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AIR QUALITY EXPERT GROUP

Linking Emission Inventories and Ambient Measurements



Prepared for:
Department for Environment, Food and Rural Affairs;
Scottish Executive; Welsh Government; and
Department of the Environment in Northern Ireland

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This is a report from the Air Quality Expert Group to the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of the Environment in Northern Ireland, on linking emission inventories and ambient measurements.

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Acknowledgements

The Air Quality Expert Group would like to acknowledge the following individuals and organisations for their help in the preparation of this report:

Dr Duncan Whyatt (University of Lancaster) and Roger Timmis (Environment Agency) for their contributions to Sections 4.1 and 9.2.2.

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TABLE OF ABBREVIATIONS

AEC	– airborne eddy covariance
AURN	– Automatic Urban and Rural Network
BaP	– benzo[a]pyrene
CH₄	– methane
CLRTAP	– Convention on Long-Range Transboundary Air Pollution
CMB	– chemical mass balance
CO	– carbon monoxide
CO₂	– carbon dioxide
CPC	– condensation particle counter
DA	– devolved administration
DECC	– Department of Energy and Climate Change
Defra	– Department for Environment, Food and Rural Affairs
DfT	– Department for Transport
DUKES	– Digest of UK Energy Statistics
EC	– elemental carbon
EEA	– European Environment Agency
EMEP	– European Monitoring and Evaluation Programme
GHGI	– Greenhouse Gas Inventory
HOA	– hydrocarbon-like organic aerosol
IIASA	– International Institute for Applied Systems Analysis
IPCC	– Intergovernmental Panel on Climate Change
LAEI	– London Atmospheric Emissions Inventory
NAEI	– National Atmospheric Emissions Inventory
NAME	– Numerical Atmospheric Dispersion Modelling Environment
NCAS	– National Centre for Atmospheric Science
NECD	– National Emission Ceilings Directive
NERC	– Natural Environment Research Council
NH₃	– ammonia
NMVOC	– non-methane volatile organic compound
NO_x	– nitrogen oxides (NO + NO ₂)
NO	– nitric oxide
NO₂	– nitrogen dioxide
O₃	– ozone
OC	– organic carbon
OECD	– Organisation for Economic Co-operation and Development
OOA	– oxygenated organic aerosol
PAH	– polycyclic aromatic hydrocarbon
PM	– particulate matter
PM₁₀	– particulate matter with a diameter less than 10 micrometres
PM_{2.5}	– particulate matter with a diameter less than 2.5 micrometres
POP	– persistent organic pollutant
POCP	– photochemical ozone creation potential
SO₂	– sulphur dioxide
SOA	– secondary organic aerosol
UFP	– ultra fine particle
UNECE	– United Nations Economic Commission for Europe
UNFCCC	– United Nations Framework Convention on Climate Change
VOC	– volatile organic compound

Executive summary

1. This report considers the linkage between emission inventories and ambient measurements and aims to review information that could help establish a stronger link between them.
2. It is generally the case that atmospheric measurements and emission inventories are collected or developed separately and are considered in isolation from one another. The feedback between these two areas tends to be *ad hoc* and the consistency between ambient measurements and emission inventories is not considered in a thorough and systematic way. This separate development leads to missed opportunities which could help to improve inventory verification and provide confidence that there is consistency between emission estimates and the response of concentrations in the atmosphere.
3. Emission inventories are a cornerstone of air quality management and incorrect emission estimates will have important consequences for the whole air quality management process. Erroneous emission estimates will have a direct bearing on the quality of policies developed to mitigate air pollution and could result in ineffective or misdirected emissions control measures being implemented. It is also important to verify emission inventories as a way of checking whether trends in ambient concentrations match those expected in emission inventories and, if not, to identify a potential cause and take the necessary action.
4. The linkage between emission source strength and atmospheric concentration is a complex one; this makes it difficult to know whether emission estimates are consistent with atmospheric measurements. It is rarely the case that a change in emissions results in a proportionate change in concentration in the atmosphere because ambient measurements tend to be a superposition of numerous sources. Similarly, it can be difficult to make or analyse ambient measurements in a way that can provide the emission estimates for a specific source sector required by emission inventories. Nevertheless, there are many measurement and analysis techniques available that can help verify emission inventories or aspects of them.
5. Ambient measurements provide the opportunity to verify localised emission sources (which are often derived from spatially disaggregating a national total). Discrepancies may therefore be caused by issues associated with the mapping process, or the emission estimates themselves. Nevertheless, information from ambient measurements may allow emission inventory improvements.
6. This report identifies some of the measurement and analysis techniques that can help inventory verification. Almost all the techniques and methods identified in this report require careful thought as to how they are applied. Few, if any, of the techniques can be applied in a direct and simple way because they do not provide the complete or specific information required by emission inventories, e.g. information on a specific source sector or spatial information. However, it is clear that considerable information does exist that could help with inventory verification and which is currently unused. Improved articulation of the feedback between measurements and inventories is needed.

7. Emission inventories such as the National Atmospheric Emissions Inventory (NAEI) are primarily designed for inventory compliance reporting to various international bodies in order to track progress towards national emission reduction targets. This imposes some limitations in terms of their flexibility to respond to emerging evidence from verification studies. The NAEI aims to provide comprehensive emission estimates across the UK at a range of scales. However, most of the techniques for verifying inventories allow consideration of only a partial set of the information.
8. It is clear for some source sectors that deviation in long-term trends in emissions from “true” values can usefully be identified. Even simple plots of ambient concentrations filtered to maximise the effect of a specific source can highlight discrepancies (e.g. the analysis of the roadside increment in concentrations to estimate road vehicle emissions). In addition, more sophisticated statistical analysis of ambient concentrations can provide time series that better reflect changes in emissions by removing or minimising the variation due to other influences, such as meteorology, that can falsely mask or emphasise trends.
9. In recent years, measurement technologies have developed so that there are now many more opportunities for verifying emission inventories than previously. These techniques cover a wide range of scales from the near field (e.g. close to a road or point source) to urban and even continental and global scales. Vertical flux measurements, for example, can provide urban (and rural) source strength estimates for a comparatively wide suite of species that can (and have) been compared with the NAEI. Satellite-based remote sensing can provide source information at a country or continental scale. In addition, these techniques can provide information on emissions not included in the NAEI.
10. The wide range of techniques available for inventory verification broadly provides either absolute emission estimates (such as flux measurements over an urban area) or information on the relative change or difference in emissions (such as the plot of the concentration ratio of two species over time). Both of these types of information can be useful for emission inventory verification. However, the extent to which such information is useful and how it is used and applied can vary widely.
11. There is also a wide variation in how well different measurement and analysis techniques match up to current inventory source categories. For example, vehicle emission remote sensing can provide highly disaggregated emissions information for many species that can match directly with detailed NAEI emission categories. Such data could be used in a relatively straightforward way in emission inventories, either for verification or to replace existing data. In contrast, vertical flux measurements can provide absolute source emission estimates for an upwind ‘footprint’ source area but require careful analysis to match the two and ensure a consistent comparison. This report highlights how different methods can link with emission inventories.
12. A valuable contribution that ambient concentration measurements can make towards emission inventories in general is the measurement of species currently not included in inventories. In this respect, rather than providing some form of verification, they can help fill important gaps in knowledge. Areas where these contributions are particularly valuable include information on source apportionment, e.g. for particle and volatile organic compound (VOC) measurements. In these cases it can be important to have detailed, speciated data, e.g. for use in atmospheric models or for their evaluation.

13. Atmospheric models provide a natural linkage between emission inventories and ambient concentrations because they rely on inventories as input and ambient data for model evaluation. However, it is often the case that when discrepancies are identified and reported it can be difficult to know whether a difference is due to deficiencies in emission inventory estimates or the model – or both. The use of emission inventories in models can help to identify inventory deficiencies because their effect on ambient concentrations can be assessed directly. Beyond the direct use of inventories in models, inverse modelling, where models are used to back calculate source strengths, has been increasingly used at a range of scales from urban to global. These methods may be useful for estimating the source strength of species such as ammonia, where emission estimates are uncertain both in terms of source strength, and spatial and temporal variation. Continued model developments are likely to increase the importance of these methods over time.
14. It is not possible to establish a universal approach for considering how each verification technique can be used to inform the inventory, nor what action the inventory community should take to respond. Each piece of evidence for each pollutant, emission source and inventory scale needs to be considered independently, but there will be a need for consideration of other potentially conflicting or supporting evidence and the wider inventory needs.

Recommendations

15. The issue of inventory verification or checking the consistency of emission estimates with ambient measurements is to a large extent an activity that is absent – or at least *ad hoc* – in the UK. There are three main opportunities for ensuring a closer linkage between measurements and emission inventories:
 - a. First, there is a large body of existing data (measurements and emissions) that lends itself to being analysed in the ways described in this report. Trends in emissions and ambient concentrations should be considered on a more routine and regular basis. Such trend comparisons would help identify important deviations between emission trends and those in ambient concentrations and provide an early warning of any discrepancies.
 - b. Second, the research community, particularly through the Natural Environment Research Council (NERC) National Centre for Atmospheric Science (NCAS), increasingly operates research programmes that provide potentially important inventory verification information, e.g. on urban fluxes, and detailed source speciation information. It is important that the Department for Environment, Food and Rural Affairs (Defra) is aware of these programmes and their outcomes to ensure the value of such information is maximised.
 - c. Third, Defra should consider the linkage between emission inventories and ambient measurements when planning and commissioning new work. This would ensure such issues are “built in” from the start of new programmes of work and encourage the closer linkage between these two areas.
16. Consideration should be given to the enhancement of the NAEI, recognising its core function. This enhancement should include development of a structure or mechanism to allow testing of scenarios and the addition of emerging science for both policy and research applications. The current NAEI has well-established methods and a life cycle that must meet a range of requirements; most notably for international

reporting. While it would be too ambitious to consider a full, alternative NAEI based on emerging information, it is clear that for some species and some sectors, more flexibility in this respect would be advantageous. The recent case of erroneous concentrations of nitrogen oxides (NO_x) and nitrogen dioxide (NO₂) emissions from road vehicles provides a good example of where an enhanced inventory would be beneficial. Such an enhancement could act as a 'test bed' for new information and if found useful could be integrated into the full NAEI.

17. Models can help provide a direct linkage between emission inventories and ambient measurements and could play a more important role in checking the consistency of emission inventories. Further work is encouraged on inverse modelling as a method of estimating both the source strength and location of emission sources.
18. There is a need to find more opportunities to engage jointly those involved with emission inventory development and ambient measurements to ensure a stronger link between the two areas. The complexity of exploiting links between inventory development and ambient measurement and analysis techniques necessarily requires a wider co-operation between these two communities. Such opportunities could include workshops to consider a specific topic, co-operation on identifying how best to exploit new measurement opportunities in inventory development and the explicit inclusion of such issues into inventory development plans.
19. We recommend co-ordinated action is taken by Defra and the research councils to bring together the research community involved in verification activities to 'make their case' and to help the inventory community decide how, based on the evidence, the inventory could be changed.
20. There needs to be an improved mechanism available to feed new information into inventories to ensure that potentially useful information is fully exploited.
21. A mechanism should be set up to make the recommended changes in the enhanced inventory which, when demonstrated to close the evidence gap, would then become the 'official inventory' for a given pollutant, provided the needs for compliance reporting is maintained. A new enhanced inventory may then evolve from this version to test further improvements. An Air Quality Inventory Advisory Group should be set up to prioritise where, based on the strength of evidence presented and Defra's policy needs, the inventory should be changed and how. Such a group could meet annually to review the most recent evidence and make recommendations.
22. An active feedback system like this should also be considered at the international level to ensure that observational evidence is fed quickly into the various inventory guidebooks.
23. Table 1 groups the main measurement and analysis techniques that can be used in inventory verification. With each grouping, some of the key advantages and disadvantages are identified, together with how they link to emission inventories. A more comprehensive treatment of these issues is considered in the main report.

Table 1: Summary of techniques that can be used to check the validity of emission estimates.

Technique	Advantages	Disadvantages	Inventory linkage
Comparing time series trends of emissions and concentrations	Straightforward, with most data readily available. Can provide a quick indication of gross mismatches. Better for time series over many years where meteorological effects are diminished.	Too simplistic for many situations. Difficult to isolate specific sources sufficiently well to allow for effective comparisons.	Can provide aggregate source-specific comparisons, e.g. urban road transport emissions. Best for longer-term trend comparisons over many years.
Comparing ambient pollutant ratios with emission inventory ratios	Simple to calculate. Removes much of the variation due to meteorology to produce clearer trends. Most useful for local sources.	Does not directly provide information on which pollutant is “wrong”.	Similar to above.
Meteorological normalisation <i>Statistical analysis of ambient measurement data to remove the effect of meteorological variation</i>	Removes much of the influence of meteorology affecting ambient trends, leaving a trend that better reflects changes in source strength.	Can require sophisticated statistical models and care in developing robust models. Not carried out on a routine basis – but could be for key sites that are well characterised.	Best for comparing long-term trends in emissions for aggregate source types, e.g. road transport or total urban emissions. Has already been used for inventory comparisons.
Flux measurements <i>Use of fast response instruments to measure vertical fluxes of pollutants and meteorological variables in the atmosphere</i>	Provides a direct estimate of source strength over an area. Consistent with current inventories, i.e. aggregate emission estimate over an area. Useful for an increasing number of species, e.g. NO _x , CO, some speciated VOCs and particle metrics.	Measurements, their analysis and interpretation can be complex. Lack of longer-term measurements, although this is being addressed for some species.	Emission estimates can be compared against inventory totals over varying spatial areas. Has already been used for inventory comparisons.

Technique	Advantages	Disadvantages	Inventory linkage
Vehicle emission remote sensing	<p>Provides highly disaggregated emissions by vehicle class.</p> <p>Large sample sizes.</p> <p>Highly consistent with inventories.</p>	<p>Emissions are fuel-based (CO₂) ratios, not absolute estimates.</p> <p>Provides information on a subset of driving conditions (typically urban).</p> <p>Commercial systems limited by lack of NO₂.</p> <p>Long-term UK measurements not available.</p>	<p>Strong and direct linkage with emission inventories, e.g. can exactly match existing NAEI vehicle class categories, providing data for new emission factor estimates or verification of existing emission factors.</p> <p>Information on specific technologies, e.g. selective catalytic reduction, is potentially very useful.</p> <p>Has already been used for inventory comparisons.</p>
Space-based remote sensing	<p>Useful for large-scale emission estimates, e.g. at a country level.</p> <p>An increasing number of species can be considered at increasingly higher resolutions.</p>	<p>Currently a limited range of species that can be measured and linked to inventories.</p> <p>Analysis and interpretation is complex.</p>	<p>Can provide country (or regional) scale emission estimates that can be compared with national emission totals.</p> <p>Has already been used for inventory comparisons.</p>
<p>Inverse modelling</p> <p><i>Where an air quality model is used to back calculate emission estimates using ambient measurements</i></p>	<p>Can provide a direct, absolute estimate of emission source strength.</p> <p>Is applicable at small (street) to large (regional) scale.</p> <p>Can account for chemical reactions.</p> <p>Models and model methods are becoming increasingly sophisticated.</p>	<p>Can require sophisticated models.</p> <p>Care needed to rule out other causes of error, e.g. inadequate treatment of dispersion.</p> <p>Detection limit of measurements, e.g. CO on AURN.</p> <p>Some methods limited by number of measurement sites available.</p>	<p>Has already been used for inventory comparisons.</p>

1 Introduction

1.1 Background

Emission inventories play a central role in air quality policy and are used in a very wide range of circumstances. These circumstances include but are not limited to: reporting of emission totals to international bodies; as input to air quality models; and for a wide range of research applications. Inventories are used as the basis to predict current pollutant concentrations at a wide range of scales and for a very wide range of issues including local and regional air quality. Furthermore, inventory projections form an essential role in predicting future concentrations and more generally for understanding the potential impact of measures to improve air quality. If inventories are erroneous, then regardless of the sophistication of other aspects of the air quality management system (e.g. air quality modelling), predictions of pollutant concentrations will also be erroneous. Despite the key role played by inventories, their verification is somewhat *ad hoc* and inconsistent. There are no formal methods for checking the accuracy of emission inventories in the UK to ensure they are consistent with ambient observations. More often than not, emission inventories are considered separately from ambient measurements with each being reported in their own way.

Many characteristics of emission inventories are important. At the simplest level it is important to know whether annual emission totals are correct. In addition, a key consideration is whether long-term trends in emission estimates are consistent with ambient measurements. Without a comparison of emissions and ambient observations it is difficult to know whether measures to control emissions have been effective or not. Equally, any disparity between emission and ambient trends may provide important information concerning deficiencies in emission inventory estimates. The spatial and temporal distribution of emissions is also an important consideration for many species, e.g. ammonia. In other situations it can be very important to understand how emissions are speciated, e.g. the individual constituents of volatile organic compound (VOC), PM₁₀ (particulate matter, PM with diameter less than 10 µm) or nitrogen oxides (NO_x) emissions.

Establishing whether emission inventories are consistent with ambient measurements is challenging. Trends in emissions of a pollutant cannot usually be directly compared with ambient measurements to establish whether there is consistency between the two. Indeed, there are only a few situations where a direct correlation between emission estimates and ambient measurements would be expected. For example, for a single source of a primary pollutant where changes in emission would result in a proportionate change in the ambient measurement, or for multiple sources of a primary pollutant that all change in a proportionate way. Even in these situations the variation in meteorology over time can introduce variation in pollutant concentrations that is not related to changes in source strength.

In most real situations however, there is no simple relationship between emissions and ambient concentrations. The reasons for this are varied, but include the following. First, ambient measurements tend to reflect the superposition of multiple sources. These sources may comprise different source sectors that respond differently over time to emission changes, e.g. road transport and power station emissions. Second, the way emissions disperse in the atmosphere is very important: a small, local source may make a disproportionate contribution to the concentration measured at a receptor. Source proximity is therefore important. Third, pollutant species may

undergo chemical transformation in the atmosphere, making it very difficult or impossible to directly gain information concerning the primary emission.

Meteorology also plays a central role in determining the concentration of dispersed pollutants and can falsely mask or emphasise ambient trends. It is sometimes stated that a particular year was a “bad” or a “good” year with respect to pollutant concentrations, but rarely are these statements quantified in any way. It can be very difficult to establish therefore whether a change was due to meteorology or a variation in source strength. This issue is at the heart of inventory–measurement comparisons.

Many of the factors that make a direct comparison between emission estimates and ambient measurements difficult can be overcome or mitigated to allow for a more consistent comparison between the two. In essence the aim is often to process the ambient measurements so as to make them more comparable with emission estimates. For example, if the interest is in road vehicle emissions then considering only monitoring sites that are strongly affected by road vehicles can help, e.g. roadside or urban sites. Data filtering techniques may also help, so rather than considering a whole time series it may in some situations be beneficial to consider particular seasons (e.g. winter when concentrations are higher) or hours of the day when road vehicles contribute a high proportion of the total emissions, e.g. Parrish (2006). Data can also be processed in other ways, e.g. using statistical models to “account” for (and remove or reduce the effect of) meteorology, leaving a trend that better reflects changes in source strength rather than meteorology.

There are also other measurements that can be made in the atmosphere that better reflect emission sources directly, for example, the use of vehicle emission remote sensing. In this case, while the measurements are made in the ambient atmosphere, they are made in such a way as to measure vehicle exhaust plumes as they disperse – thus avoiding issues of competing sources or dispersion effects. Another example is the measurement of vertical fluxes of pollutant concentration, which can be used to infer source strength. Both of these techniques require sophisticated measurements and can only provide information on a limited number of species. While these techniques do not provide a direct linkage between ambient measurements and emission inventories, they do provide a means of checking the validity of emission estimates.

It is worth noting that there is no single accepted method for checking whether emission inventory estimates are consistent with ambient observations. Work in this area tends to be *ad hoc* and strongly influenced by the data available. Furthermore, emission inventories and air quality networks in general are not developed with these issues in mind. And for this reason a very wide range of techniques have been developed and applied over the years, each with its strengths and weaknesses. Nevertheless, there are many techniques and data sources available that can help determine the accuracy of emission inventory estimates.

1.2 Aims

The area of inventory verification is very large and it is not the intention of this report to cover the area comprehensively. Instead the aim is to focus on the pollutants most relevant to UK air quality management. The main aims of this report are:

1. To provide some background information concerning the comparison of emission and ambient trends by highlighting the key issues involved.
2. To critically review some of the commonly used inventory verification techniques in the literature, in particular checking the consistency between emission and ambient measurement trends.
3. To provide examples using data available in the UK of how some of these techniques can be applied.
4. To provide recommendations to the Department for Environment, Food and Rural Affairs (Defra) relating to these issues. In particular, the aim is to comment on the applicability of various methods for pragmatic (routine) use. An additional aim is to identify other work, e.g. funded by the research councils, that is likely to be valuable to Defra in considering these issues.

2 Emissions inventory background

2.1 Introduction

Emission inventories have traditionally been developed in the UK and the rest of Europe in order to meet international inventory reporting commitments to bodies such as the UN Framework Convention on Climate Change (UNFCCC), the UN Economic Commission for Europe (UNECE) and the European Union. For this purpose, national inventories must be produced following internationally agreed guidelines so that inventories reported by different countries are consistent and comparable. They also enable progress towards meeting national emission reduction targets to be tracked. The UK has to meet ceilings in national emissions set under the Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-Level Ozone, part of the Convention on Long-Range Transboundary Air Pollution (CLRTAP), and the EU's National Emission Ceilings Directive (NECD).

To meet the needs of international inventory reporting, key considerations must be given to spatial coverage (i.e. over what areas the country is responsible for emissions reporting), consistency with other national statistics (e.g. energy statistics), consistency in methodologies and source sector definitions, and consistency in the time series covered. National inventories must report emissions as an annual emission rate each year across a time series going back to at least 1990, and in some cases 1980. This is important so that any changes in the methodology used to estimate emissions are applied to all the reported years, and the time series reflects real changes in emissions over time and not changes in methods applied between years.

National inventories are normally the primary source of inventory information for air quality modelling but, essential though they are, the inventories developed for compliance reporting may not provide all the information required for modelling. The key additional requirements include:

- greater spatial and temporal resolution;
- greater source coverage – not all emission sources (e.g. natural sources) are included in compliance inventories;
- greater chemical speciation, e.g. in terms of the breakdown in VOCs, PM and NO_x into their chemical components; and
- an appreciation of inventory uncertainties.

The most accessible and complete emissions inventory covering the whole of the UK is the National Atmospheric Emissions Inventory (NAEI, see www.naei.defra.gov.uk/index.php) which is updated on a yearly basis with a time series extending back to 1970. Emission inventories for other parts of Europe are provided through the European Monitoring and Evaluation Programme (EMEP, see www.emep.int).

The NAEI also provides the UK inventory for emissions from anthropogenic sources for the latest year spatially resolved at 1 km x 1 km resolution.

The NAEI is normally the primary source of inventory information for the UK. The air quality modelling and assessment community is a key stakeholder of the NAEI. However, it is not the only one and the data from emission inventories are used by a wide range of different stakeholders. Figure 1 shows some of the main user groups of emissions datasets. These stakeholders can have very diverse needs, and the resulting demands on a national emissions inventory programme are therefore extensive.

Policy-makers have a particular interest in the current and future trends in national emissions from different source sectors and how these might respond to policy interventions, for example, in industry, transport and power generation. Econometric studies and environmental impact assessments may require simplified outputs such as activity datasets and aggregated or implied emission factors (e.g. emissions per unit energy consumed). Air quality modellers require more spatially- and temporally-resolved emissions covering all known sources, not just those included in compliance inventories, and with greater chemical speciation.

The levels of certainty associated with datasets developed for different purposes vary greatly, and the user needs to have an appreciation of how the data have been tailored to ensure that they are fit for purpose. One of the most important issues associated with emission inventories is that the users of the data do not always have an appreciation of what the data are or are not suited for.

The following chapter elaborates on some of these points and in particular addresses the key concerns of air quality modellers on the spatial and temporal variability of emissions, their chemical speciation and associated uncertainties. To put this into context, Section 3.1 summarises the key principles of emission inventories and the treatment of inventory uncertainties as they relate to compliance reporting. Uncertainties associated with quantifying the spatial and temporal variability of emissions are addressed in later sections dealing with these specific areas of interest to modellers.

Local inventories provide an additional and very useful source of information for air quality modelling and assessments and have the potential advantage of using much more localised knowledge and information. Section 3.3 gives a brief overview of how local inventories relate to the NAEI, using the London Atmospheric Emissions Inventory (LAEI) as an example.

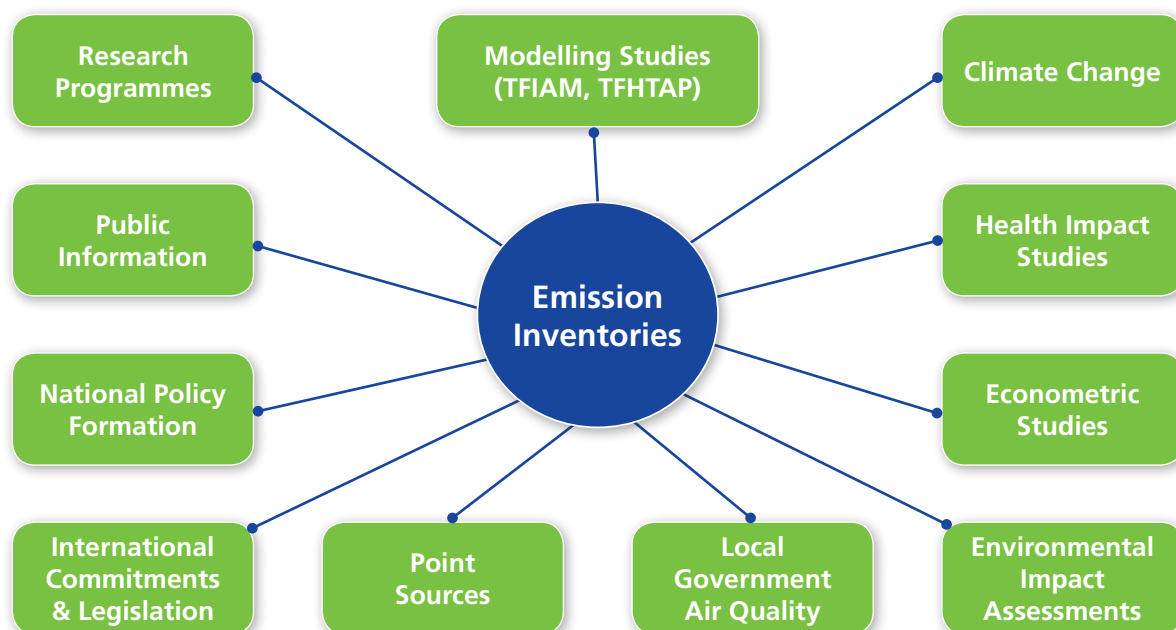


Figure 1: A selection of emission inventory stakeholder groups.

The final sections of Chapter 3 aim to provide information on the main strengths and weaknesses of the different datasets that are generated from the national inventory programme, so that they can be used appropriately by different stakeholders.

3 Emission inventories in detail

3.1 Principles of emission inventories for compliance reporting and their use

3.1.1 Annual cycle and version control

National emission inventories are typically updated on an annual basis, and are two years behind the latest year in the emissions inventory time series. So, for example, the dataset for 1970-2011 will first become available early in 2013. The time lag is due to the time it takes for the necessary UK activity data (e.g. fuel sales, transport and industry statistics, etc.) to be published by various organisations after the end of a calendar year, in addition to the amount of inventory processing time required.

However, as part of the annual update, the entire historic time series is updated to incorporate any improvements to methodologies or any new data. This ensures that all years of the emissions inventory are consistent. As a result, it is important that users always identify the *version* of the emissions inventory that is being used, and not just the *year* in the dataset. This is typically achieved by specifying the range of the time series (e.g. 2010 data from the 1990-2011 version of the emissions inventory).

Figure 2 shows a data flow diagram for the NAEI. Each year, activity data are provided from a variety of sources including government departments, statistical offices, regulators, industry, and trade associations. These may include data provided for previous years that have been revised. A formal system is used to apply quality assurance/quality control (QA/QC) to the activity data before it is incorporated into a number of sector-specific calculation spreadsheets and databases which contain the emission calculation algorithms and emission factors. The emission factors and calculation methodologies may occasionally be updated if new sources become available. This may be when emission inventory guidebooks are updated by EMEP and the European Environment Agency (EEA). The process for updating these is a formal one involving various international task forces and expert groups which aim to harmonise inventory approaches across all EU Member States. Calculation procedures may also be updated if new, usually more detailed, activity data become available. There are various tiered approaches given in the inventory guidebooks (see for example the EMEP/EEA Inventory Guidebooks at <http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009>) and it may sometimes be possible to switch to more detailed, higher tiered approaches when more detailed activity data become available. In the UK, the highest tier 3 approaches are used for many source categories because of the availability of detailed activity data (e.g. transport statistics).

