of climate. As the focus increasingly moves towards the control process, much more attention will be paid to validation, if only because the costs of the controls are so large.

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