The NAEI has a continuous improvement programme operating through a formal process managed by Defra and the Department of Energy and Climate Change (DECC). The process involves a National Inventory Steering Group and other stakeholder meetings where improvements to be adopted in the coming year are agreed. No improvements are carried out (other than routine changes to activity data) unless agreed through this process.

The whole inventory compilation process conducted annually is tightly managed with various QA/QC procedures along the way before the final outputs are submitted to Defra and DECC and then disseminated and reported in specified formats to the various international bodies. The UK inventory is periodically peer reviewed by expert groups appointed by the UNECE and UNFCCC. Some members of the UK inventory team participate in international inventory expert panels and reviews of other countries' inventories.

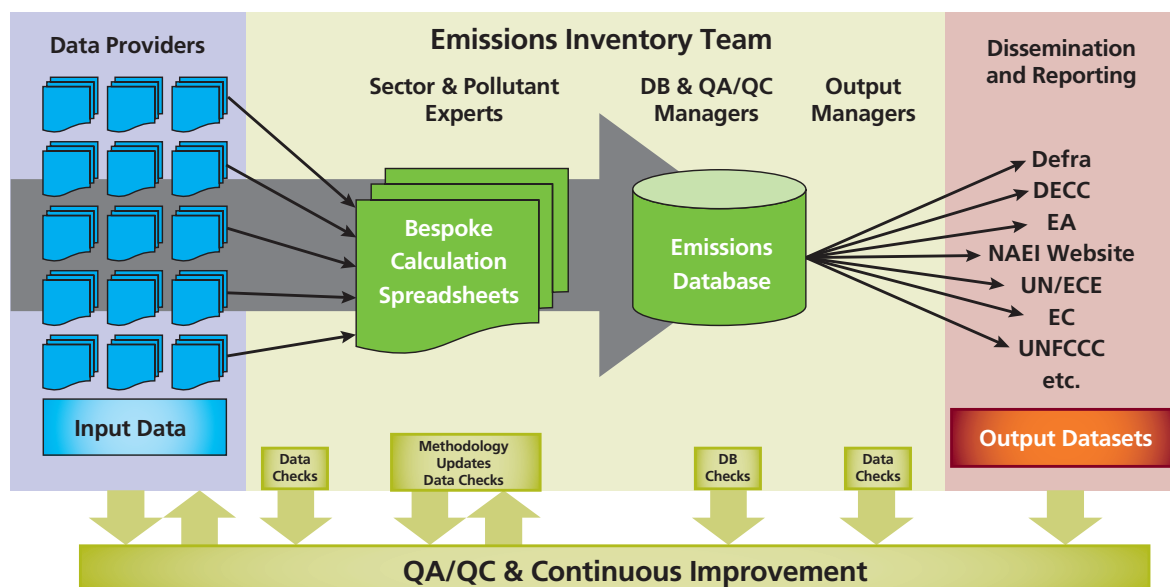


Figure 2: Data flow diagram for the UK's emissions inventory.

3.1.2 Pollutant definitions and speciation/fractionation

The precise definition of pollutants is driven by the guidance from international legislation. All emissions included in the inventories are primary emissions occurring directly from the source, i.e. components such as resuspension of PM are not included.

For compliance reporting, it is not necessary to separate emissions of groups of pollutants reported into their chemical component parts. For example, PM emissions are reported only as particle mass in the different size ranges as PM₁₀ and PM_{2.5}, although the UK also reports emissions in the PM₁ and PM_{0.1} ranges, and in future black carbon emissions will be reported separately.

The UK provides a means of separating NO_x emissions into nitric oxide (NO) and nitrogen dioxide (NO₂), and non-methane volatile organic compound (NMVOC) emissions are chemically speciated into over 600 individual compounds. Emissions of "SO₂" (sulphur dioxide) are in fact the emissions of all sulphur compounds expressed as SO₂. In the UK emissions inventory, metal emissions are also available as emissions of the different valencies/chemical states.

Further discussion on the speciation and fractionation of emissions in the inventory is in Section 3.5.

3.1.3 Source sector coverage

The sector coverage of emission inventories is typically driven by the definitions used for international legislation. National totals typically include all primary emissions of domestic anthropogenic sources. Some components of international sources (aviation and shipping) may also be included. “Natural” sources are not included in the national totals, although estimates of a number of these non-anthropogenic sources are made.

Natural sources of VOC emissions are not covered in national inventories and models usually calculate them internally using land cover datasets, emission potentials and environmental correction factors that depend on meteorological conditions. These show great spatial and seasonal variability and differ from year to year depending on weather conditions. Modellers need to state the sources of biogenic emissions used or the land cover, vegetation species and meteorology data used, and the emission potentials and methodologies used to calculate them in their models.

3.1.4 Geographical coverage

Data from the NAEI typically represent the whole of the UK. However, there are subtleties in the datasets, as some include emissions from crown dependencies and overseas territories, and others do not.

Emissions data for the devolved administrations (DAs) are derived from the UK emissions estimates primarily using a top-down approach so that the total sum of each constituent country is the same as the UK. This is significant because a bottom-up approach based solely on detailed information from each country may not yield exactly the same result for the UK, although the majority of the DA inventories are based on DA-specific data.

Other emission inventories are also available, typically at a more local level. London and several other large cities compile their own inventories using a bottom-up approach to sum the individual sources within the relevant geographical area. The emission estimates can be compared with data from the relevant portion of the UK emission maps. The estimates derived from the national emission maps use a top-down approach, and therefore differences are to be expected with the locally compiled emission estimates.

The relationship between the UK and local inventories is considered further in Section 3.3, but *it is not the case* that the UK inventory is made up of the sum of the parts.

3.1.5 “Top-down” vs. “bottom-up”

The UK inventory uses a large amount of statistical information on energy consumption, transport and other nationally held public information. The Digest of UK Energy Statistics (DUKES) published annually by DECC is a crucial information source. This high quality information, much of which has national statistics status, enhances the quality of the UK’s emissions inventory at the national scale. Inventory reporting guidelines require that this information, where available, is used so that a country’s inventory is consistent with other statistics provided to bodies such as Eurostat and the Organisation for Economic Co-operation and Development (OECD).

The UK inventory uses a combination of bottom-up procedures, using local information where possible, and top-down procedures using national statistics. However, even if it was possible to develop the entire UK inventory from local information and adding up the parts, there would still need to be a top level adjustment or normalisation to ensure the end result is consistent with national energy and transport data. The likelihood is that the amount of fuel used by every home and business in a particular area is not known with great accuracy, so if such information was summed across the country, it would not yield the same result as is published in the national energy statistics. The latter always takes precedence in the UK inventory compilation.

The UK's inventory for road transport emissions is based on vehicle kilometre data published by the Department for Transport (DfT). These match accurately the sum of traffic levels reported in individual areas, but there will be differences in the local age distribution and fuel mix of the fleet from the national trends. Other countries produce emission inventories for road transport that are based on sales of road fuels rather than detailed traffic data; the latter is more aligned with fuel consumption rather than fuel sales. A fuel sales-based inventory will be strongly affected by "fuel tourism", whereby fuel is purchased in one country and consumed in another. Although not practised in the UK, such a procedure could break the link between where traffic emissions occur and which country reports the emissions in such a way that it makes interpretation of air quality data more difficult.

3.1.6 Quality criteria

There is extensive guidance on the definition of quality in the emission inventory field, at least for national inventory reporting. In short, the following are used to assess the overall levels of quality in an emissions inventory.

Transparency: Documentation should accompany the inventory data, and data should be reported at a level of disaggregation that allows individuals or groups other than the inventory compiler to understand how the inventory was generated and to assure it meets good practice requirements. The transparency of emission reporting is fundamental to the effective use, review and continuous improvement of the inventory.

Consistency: Estimates for different inventory years, pollutants and source categories should be made in such a way that differences in the results between years and source categories reflect real differences in emissions. Annual emissions, as far as possible, should be calculated using the same method, and data sources for all years and resultant trends should reflect real fluctuations in emissions and not the changes resulting from methodological differences.

Comparability: The emissions inventory should be reported in such a way that allows it to be compared with other inventories. This can be achieved by using accepted reporting structures, or ensuring that definitions of sources are consistent with those used in international reporting.

Completeness: Estimates should be reported for all pollutants, all relevant source categories and all years, and for the entire area of the inventory. However, it should be noted that the precise definitions of each of these criteria (and hence the scope of the inventory) may vary from dataset to dataset.

Accuracy: Emissions should neither be systematically overestimated nor underestimated, as far as can be judged. This implies that parties will endeavour to remove bias from the inventory estimates and minimise uncertainty.

3.1.7 Emission projections

It was stated in Section 3.1.1 that the use of common terminology is vitally important when referring to inventories so that the *version* of the inventory is recognised as well as what *year* the inventory refers to. This recognises that inventories for previous years are updated.

The same holds for emission projections which are used to predict future air quality. Again, different versions of projections exist as they are updated periodically with the latest national energy, economic and traffic forecasts, and other assumptions. Emission projections are often made for different scenarios, for example, reflecting different economic growth rates, fuel demand and levels of ambition for reducing emissions (e.g. 'business as usual' or 'maximum feasible reduction' scenarios).

Again, it is essential that modellers state which version of the NAEI projections are being used. These details are always provided by the NAEI in terms of what the inventory base year is, what DECC energy projections are used (e.g. UEP34) and what DfT traffic projections are used.

Emission projections for sources in Europe can be taken from various sources on-line to apply to the EMEP gridded inventories, e.g. the EMEP site itself or the International Institute for Applied Systems Analysis (IIASA) RAINS/GAINS (Regional Air Pollution Information and Simulation/Greenhouse Gas and Air Pollution Interactions and Synergies) projections might be used (Amann *et al.*, 2011). The latter are periodically updated and are available for different emission scenarios, so it is vital that modellers state which version of the EMEP or IIASA projections are used by referring to the version names provided.

3.1.8 Uncertainties

Introduction

The concept of uncertainty in emission inventories is important, but is by no means simple. There are different types of uncertainty – the uncertainty in the trend with time and the absolute uncertainty of an emissions estimate. There are also several different statistical approaches that can be used for assessing levels of uncertainty. However these do not necessarily account for all influencing factors, such as detailed speciation.

Statistical uncertainty analysis techniques

Propagation of errors: Uncertainties are assigned to each activity data point and each emission factor in the inventory. The uncertainties are then combined to give an overall uncertainty on the emission total.

Monte-Carlo: An uncertainty distribution is assigned to each activity data point and each emission factor in the inventory. The uncertainties for each data point are randomly selected according to the uncertainty distributions and then combined (taking into account dependence/independence) to give an overall value. This process is repeated many times, typically several hundred, to provide an average uncertainty on the total emission and a statistical range. This approach is more sophisticated than the propagation of errors and is the favoured approach in emission inventories.

There are some important limitations with both of these approaches:

- The uncertainties that are assigned to data points are often based on expert judgement. For example, only a very small fraction of emission factors are determined from large enough datasets to include an uncertainty value that has been statistically derived. As a result, the uncertainties are based on limited information, and have a tendency to be underestimated. This is particularly the case for forecast datasets that underpin emission projection estimates.
- As statistical approaches, neither the propagation of errors nor Monte-Carlo approach can account for unforeseeable changes, an example of which might be the recent global economic downturn. The impact of this event on emission projections has been significant, but would not have been included in the uncertainty ranges used for determining the overall uncertainty in the emission estimates from the national emissions inventory.

The NAEI reports uncertainty estimates in the *annual* rates of emissions reported at the national level. The NAEI makes quantitative estimates of uncertainties based on calculations using a direct Monte-Carlo simulation technique corresponding to the Intergovernmental Panel on Climate Change (IPCC) Tier 2 approach recommended for greenhouse gases, and also the methodology proposed in guidance produced by the UNECE Taskforce on Emission Inventories. This is explained in detail in the National Greenhouse Gas Inventory (GHGI) Report (Webb *et al.*, 2013) and by Passant (2003). Table 2, taken from the 2010 version of the NAEI (Passant *et al.*, 2012), shows the levels of uncertainty in total UK emissions of the main air quality pollutants.

Table 2: Uncertainties in the estimates of total UK emissions in 2010.

Estimated uncertainty (%)	
NO _x	±10%
PM ₁₀	-20 to +30%
NMVOCS	±10%
SO ₂	±4%
NH ₃	±20%
CO	±20%

It is very important to understand how to interpret these uncertainties. They refer to uncertainties assessed within the emission inventory compilation process. They refer to statistical uncertainties in total emissions for the UK as a whole over one year covering all source categories, which will be known with various degrees of certainty.

They are based on expert judgement on the uncertainties in the emission factors and activity data for every source and represent the statistical range of uncertainties in the total inventory of emissions estimated from them. It does not reflect the fact that an emission factor for a specific source taken from the inventory guidebook, for example, could be biased in any way. For example, there was probably unidentified bias in the emission factors for NO_x used for some types of vehicles that led to 'errors' in the national totals, and trends in particular, in excess of 10%.

It may be surprising that the uncertainty in the inventory for carbon monoxide (CO), for example, is higher than for NO_x, but there are several reasons for this. Emissions of both of these pollutants have a significant contribution from the road transport sector. However, a number of significant sources of CO emissions are from stationary combustion, where there have been far fewer measurements of CO than for NO_x. Furthermore, road transport emissions of CO are dominated by emissions during cold start and the uncertainties in methods for estimating cold start emissions are much higher than those for estimating hot exhaust emissions which tend to dominate NO_x emissions overall. The linkage between transport NO_x and CO emissions and ambient measurements is considered in more detail in Section 4.1.

Uncertainty estimates of the type given in Table 2 are required for compliance reporting. They may be used to understand the uncertainty in a country's inventory in relation to the national emission ceiling. However, these estimates, while relevant to the national UK emission inventory totals, give a rather false impression when it comes to uncertainties relevant to the emission rates used in air quality models. The uncertainties in emission estimates for specific sectors and at specific locations and times will be considerably higher than this, but are much more difficult to quantify. There are several reasons for this and it helps to understand these reasons when considering uncertainties in emission inventories used for modelling a particular air quality issue, whether it be ground-level ozone, acidification and eutrophication, or urban air quality, even if the uncertainties cannot be quantified. These will be considered in terms of the spatial variability, temporal variability and chemical speciation of emissions in the following sections.

Absolute and trend uncertainties

Absolute levels of measured air pollutant concentrations, deposition rates and their trends over time can point out the accuracy of emission inventories, their deficiencies and gaps. This is provided that other factors that influence ambient concentrations are well understood and represented or can be accounted for, such as meteorology and dispersion effects. A key question is how well do the measured concentrations or ratios in concentration reflect the trends in emissions. More consideration of this is given in Section 4 where the usefulness of different measurement approaches to evaluate and inform emission inventories are discussed.

Other forms of validation and verification

There may be other verification methods, besides using air pollution concentration measurements, that can be used to indicate whether an inventory for a specific source or sources is valid, or at least that the method used to estimate them is sound.

An example of this is used for the UK road transport sector. For this sector, the bottom-up modelling approach based on vehicle activity data (fleet composition, distances travelled and average speed) and emission factors is used to calculate total petrol and diesel consumption. These figures can be compared with total fuel sales figures given in the Digest of UK Energy Statistics (DUKES) which are known with high accuracy. The UK road transport sector benefits from the fact that the UK is an island so “fuel tourism” occurs on a relatively small scale and the fact that these two fuels are used almost exclusively for road transport purposes. This is not the case for other fuels which are used in a variety of sectors.

The bottom-up estimation method for fuel consumption has agreed with the fuel sales figures in DUKES to within 8% for both fuels and for all years back to 1990 (Passant *et al.*, 2013). Whilst this gives no guarantee that air pollutant emissions are estimated to this level of accuracy, nor does it imply that traffic fuel consumption and emissions at any specific location are known with this level of accuracy, it does give some confidence in the overall approach for estimating UK emissions from the road transport sector.

Further means of verification involve developing implied emission factors for a specific sector by dividing total emissions by fuel consumption or other activity driver and comparing them with the implied emission factors reported by other countries. Again, consistency with the implied emission factors from other countries does not imply the calculated emissions are “correct”, but it does imply they are consistent with other reported inventories. The process is also useful in identifying ‘outliers’ compared with other countries, pointing out potential problems in a particular inventory source that may warrant further investigation.

Emission projections

Uncertainty in emission projections extends to our ability to predict the future; whatever the uncertainties are in current estimates of emissions, the uncertainties will be higher in predicting future emissions.

Here it is useful to consider projections in terms of alternative scenarios. These may be expressed as high, medium and low growth rates in future economic indicators (e.g. fuel price, taxation, GDP, etc.), population, energy consumption, traffic, alternative fuel and technology uptake rates, international legislation and the effect of national and local policies. DECC and DfT produce a range of growth rates for future energy consumption and transport. Emission projections can be developed for any combination of future change scenarios. The range of outcomes provides a measure of sensitivity to the unknown activity drivers and emission factors in the emission calculations, and it is probably more useful for the range to be assessed in the modelling of future ambient pollutant concentrations rather than a single emission projection.

3.2 Spatially-resolved emissions

3.2.1 The UK NAEI emission maps

The UK NAEI is largely based on national statistics which are known with high levels of accuracy, for example the total consumption of coal, gas or petrol. Comprehensive traffic surveys conducted by DfT provide the total number of vehicle kilometres travelled by vehicles in the UK and are known with reasonably good levels of accuracy. The NAEI 1 km x 1 km maps are produced by spatially disaggregating national emissions using traffic flow data on individual roads and by using proxy statistics such as household and population census, land use and employment data. In reality, with the possible exception of traffic, levels of domestic, industrial and agricultural activity occurring in every square kilometre are not known with high accuracy. On the other hand, emissions from major point sources such as power stations and refineries can be spatially assigned with reasonably high levels of accuracy because the location of the sources are known and the operators themselves may provide specific emissions data for their operations on the site, either from measurements or calculated from known activity levels at the site (e.g. fuel consumption).

In the case of traffic, although we may know the flows of vehicles on individual roads, even broken down by vehicle type, there is seldom information available to break traffic flow down further by fuel type or engine size and age of vehicle. For example, the flow of cars along a road section may be known, but not the mix of petrol and diesel cars and the age distribution which determines the mix of Euro emission standards. These data can only usually be gathered at national level from licensing statistics, although the increased availability of Automatic Number Plate Recognition data is providing greater opportunity to apply more road or area specific features. The NAEI has started to use this information to define the variability in the fleet mix on different road types.

Assuming the fleet mix is the same everywhere in the country, with no regional differences, introduces a significant source of uncertainty in the emissions data used in urban air quality models. For example, trends in roadside NO₂ concentrations at a given location have been interpreted in terms of trends in national traffic emissions, when in fact the fleet mix in areas like central London has been evolving quite differently from the national fleet. Traffic data cannot separate cars from taxis, but relatively high levels of taxi activity, which mainly have diesel engines, are evident in central London, while buses in the area are known to have been renewed or equipped with diesel particulate filters. The NAEI is currently undertaking more detailed analysis of emissions based on traffic flows on individual roads near air quality monitoring sites in London, but area-specific activities like this in all other cities are not currently being carried out.

What all this means is that the accuracy of the information about the spatial distribution of emissions will vary from one pollutant to another according to the relative importance of point source emissions which might be known reasonably well, and the line and more diffuse area sources, such as domestic combustion and the many fugitive sources, which are less well known. So for a pollutant like SO₂, the spatial distribution may be known reasonably well because it is dominated by major point sources, but for VOCs and ammonia (NH₃), which are dominated by more diffuse area sources, the distribution is known with much less accuracy.

3.2.2 The importance of constituent source characteristics

In providing the 1 km x 1 km maps of UK emissions, the NAEI has considered the quality of the maps in terms of the contribution of point and area sources to mapped emission totals for each pollutant. These contributions are shown in Table 3.

Table 3: Contribution of point sources to UK mapped emission totals in the 2006 NAEI (Bush *et al.*, 2008).

Pollutant	Point sources (%)	Area sources (%)
CO	24%	76%
NH ₃	2%	98%
NMVOCS	20%	80%
NO _x	32%	68%
PM ₁₀	20%	80%
SO ₂	78%	22%

From this table it can be seen that 78% of SO₂ emissions in the UK are from point sources, while only 2% of NH₃ emissions are from point sources, the remainder occurring from area sources.

Sources where the spatial disaggregation of pollutant emissions is particularly uncertain are:

- VOC emissions from solvent use and from biogenic sources;
- NO_x and SO₂ emissions from domestic combustion, off-road machinery and shipping;
- PM emissions from domestic combustion, off-road machinery and shipping, and activities such as construction, agriculture and other fugitive releases of dust; and
- NH₃ emissions from agricultural activities.

Uncertainties in the spatial distribution of emissions are influenced not only by lack of knowledge about what activities are occurring in specific places, but also by the methods used to calculate the emissions. In many cases, emissions are calculated by combining an emission factor with activity data; so if you know where the activity is occurring, then the emission can be estimated locally with the same level of certainty as can the emissions from the same source at national level.

This is not necessarily the case for road transport, and different procedures are best used at the national and local scales. The national inventory combines vehicle kilometre data with grammes per kilometre emission factors derived from functions that relate emission factor to average vehicle speed. Further methodologies are used to calculate cold start excess emissions and evaporative emissions from vehicles. All these methodologies are designed to do the job well for application to national scale inventories, but they can break down if applied at a much more local level.

For example, using average speed-related emission functions to calculate emissions on the whole of a national road network is fine, but using them with average speed data to calculate emissions occurring at a specific road junction is not strictly valid. This is because of the transient nature of emission processes at the location resulting from the mix of acceleration, deceleration and idling conditions occurring there. At this more local level, more complex transient emission modelling approaches are required to account for the variation in emissions over different parts of the vehicle operational cycle. Local cold start emissions need information on local parking durations, ambient temperatures and lengths of trips. Thus, road transport emissions used in urban air quality models are to some extent compromised by the necessary simplifications and empiricism of the methodologies and emission factors used to calculate them.

Mapping emissions from certain sources such as off-road machinery and construction activities is particularly problematic because of the transient nature of the activities. The activity may occur in a certain area for a certain period of time, and then move on. Agriculture dominates NH_3 emissions, but while the total number of livestock may be known, spatially distributing the emissions depends on knowledge of farming practices and livestock movements in different areas.

Spatially resolving biogenic emissions of VOCs might appear to have the advantage that major forests are largely fixed positionally, but fully establishing the spatial pattern of biogenic emissions also depends on understanding how different classes of vegetation are spread around the country. The use of land for growing different types of vegetation can change over time.

Emissions from shipping have until recently not been well characterised, but they are making an increasingly large contribution to emissions impacting on local and regional air quality and acidification. This is because fuels and emissions from ship engines have not been subject to the same level of control and regulation as have those from industry and road transport, so the relative contribution made by shipping to national NO_x and SO_2 emissions has been growing.

Part of the problem in defining an inventory for shipping emissions has largely been because it has been seen as an international emissions problem, since it occurs across national boundaries and sea territories. Following national inventory reporting rules, emissions from international shipping are excluded from national totals, thus shipping has contributed a relatively small proportion to the emissions reported by individual countries. However, the emissions are occurring and contributing to local and regional air quality, regardless of who is politically responsible for them. The problem has required a centralised shipping inventory approach and the situation has been improving with shipping inventories developed by Entec for the European Commission (Entec, 2005). The problem with developing a spatially-resolved inventory for shipping has been having reliable activity data indicating where different types of shipping movements occur. Entec has used actual shipping movement data held by Lloyd's Registry to map pollutant emissions around UK waters in 2007 at 5 km resolution (Entec, 2010), but this is a resource-intensive process that can only be undertaken periodically. And even this source of shipping emissions data may not be of a fine enough resolution to understand the impact of localised emissions on air quality near major sea ports.

3.2.3 Uncertainties in the UK emission maps

Although it is not possible to quantify the uncertainties in the spatial distribution of emissions in terms of confidence levels, the NAEI has developed a fairly sophisticated approach to provide an overall data quality confidence rating for each pollutant map (Bush *et al.*, 2008). A rating index is assigned to each pollutant–source combination from 1 (highest quality) to 5 (lowest quality). An overall ‘confidence rating’ can be calculated for each pollutant map thus:

$$R = \frac{\sum_i (E_i \cdot R_i)}{E_T}$$

where R is the overall confidence rating for a given pollutant, E_i is the emission estimate for source i , R_i is the data quality ratings applied to the mapping of emissions for source i and E_T is the total emission of the pollutant.

Some general rules of thumb were followed when choosing data quality ratings for mapping procedures. Point source data from the Environment Agency’s Pollution Inventory, industry or regulators are given a rating of 1 because the locations of emissions are ‘known’ precisely. Modelled point source data were given a quality rating of 2 to reflect the fact that, although all point sources are known, there is uncertainty regarding the distribution of emissions over these sources. Mapping of area sources is by use of various ‘grids’ which utilise spatially-resolved data such as traffic flows, population or employee numbers. Quality ratings for each set of area/line sources were allocated following assessment of:

- the quality of the spatially-resolved data used to make the distribution grid; and
- the reliability of the distribution grid as a measure of emissions from the source.

A rating was applied to the bulleted criteria and the mean is used as the data quality rating for that set of area source data. For example, a grid based on 2001 census population data has been allocated a rating of 2, since it is based on accurate census data generalised across the 1 km grid resolution. The use of such a grid to map emissions from decorative paint use is considered appropriate and was assigned a rating of 1. The area source data for decorative paints therefore has an overall quality rating of 1.5. On the other hand, while a grid based on suburban land cover is also of good quality and assigned a rating of 2, its use to map emissions from small-scale waste burning (bonfires) is considered much less reliable and is given a rating of 4. Area source data for these emissions have an overall quality rating of 3. Figure 3 shows the resulting confidence ratings for all the NAEI pollutant maps.

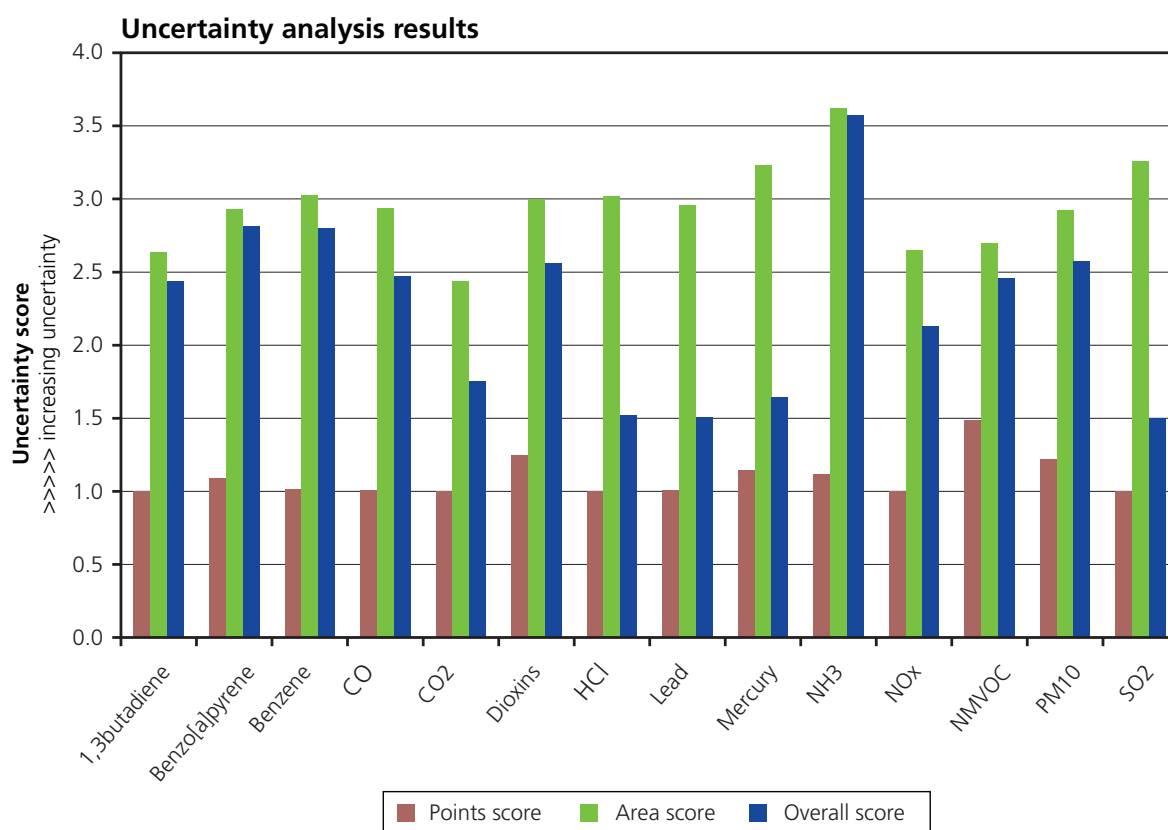


Figure 3: Confidence ratings for mapping elements of the 2006 NAEI (taken from Bush *et al.*, 2008).

From this, it can be seen how the overall quality ranking is good for SO₂ at around 1.5, but poor for NH₃ at about 3.6. Among the key air quality pollutant emissions relevant to the modelling of ground-level ozone, acidification and eutrophication and urban air quality, the ranking in order of decreasing mapping quality is:

SO₂ > NO_x > NMVOCs > PM₁₀ > NH₃

Whilst not quantitative, this ranking system does at least allow one to appreciate what performance might be expected of the model in terms of the quality of the spatially-resolved emissions inventory used.

Another aspect of the NAEI emission maps is that whilst a new map is developed for the latest inventory year, maps produced for previous years are not updated when any methodological improvements or changes to emission factors are made to the inventory time series reported as UK emission totals. This means that UK maps for different years are not necessarily consistent with each other nor do they give a true indication of the changes in emissions over time at specific locations. One way round this, if an up-to-date inventory map for an earlier year is required, is to apply a year-, sector- and pollutant-specific scaling factor to the map of emissions from that sector for the latest year. The scaling factor would be the ratio of total UK emissions for the sector in the year of interest divided by the UK emissions for the sector in the most recent year, as defined by the latest NAEI emission time series trend. This assumes that the spatial distribution of emissions from a specific sector has not changed over time, only their magnitude.

The EMEP inventory for Europe is at a 50 km resolution and it brings together emission inventories for many countries on a common basis. It is bound to have a more uncertain spatial representation than, for example, the UK NAEI.

3.3 Local emissions inventories

Local inventories have been developed for a number of cities and conurbations in the UK. They generally use the same estimation methods as the NAEI and rely on the same types of information and emission factors, but can potentially use more localised activity data, particularly road traffic and fleet information.

Emission inventories for cities do not typically include power stations, large industrial sources, agriculture, aviation and a number of other sources that may be relevant at the national scale. So it is possible to focus efforts on fewer sources, and in particular on those making the most important contributions to the emissions totals (e.g. road transport and domestic combustion). They can also potentially take account of specific activities occurring in the area that may be only temporary in nature, such as major construction projects. They may also be able to provide locally specific data on temporal variations in emissions, e.g. due to local traffic patterns and how they vary with time of day and day of week. Local inventories can take account of local policies and measures (e.g. transport schemes), and local practices and behaviours which are more difficult to capture on the national scale.

There is scope for applying more detailed emission calculation methodologies to local inventories, for example, for traffic sources the use of more transient emission modelling techniques to take account of congestion and road junction effects that are more difficult to account for on the national scale.

However, there are still many sources that local inventories cannot cover any better than the NAEI, particularly fugitive sources, off-road machinery, etc., because of lack of local activity data. For these sources, the gridded data from the NAEI may have to be used. In reality then, local inventories use a hybrid of top-down and bottom-up approaches for estimating emissions from many sources.

Construction of a local inventory has the advantage, compared with the national inventory, that fewer constraining factors have to be applied. For example, there is a need for the national inventory, and the gridded data derived from it, to be consistent with national energy and other statistics. This is not the case for local inventories. However, this can also put local inventories at a disadvantage and the smaller geographical extent does also present some challenges. Many key datasets that underpin emission inventories are compiled at the national scale. For example, it is straightforward to obtain a national energy balance. Compiling similar data at the city level can be considerably more difficult and may be less meaningful.

Local inventories are considerably freer to structure the emissions output datasets in a format that is suited to their specific users, and to modellers in particular. This is particularly helpful in ensuring that the emission inventories are designed to investigate the impacts of policies and measures, which may require the emission estimates of some sectors to be determined in great detail.

Local inventories are generally developed on a less regular cycle and on a less rigid timetable than the NAEI. Some may be developed on an *ad hoc* basis, others once every few years. This can be both an advantage and a disadvantage. One advantage is that there may be more time available to gather information and to develop and apply more detailed estimation techniques; there may also be greater scope and freedom to introduce research findings. On the other hand, resourcing levels may be more limited. Another disadvantage is that they may not be kept as up to date as the NAEI, nor offer a consistent time series in emissions developed under the same methodology extending over many years. This makes it more difficult to interpret trends in local emissions.

Another issue is one of consistency and comparability between local inventories, especially when they are developed at different times by different organisations. Not all local inventories may apply best practice and their quality may be variable. The NAEI is a very mature inventory and is peer reviewed regularly because of its status as a compliance inventory and source of national statistics.

There are some high quality local inventories, the LAEI being an example. In an effort to ensure consistency with local/regional emission inventories, the NAEI periodically reviews the information that is available from emission inventories such as those for London, Merseyside and Greater Manchester. The underlying structures can, however, be very different, making direct comparisons difficult. Comparisons have been made between the NAEI portion for London and the LAEI and these highlight differences and similarities for the reasons outlined above. In many respects it is not realistic to expect them to be exactly the same, but an increasing amount of information is being exchanged and experiences shared between the NAEI and LAEI enabling the gap to be closed.

3.4 Finer time-resolved emission estimates

3.4.1 Introduction

National emission inventories and spatial distributions are only ever provided in terms of annual emission rates, which is not adequate for most air quality models which can require emissions on at least an hourly basis. Models get round this problem by using a temporal profile for each pollutant and main emission source that takes into account the relative variation in activity levels of anthropogenic sources with time throughout the course of a calendar year or, for some sources, the variation in meteorological factors such as temperature if this affects emission rates.

3.4.2 NAEI temporal profiles

The NAEI developed a default set of temporal profiles for ozone precursors and 11 source sectors (SNAP 1 level) by time of day, day of the week and month of the year. These profiles, developed by Jenkin *et al.* (2000), take into account the temporal variations in activity levels and the impact these have on emissions. They are currently being reviewed and updated. Other temporal profiles are available from other European inventory programmes (e.g. TNO in the Netherlands).

Temporal profiles are known with varying degrees of confidence. The temporal variation in traffic exhaust emissions, for example, is known with reasonable confidence because the diurnal and daily pattern in traffic levels is well characterised, although one might expect some variation on different road or area types, for example, in central urban areas and on rural motorways. The change in industrial combustion and process emissions with day of the week is probably known reasonably well. High quality data are available on power generation output by time of day, day of the week and month of the year, which helps define a profile for this sector. Domestic combustion is expected to follow a consistent diurnal and seasonal pattern, though one might expect year-to-year variability according to weather patterns.

The temporal profiles for some of the more diffuse sources are known with much less certainty, just as is the case for their spatial distribution. PM emissions from construction activities, for example, are likely to be intermittent and may start or cease at any time throughout the year. The temporal profile for VOC emissions from solvent use (industry and domestic) is likely to be more uncertain, although one might expect a seasonal pattern with higher emissions occurring in warmer months due to evaporation. Similarly, the profile for evaporative VOC emissions from vehicles and fuel handling is expected to be seasonal, but the temperature dependence of evaporative losses is difficult to quantify with any certainty. Agricultural practices are seasonal, so one would expect some seasonal dependence in NH₃ emissions, but again the temporal nature of the emissions is difficult to quantify and is likely to vary from year to year and across different parts of the country.

Biogenic emissions of VOCs depend critically on meteorological conditions and the question here is how well the emission potentials and environmental correction factors combined with the appropriately time-resolved meteorological data fields used in models are able to reproduce the variation in biogenic emissions with time of day and season, especially under extreme summer episode conditions. It has been estimated that biogenic emissions are uncertain by at least a factor of four (Stewart *et al.*, 2003).

Even for point sources, where one might expect a fairly accurate annual emission rate following a general industry- or power generation-based temporal profile, it is impossible to know with confidence what emissions from a particular stack might be at every hour of the day, yet these variations could be important in a number of air quality model applications.

3.4.3 The EMEP emissions inventory

The EMEP inventory for Europe brings together emission inventories for many countries on a common basis. Whilst one would expect emissions from the same source across Europe to exhibit a common temporal profile, there are bound to be some differences due to different weather patterns and climatic conditions, and industrial and agricultural practices.

Emissions from sporadic or irregular events such as forest fires or accidental releases are not usually captured in national emission inventories. Modellers may require other techniques to cover these.

3.5 Chemical speciation in emissions

Some of the pollutants reported in inventories are actually groups or families of individual chemical species, most notably, the VOCs, NO_x and PM.

3.5.1 NMVOC speciation

VOC emissions consist of many hundreds of individual organic species each with different reactivity in the atmosphere. Models of ozone and organic aerosol formation require the breakdown of the reported VOC emissions into as many of these individual compounds as possible and for each source sector. The NAEI provides a VOC speciation profile describing the relative mass proportions of individual VOCs emitted from each detailed source category. The speciation profile covers 664 individual compounds or groups of VOCs emitted from around 250 different sources (Passant, 2002). The profile is known reasonably well for some sources, e.g. solvent emissions, because the manufacturer or user knows the chemical composition of the product. It is known less well for vehicle exhaust emissions, but is still expected to be adequate for the most abundant and reactive compounds. For other combustion sources and process emissions, the profile is known much less well. However, when their photochemical ozone forming potential is taken into consideration, solvent use and road transport emissions of VOCs are calculated to make the most significant contributions to episodic peak ozone concentrations (Derwent *et al.*, 2008).

The NAEI profile is held constant each year in relative terms and applied to a new total VOC inventory. The profile itself is only periodically updated. The constancy in the profile is a reasonable approximation for many sectors, but changes could occur, for example as a result of solvent substitution, process changes in the chemicals and food and drink industries, or new fuel formulations (e.g. biofuels). This adds to the uncertainty associated with using the profile across a time series, perhaps especially in forecasting the effect of future emissions on ozone formation.

The application of the NAEI speciation profile, which is UK-biased, to VOC sources in other countries (e.g. by combination with the EMEP inventory of VOCs) is questionable given the potentially different processes, fuels and solvents used.

The overall uncertainty in the NAEI VOC speciation profile has not been quantified, however, in the context of modelling ground-level ozone, the result can be quite sensitive to assigned speciation. For example, the top ten components have photochemical ozone creation potentials (POCPs, an index reflecting the ozone-forming reactivity of a VOC relative to ethene, Derwent *et al.*, 1996) varying from 14 to 100. Formation of secondary organic aerosol (SOA) is likely to be even more sensitive to VOC speciation than ozone formation.

3.5.2 Oxides of nitrogen

The separation of the NO_x inventory into NO and NO₂ is now understood to be important in modelling urban concentrations of ozone and NO₂. Primary NO₂ emissions influence the presence of local oxidant in urban areas. In recent years, emissions have been affected by increased diesel vehicle activity and exhaust abatement technologies introduced to curb vehicle emissions. Primary NO₂ fractions given as the volume fraction of NO_x directly emitted as NO₂ have been developed for a range of vehicle categories and other combustion sources of NO_x. These are developed and provided by the NAEI, but their uncertainties are large. The NAEI

provides primary NO₂ factors (f-NO₂) for different road vehicle emission sources and other transport sources.¹ Consideration is given to the estimation of primary NO₂ emissions in Section 4.2.1.

3.5.3 Fractionation of particulate matter

Inventories for emissions of primary PM in the NAEI are broken down into various size classes (PM_{2.5} and smaller) for each emission source. They are usually derived from fractions relative to PM₁₀. Uncertainties in the PM size fractions for many sources are high. To date, they have not been broken down into their chemical constituents because of lack of speciation data applicable to different source categories, and the fact that it has not been necessary to do so for compliance inventory reporting. Information is becoming available from national inventory guidebooks to enable inventories to be developed for black carbon and organic carbon for some sources.

3.5.4 Metals and persistent organic pollutants

In the UK emissions inventory metal emissions are also available as emissions in terms of the different valencies/chemical states. Work has also been conducted to chemically speciate emissions of the different polychlorinated biphenyls (Goodwin *et al.*, 2001).

3.6 Strengths and weaknesses of the national inventory

The UK's inventory is regularly peer reviewed for compliance reporting by international inventory experts working for the UNECE. It is considered a high quality inventory, using the most detailed (high tier) methodologies and approaches for many source categories. This has been possible thanks to the investment in the NAEI made by Defra and DECC over many years, the availability of detailed and high quality activity data from among the UK's national statistics and the co-operation and willingness of other government departments, agencies, regulators and industry groups to help retain and improve data quality.

The inventory has many strengths, but also some weaknesses for certain stakeholder groups, including the air quality modelling and science community. These are evident from the previous sections of this chapter. The strengths and weaknesses of the NAEI are summarised in the following sections. It is the case that some of the strengths can also be considered weaknesses by certain stakeholder groups.

3.6.1 Strengths

- The NAEI is produced at high source category resolution using advanced methods and detailed activity datasets.
- It is based to a large extent on emission factors measured at source, rather than interpreted from other observations, and a high proportion of emission factors are UK specific.
- The source categories are well defined and understood.

¹ <http://naei.defra.gov.uk/data/ef-transport>

- The inventory covers a long and expanding time series going back to 1970 and forward to 2030; the whole time series is assessed and if necessary updated annually so emissions across different years can be compared on a consistent basis.
- The inventory is generated annually on a fixed and predictable timetable to meet the needs of compliance reporting and for the UK's own national statistics.
- The inventory operates to a mature and well managed reporting system which ensures the UK meets its reporting obligations, generating outputs that can be compared with those from other countries.
- The time series enables UK policy-makers to track progress towards meeting emission reduction targets.
- The inventory is consistent with other national statistics on energy consumption, industrial output, transport and agriculture – this can also be perceived to be a weakness, as the need for consistency with national statistics imposes restrictions on the consistency between local and national level inventories.
- The inventory provides outputs in various formats including those which are convenient for policy-makers. Formats include emission projections and results from “what if” scenarios closely linked to energy and other policy drivers. This allows the effect of policies on air pollutant emissions to be easily understood and interpreted.
- The inventory is set up to produce simplified outputs (emission factors and activity data) to allow local and regional inventories to be developed on a consistent basis, and for local air quality management.
- The inventory covers the whole of the UK, including crown dependencies and overseas territories.
- The inventory is spatially resolved at 1 km x 1 km resolution each year, covering the whole of the UK on a consistent basis.
- The inventory is regularly peer reviewed by independent international experts. A continuous improvement programme is agreed with Defra and stakeholder groups.

3.6.2 Weaknesses

Table 4 describes the weaknesses or limitations in the current UK inventory considered relevant to the air quality modelling and science communities, divided into key groups. These include items that the NAEI is not (or has not been) set up to cover. The table also includes comments on where some of these weaknesses are currently being addressed.

Table 4: Weaknesses or limitations in the current UK inventory.

Issue	Weakness	Action currently being taken
Spatially-resolved emissions	Spatial representation includes a large amount of top-down treatment of local emissions, the accuracy of which is limited by the availability of suitable local data, e.g. domestic fuel use.	
	Some national inventory methods may not be robust at local level, e.g. the parameterisation of traffic emissions (exhaust and non-exhaust) is oversimplified for local traffic situations.	
	May not pick up local policies, measures and behaviours.	
	Resolution in shipping emissions is not fine enough around port areas.	A scoping study is currently being undertaken to assess how higher resolution shipping emissions can be developed around key port areas.
	Historic emission maps not updated when emission factors and methods are updated.	Revised maps for 2005 are currently being developed, together with sector-specific scaling factors that can be used to generate further maps from current ones covering other past and future years.
Completeness – not all sources covered	Biogenic and other natural source emissions (e.g. dust and sea spray) and resuspension are not included.	Work is currently underway to assess the most suitable biogenic VOC inventories for modelling purposes.
	Sporadic events are not well covered, e.g. fires, intermittent construction projects and civil emergencies.	
Temporally-resolved emissions	Profiles by hour of day, day of week and month/season exist but are not routinely updated.	Work is currently underway to generate new and update existing temporal profiles for transport, power generation, industrial and domestic combustion, and agriculture.

Issue	Weakness	Action currently being taken
Chemical speciation	PM emissions are not chemically speciated.	An inventory for black carbon is being developed. Factors for organic carbon are becoming available in inventory guidebooks for the first time.
	VOC and NO _x emissions are speciated, but not regularly updated.	The UK does have a very detailed chemical speciation of VOCs from over 200 source categories. This is currently being reviewed across key sectors (e.g. solvents, coatings, chemicals industry and road transport). The UK does provide factors for direct NO ₂ emissions which are maintained for road transport sources. Factors for other sources are being developed.
Emission factors	Poor quality for some sectors due to insufficient measurements at source.	An international inventory problem under constant review.
	Process takes too long to bring emission factors for new sources, technologies and fuels to the inventory community.	
	Transferability of emission factors measured abroad to sources in the UK.	
Activity data	Diffuse sources very difficult to quantify nationally and locally, e.g. solvent evaporation, small combustion, fugitive sources, etc.	
	Air quality models require additional information to the quantity of emissions, e.g. stack heights and release parameters.	Work is underway to review stacks data held by the NAEI and potentially update it with new information to benefit the wider community.
Inventory development process	Can have a lot of inertia. Takes a long time and not a good mechanism to bring research findings into the inventory community.	
	Compliance reporting requirements and guidelines may restrict the application of new research findings to national inventories in a given country.	

3.7 Inventory improvements through verification

There is clearly a role for air quality science, atmospheric measurements and models to improve the quality of emission inventories and to show where the inventories are weak and could be improved. This can be done through a process of verification which essentially considers whether the observed concentrations or other types of measurements made in the atmosphere are as they would be expected from the emission inventories and, if not, how the inventories might be in error.

The remaining chapters of this report provide details of a range of different verification techniques and at the end of each chapter, some consideration is given to their strengths and weaknesses in informing inventories. It may be that the technique simply points out that there is a discrepancy between the measurement and the inventories without explaining what part of the inventory may be in error, thus leaving it to the inventory community to examine possible causes. In some cases, the technique may provide much more useful information and pinpoint the sources that may be causing the discrepancy and whether it is related to the emission factors used, activity levels assumed or how the inventory is parameterised.

Models play a vital role in inventory verification. If modellers flag concerns over the accuracy of emissions data, it is important that their feedback provides enough detail for the emissions inventory compilers to then review their estimates, for example by suggesting that it is either a particular source or location that is considered to have erroneous emissions estimates.

It should also be stressed that the accuracy of emission inventories is generally limited by the data that are available from the measurement community (typically emissions measurements). To date, the emissions inventory community has not been particularly active in presenting their needs to the measurement communities, to ensure that emissions measurement programmes address the needs of national emission inventories (and in turn the modelling community).

All of these points were particularly well demonstrated by recent developments regarding metal emission estimates. Following a number of modelling studies to determine ambient concentrations of metals, the Meteorological Synthesizing Centre – East (MSC-E, the organisation responsible to EMEP for the transboundary modelling of heavy metals and persistent organic pollutants (POPs), see <http://www.msceast.org/>) suggested that national emission inventories for some metals represented substantial underestimations. They did not indicate that this might be caused by underestimation of a particular source or by particular countries. The international emissions inventory community reviewed the data and methods used for estimating metal emissions and were not able to identify any significant underestimates. It was only when new measurement data became available (updated metal contents of motor vehicle lubricants) that it was possible to suggest the source that was being significantly underestimated. The guidance has now been revised so that national emission inventories can provide more accurate metal emission estimates for the modellers to use.

4 Simple trends in emissions and concentrations

4.1 Trends in emissions and concentrations

The simplest way of comparing emission trends with ambient concentration trends is to plot each time series. Plotting the two together, while straightforward, is rarely done. Even though, as discussed previously, there are issues with direct comparisons, some of these issues can be avoided or reduced. For example, with a sufficiently long time series over many years, the effect of meteorology on trends can be diminished. Also, plotting the data in a way that allows for the different scales of emissions and ambient measurements helps with the comparison.

Figure 4 shows a comparison between UK national emission trends in CO and NO_x together with ambient measurement trends at Marylebone Road. To assist the comparison, all data have been normalised to 100 in 1998. CO and NO_x emissions tracked each other very well until around 1998, peaking around 1990. From the late 1990s CO emissions decreased steeply, such that in 2009 emissions were approximately 20% of their value in 1998. NO_x emissions have also decreased considerably since the late 1990s but not as much as CO. In 2009 NO_x emissions were about 40% of their value in 1998.

Ambient concentrations of CO match the emissions trend very well from 1998-2009, although in 2009 ambient concentrations were about 30% of their 1998 value compared with 20% for the emissions. There is also some indication from the ambient concentrations of CO that the rate of decrease in recent years has slowed compared with the rate of decrease in emissions. However, the clearest discrepancy is between NO_x emissions and concentrations. NO_x concentrations in 2009 were about 20% less than their 1998 value, compared with emissions that were approximately 60% less than their 1998 value. These results, if borne out more generally across the UK, would indicate that the emission inventory for CO is consistent with ambient measurements whereas that for NO_x is overestimating the reduction.

It should be noted that we are reaching the point with CO where the northern hemisphere background of around 0.1 ppm is becoming a significant component of urban measurements. This is likely to affect the relationship between inventories and ambient data as well as ratios (see, for example, Section 4.2 concerning NO_x/CO ratios). In addition, detecting much lower concentrations of CO could become increasingly problematic with existing instrumentation.

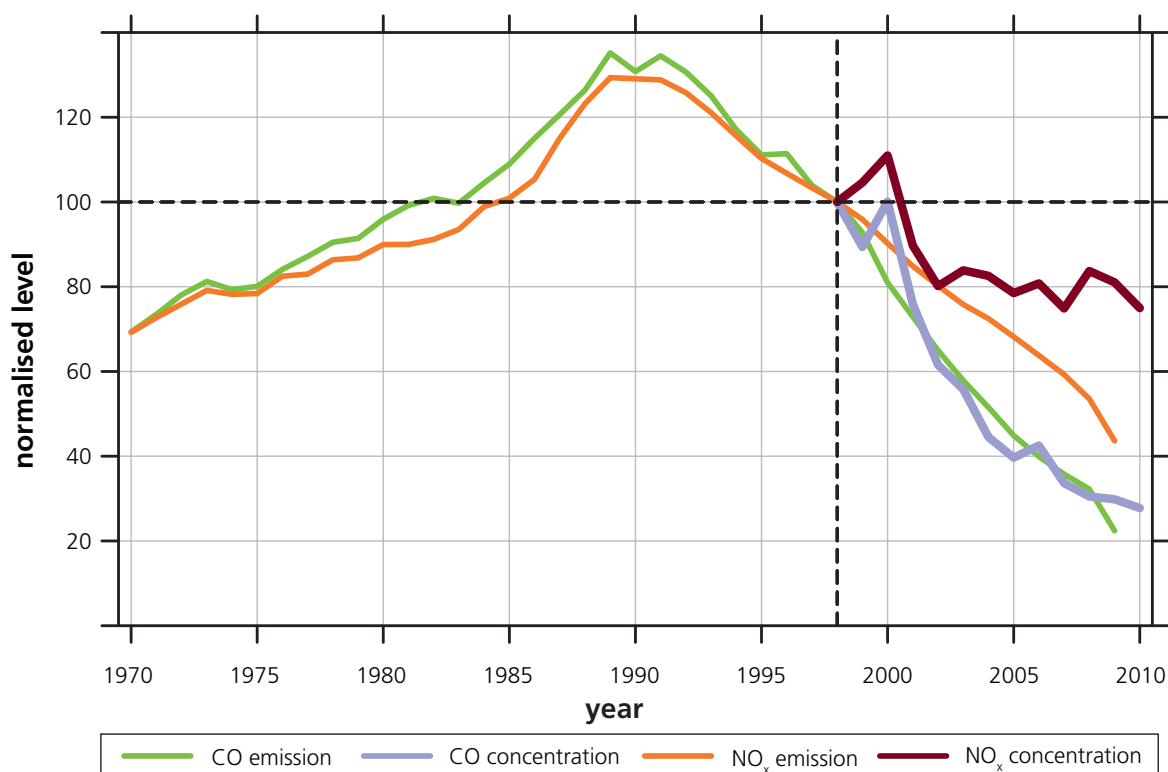


Figure 4: UK emission total trends and ambient trends at Marylebone Road for CO and NO_x normalised to 100 in 1998 (analysis carried out for this report).

Some caution is necessary when considering trends in emissions and ambient concentrations because it is important to know the extent to which sites are affected by particular sources. An example of annual emission and concentration trends is given in Butterfield and Brown (2012) for UK emissions and concentrations of benzo[a]pyrene (BaP). The ratios of emission estimates of BaP to other polycyclic aromatic hydrocarbons (PAHs) are very strongly correlated, although BaP only accounts for 0.3% of the total emissions of the 16 PAHs considered by the NAEI. The NAEI includes estimates of PAH emissions since 1990, as shown in the left panel of Figure 5. BaP emissions have shown a 95% decrease in the last 20 years: from 66 tonnes in 1990 to only 3 tonnes in 2008.

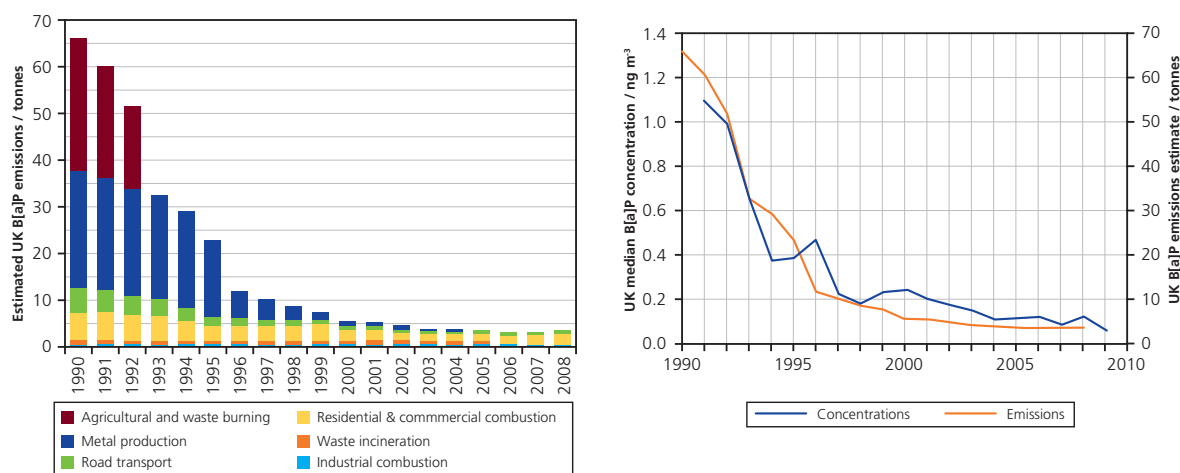


Figure 5: Comparison of UK BaP estimated emissions and UK median BaP measured concentrations from 1990 to 2009.

The greatest reductions over the period, in absolute terms, have been from:

- field burning of agricultural wastes: 28 tonnes
- aluminium production: 25 tonnes
- road vehicles: 5 tonnes
- residential emissions: 3 tonnes.

UK data show that PAH concentrations have decreased since 1990, shown by the decrease in BaP concentrations in the right panel of Figure 5, which also shows the emissions change. It is difficult to produce a representative average UK value for PAH concentrations because of the changes in monitoring site location and number that have occurred in the PAH monitoring network over the last 20 years. However, according to Butterfield and Brown (2012), a reasonable representation of an average UK PAH concentration can be provided by the median yearly value across all sites on the PAH Network.

It is clear from Figure 5 that both emissions and measured concentrations of BaP have decreased dramatically over the last 20 years. It is also clear that these decreases are highly correlated. For a long period such as 20 years, the effect of interannual variations in meteorology will be small, but will account for some of the variation shown for BaP concentrations in Figure 5.

The high degree of correlation between emissions and concentrations is somewhat surprising given the changes to the PAH monitoring network over this period and the large decreases in emissions from agricultural field burning and aluminium production, which might be expected to have very different impacts on ambient concentrations at different locations. The reductions in emissions from aluminium production would only be expected to have an impact at monitoring sites close to specific plants, such as the decline of the annual mean BaP concentration at Kinlochleven from 6.8 ng m^{-3} in 1999 to 0.34 ng m^{-3} in 2001 associated with the closure of the plant. Reductions in emissions from road traffic and residential emissions would be expected to have a more widespread impact at monitoring stations across the UK. Therefore, while it is clear that emissions and concentrations have decreased over time, the *reasons* for the decrease cannot be identified with confidence unless more consideration is given to how individual sites are affected by specific emission sources.

The application of data filtering techniques to ambient measurements can help to isolate emission trends at a particular source. An example from Lancaster University and the Environment Agency has tracked the emissions performance of Ferrybridge power station in West Yorkshire using ambient sulphur dioxide (SO_2) data from a monitor ~4 km east of the station (Whyatt, D., personal communication).

Bivariate polar plots (Carslaw *et al.*, 2006; Carslaw and Ropkins, 2012) can be used to identify plume impacts, which can then be tracked over time in order to infer trends in stack emissions. At Ferrybridge, different percentile impacts of SO_2 were derived for overlapping periods and plotted as smoothed time series between 2001 and 2005 (Figure 6).

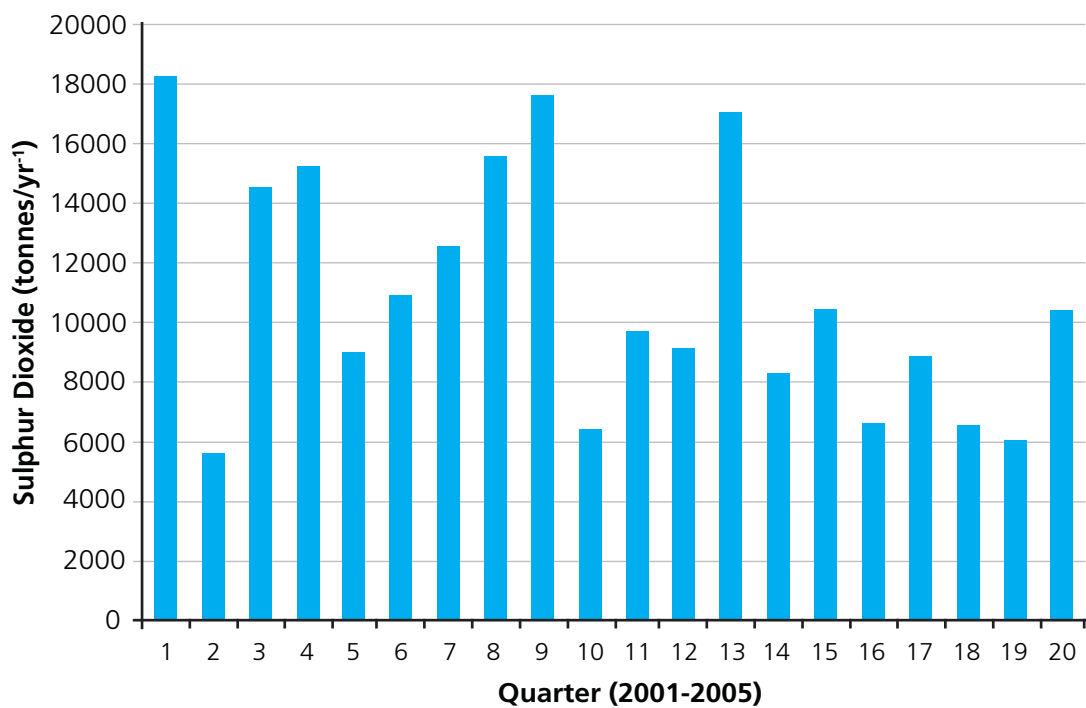
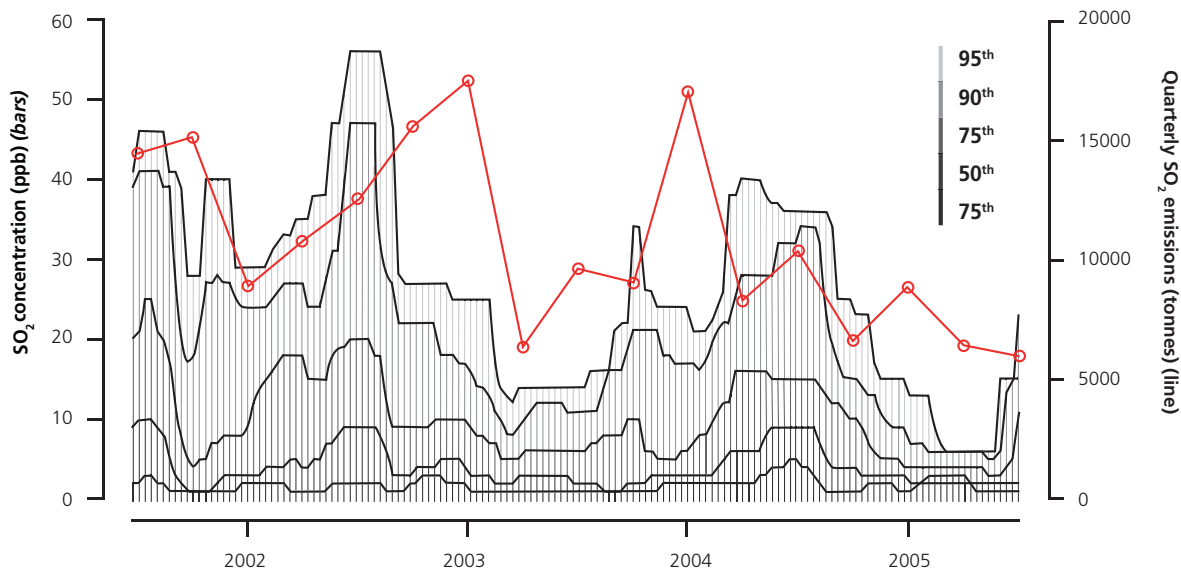
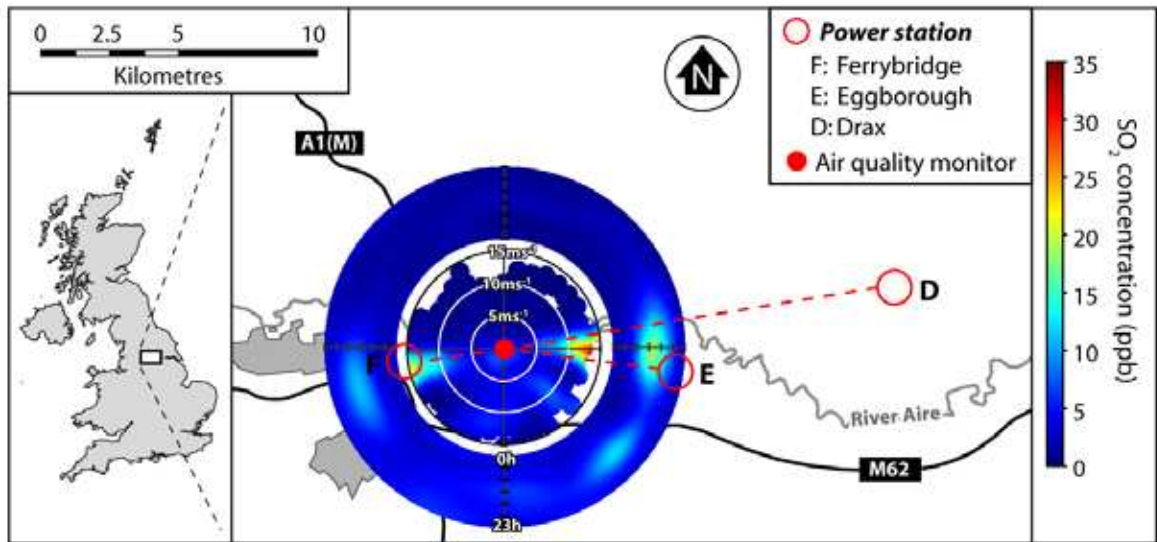


Figure 6: Data filtering techniques applied to ambient SO₂ concentrations from power stations in the Aire Valley, Yorkshire. Top panel shows how a bivariate polar plot can be used to isolate a specific source, e.g. Ferrybridge power station. Middle panel shows the different percentile levels of SO₂ from Ferrybridge as a time series and suggests a general decline in ambient impacts over ~4 years, which broadly agrees with reported emissions (bottom panel).

The percentile series suggest there has been a general decline in SO₂ impacts over these five years, although there are significant variations, e.g. between seasons and years. Figure 6 also shows quarterly SO₂ emissions, as reported by the power station; these emissions have fallen by ~40% over the period considered which is broadly consistent with the trend in ambient percentiles.

Tall stacks are designed to disperse emissions at heights that are well above the surface, so that ground-level impacts from stack plumes are relatively well diluted and only occur infrequently, e.g. under adverse meteorological conditions. The reduced magnitude and frequency of impacts at ground level can make it harder to use ambient data to track emission trends from elevated sources, compared to the greater and more frequent impacts caused by low level sources. The Ferrybridge example suggests that ambient data can only be used to track longer-term emission trends from elevated sources, for example, over a few years.

Clearly it is not always possible to isolate specific sources, but by careful siting, the opportunities for detecting a specific source can be maximised. In the case of the Ferrybridge example, there are relatively few occasions when the plume grounds at the monitoring site and this can make inference difficult. Another important issue is the availability and adequacy of the emission source information. Often such information is not available, or not available at a sufficient level of detail, which can frustrate any analysis that attempts to link ambient measurements with emission source changes.

4.2 Ratios of pollutants

One of the common methods for comparing emission inventories with ambient measurements is to consider pollutant ratios. The principal advantage of comparing ratios of concentrations in the atmosphere is that the effect of meteorology is largely accounted for. For a location that is dominated by a source (such as a roadside site) it can be assumed that primary pollutants are dispersed in exactly the same way. This technique is also valid for pollutants where the background contribution is high, e.g. PM₁₀.

As an example, consider the concentrations of NO_x and CO at Marylebone Road shown in Figure 7. Marylebone Road was chosen because the contribution from the road itself to concentrations of NO_x and CO is high and therefore the “signal” due to road vehicles is clear. Even with monthly averaged concentrations the time series have considerable variation – particularly for NO_x. However, calculating the gradient of CO/NO_x through a linear regression each month produces a much clearer trend shown in Figure 8. This much clearer relationship shows that the ratio of CO/NO_x decreased substantially from 1998-2006 but has since levelled off.

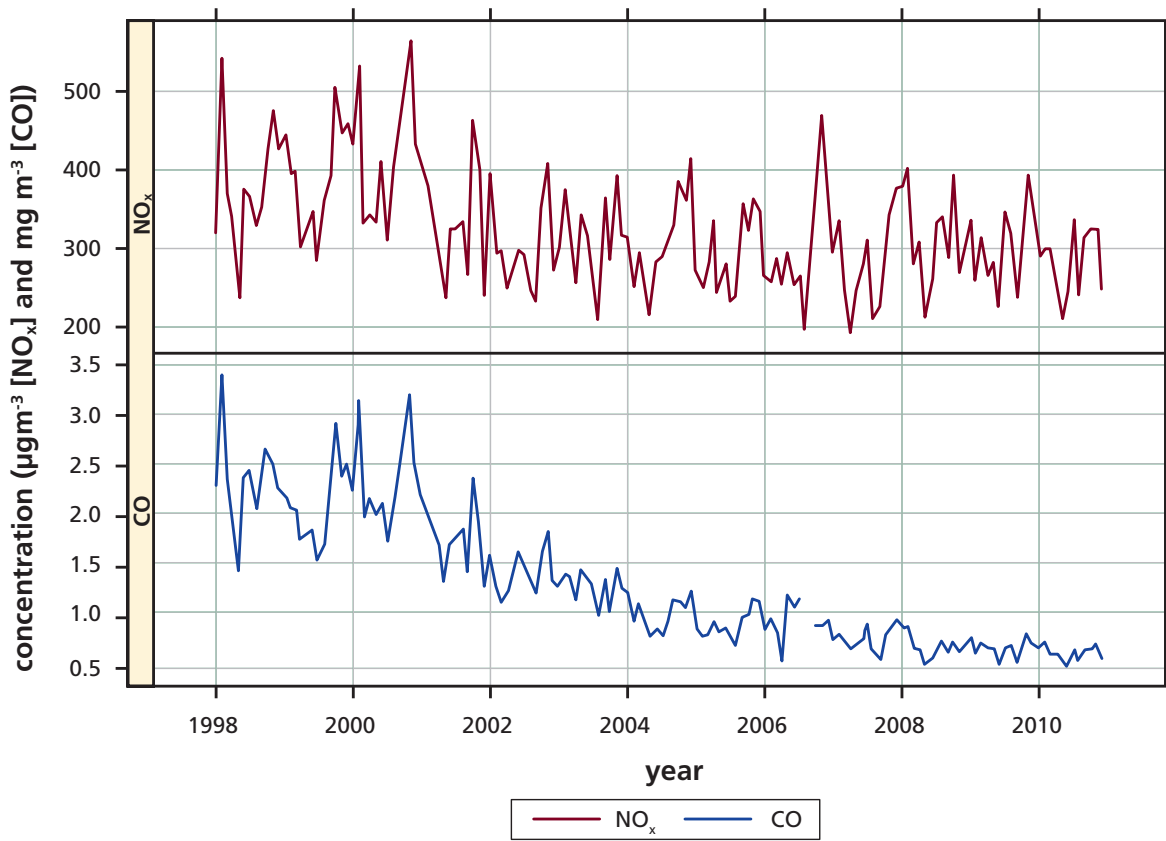


Figure 7: Monthly mean concentrations of NO_x and CO at Marylebone Road.

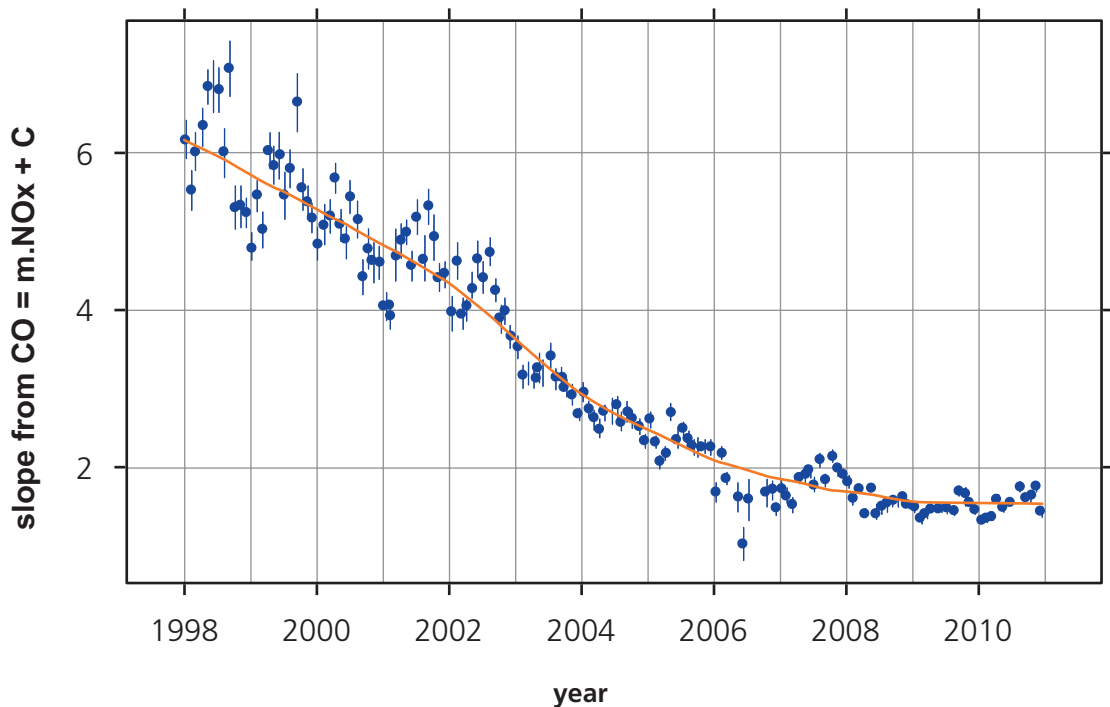


Figure 8: Monthly mean ratio of CO/ NO_x at Marylebone Road on a mass basis. The error bars show the 95% confidence interval in the slope estimate (analysis carried out for this report).

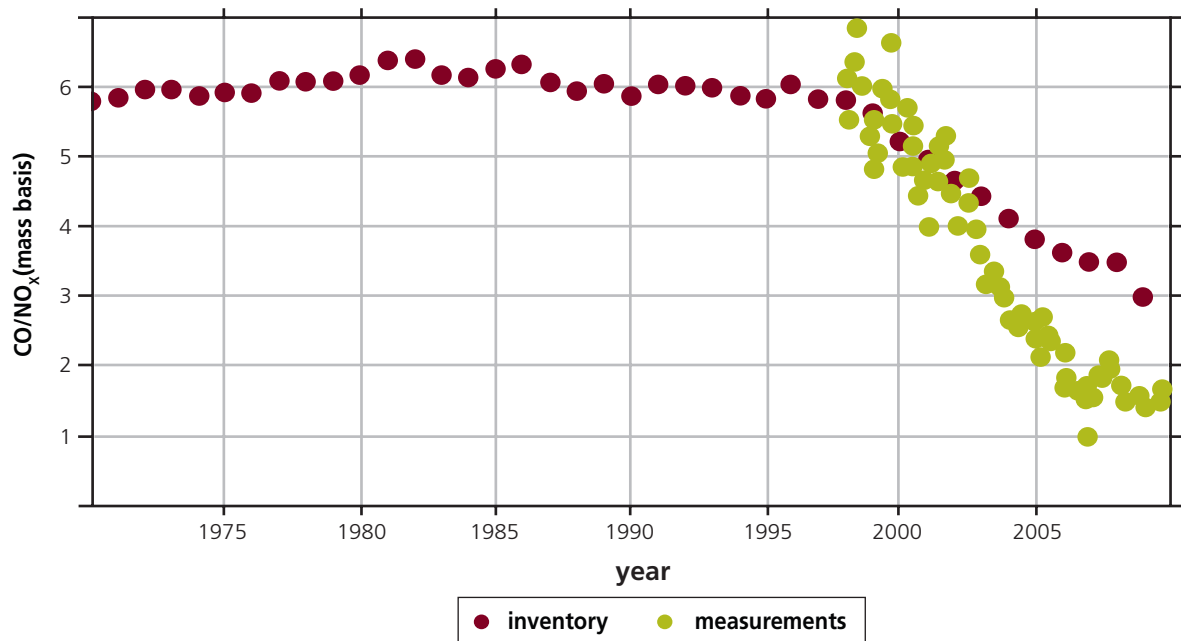


Figure 9: CO/NO_x ratio for UK road transport emissions and ambient measurements at Marylebone Road (analysis carried out for this report).

The ratio of measurements can also be compared directly with emission inventory estimates of CO/NO_x. In this case the comparison is with UK road transport totals rather than emissions estimates for vehicles using Marylebone Road. A more refined analysis would use annual emission estimates for Marylebone Road from 1998-2009, but these are not available. However, the principles of such a comparison can be illustrated. Figure 9 shows the ratio of CO/NO_x emissions for UK road transport from 1970-2009 (red circles) from the NAEI.

According to the emission estimates, the ratio of CO/NO_x was around six from 1970 to around 1998, i.e. CO emissions were six times greater than those for NO_x. Also shown is the ratio based on the analysis of ambient measurements at Marylebone Road (green circles). The ambient trend in the CO/NO_x ratio was very similar to the UK measurement ratio around 1998, but decreases much more rapidly than indicated by the emission estimates. Indeed, comparing the two estimates in 2009 shows that the inventory gives three times as much CO as NO_x, whereas the measurement analysis gives a ratio of about 1.5. The divergence in these ratios provides a strong indication that there is a discrepancy in the CO/NO_x ratio between the two estimates. The limitation of this approach is that the divergence could be caused by either NO_x or CO, or even a combination of both. However, with other information (e.g. the evidence from plotting simple trends), this type of analysis provides an effective way of identifying discrepancies between emission inventories and ambient measurements.

4.2.1 Primary NO₂

In some cases it is useful to know the ratio of two species directly. In the case of vehicular NO_x emissions, the proportion that is NO₂ has become increasingly important in its own right. The ratio of NO₂/NO_x in exhaust emissions is an important factor that contributes to ambient concentrations of NO₂, particularly those close to the source of emission. The NO₂/NO_x exhaust emission ratio is a quantity that can be estimated from an analysis of ambient concentrations of NO_x and NO₂ directly, thus allowing for a direct comparison with emission inventory estimates. Clapp and Jenkin (2001) provide details of how the local oxidant contribution (defined as the sum of NO₂ and ozone, (O₃) in ppb) can be estimated at sites that measure NO, NO₂ and O₃. The local contribution to the total oxidant provides an estimate of the ratio of NO₂/NO_x in the exhaust of vehicles. Figure 10 shows the trend in the estimated ratio of NO₂/NO_x (expressed as a percentage) at Marylebone Road based on the analysis of monthly mean concentrations. The figure shows that prior to 2003 the ratio was very close to 10%, before increasing over a short period of time to over 20%. The analysis can be refined by removing background concentrations first.

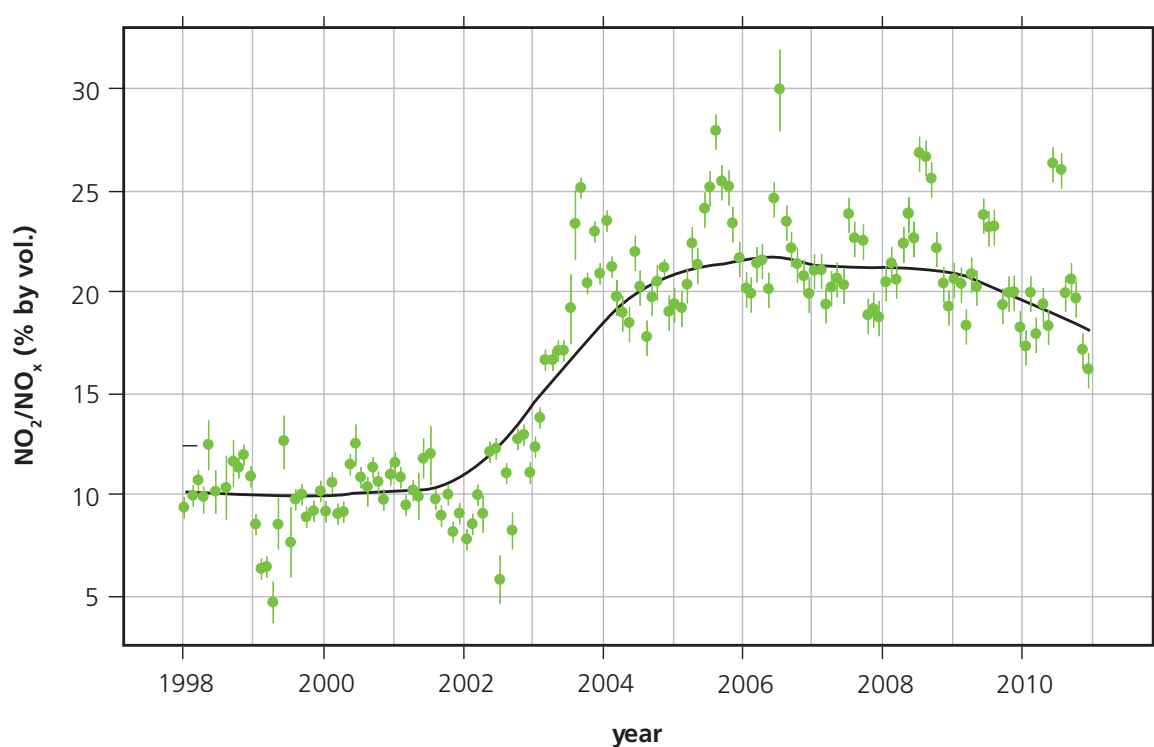


Figure 10: Local oxidant (f-NO₂) calculated at Marylebone Road.

The type of analysis shown in Figure 10 is useful because the results can be compared with emission inventory estimates of the NO₂/NO_x ratio. One limitation of the method is that it requires a measurement of O₃, which is only available at a few roadside locations. However, other methods, still based on the analysis of ambient measurements, have been developed to estimate the NO₂/NO_x ratio at roadside sites that do not measure O₃, e.g. Carslaw and Beevers (2005). Figure 11 shows an analysis of London roadside sites where most did not measure O₃. In this case a clear upward trend in the NO₂/NO_x ratio is apparent, which can be linked to changes in emissions control technologies used on diesel vehicles.

From an emissions inventory perspective, such information provides a mean NO_2/NO_x ratio for a specific road link, rather than by vehicle class. Nevertheless, such information can be used to check whether emission inventory assumptions are valid.

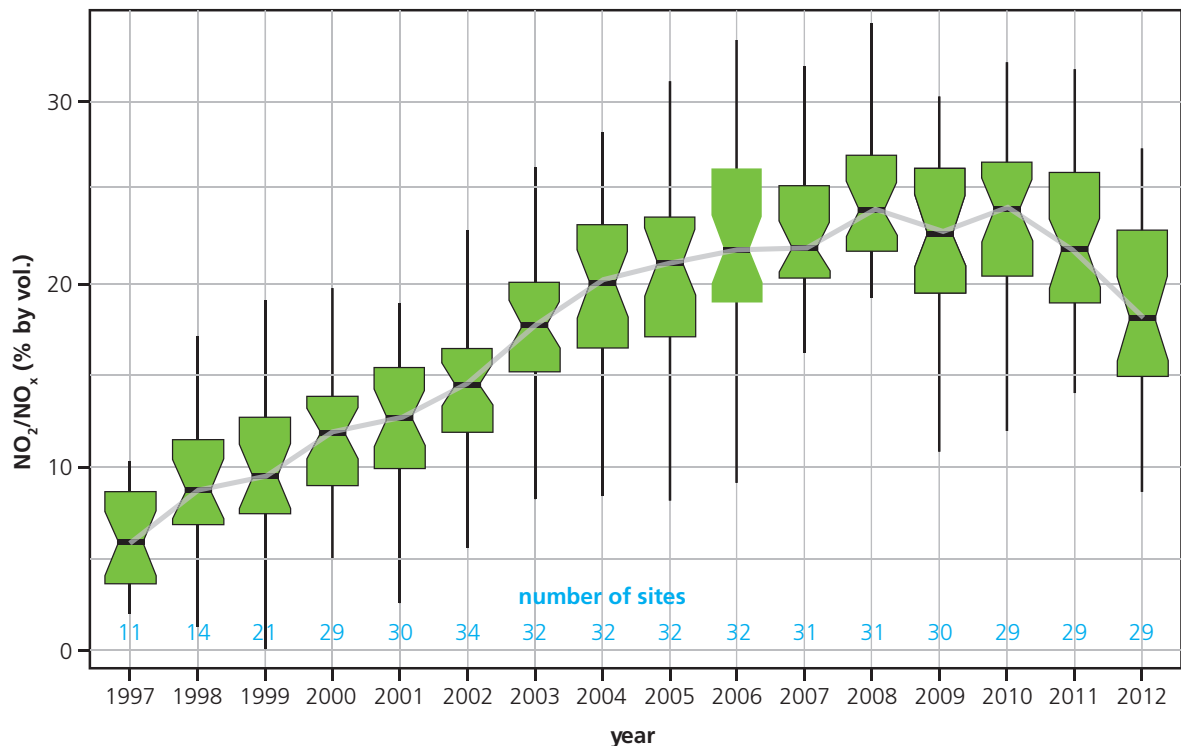


Figure 11: Estimates of the f-NO_2 for roadside monitoring sites in London.

4.3 Summary points

4.3.1 Strengths

- Long-term trends in emissions and ambient concentrations are easily calculated and can quickly provide a “first order” analysis of the consistency between the two.
- Considering ratios of pollutant concentrations can greatly reduce the “noise” introduced by meteorological variation.
- In some cases, ratios of pollutants, e.g. NO_2/NO_x , can provide information of direct use to inventories.

4.3.2 Weaknesses

- It can be difficult to isolate the effect of specific source types by analysing ambient measurements and source specific information is usually needed for comparison with inventories.
- Inventory information is not necessarily available at sufficient detail. For example, estimated trends in emissions along specific road links may be based on national fleet ages.

4.3.3 Conclusions and recommendations

- The comparison of emission and ambient concentration trends should be carried out more often because it can provide the first indications of inconsistencies between the two, which can be followed up with more detailed work.

4.3.4 Linkage with emission inventories

- This is a very useful technique that can alert inventories to incorrect trends in emissions from a specific source or group of sources (e.g. road transport) and direct inventory groups to where these may need to be reassessed.
- The most relevant linkage with emission inventories is the comparison with long-term trends for specific source sectors. Depending on how the ambient data have been processed these source sectors may include, for example, urban road transport emissions.
- However, the technique may not pinpoint the exact source which is “in error”, e.g. which specific vehicle type, and whether it is a problem with emission factors or treatment of activities, or in the inventory estimation methodology.
- In most cases, the technique is only useful for informing problems with local inventories developed from local knowledge (e.g. the evolution of the vehicle fleet and traffic flows). However, if this information is known accurately, it could pinpoint issues with emission factors relevant to national inventories.
- Concentration ratios are also very useful for alerting inventories to conflicts, but less useful for pointing out what element of the inventory should be “fixed”, e.g. which pollutant, emission factor or activity data. It is potentially useful for identifying errors in inventories regarding the mix within groups of similar pollutants. For example, it can inform the inventory directly on whether the VOC speciation for a specific source such as road transport is correct if the measurements are made at the roadside.

5 Meteorological normalisation

5.1 Application to ambient concentration trends

Meteorological normalisation refers to statistical techniques that can be applied to time series of ambient concentration to account for or “remove” the effect of meteorology. As noted previously, meteorology can falsely mask or emphasise trends, making it difficult to know the extent to which a trend reflects changes in source strength or changes in meteorology. The basic idea is that a statistical model is developed to explain concentrations in terms of different variables. Having modelled these relationships and accounted for their influence, the remaining (unexplained) contribution should better reflect the variation in source strength. Similarly, if a good explanatory model can be developed, then it is possible to remodel a time series with a fixed set of assumptions, e.g. assuming the same wind speed, etc., every day. In this way, these techniques can provide estimates of time series concentrations assuming the same weather conditions every year. The variables used will depend on the availability of meteorological and other data, but may for example include ambient temperature, wind speed, wind direction and humidity.

For almost all practical situations there is not a straightforward, linear relationship between the concentration of a pollutant and a variable such as wind speed or temperature. Indeed, not only do these relationships tend to be highly non-linear, there are also interactions between them. For example, wind speed and direction do not act independently of one another. For this reason, the best explanatory models tend to use quite sophisticated techniques that can account for both non-linear relationships and interactions between variables.

Meteorological normalisation has been used extensively on a range of problems including sulphate and nitrate trends in the USA (Holland *et al.*, 1999), SO₂ trends (Holland *et al.*, 2000), ozone (Gardner and Dorling, 2000a; 2000b), PM₁₀ and NO₂ (Kukkonen *et al.*, 2003; Carslaw *et al.*, 2007). Many of these studies show that not taking account of meteorological variation in trend assessment can sometimes lead to very different results compared with those that do account for meteorological variation. In the context of this report, the emphasis is on the use of these techniques to provide long-term trends (or other temporal variations, e.g. diurnal variations) that should relate better to changes in source strength. In this respect, the techniques provide a means of comparing emission trends with trends in ambient observations on a more like-for-like basis.

As an example of the usage of meteorological normalisation, an analysis has been undertaken of hourly NO_x concentrations at Marylebone Road from 1998 to 2010 using hourly meteorological data from Heathrow Airport. The model is based on that described in Carslaw *et al.* (2007). Among the variables used in the model were the wind speed and direction (u and v components of), temperature, and variables representing diurnal, weekly, seasonal and long-term trend variation. The aim was to establish the trend in NO_x concentrations given fixed meteorological conditions.

Figure 12 shows the trend in observed (raw) monthly mean NO_x concentration at Marylebone Road. Even a monthly mean shows considerable scatter. The smooth fit line shows that concentrations decreased from around $400 \mu\text{g m}^{-3}$ in 2000 to about $300 \mu\text{g m}^{-3}$ in 2010.

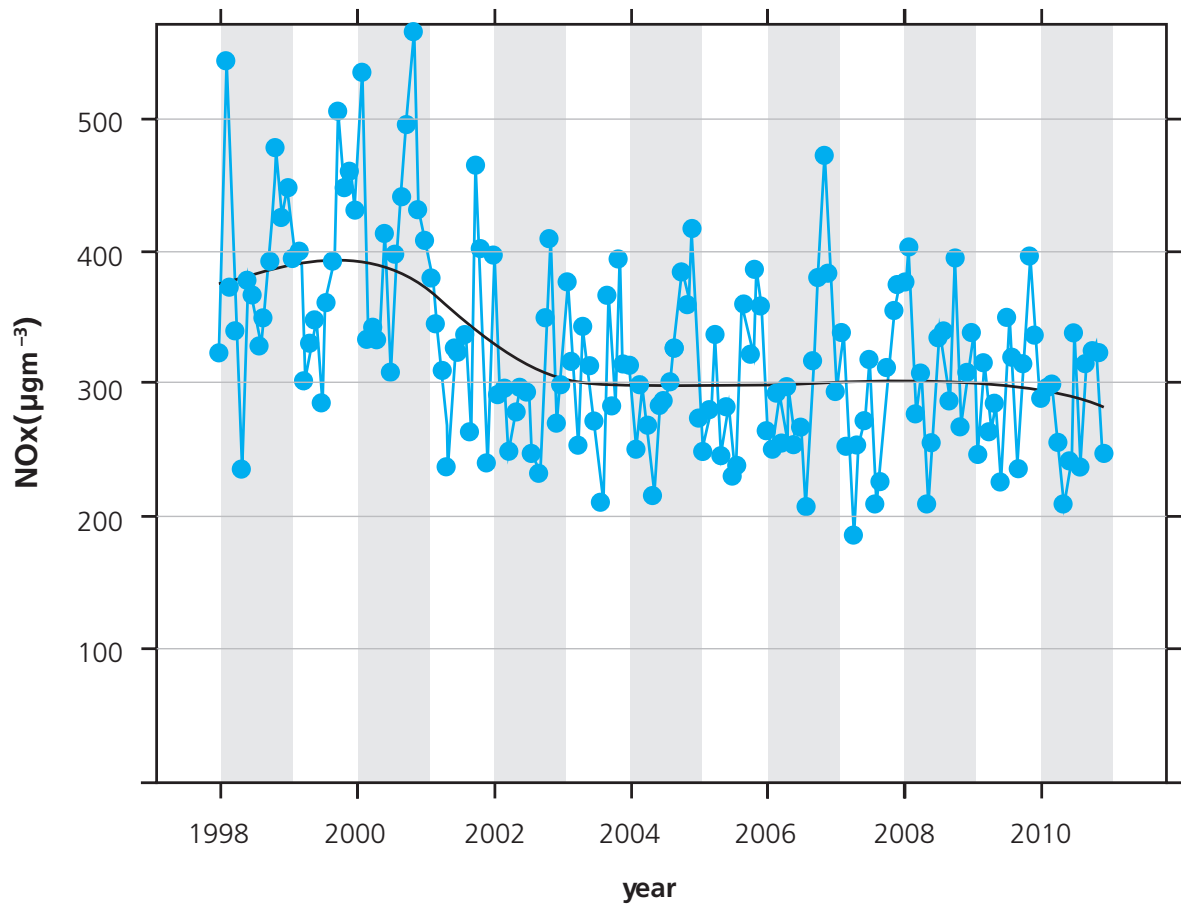


Figure 12: Trend in monthly mean NO_x concentration at Marylebone Road, shown with a smooth fit to highlight the trend.

In order to understand the effect of meteorology it is useful to predict trends based on the meteorology for a range of years. This process has the advantage of highlighting those years that tend to result in elevated NO_x concentrations and those that do not. The model was therefore run separately for each “meteorological year”. First, 1,000 hours of meteorological conditions (and other variables) were randomly sampled from that year. Second, the model was used to predict the NO_x concentration over the period 1998-2010 using these 1,000 hours. The averaged results provide an estimate of what the trend in NO_x is for a given year of meteorological conditions. This process was repeated for each year between 1998 and 2010, yielding 13 time series for different meteorological years.

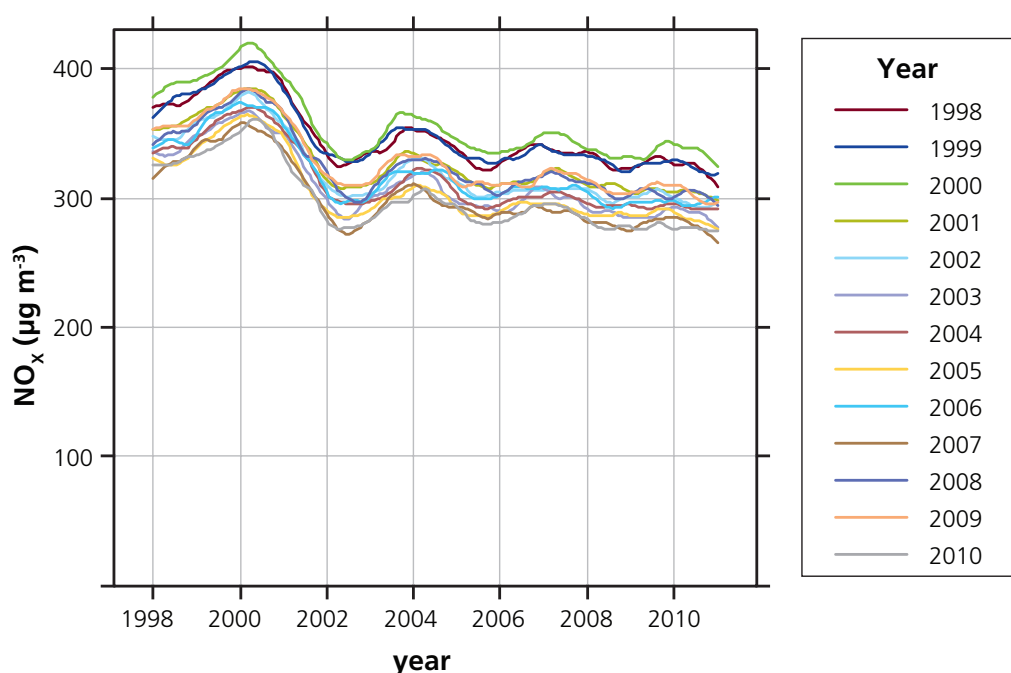


Figure 13: Generalized Additive Model (GAM) predictions of the trend in NO_x concentration at Marylebone Road. Each line shows the mean result of running the model by randomly sampling meteorological conditions from that year and applying them to the whole time series. The analysis was carried out for this report.

Figure 13 shows the results from the modelling and highlights the following features:

- The range in predicted concentrations is quite large when using different “meteorological years”. The minimum to maximum concentration range is about $80 \mu\text{g m}^{-3}$.
- Three years, 1998 to 2000, stand out as leading to higher concentrations than the others, with the year 2000 resulting in the highest concentrations and 2010 the lowest.

It is clear from the results above that meteorology plays an important role in controlling NO_x concentrations. However, perhaps the most important feature of Figure 13 is the information it provides on the trend in NO_x . As noted previously the observed concentration of NO_x decreases from about $400 \mu\text{g m}^{-3}$ to $300 \mu\text{g m}^{-3}$ from 2000 to 2010. However, the GAM modelling indicates that those early years (1998-2000) were somewhat unusual because they result in higher concentrations due to the meteorology in those years. If the *same meteorology* had been experienced over those 13 years then the change from 2000 to 2010 would typically be expected to be about $370 \mu\text{g m}^{-3}$ to $300 \mu\text{g m}^{-3}$ NO_x . Expressed as a mean annual reduction from 2000 to 2010, the observed data suggest a trend of -1.9% /year compared with about -1.4% /year for the normalised trend. In other words, the observed decrease in NO_x over the period 1998-2010 is exaggerated due to meteorological conditions early on in the time series that led to higher than normal concentrations.

A consideration of *why* concentrations may have been higher in the years 1998-2000 reveals that part of the answer may lie in the fact that for those years the wind was from a south-westerly direction more than for other years – about 15% more. Figure 14 shows that when the wind is from the south-west (even for high wind speeds) the concentration of NO_x at Marylebone Road is high. These high concentrations are due to street canyon recirculation at this location, which yields high concentrations at high wind speeds. Therefore, an increase in the frequency of winds from those directions would tend to lead to higher concentrations. Similarly, 2010 had the highest proportion of northerly winds, when concentrations at Marylebone Road tend to be much lower, and this is likely to be the dominant factor explaining why the 2010 meteorological year results in the lowest predicted concentrations.

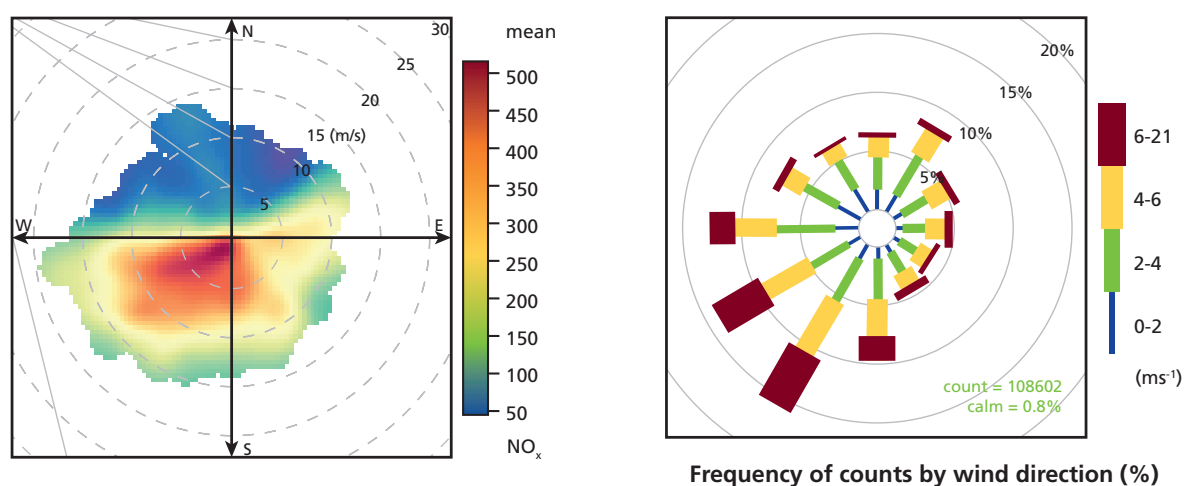


Figure 14: Left: Bivariate polar plot of NO_x concentrations at Marylebone Road. Right: Wind rose. Both plots are based on hourly data from 1998-2010 (analysis carried out for this report).

The effect of different meteorological years can differ considerably depending on the local factors affecting a site. For Marylebone Road it was shown that the dominant wind directions leading to elevated local pollutant concentrations were from the south-west. However, other sites can show a very different response to different meteorological years. As an example, the Cromwell Road 2 site in inner London – in contrast to the Marylebone Road site – is predicted to have the highest concentrations for 2010 meteorology, as shown in Figure 15. Statistical modelling can therefore help understand differing trends across sites and rationalise them in terms of meteorological effects. When several sites are compared, meteorological normalisation can help ensure that the trends are compared on a consistent basis.

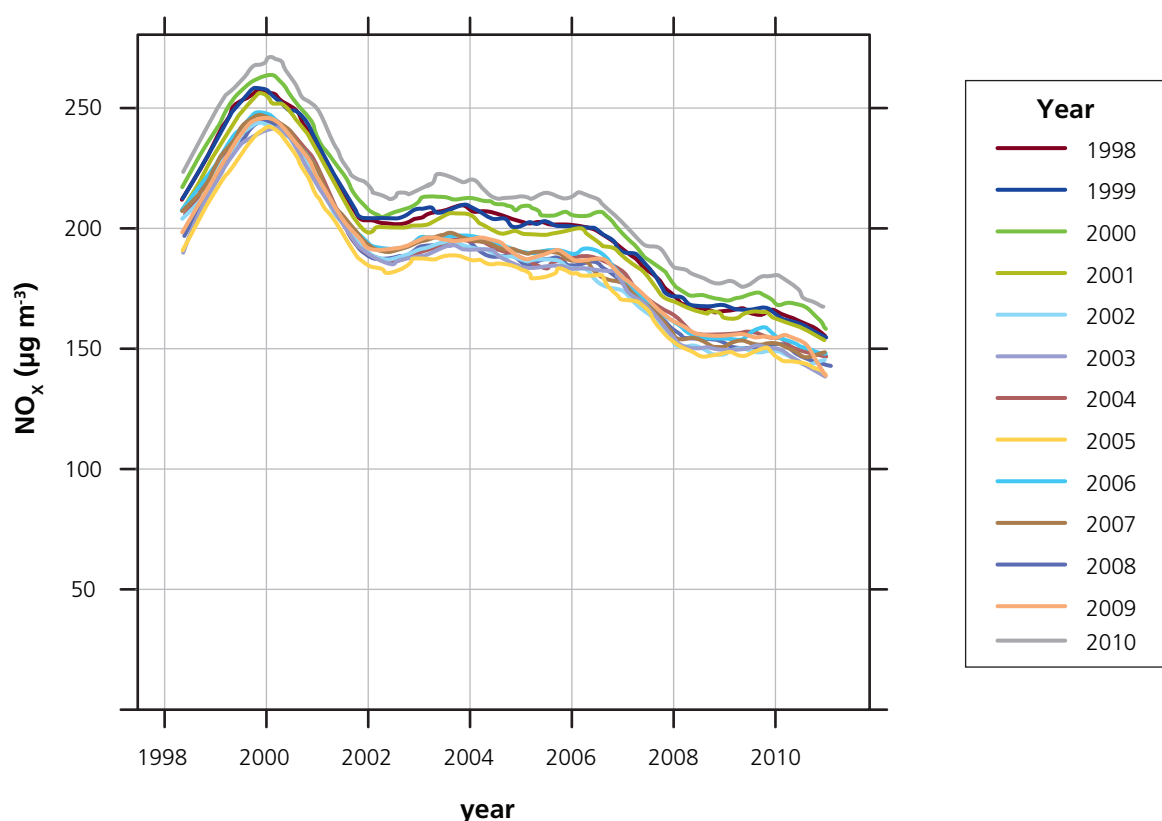


Figure 15: GAM predictions of the trend in NO_x concentration at the Cromwell Road 2 site. Each line shows the mean result of running the model by randomly sampling meteorological conditions from that year and applying them to the whole time series.

Note also that such information is useful when considering time series of trends generally. For example, it might be thought encouraging that concentrations started to decrease in 2010. However, this type of modelling helps to explain that the most likely reason is an unusual set of meteorological conditions (at least for Marylebone Road), rather than a reduction in emissions. An additional benefit of these techniques is that they can often reveal changes that can be linked to specific events or changes in local conditions, e.g. a closer analysis of Marylebone Road reveals that a reduction in concentration in NO_x around 2001 was most likely linked to the introduction of a bus lane. Therefore, these techniques can help to make sense of the observed change in concentrations.

The results of this analysis show that it can be important to consider meteorological variation when considering trends, even in time series that are quite long. It also shows that statistical modelling can improve insight into and understanding of the factors affecting trends. As noted previously, these models can be complex, but there is no reason why they could not be developed for a few well-characterised sites to provide a more robust understanding of measurement trends on an ongoing basis.

An approach that is often used is to compare ambient trends in pollutant concentration with the trends in UK pollutant emissions reported annually by the NAEI or with the spatially-resolved emission maps for a single year. In the case of road transport, analysis may be carried out by comparing trends in urban traffic emissions with roadside measurements, but even here the comparison is usually with total urban UK traffic emissions. The problem with this approach is that the UK and even urban UK emissions for road transport reported by the NAEI mask a great deal of

regional, site-to-site variation which exists due to differences in the traffic mix and how these have developed over the years. The NAEI maps account for road link-specific traffic levels, but maps for previous years are not updated when emission calculation methodologies or emission factors are revised.

5.2 Comparison with emission estimates at roadside sites

More recent work has attempted to compare estimates of NAEI emissions at individual road links with ambient measurements in London using a consistent approach to emission calculation based on COPERT 4 v8.1. Emissions were calculated at 15 individual road links where long-term air pollution measurement data exist (mostly data from the London Air Quality Network). The benefit of this approach is that there should be closer correspondence between the emission and ambient trends because specific road link and roadside monitoring sites are compared. Nevertheless, the emissions data from the NAEI would still only be expected to represent 'typical' conditions and could not, for example, account for all local influences close to a monitoring site.

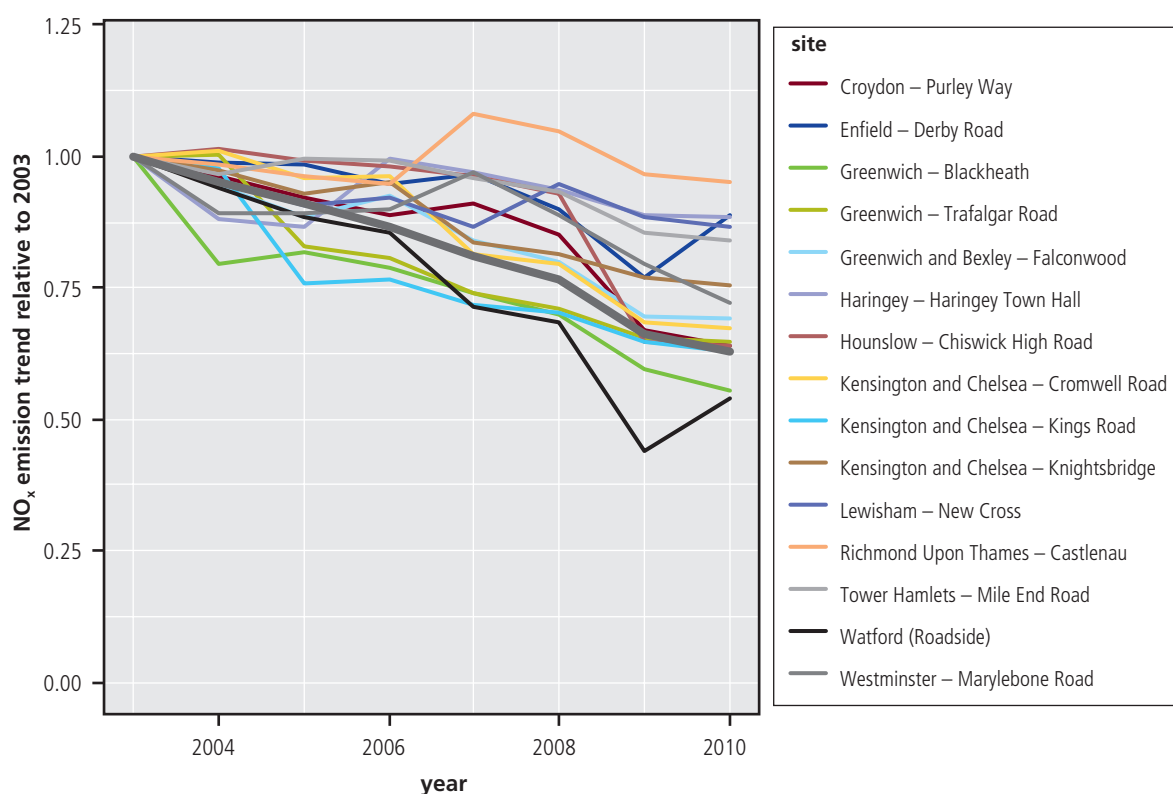


Figure 16: Relative change in road link NO_x emission estimates for 15 roadside sites in London. The thicker grey line shows the mean for NAEI urban traffic emissions.

The analysis to date shows that there is considerable variation in NO_x emission trends between roadside sites, which is affected by both the variation in vehicle stock and changes in vehicle flow over the period 2003 to 2010, as shown in Figure 16. For example, the data show that the relative change in NO_x emissions over the period 2003 to 2010 varies from approximately no change to a reduction of 50%. These results show that it is very important to understand vehicle emissions on individual road links if comparisons are to be made with roadside ambient measurements. Viewed another way, the results also suggest that many (i.e. more than ten) sites may be required to provide a reasonable overall estimate of *typical* urban emission trends

for road vehicles and that it can still be difficult to reconcile the differences on an individual site basis. Figure 16 does not demonstrate that calculating emission trends using local traffic and fleet data provides a better agreement with trends in ambient concentrations at these sites, as no such comparison has been carried out. However, it does indicate that significant variations in the rate of change in emissions over this time period should have been expected simply on the basis of differences in how traffic flows and fleet have changed over time near these different London sites. The point of Figure 16 is simply to show how the trend in total UK emissions cannot be taken to be representative of the trend in traffic emissions at specific sites. Further work is required to quantify the extent to which the use of road link emissions data improves the emissions quantification compared with using national fleet data.

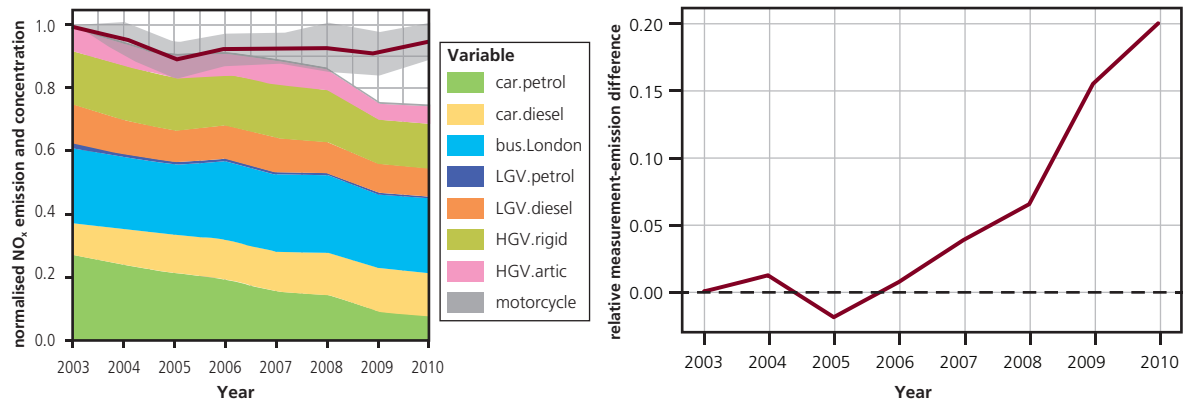


Figure 17: Left panel: Mean change in vehicle emissions and normalised roadside increment NO_x concentrations across 13 roadside sites in London. The red line shows the trend in normalised NO_x concentration and the shading the 95% confidence interval in the mean due to the variation across sites. Right panel: Deviation in NO_x concentrations from emissions normalised to 2003.

The relative variation in meteorologically-normalised trends is shown in Figure 17 with the 95% confidence interval calculated as a mean across the 13 sites. Again, it can be shown that accounting for meteorology is important for individual sites and that there is large variation in the relative trends between the sites. The pooled results shown in Figure 17 (left panel) do show that when averaged across 13 sites there has been little change in NO_x concentration, whereas the emissions totals have decreased by about 25% over the period 2003 to 2010. This disagreement between emission and concentration trends is more clearly seen in the right panel of Figure 17 where the difference between the two normalised estimates is shown. These results show that from 2003 to 2006 there was good agreement between the emissions and ambient trends in NO_x concentration. From 2006 onwards it is then clear that the two deviate – corresponding to a period where there continues to be a reduction in emissions but little or no change in concentration. One tentative conclusion from this work is that the introduction of Euro IV diesel cars and vans in 2005 could account for the discrepancy, as it is known that these vehicles are higher emitters of NO_x than previously thought (Carslaw *et al.*, 2011). However, the emission factors used in the calculations are meant to account for these increased emissions, which perhaps is indicative of the ongoing need for further work to improve the emission estimates for these vehicles.

5.3 Summary points

5.3.1 Strengths

- Accounting for (removing) the effect that meteorology has on ambient trends using statistical models can reveal trends that are much more closely aligned with trends in emissions.
- The techniques for meteorological normalisation are practical enough to be used on a routine basis and the statistical tools for doing so are available.
- The techniques can be used to provide useful information on long-term trends as well as diurnal and seasonal variations.

5.3.2 Weaknesses

- Care and expertise is required to develop models in the first place.
- Local, good quality meteorological data are required to develop models with sufficient explanatory power. However, good models can be produced using routinely available meteorological data, e.g. wind speed, wind direction and temperature.
- The techniques are most suitable for site-specific analyses of local emissions.
- They do not provide direct information to allow inventories to be adjusted but highlight potential areas of inconsistency.

5.3.3 Conclusions and recommendations

- These techniques could be used on a routine or regular basis to allow a comparison between ambient concentrations and emission source estimates.

5.3.4 Linkage with emission inventories

- Many of the comments made in Section 4.3 concerning the linkages between trends analysis and emission inventories apply to this technique.
- However, this technique, if carefully done in the right locations, has the additional advantage of pinpointing problems with inventories for a specific source, if this cannot be determined from the trends analysis alone.
- The most relevant linkage with emission inventories is the comparison with long-term trends in aggregate emissions for specific source sectors. In addition, these techniques can provide some information on other variations, e.g. diurnal or seasonal, that could be useful to either confirm or provide new information for emission inventories.

6 Vehicle emission remote sensing

6.1 Introduction

Emissions from road vehicles represent one of the more significant areas where information concerning the accurate estimate of emissions is important. This sector is also diverse and constantly evolving. For example, there are numerous vehicle types, fuels and emissions control technologies in use. Furthermore, new technologies are continually entering the vehicle fleet and emissions themselves are very dependent on driving conditions. This complexity is also reflected in emission inventories where it is generally the case that emission factor estimates (in grammes per km) are made for a highly disaggregated list of vehicle types (e.g. by fuel, vehicle type, engine size, etc.) and as a function of vehicle speed. For these reasons checking whether emission factors are accurate is not straightforward.

Vehicle emission remote sensing offers an effective way of understanding vehicle emissions and the extent to which inventories agree with observations (Bishop *et al.*, 1989). Remote sensing of vehicle exhaust was developed about 20 years ago at the University of Denver (e.g. Stedman *et al.*, 1997) and has been extensively used on many campaigns worldwide. Remote sensing does not provide a link between ambient measurements and emissions directly, but can be used to assess the accuracy of vehicle emission factors in a highly disaggregated way. For this reason, remote sensing measurements can provide information that can be used to directly judge the validity of emission inventories.

Remote sensing does not directly provide information on absolute vehicle emission rates, e.g. in g/km, but on pollutant ratios with carbon dioxide (CO₂). However, a ratio of a pollutant to CO₂ can be compared directly with fuel-based emission factors in emission inventories. Remote sensing campaigns complement the rolling road measurements, which generally form the basis of Type Approval Testing and emission inventory estimates. On the one hand they have the advantage over rolling roads in that they can be used to sample thousands of vehicles *in use*. However, on the other hand, remote sensing can only provide information for a subset of driving conditions, e.g. not high speed motorway driving.

Recent analyses of remote sensing data from surveys in the UK are reported in Carslaw *et al.* (2011). Together, the emission measurement campaigns in 2008-2010 sampled over 80,000 vehicles. These data were processed to derive absolute g/km estimates of emissions of NO_x and NO₂. A summary of the findings for key vehicle categories is shown in Figure 18, which shows clearly where there may be discrepancies between currently used UK estimates of emissions and those derived through remote sensing campaigns.

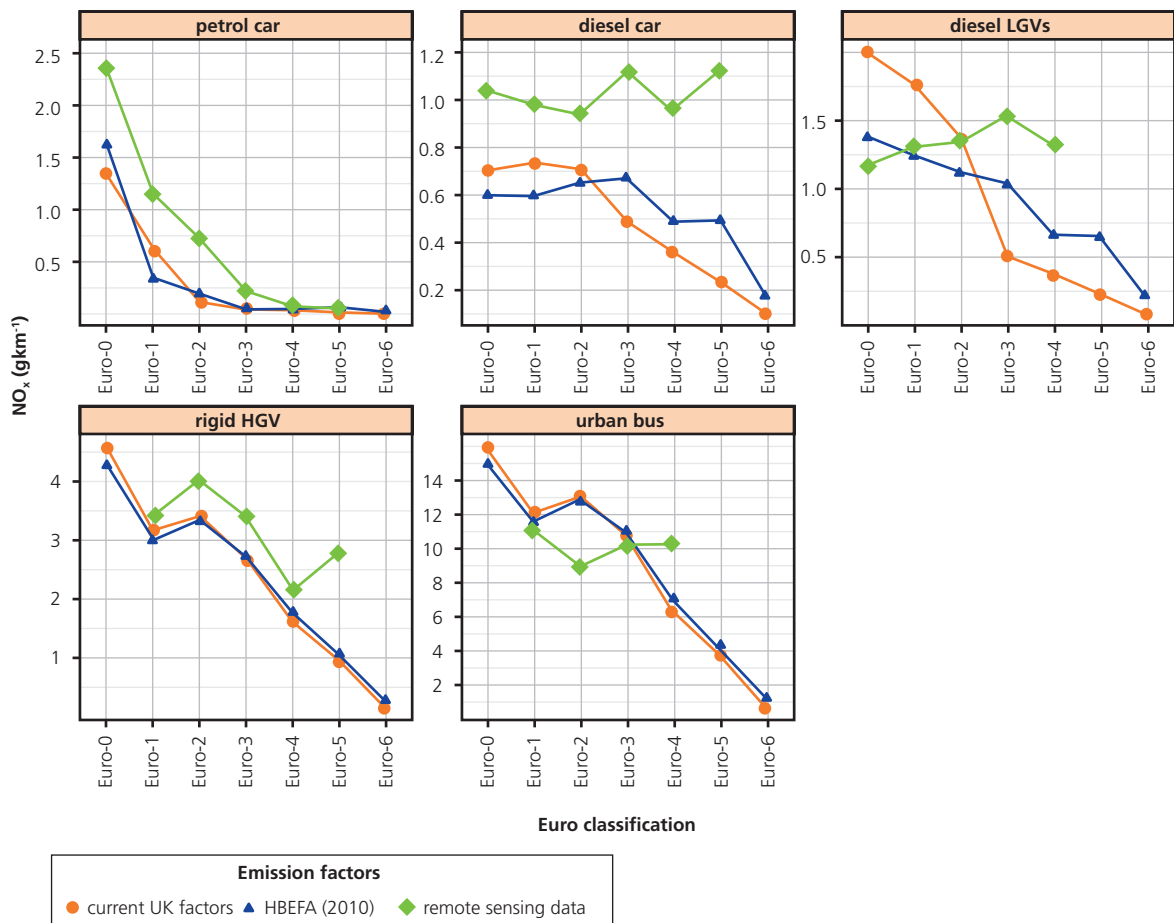


Figure 18: Comparison of three different emission factor estimates: UK factors from 2010, the ‘Handbook Emission Factors for Road Transport’ (HBEFA) and estimates based on the analysis of remote sensing data. The uncertainties for the remote sensing data are the 95% confidence intervals in the mean. More details can be found in Carslaw *et al.* (2011).

The principal benefit of vehicle emission remote sensing is that it is capable of easily sampling thousands of vehicles. Moreover, if individual vehicle information, such as emissions Euro class, year of manufacture, vehicle weight, etc., can be linked to emissions measurements, then potentially highly disaggregated emissions information can be gained. Such information can in turn be used to link emissions estimates directly with existing vehicle categories in emission inventories; this is a significant benefit of the technique. In this way it is possible to gain information on a wide variety of vehicles, technologies and fuels.

While vehicle remote sensing is valuable, there are nevertheless some potentially important limitations. First, only a subset of road types can be sampled. Second, it is not possible to sample every vehicle type, e.g. articulated HGVs where the exhaust plume is released at height. Third, unlike rolling road measurements, remote sensing only provides a snapshot of what an individual vehicle is emitting at a particular time. Many of these effects can be mitigated, e.g. large sample sizes over a range of vehicle speeds and accelerations can provide detailed information on driving condition effects. Finally, remote sensing does not provide an absolute measure of vehicle emissions in g/km, but a ratio with CO_2 . Nevertheless, such measurements do help to provide important information concerning vehicle emissions that has the potential to indicate where current inventory assumptions are likely to be erroneous.

While not considered further in this report, measurements made in road tunnels can provide useful information on emission rates of gaseous species from vehicles.

6.2 Summary points

6.2.1 Strengths

- Vehicle emission remote sensing can provide very detailed emission ratio (and through post-processing, emission factor estimates in g/km) information apportioned to a comprehensive range of vehicle types.
- The output from remote sensing campaigns is, or can be, very closely aligned with existing inventory methods. For example, it is possible to match the same vehicle fuel, engine size and Euro class.
- A large amount of in-use vehicle emissions data can be collected over a relatively short period of time.
- Remote sensing can provide up-to-date information on the impact of new vehicle technologies as they enter the fleet.

6.2.2 Weaknesses

- Remote sensing is not carried out on a routine basis and requires specialist equipment. There is only one remote sensing set-up in the UK and that does not measure NO₂.
- Remote sensing can only usefully provide information on urban and to some extent suburban driving and therefore does not cover the full range of conditions required by emission inventories.
- Remote sensing provides information on the ratio of a pollutant to CO₂ and not the absolute (g/km) emissions used in emission inventories.

6.2.3 Conclusions and recommendations

- Remote sensing has a proven capability for use in the UK.
- Regular remote sensing surveys, e.g. on an annual basis, would provide valuable, up-to-date information on the vehicle emissions for a key sector.

6.2.4 Linkage with emission inventories

- Vehicle emission remote sensing arguably provides the closest match between “ambient” measurements and emission inventory source categories when compared with the other techniques outlined in this report. This close matching is due to remote sensing directly providing emission information by detailed vehicle type that can exactly match those categories used in the NAEI. Moreover, such data can also provide information on the speed dependence of emissions, also a key characteristic of how road transport emission inventories are compiled.

- Although the technique can only provide ratios of emissions to CO₂, this is not a significant limitation because CO₂ emissions from vehicles are known with relatively high confidence compared with air pollutant emissions. The technique can therefore be used directly to verify and suggest changes in individual vehicle type emission factors.
- A disadvantage is that measurements are made at a specific location and vehicle operational conditions (e.g. speed or part of a drive cycle), so may not be appropriate for other conditions.
- The technique can very usefully pinpoint the number of “failing” vehicles and high emitters in the fleet because of the large sample sizes and this in itself can feed directly into an inventory.
- We recommend that results from remote sensing programmes are considered alongside those from other, more direct emission test programmes when developing compilations of emission factors for inventories.

7 Flux and satellite-based measurements

7.1 Introduction to flux measurements

Flux measurements from an elevated platform provide a top-down method of calculating vertical fluxes integrated over spatial scales of hundreds of metres to city wide. They can be used to evaluate traditional bottom-up emissions inventories or to provide emissions data on new metrics, which is the case for most particle-related emissions, such as particle number and chemically-speciated particle components. In brief, the usual methodology involves correlating high frequency changes in species concentration with the up and down air movements at the sampling point so as to extract the net direction and magnitude of mass flux passing through the horizontal plane of the measurement height. These eddy covariance techniques require sub-second sampling frequency (several Hz) and/or short dwell times (a few milliseconds) which is a considerable challenge for analytical instrumentation, particularly for particle metric instrumentation. (Note that this type of measurement of vertical emission fluxes from a surface, e.g. a city, is different from the approach that derives the emissions by mass balance of the horizontal fluxes passing through the vertical plane of the circumference of the source region – see Section 7.4.2.) The area of the surface over which the measured vertical flux is integrated – the ‘flux footprint’ – depends on, amongst other factors, the vertical height of the measurement, horizontal wind speed and atmospheric stability (Kljun *et al.*, 2004).

7.2 Gases

Historically, flux measurements of gases have focused on biogenic sources, where the source itself tends to be homogeneous and the terrain flat. However, recent instrument developments together with a careful consideration of how the measurements are made have resulted in estimates of the source strength for several key urban pollutants.

Recent work carried out using measurements located at the top of the BT Tower in central London (~190 m above street level) has provided estimates of emission totals that could be compared with NAEI totals (Langford *et al.*, 2010). This height has the advantage of integrating fluxes over a large urban area and minimising artefacts from the heterogeneity of the urban canopy, but has the disadvantage that it is sometimes above the boundary layer (particularly at night) and fluxes may not remain constant over this vertical distance. In unstable atmospheres the footprint for the BT Tower corresponds to a small area extending about 500 m from the measurements, whereas under stable conditions the footprint can extend to >14 km. The average conditions during the campaign corresponded to a footprint extending to 4.7 km. The footprint area was matched with the NAEI km² grid emissions for 2009 allowing a comparison (scaled up to annual totals) to be made between the two (Figure 19). Considering, for example, emissions of CO there is remarkably good agreement between the flux and NAEI estimates (329 t km⁻² yr⁻¹, within 10% of the NAEI estimate).

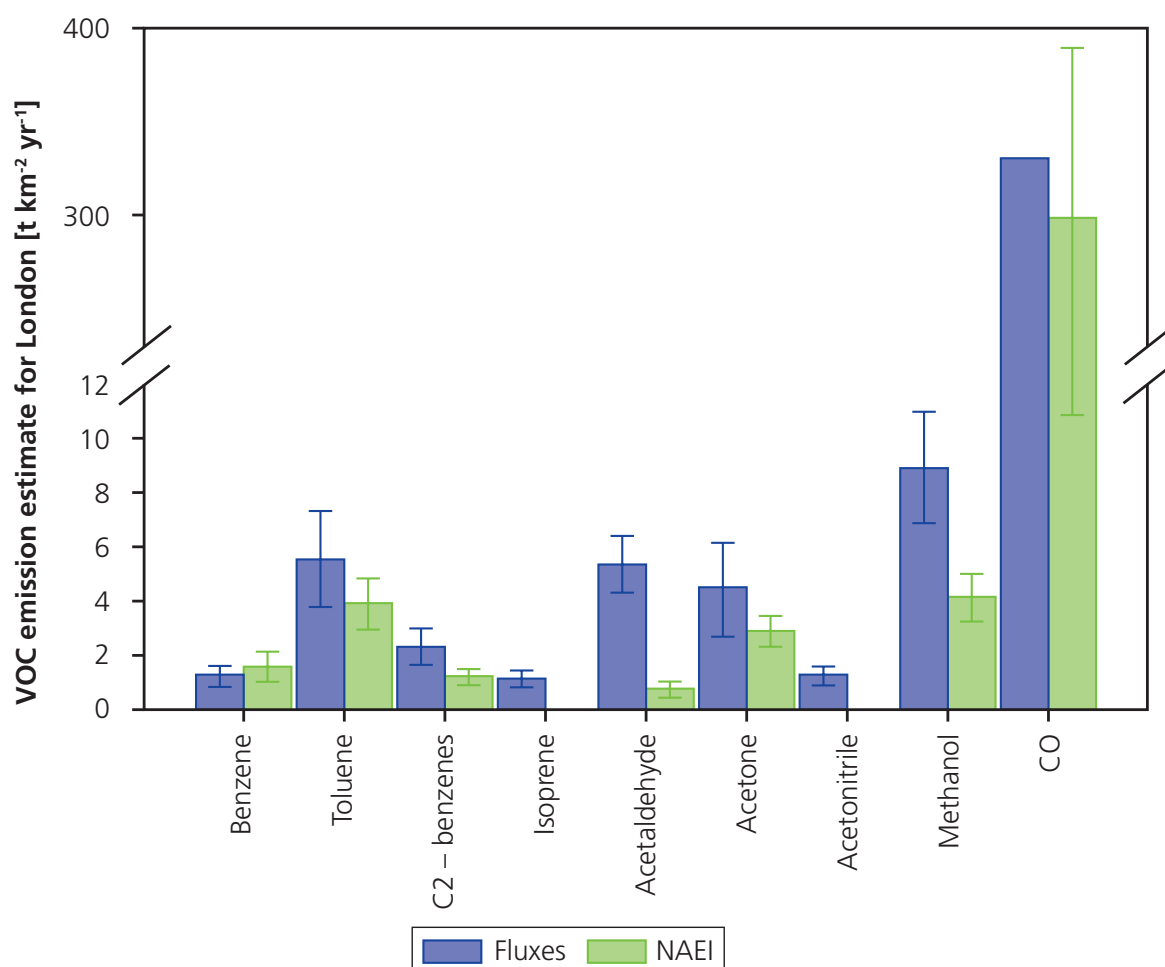


Figure 19: Comparison between NAEI estimates of emissions and those derived from flux measurements in London (Langford *et al.*, 2010).

Flux estimates have also been made for some common VOCs measured at 80 m elevation in Manchester by disjunct eddy covariance and PTR-MS (proton transfer reaction mass spectrometry). Fluxes of oxygenated VOCs were highest on average, ranging between $0.15 \text{ mg m}^{-2} \text{ h}^{-1}$ and $1 \text{ mg m}^{-2} \text{ h}^{-1}$; the fluxes of aromatic compounds were lower, between $0.12 \text{ mg m}^{-2} \text{ h}^{-1}$ and $0.28 \text{ mg m}^{-2} \text{ h}^{-1}$ (Langford *et al.*, 2009). The observed fluxes were up-scaled to give annual emission estimates to compare with estimates from NAEI for the same flux footprint (radius of footprint for 80% flux under average friction velocity was 1.62 km) (Figure 20). Fluxes of toluene and benzene compared most closely, differing by approximately 50% from the annual average predicted by the NAEI, while the oxygenated VOC fluxes were found to be larger by 3.6 (methanol), 4.7 (acetone) and 6.3 (acetaldehyde) times. This suggests the NAEI is accurately characterising the sources of aromatic compounds, whose emission is dominated by a single source, in this case road transport, but performs less well for the oxygenated VOCs whose emissions may be dominated by numerous diffuse sources. In such instances direct top-down flux measurements may provide a more robust approach.

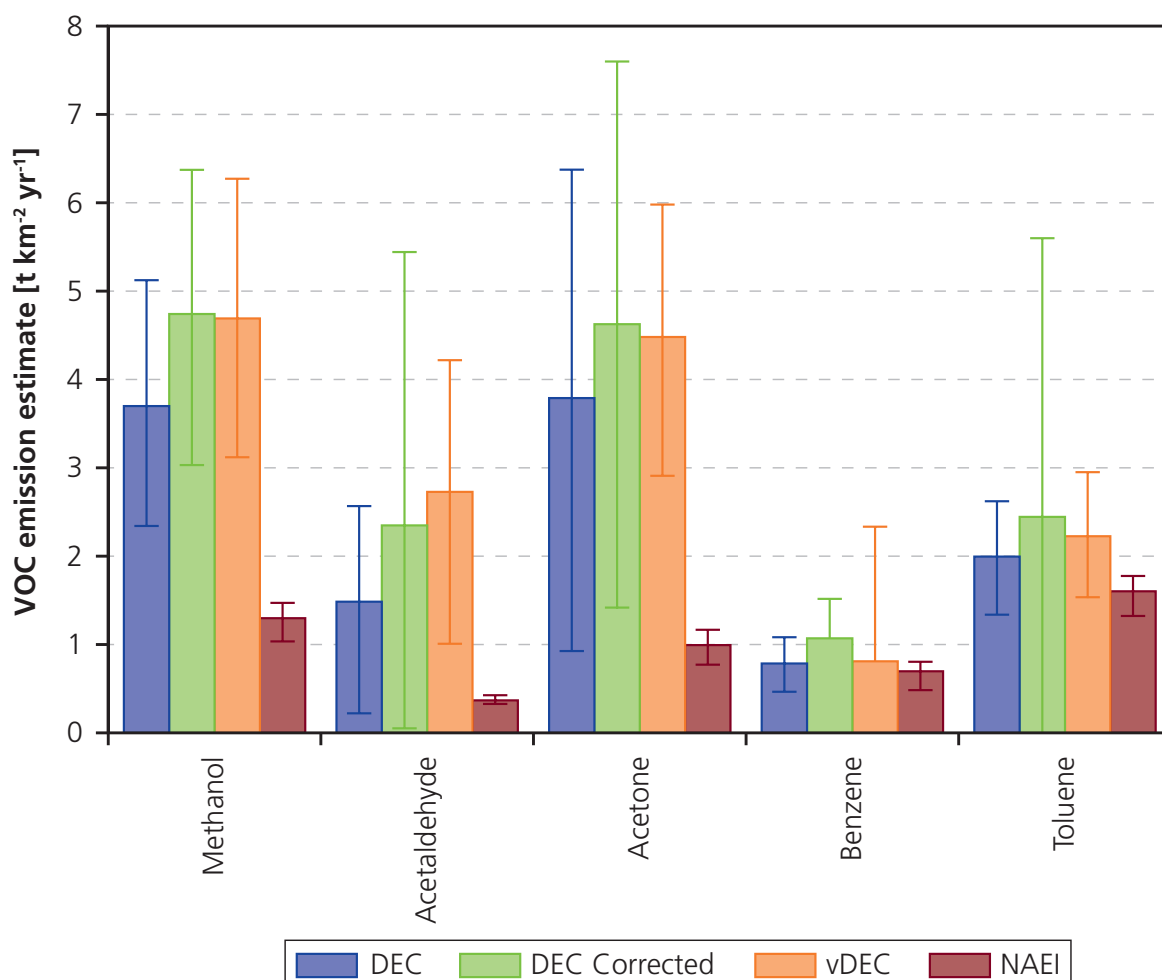


Figure 20: Comparison of annual emissions of individual VOCs in Manchester from up-scaled eddy covariance measurements and NAEI estimates. The uncertainties on the eddy covariance data are based on the standard error of the flux measurements (Langford *et al.*, 2009).

In addition, the Centre for Ecology & Hydrology (CEH) has started long-term (two year) measurements of fluxes of CO₂, CO, methane (CH₄), NO, NO₂ and O₃ on the BT Tower (Nemitz, E., personal communication). These measurements will offer the opportunity to provide estimates of emission rates for a wider range of species for comparison with emission inventories. In the context of recent evidence concerning emissions of NO_x the measurements should prove to be valuable.

7.3 Particles

Owing to the requirement for very fast sampling, the first eddy correlation particle flux measurements were of particle number (which is dominated by the ultra fine particle, UFP, fraction) (Dorsey *et al.*, 2002). UFP vertical fluxes over four European cities (including Edinburgh, Manchester and London in the UK) show clear diurnal trends linked to traffic activity and local sources, with wind sector analysis also showing UFP flux contribution from local, heavily urbanised areas (Martin *et al.*, 2009). Fluxes were parameterised by a simple model including traffic activity, sensible heat and friction velocity above the city – see discussion later in this section. Size-resolved particle number fluxes have also been measured, for example in London in the REPARTEE campaigns, also discussed further later in this section.

Eddy covariance measurement of particle chemical components was first reported by Nemitz *et al.* (2008) over an urban environment in Boulder, USA, using the Aerodyne quadrupole aerosol mass spectrometer which quantifies non-refractory components of the sub-micron (PM₁) particle ensemble (ammonium, sulphate, nitrate (NO₃⁻) and different classes of organic compounds). The authors were able to demonstrate diurnal, presumably traffic-related, patterns in the emissions of hydrocarbon-like organic aerosol (HOA), identified as primary emissions and nitrate, with indication of fast production of moderately oxygenated organic aerosol (OOA) below the measurement height of 45 m, averaging about 15% of HOA emission. The average emission factor for HOA was 0.5 g (kg fuel)⁻¹, similar to those found in previous studies. For NO₃⁻, an emission factor of 0.09 g (kg fuel)⁻¹ was estimated, implying oxidation of 0.5% of the traffic-derived NO_x below 45 m height. Further improvements on chemically-speciated PM fluxes now derive from the coupling of eddy covariance with the higher resolution time-of-flight aerosol mass spectrometer (Farmer *et al.*, 2011).

Probably the most comprehensive dataset on urban particle fluxes anywhere was obtained during the REgents PARk and Tower Environmental Experiment (REPARTEE) campaigns in London in October 2006 and October-November 2007 (Harrison *et al.*, 2012a). Flux measurements were made near the top of the BT Tower, with the associated advantages and disadvantages described above. Particle number fluxes for particles in the diameter range 0.01-2 µm (measured by a condensation particle counter, CPC) showed strong diurnal cycles peaking during the day at 14.00h and minima in the early morning at 04.00h. Smaller peak emission fluxes were observed at 11.00h and between 13.00h and 14.00h; further support for the dominance of traffic sources comes from analyses of data according to wind sector. The following multi-regression emission model was derived,

$$f_p = C[(EF_{\text{friction}}u^*) + (EF_{\text{heat}}H)] + (EF_{\text{traffic}}TA) - f_0$$

where f_p is the predicted number flux (# cm⁻² s⁻¹), $EF_{\text{traffic/friction/heat}}$ are the factors associated with traffic activity (TA), friction velocity (u^*) and sensible heat (H), respectively, C is a dimensionless coefficient and f_0 a compensation or sink term whose sign may vary depending on the urban surface type as well as the source or sink density within the footprint (Harrison *et al.*, 2012a). The $EF_{\text{traffic}}TA$ term is the source term due predominantly to anthropogenic activity as described through the proxy of traffic activity, whereas the $EF_{\text{friction}}u^*$ term describes the turbulent transport of particles to the measurement height. The sensible heat flux term $EF_{\text{heat}}H$ describes the coupling between particle emission and boundary layer transport due to convection but this contribution was significantly weaker than that due to turbulent transport. A limitation in this analysis is that non-traffic UFP emissions are not separately segregated. Also, the coefficients need to be determined experimentally. However, those for London were found to be similar to those from other UK cities (Martin *et al.*, 2009), and explained more than 90% of the observed variance in UFP flux, suggesting that simple model parameterisations of emission based on flux analyses perform well over urban surfaces. The UFP flux was also well correlated with fluxes of CO and CO₂ which are tracers of combustion.

Size-resolved particle number fluxes were also measured during REPARTEE. Particle number fluxes were dominated by particles <0.2 µm. Comparing fluxes determined using the ultra high sensitivity aerosol spectrometer and the CPC showed that, on average, 61% of the particle flux was in the size range 10-50 nm, although this

proportion varied considerably from about 10% to nearly 100% (Harrison *et al.*, 2012a). Mass and surface area particle fluxes were bimodal with contributions from modes centred around 100 nm and 400 nm. The observation of accumulation mode emissions in these London data may reflect the formation of secondary organic aerosol between the surface and the measurement height of 190 m.

Fluxes of non-refractory components of PM₁ were measured via disjunct eddy correlation with both Q-AMS (quadrupole aerosol mass spectrometer) and ToF-AMS (time of flight aerosol mass spectrometer). The measured fluxes were dominated by the organic component. Fluxes of OOA were small and bidirectional, but fluxes of HOA showed clear diurnal cycles with an average emission of 136 ng m⁻² s⁻¹ and midday values up to 600 ng m⁻² s⁻¹. Comparison of the HOA and estimated sub-micron particle mass flux (from the size resolved particle counts) confirmed that HOA accounted for the bulk of the sub-micron mass flux (Harrison *et al.*, 2012a). The HOA flux lagged the CO flux somewhat with an HOA/CO ratio peak in the evening, indicating a change in the source over the day, with a new source in the evening. It is suggested that this is a cooking source of organic aerosol, which is consistent with diurnal trends in concentrations of a cooking organic aerosol source measured at ground level and the lack of a quantitative link between HOA and CO in multi-linear regression (Allan *et al.*, 2010). Fluxes of sulphate (SO₄²⁻) were near zero, which is consistent with measurements above other cities in the developed world and suggests there are no significant sources of sub-micron SO₄²⁻ in the urban environment (Harrison *et al.*, 2012a). Fluxes of sub-micron nitrate (NO₃⁻) were more variable. The variability likely reflects varying contributions from ammonium nitrate (NH₄NO₃) formation at roadside and efficient deposition in urban parks (via NH₃ and nitric acid, HNO₃).

The above measurements demonstrate the utility of elevated particle flux measurements to provide data for chemically-resolved particle emissions.

Eddy covariance and aerodynamic gradient methods have also been applied to measure fluxes of particle number, size distribution and composition over non-urban terrain such as heathland (Nemitz *et al.*, 2004) and tropical rainforest (Whitehead *et al.*, 2010). These studies reveal complex behaviour in particle vertical dynamics in these environments related to changes in gas-particle partitioning (e.g. between NH₃, HNO₃ and NH₄NO₃) and associated deposition to vegetation (Nemitz *et al.*, 2004), and to the transport of particles through the canopy and the coupling between canopy space and above-canopy air through sporadic large-scale turbulent ventilation events (Whitehead *et al.*, 2010).

7.4 Aircraft-based measurements

7.4.1 Vertical flux measurements

Tower-based methods of VOC flux measurement are limited to relatively small footprints. One approach to widen the footprint to landscape or city scales is to use a mobile platform for flux measurements. Mobile platforms can be in the form of a movable tower (Moore *et al.*, 2009) or an aircraft. Airborne flux measurements offer the possibility of obtaining large-scale (city and regional) flux estimates, but at the spatial and temporal resolution necessary for understanding ground-level pollutant formation and exposure. Applications of airborne eddy covariance (AEC) have been rather few to date, due to the stringent sampling technology requirements (the method requires a data rate of ~5-10 Hz) and the availability of suitable turbulence

probes on aircraft. However, recent advances in sensor technology now begin to make AEC possible for ozone precursors such as NO_x and VOCs, as well as for more easily measured scalars such as carbon dioxide (CO₂) and water vapour. An existing NERC research project is trialling this approach in the UK with support from Defra for city-scale NO_x flux estimates.

One conceptual difference between AEC and ground-based eddy covariance is that, with AEC, the flux calculation is performed in a spatial, rather than a time, domain, based on Taylor's hypothesis of frozen turbulence (i.e. the spatial scale of turbulent motion can be accurately captured if the speed of the aircraft is much faster than motions related to turbulence) (Taylor, 1938). The mathematical foundation for AEC has been extensively reviewed (e.g. Lenschow *et al.*, 1994). To date AEC measurements of ozone (Mauder *et al.*, 2007), dimethyl sulfide (Faloona *et al.*, 2005) and VOCs (Karl *et al.*, 2009b, over Mexico City) have been reported, but the method has not yet been demonstrated for NO_x.

AEC methods are reliant on suitably fast responding instrumentation, and at present this means the only approach is through PTR-MS (proton transfer reaction mass spectrometry). This captures only a subset of the total VOC emissions from anthropogenic sources, and so alternative, more chemically comprehensive methods are also required.

7.4.2 Mass balance measurements

Aircraft also offer a means to determine large-scale emissions via a mass balance approach. Given an approximately closed-loop flight track of an aircraft, a uniform boundary layer and no vertical exchange of compound, the horizontal flux of compound out of an area can be calculated by adding up the components of the observed pollutant mass fluxes perpendicular to the path of the aircraft, i.e. by calculating the flux out of the closed loop at each stage around that loop:

$$F = \int C(x) (v(x) \cdot \hat{V}(x)) Z(x) dx$$

where F is the flux in kg s⁻¹, $C(x)$ is the concentration of the compound in kg m⁻³ at position x (m) along the loop, v is the horizontal wind vector (m s⁻¹) at position x along the loop, V is the aircraft horizontal flight vector (m s⁻¹) at position x along the loop, Z is the boundary layer height (m) at position x along the loop, $\hat{\cdot}$ represents the unit normal operator, and \cdot is the dot product operator.

As $\hat{V}(x)$ represents a unit vector in the horizontal perpendicular to the path of the aircraft (i.e. a vector pointing out of the loop around the measurement location), $v(x) \cdot \hat{V}(x)$ represents the magnitude of the component of the horizontal wind out of that loop. By multiplying this flow out of the loop by the concentration and the boundary layer height, and integrating over the closed loop, the total flux out of the loop is derived. Other than the boundary layer height, all these parameters can be directly observed. An example of such an approach (Figure 21) for estimating speciated VOC emissions is given in Hopkins *et al.* (2009) for the city of Lagos.

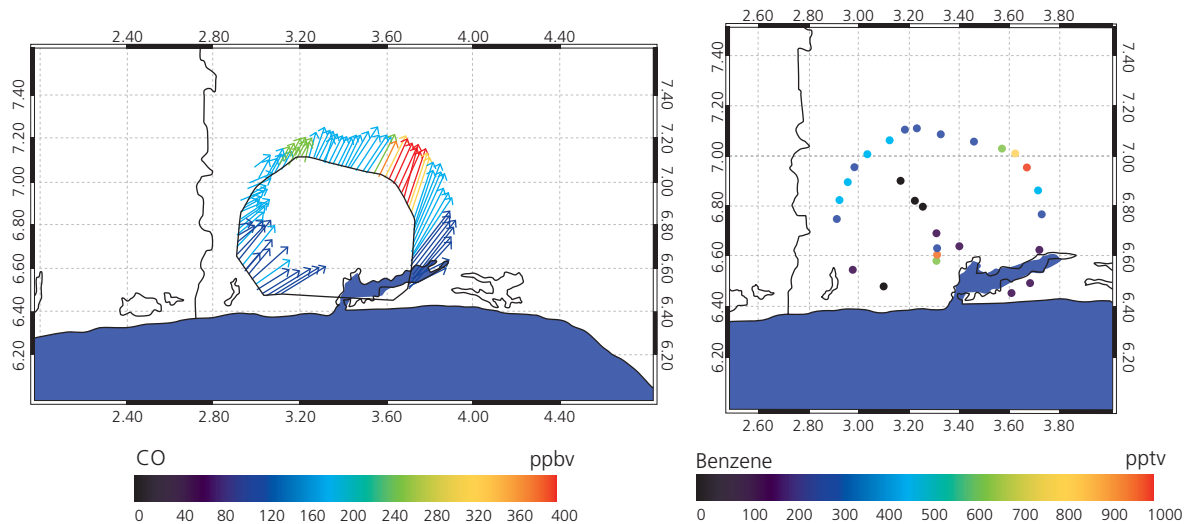


Figure 21: Example of ‘closed loop’ measurements from flights downwind of Lagos (Hopkins *et al.*, 2009).

Whilst conceptually simple, this is a difficult approach to use experimentally, since it relies ideally on a close to zero VOC concentration inflow, a boundary layer not changing in time, and the ability to keep an aircraft within that boundary layer for the full circuit. This has been attempted around London, but practical issues such as air traffic permissions have resulted in only a limited number of successful demonstrations, and it has yet to yield a London VOC emissions estimate.

McMeeking *et al.* (2012) reported results from ground-based and airborne measurements of gases and particles entering and leaving the periphery of London in June 2009. Sub-micron aerosol composition was dominated by secondary species including sulphate (24% of sub-micron mass in the London plume and 29% in the non-plume regional aerosol), nitrate (24% plume; 20% regional) and organic aerosol (29% plume; 31% regional). The primary sub-micron aerosol emissions from London were minor compared to the larger regional background, with only limited increases in aerosol mass in the urban plume compared to the background (similar to 12% mass increase on average). Black carbon mass was the major exception and more than doubled in the urban plume.

7.5 Space-based methods

The measurement of distributions and quantities of trace constituents in the troposphere using satellite instruments that typically orbit some 800 km above the earth in space is a discipline that has really only been developed recently. The challenge initially was to retrieve with accuracy a tropospheric column of the target species (see Figure 22); since this has been achieved, the focus has been using these as quantitative data in air quality applications. The main chemical species measurable from satellite remote sensing in the lower troposphere that are of relevance to air quality are nitrogen dioxide, sulphur dioxide, carbon monoxide and aerosols (via the measurement of aerosol optical depth) (Monks and Bierle, 2011).

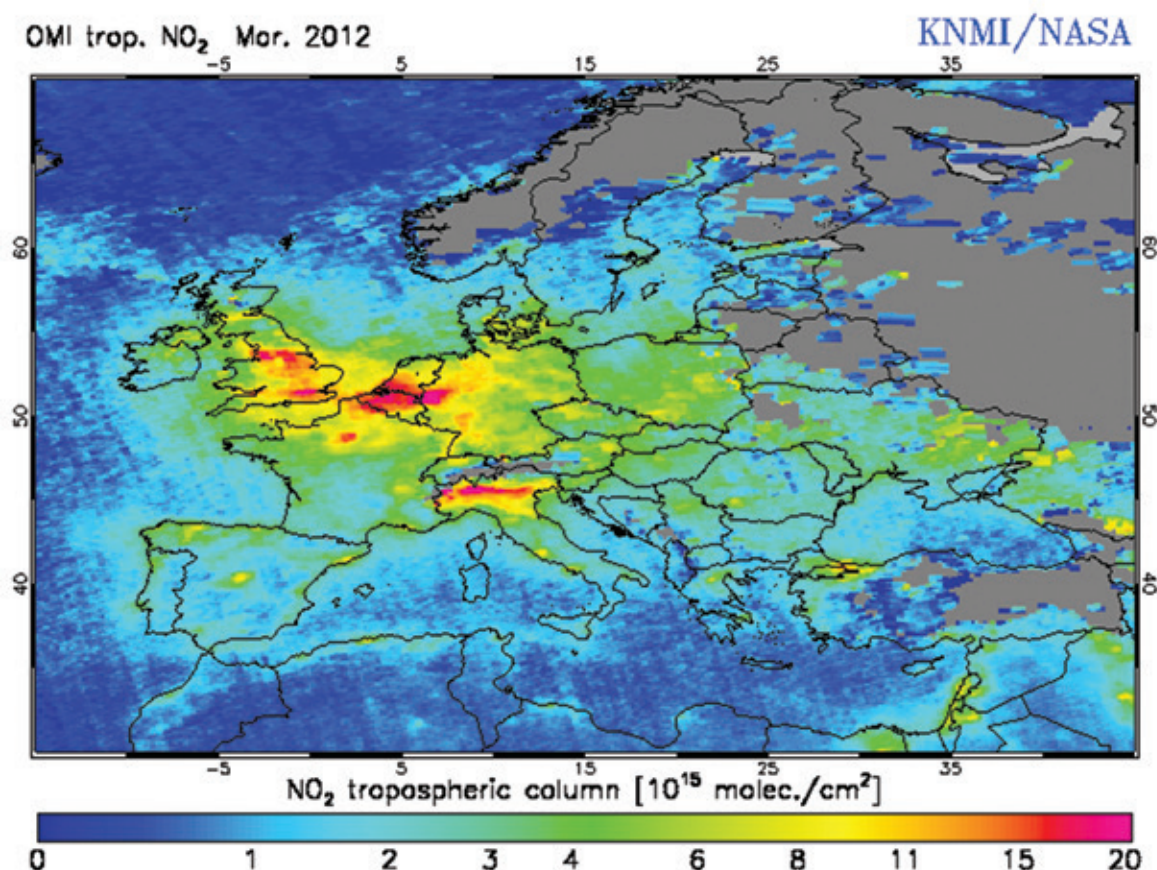


Figure 22: Monthly mean tropospheric NO₂ column from the OMI satellite (Monks and Bierle, 2011).

Much of the air quality work has focused on the exploitation of nitrogen dioxide from space-based measurements, where high quality records go back to 1996 with the launch of GOME (the Global Ozone Monitoring Experiment) (Burrows *et al.*, 1999). There have been comparisons of tropospheric NO₂ measurements with ground sites, as well as data being used to quantify NO₂ emissions from soil, shipping, power plants and lightning (Monks and Bierle, 2011). The length and quality of space-based NO₂ records have allowed observations of trends. Trends in tropospheric column densities of NO₂ can highlight the effectiveness of abatement as well as the accuracy of emission inventories. For example, there has been particular interest in the NO₂ trend over the developing countries in eastern Asia and in particular China (Richter *et al.*, 2005; Lamsal *et al.*, 2011). Richter *et al.* (2005) showed that there had been a 50% increase in emissions of NO₂ over China in the period 1996-2004. There has been a plethora of studies that use satellite data in combination with other data sources and models to constrain emission budgets.

Some of the most effective techniques, in terms of quantification and relationship to emission inventories, are often based around inverse modelling. Inverse modelling uses observational data as constraints to emission parameters, which are used as input for an atmospheric model. The method implicitly assumes that the model comprises an adequate description of the chemical and physical processes which determine the amount and distribution of the species in the atmosphere. NO₂ is an ideal species for formal inversion modelling, as the satellite data products are

abundant and the relationship between the NO₂ columns derived from satellite measurement and emissions is direct and easy to interpret because NO_x emissions are the major driver of variability on the columns. One of the more common approaches used is a Bayesian inverse modelling approach (Martin *et al.*, 2003; Konovalov *et al.*, 2006; 2008). These techniques perform a probabilistic combination of top-down and bottom-up approaches and emission estimates provide in some cases a global or regional NO₂ emission inventory constrained by the satellite measurements. These are often claimed to be more accurate than bottom-up inventories. Figure 23 and Figure 24 show some typical results. In Figure 23, long-term satellite measurements of nitrogen dioxide in the troposphere (in orange) are used in combination with a continental-scale air quality model (EMEP, in blue and green) in order to verify and improve available estimates of multi-annual changes of emissions of nitrogen oxides. In the UK they have been compared with the Automatic Urban and Rural Network (AURN) (Konovalov *et al.*, 2008). Figure 24 shows similar techniques at the city scale (London), where good quantitative agreement is found between the linear trends in the simulated and measured near surface NO_x concentrations.

Inversion techniques have been expanded beyond NO₂ to other air pollutants such as CO (Muller and Stavrakou, 2005) and methane (Bergamaschi *et al.*, 2009; Bloom *et al.*, 2010).

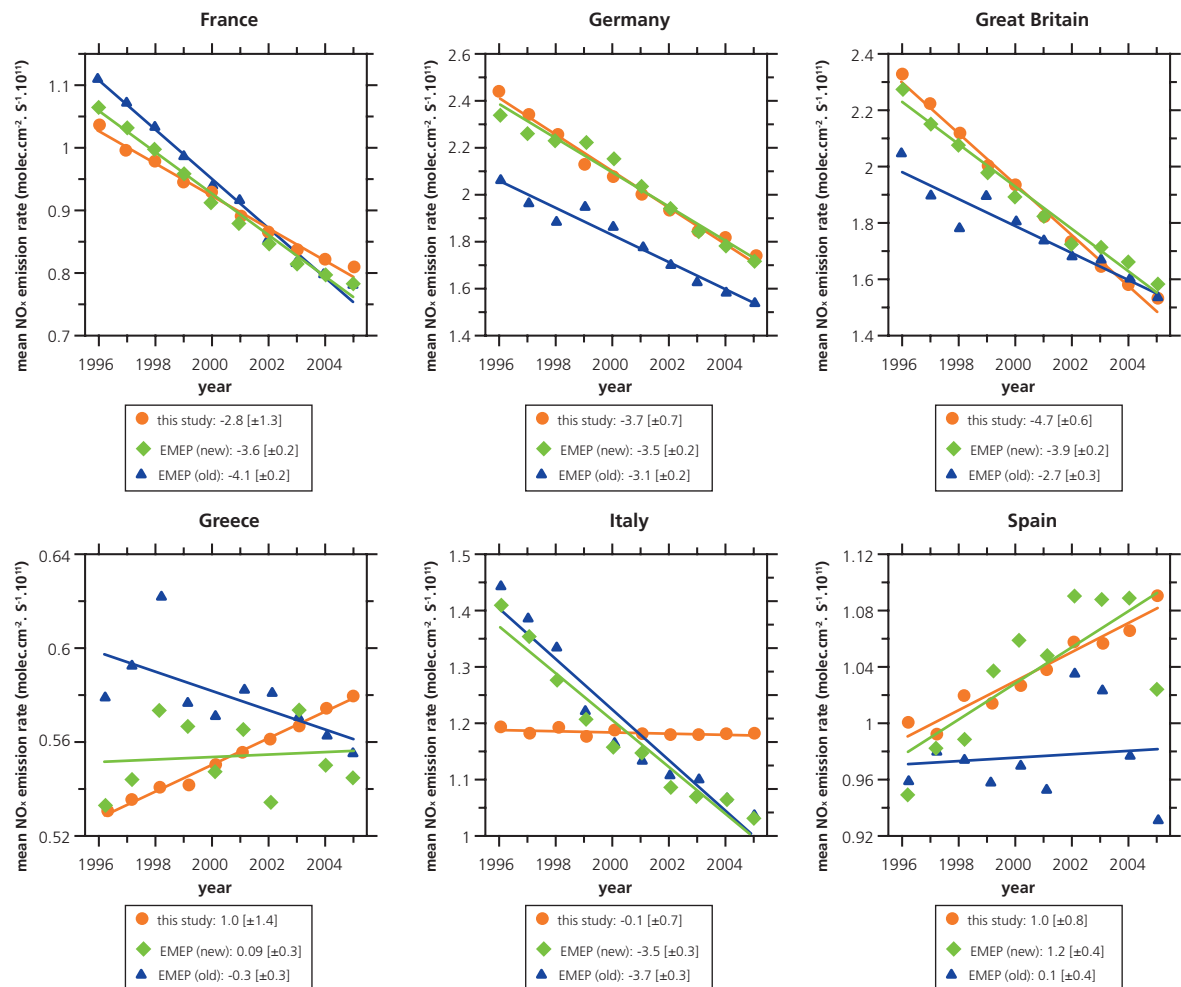


Figure 23: Comparison of satellite-derived NO_x emission trends versus EMEP emission inventories (Konovalov *et al.*, 2008).

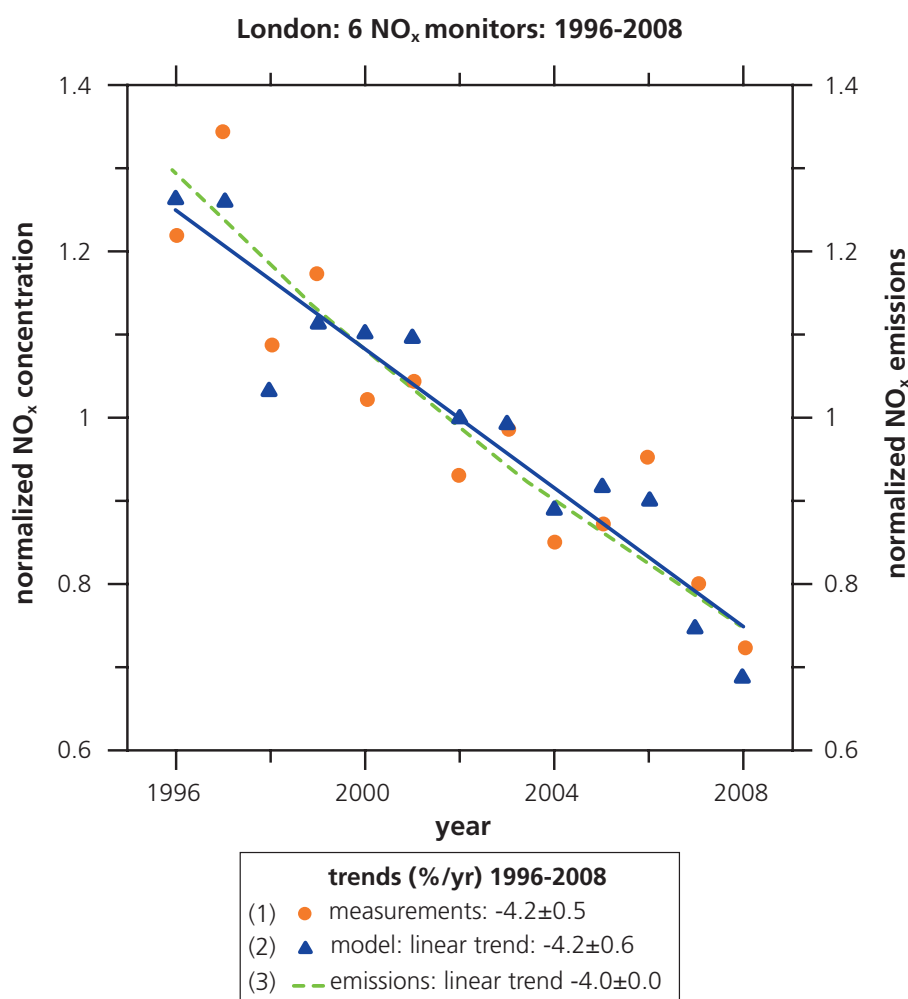


Figure 24: Comparison of (1) air quality monitoring data in London with (2) simulations based on the relative linear trend in NO_x emissions. The trend estimated as an exponential fit to emission estimates derived from satellite data is also shown (3). The range of uncertainties reported along with values of trends is estimated as the standard deviation of the slope of the linear fit (Konovalov *et al.*, 2010).

7.6 Summary points

7.6.1 Strengths

- An advantage of flux measurements over many alternative methods is that they provide a means of estimating absolute source strength, as opposed to pollutant ratios, which can then be compared directly with emission inventories totals.
- Depending on the time resolution of the data averaging, flux measurements provide temporal information on diurnal and day of week changes in emissions that can provide insight into the nature of the sources; for example, they can be associated with specific activity patterns such as traffic movements and fleet make-up, and meteorological variables such as temperature, wind speed and boundary layer stability.
- Universality – a wide variety of gas and particle components can now be measured by these flux approaches.

7.6.2 Weaknesses

- Quantitative interpretation of the vertical fluxes requires the assumption of homogeneity of emissions from the ‘footprint’ area at the surface to which the measurement height is sensitive. The footprint area increases with horizontal wind speeds. On the other hand, vertical flux measurements have large uncertainty at very low wind speeds (e.g. at night or during stagnant episodes).
- Whilst the integrated nature of the flux measurement over the footprint can be an advantage, it can also be a weakness where the surface has multiple sources, because there is no direct link between fluxes and individual sources.
- For reactive species, the flux measured at elevation may not be the true surface flux because of loss or gain of the species on the few seconds time scale between emission and transport to the measurement height.
- Measurement heights of a few 100 m (e.g. tops of tall towers) may sometimes be above the boundary layer and therefore meteorologically decoupled from the surface.

7.6.3 Conclusions and recommendations

- Tower (and aircraft) based measurements of vertical fluxes are now coming into their own with the development of gas and particle analytical instrumentation with the required high frequency of sampling and reliability for unattended operation, and have the potential to provide new estimates of emission source strengths for use in inventory development.
- A wide range of gas and particle components can now be measured; most of the particle flux measurements are of particle components for which there are no existing traditional inventories. For other species, these flux measurements provide an independent comparison.
- Fluxes are derived with high time resolution, typically hourly or better, which can provide considerable insight into the nature of the underlying sources.
- Although these flux measurements are becoming more routine, investment in infrastructure would be required to provide data from more than just a few campaigns, i.e. for data over the long term and at more than an isolated site.

7.6.4 Linkage with emission inventories

- Flux measurements are very useful for assessing the quantitative accuracy of emission rates implied by an inventory over a period of time and in a specific area.
- Flux measurements have the advantage over many other methods of providing a direct, absolute measure of emissions that can (and have) been compared with emission inventory estimates. However, the method of comparison is not straightforward because estimating the source footprint and understanding specific sources contributing to the fluxes is difficult.

- It may not be possible to pinpoint the accuracy of emission inventories for a specific source, although analysis of temporal behaviour may help with this. It does not allow the inventory compiler to know what part of the inventory might be “wrong” and needs changing, for example, whether the problem is with an emission factor, the activity rates or the way they are parameterised. This is important because otherwise the inventory compiler does not know how transferable the findings are to other areas, e.g. if the problem is with an emission factor rather than an activity rate.
- The technique may be best used to indicate where the emission inventory has omissions, for example from natural sources, or where it is making gross overestimates. The technique could also provide useful information on the temporal variability in emissions of different pollutants, e.g. diurnal or day of week variations.
- This information is difficult to quantify and flux measurements could at least be used to verify whether temporal profiles provided with inventories are valid.

8 Analyses of speciated NMVOC and particulate matter composition data

8.1 Analyses of network NMVOC data and inventory evaluation

8.1.1 Introduction

The majority of pollutants considered in the NAEI consist of single species (e.g. CO) or very simple mixtures of species (e.g. NO_x). In contrast, non-methane volatile organic compound (NMVOC) emissions are made up of highly detailed speciations of individual compounds that are emitted from a large number of different sources within a number of broad source sectors (e.g. solvents and other product use, extraction and distribution of fossil fuels, transport, etc.). The NAEI currently defines 111 species profiles representative of different sets of sources (Passant, 2002), which result in a full speciation which contains 664 NMVOC species emitted from 295 anthropogenic sources. The NMVOC species considered come from a variety of classes of organic compound, including hydrocarbons (e.g. alkanes, alkenes and aromatics), oxygenates (e.g. alcohols, esters, aldehydes and ketones) and halogenated species (e.g. chlorocarbons). It should be noted that the air quality strategy pollutants benzene and 1,3-butadiene are also component NMVOCs.

Due to the highly detailed speciation of NMVOC emissions, ambient measurements inevitably cover only specific compounds or specific subsets of compounds. Since 1993, routine monitoring of NMVOCs in the UK has been carried out via Defra's Automatic Hydrocarbon Network, using automated gas chromatography with flame ionisation detection (e.g. Derwent *et al.*, 2000; Dollard *et al.*, 2007). Over the period 1993-2004, hourly measurements of up to 31 light hydrocarbons (C₂-C₈, including benzene and 1,3-butadiene) were made at 11 urban background sites, one kerbside site and one rural site (Dollard *et al.*, 2007). In more recent years, measurements have been made at a more limited number of locations, and are currently taken at four sites, namely Auchencorth Moss, Midlothian (rural), Harwell, Oxfordshire (rural), London Eltham (urban background) and London Marylebone Road (kerbside). Although the 31 monitored hydrocarbons are only a small subset of the 664 species identified in the inventory speciation, they include several species that are among the most abundant, including seven of the top ten entries. As a result, these 31 compounds represent an average of about 45% (by mass) of emitted anthropogenic NMVOCs, based on their collective contribution to the UK total in 2002. The Automatic Hydrocarbon Network data, and similar speciated measurements conducted elsewhere, therefore provide the potential for elucidating information about NMVOC sources and evaluating NMVOC emission inventories.

Although classed as a single pollutant (on the basis of their collective atmospheric role as ozone precursors), the individual NMVOC components cover a very large range in reactivity, such that their speciation changes as the air mass ages. Considering only the C₂-C₈ light hydrocarbons that are routinely measured (e.g. Dollard *et al.*, 2007), typical (average) atmospheric lifetimes vary from about 3 hours for the most reactive alkene (isoprene) to about 50 days for the least reactive alkane (ethane). For a single well-defined source, therefore, the differential depletion rates of the hydrocarbons allow the relative concentrations of two or more species to be used as an indicator of air mass age (e.g. Blake *et al.*, 1993).

Because an individual source profile essentially provides a “fingerprint” for that source, speciated hydrocarbon data at a given location can potentially be used to quantify contributions from different sources, provided the measurements are precise and the source profiles are well defined and reproducible. The effect of air mass ageing on the source profiles (as indicated above) may also need to be factored into the analysis, and the longer-lived hydrocarbons may have residual background contributions from remote (e.g. transboundary) sources. Reported analyses of hydrocarbon data have derived source information using concentration ratios of hydrocarbons (Derwent *et al.*, 2000) or statistical methods such as principal component analysis, positive matrix factorisation and chemical mass balance modelling (e.g. Borbon *et al.*, 2003; Badol *et al.*, 2008; Gaimoz *et al.*, 2011; Morino *et al.*, 2011; Niedojadlo *et al.*, 2012).

It should be noted that some of the monitored hydrocarbons are also emitted from biogenic sources, which are not considered in detail by the NAEI, but which can make important contributions to the ambient measurements. In particular, biogenic emissions have been shown to make an increasingly dominant contribution to the measured concentrations of isoprene in a number of analyses of UK Automatic Hydrocarbon Network data (AQEG, 2007; 2009; von Schneidemesser *et al.*, 2011), and are particularly important at the elevated temperatures characteristic of photochemical ozone episodes (e.g. Lee *et al.*, 2006; Murrells *et al.*, 2012). The emission of other reactive light alkenes (specifically propene and butenes) from biogenic sources has also been reported (Klemp *et al.*, 1997). Other NMVOC species that are estimated to have significant biogenic inputs, most notably monoterpenes, for which the reported UK emissions are several times larger than that for isoprene (NATAIR, 2007; AQEG, 2009; Karl *et al.*, 2009a) are currently not monitored routinely in the UK.

8.1.2 Existing analyses of UK data

Correlation and trend analyses

A number of analyses of UK Automatic Hydrocarbon Network data have been carried out. Derwent *et al.* (2000) considered 1996 data from 11 urban background sites and one rural site, and used correlation plots to determine relative source strengths for each of the measured hydrocarbons. The results were consistent with the measurements being dominated by road transport sources, with the measured speciation providing broad support for the corresponding source profiles used in the NAEI. Evidence was also found for intermittent sources related to petrol evaporation from refilling operations at petrol stations and petrol distribution depots, and at sites close to oil refineries and petrochemical industries.

Dollard *et al.* (2007) carried out an analysis of hydrocarbon data monitored for varying subsets of the period 1993-2004 at 11 urban background sites, one rural site and one kerbside site. The results demonstrate significant and sustained reductions in the concentrations of the majority of hydrocarbons over this period, typically at rates between about 15% and 25% per year. These reductions are compatible with the decline in NMVOC emissions from road transport sources over the same period as represented in the NAEI, and again demonstrate a dominance of road transport sources in the measured data. The concentrations of ethane and propane displayed weaker downward trends, consistent with natural gas leakage being the dominant source for ethane and a major contributor (along with road transport emissions) for propane.

Modelling analysis

A preliminary analysis has recently been performed using an idealised, multi-layer column model to simulate oxidant formation over the London conurbation under photochemical episode conditions, in relation to observations over the period 1999-2006 (Murrells *et al.*, 2012). Simulation of the conditions of an episode on the 30th July 1999 also allowed comparison of simulated hydrocarbon levels with those measured at the Automatic Hydrocarbon Network sites at Marylebone Road, Bloomsbury (UCL) and Eltham. The model received speciated NMVOC emissions at spatially-averaged rates based on the totals reported for 1999 by the LAEI and the area covered by the inventory. The NMVOC speciation was based on the NAEI (Passant, 2002) for the distribution of component sources, as reported by the LAEI, which was dominated by about equal contributions from solvent usage (40.5%) and road transport (39.3%). The emissions were processed using the Common Representative Intermediates mechanism (CRI v2.1, see <http://mcm.leeds.ac.uk/CRI/>), the performance of which was initially validated against that of the Master Chemical Mechanism (MCM v3.2, see <http://mcm.leeds.ac.uk/MCM/>) in a single-layer version of the model.

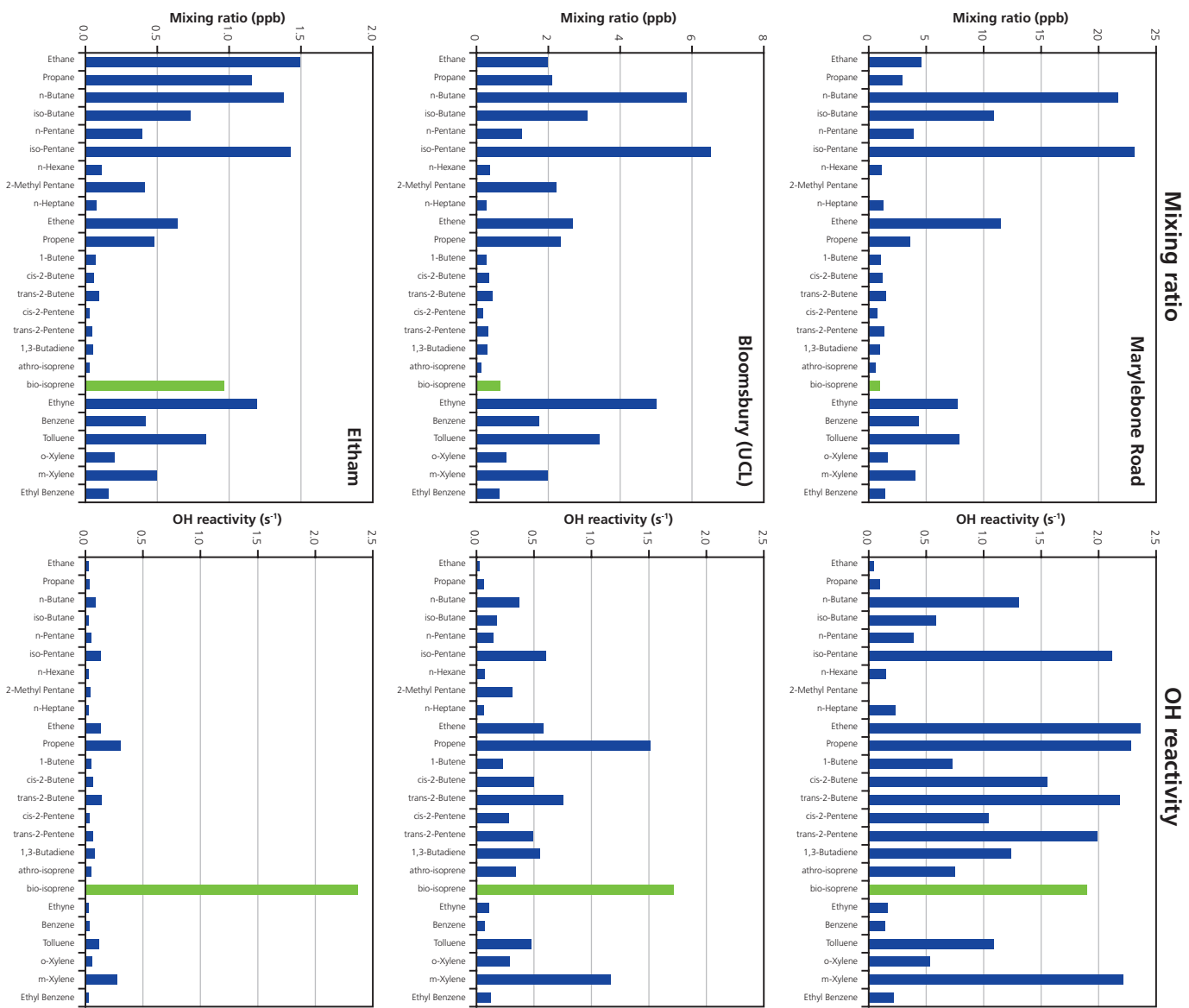


Figure 25: Observational data for 24 hydrocarbons at London sites on the afternoon of 30th July 1999, based on the average of data over the period 12:00-18:00h. Note that isoprene is divided into anthropogenic and biogenic contributions (biogenic in green), using 1,3-butadiene as a marker for the anthropogenic contribution, based on the method described in AQEG (2009).

The measured data from the three sites demonstrate a wide range of conditions reflecting the proximity of primary pollution sources (Figure 25). The collective hydroxyl (OH) radical reactivity of the measured anthropogenic hydrocarbon set therefore logically falls from 23.2 s⁻¹ at Marylebone Road (a central London kerbside site) to 9.0 s⁻¹ at Bloomsbury UCL (a central London background location) and to 1.8 s⁻¹ at Eltham (a suburban background site towards the east of the Greater London conurbation). The total OH reactivity of the simulated anthropogenic hydrocarbon set in the lowest model layer (2.1 s⁻¹) is similar to that observed at Eltham, suggesting that the conditions at this site might be the most representative of the average over the London conurbation.

Figure 26 compares the contributions of the main hydrocarbon classes to the measured and simulated anthropogenic speciations, again in terms of their collective reactivity with OH radicals. Although a small trend is apparent in the measured data, the speciation is consistent with the dominance of the road transport source at all sites, in agreement with the results of Derwent *et al.* (2000) and Dollard *et al.* (2007). In contrast, the simulated data reflect the approximately equal contributions of road transport and solvent use to the hydrocarbon speciation, leading to a higher contribution from the alkanes and a lower contribution from the alkenes.

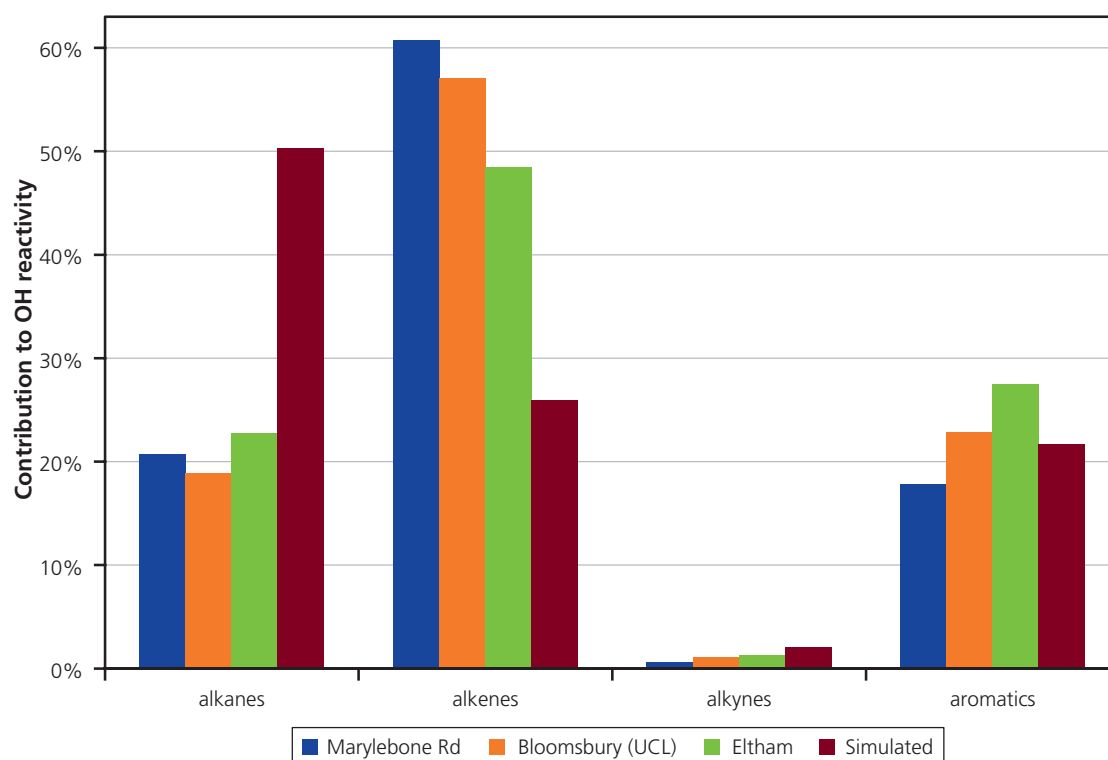


Figure 26: Comparison of the contributions of VOC classes to the observed anthropogenic speciation (in terms of OH reactivities) on the afternoon of 30th July 1999, with that simulated in the lowest layer of the multi-layer model (analysis carried out for this report).

Figure 25 also shows that the mixing ratio of biogenic isoprene is comparable at the three London sites (approaching 1 ppb), consistent with a diffuse background vegetation source. This results in an associated OH reactivity of about 2 s^{-1} , which should be broadly indicative of the average reactivity of biogenic isoprene near the surface over Greater London. This suggests that the impact of biogenic isoprene on oxidant formation under the high temperature conditions of an ozone episode is potentially comparable to the collective impact of all the other measured hydrocarbons, for conditions averaged over the London conurbation on 30th July 1999. Taking account of the likely stronger vertical profiles of reactive hydrocarbons such as isoprene, Murrells *et al.* (2012) estimated the boundary layer average impact of biogenic isoprene on oxidant formation to be about 40% of that of all the measured anthropogenic hydrocarbons.

The trends in NMVOC emissions over the past decade, and the continued decline in road transport emissions, indicate that emissions from both the solvents sector and from biogenic sources, under appropriate conditions, should be relatively more important than in 1999. As indicated above, none of the analyses of UK data clearly reveal contributions from sources in the “solvents and other product use” category, which have accounted for a progressively increasing fraction of the UK emissions (44% of the NAEI total in 2010), as the road transport emissions have declined (9% of the NAEI total in 2010). Likely reasons for this include: (i) the sites are better located to characterise road transport sources (which are relatively well defined spatially and temporally) compared with more diffuse solvent emissions; and (ii) the monitored light hydrocarbon set is estimated to cover only 19% of the aggregated solvent speciation, compared with 65% of the road transport speciation.

8.2 Use of particulate matter composition data

Airborne particulate matter is highly diverse in both size and chemical composition, which provides both challenges and opportunities when using ambient data to inform or to test emission inventories. The challenges arise from the fact that particulate matter has many sources and hence airborne concentrations are made up of contributions from multiple sources; it is only in unusual circumstances that a mass concentration of particulate matter can be attributed to a single source. Examples are road tunnel measurements and twin site studies (roadside and urban background). Even then, multiple sources (exhaust, tyre abrasion, particle resuspension, etc.) contribute, and chemical and size information is needed to distinguish them (Harrison *et al.*, 2012b).

The availability of chemical composition information can provide direct or indirect information about individual sources, therefore allowing emissions inventory data to be tested through the intermediate stage of running a numerical dispersion or chemistry–transport model. For this purpose, ideally a chemical tracer can be found which will be specific to an individual source category for which emissions data are available. There are few such tracers and one of the best examples is levoglucosan. This is an anhydrosugar which comprises a significant (about 10%) proportion of the smoke generated by burning biomass fuels. It has been widely used as a tracer of wood smoke as it is virtually specific to the biomass burning source and fairly stable in the atmosphere; levoglucosan therefore meets the first criteria for a good source tracer. However, it remains highly imperfect as its abundance in wood smoke is heavily dependent upon the type of wood and combustion conditions, including the combustion appliance in use. As such, it provides indicative rather than definitive information on wood smoke concentrations (Harrison *et al.*, 2012c).

Other examples of relatively specific source tracers are the metals barium, antimony and copper which arise predominantly from the wear of brake pads. There will be locations where other sources (e.g. industrial emissions) contribute to concentrations of these elements, but at most urban sites their concentrations are dominated by emissions from automotive brakes. However, since there is considerable diversity in the composition of individual brake pads, there are no agreed data providing a numerical factor to convert tracer element mass to the mass of brake dust particles. Such data need to come from atmospheric measurements and Gietl *et al.* (2010) used a combination of atmospheric measurements and emission factors to estimate the abundance of barium in brake dust. However, without independent information on the abundance of barium in brake dust, the work of Gietl *et al.* (2010) does not provide an independent test of emission inventory data.

The other way in which chemical composition information may be used is through receptor modelling. Receptor modelling uses atmospheric measurement data to infer the quantitative contribution of individual sources to concentrations of airborne particulate matter. Both the chemical mass balance (CMB) and multivariate statistical approaches require multiple measurements of a wide range of components of airborne particulate matter which are then processed to provide estimates of individual source contributions to those chemical components and to particulate matter mass. The CMB approach requires prior knowledge of the composition of emissions from individual sources, but not of the magnitude of those emissions. Consequently, the inferences derived from CMB modelling in terms of, for example, the contribution of diesel vehicle emissions to PM_{2.5} concentrations, can be used to test estimates derived from dispersion modelling approaches. The other generic group of receptor modelling methods referred to as multivariate statistical methods, of which positive matrix factorisation is the most widely used, requires no advanced knowledge of the composition of emissions of contributing sources. These techniques use atmospheric composition data to identify those chemical components which have similar temporal patterns of fluctuation, hence providing a chemical source profile which can be used to infer the source. Subsequent data processing can provide a quantitative estimate of the contribution of that source to the airborne concentrations measured, which again may be used to test inventories through the intermediary of an atmospheric dispersion or chemistry–transport model.

An example of the CMB approach is provided by Yin *et al.* (2010), who applied this approach using organic molecular markers as source tracers to PM_{2.5} sampled in the UK West Midlands. Their work apportioned the mass of carbonaceous aerosol to a range of sources including diesel engines, gasoline engines, smoking engines, natural gas combustion, coal combustion, vegetative detritus, soil dust and meat cooking. There are many examples of the application of multivariate statistical methods (e.g. Mooibroek *et al.*, 2011) which are frequently successful at assigning contributions of sources such as sea salt, crustal matter, secondary sulphates, secondary nitrates, road traffic emissions and emissions from metallurgical industries to their respective sources.

Other specific issues arise with carbonaceous particles; methods have been devised to distinguish between primary and secondary organic carbon, based upon chemical analysis and a radiochemical technique (carbon-14 analysis) to distinguish between contemporary and fossil sources of carbon (e.g. wood burning in the former and coal burning in the latter category). The distinction between primary and secondary organic carbon is typically based upon the elemental carbon tracer method (Castro *et al.*, 1999). This method involves plotting concentrations of organic carbon against

those of elemental carbon and constructing a line through the lowest organic carbon/elemental carbon (OC/EC) ratios. Such low ratios are assumed to arise from occasions when only primary organic carbon is present, and concentrations above that minimum ratio line are assumed to arise from formation of secondary organic carbon in the atmosphere. However, recently Pio *et al.* (2011) have cast doubt on the assumption that circumstances exist where the only organic carbon present is primary and have suggested that true primary OC/EC ratios, at least in locations where the main primary source is road traffic, are in the range of 0.3-0.4, which is well below the minimum values typically seen in atmospheric measurements.

The use of carbon-14 as a tracer depends upon the fact that contemporary carbon contains this radioisotope, but that its presence in fossil carbon is minimal due to decay over many half-lives. The combination of techniques such as the elemental carbon tracer method with measurements of the carbon-14 in different components of carbonaceous particles has been pioneered in Europe by Szidat and co-workers (for example in Szidat *et al.*, 2006), and applied to particulate matter sampling in the UK atmosphere by Heal *et al.* (2011).

8.3 Summary points

8.3.1 Strengths

- A key strength of the measurement and analysis of speciated VOC data or PM composition data is the ability to provide emissions information that would be difficult or impossible to obtain by other means.
- Gas chromatography with flame ionisation detection allows continuous automated monitoring of a set of light hydrocarbons at high temporal resolution.
- Such techniques help to differentiate emissions that are multi-component in nature into categories that can often be aligned with specific sources or activities.

8.3.2 Weaknesses

- It is not always clear how information from compositional studies can be practically implemented in emission inventories.
- Speciated measurements inevitably cover only a subset of the emitted compounds, with variable levels of coverage of compounds emitted from different source sectors.

8.3.3 Conclusions and recommendations

- It would be valuable to use archived and emerging speciated hydrocarbon monitoring data to carry out an extensive evaluation of NMVOC emissions inventory data and source profiles. Where possible, such analyses should make use of the methods and techniques described in earlier sections of this report to establish temporal trends (long-term, seasonal, day of the week and diurnal) for each of the monitored hydrocarbons at UK sites. Supplementary measurements of vertical profiles would also be informative.

- Detailed hydrocarbon speciation lends itself to the application of statistical methods such as principal component analysis, positive matrix factorisation and chemical mass balance modelling, as has been reported for analyses of light hydrocarbon data at sites outside the UK. In conjunction with ancillary data (e.g. temperature), such methods can potentially be used to quantify contributions from different NMVOC sources.
- Particular attention should be directed towards using measured data from appropriate locations to help identify and confirm contributions from anthropogenic sectors other than road transport, in particular the “solvents and other product use” category. Although the C₂-C₈ light hydrocarbons that are routinely monitored have some overlap with the source profiles for the solvents sector, measurements of additional NMVOCs making significant source profile contributions (e.g. ethanol and methanol) would be valuable.
- Further assessment of NMVOCs emitted from biogenic sources would be valuable, including studies to help identify and confirm contributions from species other than isoprene. In particular, monoterpenes are typically estimated to account for about 50% of UK biogenic emissions. Confirmation of this would require measurements of monoterpenes collectively, or of the more abundant contributors (e.g. α-pinene, β-pinene, limonene, etc.). It is also noted that evidence for the emission of some reactive light alkenes (specifically propene and butenes) from biogenic sources has been reported at a site in Germany; these hydrocarbons are normally regarded as derived from anthropogenic sources (e.g. road transport). It would therefore be valuable to establish whether or not biogenic sources make any contribution to UK emissions of any of the routinely measured light hydrocarbons other than isoprene.
- Chemical tracers, both elemental and molecular, offer the possibility to quantify airborne concentrations of particulate matter arising from sources which are difficult to capture adequately in emission inventories. Such sources include non-exhaust emissions from road vehicles (brake wear, tyre wear, road surface abrasion and road dust resuspension) and domestic wood burning. Work to date has not been directed at testing emission inventories, but determination of source-related concentrations of particles offers the potential to do so.
- Chemical tracers, including both levoglucosan and fine fraction potassium (corrected for sea salt and soil contributions), are available for the quantification of atmospheric woodsmoke.
- Carbon-14 analysis is a powerful means of distinguishing between contemporary and fossil carbon in airborne particles. It can aid in the separate quantification of particle mass arising from sources such as wood burning and diesel combustion, but suffers from poor knowledge of carbon/total particle mass ratios. It also cannot differentiate between sources of fossil carbon (e.g. diesel exhaust and coal burning), and differentiation of sources of contemporary carbon require assumptions over particle composition.

- Multivariate receptor models such as positive matrix factorisation require extensive multi-element datasets which have not to date been collected in the UK. However, there is a potential for their use in future with the likely ability to give quantitative estimates of particulate matter in the atmosphere arising from sources such as road traffic (exhaust and non-exhaust), wood burning, metallurgical industries, sea salt and soil resuspension. Chemical mass balance models are less demanding of large analytical datasets, and have been applied in the UK giving separate quantification of diesel exhaust, gasoline exhaust, wood smoke, road dust, vegetative detritus, coal smoke and natural gas smoke, and can be extended to cooking particles. Aerosol mass spectrometry is also capable of estimating the contributions of solid fuel combustion, road traffic and cooking to airborne particle mass.
- Source-specific concentrations of airborne particles offer the opportunity to test emission inventories, if those inventories provide data adequately disaggregated in terms of both source type and spatial distribution for use in urban or regional air pollution models. For particle sources which are captured ineffectively in emission inventories, this is recommended as an effective approach to enhancement of knowledge.

8.3.4 Linkage with emission inventories

- The key information provided by these methods relates to speciated source data, which can help differentiate emissions that are multi-component in nature. A potentially important aspect of these measurements and related analyses is that they can provide information on emissions of species that are absent from emission inventories.
- The links with inventories are similar to those discussed in the section on trends in concentrations and ratios of pollutants. Provided the data are analysed and interpreted in appropriate detail, these techniques can provide valuable information to verify the chemical speciation of sources in the inventory and at least indicate whether there are major discrepancies. However, the analysis would need to consider the effect of atmospheric transformation of species and conclusions would depend on how well these processes are understood. Another constraining factor is that the measurements may not cover all the VOC species emitted from a particular source. The links with inventories are therefore not so direct and the techniques are most likely to be used to indicate overall conflicts or consistency with inventories rather than provide the means (such as factors) to develop or correct them.
- Similar to flux measurements, the techniques can be particularly useful for identifying and giving some indication of sources not included in inventories, such as natural sources. The particulate matter compositional data could also provide information on PM speciation lacking in inventories for primary PM sources.

9 Inverse modelling techniques

9.1 Background

Even when compiled using the most detailed approaches, emission inventories derived using bottom-up methods will contain inherent errors and uncertainties. The extent of these errors can be partially evaluated by comparing predicted concentrations from models incorporating the emission inventories with atmospheric measurements. Measurements can also be used to evaluate and further constrain errors in predicted emission profiles using inverse modelling techniques. Inverse modelling encompasses a range of methodologies that combine information from atmospheric measurements with an understanding of where the air has come from (i.e. dispersion processes) to estimate emissions on local to regional scales. The methods can address the question – *how should the emission inventory for a given species be adjusted/estimated to provide the best match between observed and predicted concentrations?* The required degree of adjustment indicates the degree of bias inherent within the bottom-up inventories used (Mulholland and Seinfeld, 1995) and can help to identify systematic errors within bottom-up methodologies. However, uncertainties inherent within both measured data and model parameterisations impact on errors within derived emissions estimates using inverse modelling. For reactive pollutants the parameterisation of reaction or deposition rates adds further sources of uncertainty.

Inverse models have been used on a range of scales from street canyon to urban air shed to regional scales utilising different passive and reactive dispersion models based on semi-empirical (e.g. Gaussian), Lagrangian trajectory and Eulerian grid-based approaches. Studies at the local scale can be used to inform emission factors within the bottom-up approaches used to develop many emissions databases. Regional-scale studies may then be used in order to evaluate and improve national emissions totals and seasonal variations. Within the UK, inverse modelling has principally been used to interpret the high-frequency observations of long-lived greenhouse and ozone-depleting gases at Mace Head on the west coast of Ireland (Manning, 2009), however the application of inverse methods to point sources has also been discussed (Rudd *et al.*, 2012). Internationally, inverse modelling has been used at many scales and hence several international studies are included in this discussion in order to explore the wider potential of the technique.

It should also be noted that use of emission inventories in models can help to identify emission inventory deficiencies because their effect on ambient concentrations can be assessed directly. For example, in the Defra model inter-comparison exercise it is clear that differences in emission inventory assumptions are important when evaluating models against observations and that in many cases erroneous assumptions can be identified (Carslaw *et al.*, 2013).

9.2 Local-scale studies

At the local scale, inverse modelling is commonly used to estimate emissions from single sources or single source types. Applications include the estimation of real world traffic emissions and ammonia sources. Model types range from simple Gaussian to more complex Lagrangian stochastic models.

9.2.1 Traffic emission sources

Ropkins *et al.* (2009) reviewed a range of methods for estimating real world vehicle emissions including inverse modelling. At the simplest level, local-scale inverse models are based on a rearranged version of the Gaussian line source model with emission factors for species n (EF_n) being estimated as a function of the measured roadside increment in concentration $[n]$, the molecular weight of n (mw_{t_n}), traffic flow rates (TFR) and a function F describing the influence of meteorology on the dilution of the emissions:

$$EF_n = \frac{[n] \times mw_{t_n}}{TFR \times F}$$

Usually the roadside increment in concentration is obtained by using measurements from two displaced monitoring sites at background and roadside locations, with F described using a Gaussian dispersion formulation based on average wind speed and dispersion parameters reflecting a specific time average and turbulence conditions. For idealised geometries the Gaussian approach has been extended within models such as OSPM (Ketzel *et al.*, 2003) to include a description of recirculation due to street canyon effects. Such approaches have been used to estimate diurnal variations in average vehicle fleet emission factors for particle concentrations, CO and NO_x (Ketzel *et al.*, 2003; Ghenu *et al.*, 2008) and benzene (Palmgren *et al.*, 1999) using in-street and rooftop measurements to derive the roadside increment in concentrations. Ketzel *et al.* (2003) showed that early morning traffic exhibited per vehicle emissions of CO, NO_x and particle numbers above the daytime averages, with the differences being attributed to factors such as cold start emissions, changes in traffic composition and traffic patterns.

Kawashima *et al.* (2006) applied inverse modelling to the estimation of 34 speciated VOC emissions from traffic on a major national road in Japan using the Gaussian-based Caline 4 model. Two measurement sites located 5 m from either side of the road were used to account for different wind directions and a background site was based approximately 300 m from the road. Some contamination from non-vehicular sources was found and differences between this roadside study and other tunnel-based emission factor estimates were found to be up to a factor of 10. These were attributed to differences in vehicle speeds between studies which strongly influence VOC emissions.

Laupsa *et al.* (2009) compared various different approaches for achieving source apportionment of PM_{2.5} in Oslo, Norway: (i) receptor modelling using multi-variant techniques and optimal chemical profiles matched to individual source categories; (ii) forward dispersion modelling using predefined emissions profiles for different source categories; and (iii) inverse modelling using regression of the model source contributions and measured PM_{2.5} concentrations. Large discrepancies were found indicating problems with the original emissions inventory, particularly for wood burning and traffic-induced suspension. They suggested that separation between PM sources from exhaust or resuspension processes could only be achieved if receptor modelling was used to re-scale the individual source category emissions. Both these studies indicate that detailed source apportionment using inverse modelling alone would be difficult.

9.2.2 Point and small area sources

Several local-scale studies have used inverse methods to estimate ammonia emissions and hence emission factors from specific sources, such as a relatively isolated swine farm (Flesch *et al.*, 2007) or the application of diluted slurries to an area source (Sanz *et al.*, 2010). These studies used an inverse model based on a backwards Lagrangian Stochastic (bLS) trajectory approach where an ensemble of trajectories describing the motion of fluid elements (or particles) is simulated backwards in time from the receptor to the source. The source strength is estimated from measured concentrations at the receptor and the calculated residence time of those fluid particles which pass through the source volume. Several thousand backwards trajectories are used, making this approach computationally expensive. Inputs are usually mean wind speed and direction, dry deposition velocity and parameters related to turbulence, all of which are potential sources of uncertainty (Flesch *et al.*, 2007). The technique is perhaps best suited to flat terrain without the presence of building structures. Rudd *et al.* (2012) suggested that for such conditions, three to four sampling points were sufficient to accurately estimate source strength and location as long as averaging times greater than five minutes were used. Flesch *et al.* (2007) however indicated that reasonable results could be obtained for more complex sources (e.g. those from locations including built structures) provided that concentration measurements used within the inverse model were far enough from the source for the flow to have readjusted. The appropriate distance was suggested to be around ten times the building height/width, therefore careful attention needs to be paid to measurement locations used in this type of analysis.

Comparisons between emission estimates derived from bLS models and those from integrated flux techniques have shown reasonable agreement despite the former requiring considerably simpler measurements (Sanz *et al.*, 2010; Sintermann *et al.*, 2011). The use of bLS could therefore be a useful tool in the estimation of point or small area sources, and in the case of ammonia has helped to identify seasonal variation in emission rates and the percentage of total ammonium nitrogen that is released from different sources.

Models can also be used as a way of estimating fugitive emissions by explicitly modelling relatively well-known sources to remove their effect and leaving a 'residual' concentration that can be analysed further. This 'residuals' method was used to identify sources of fugitive emissions at a major steelworks at Scunthorpe (Malby, 2009; Abbott, 2010; Malby *et al.*, 2013). The background to the work was that PM₁₀ concentrations downwind of the steelworks regularly exceeded UK Air Quality Standards. However, there was considerable uncertainty about which sources were contributing most to exceedences because of the complexity of the site and its activities. Bivariate polar plots were used to examine spatial and temporal signals in the ambient record (upper left plot of Figure 27), and to show the impacts of non-fugitive sources – based on ADMS dispersion modelling with a non-fugitive source inventory (bottom left plot of Figure 27). The difference between the ambient plot and the non-fugitive plot is shown as a residual plot (right plot of Figure 27), which highlights the impacts of the remaining contribution from fugitive sources.

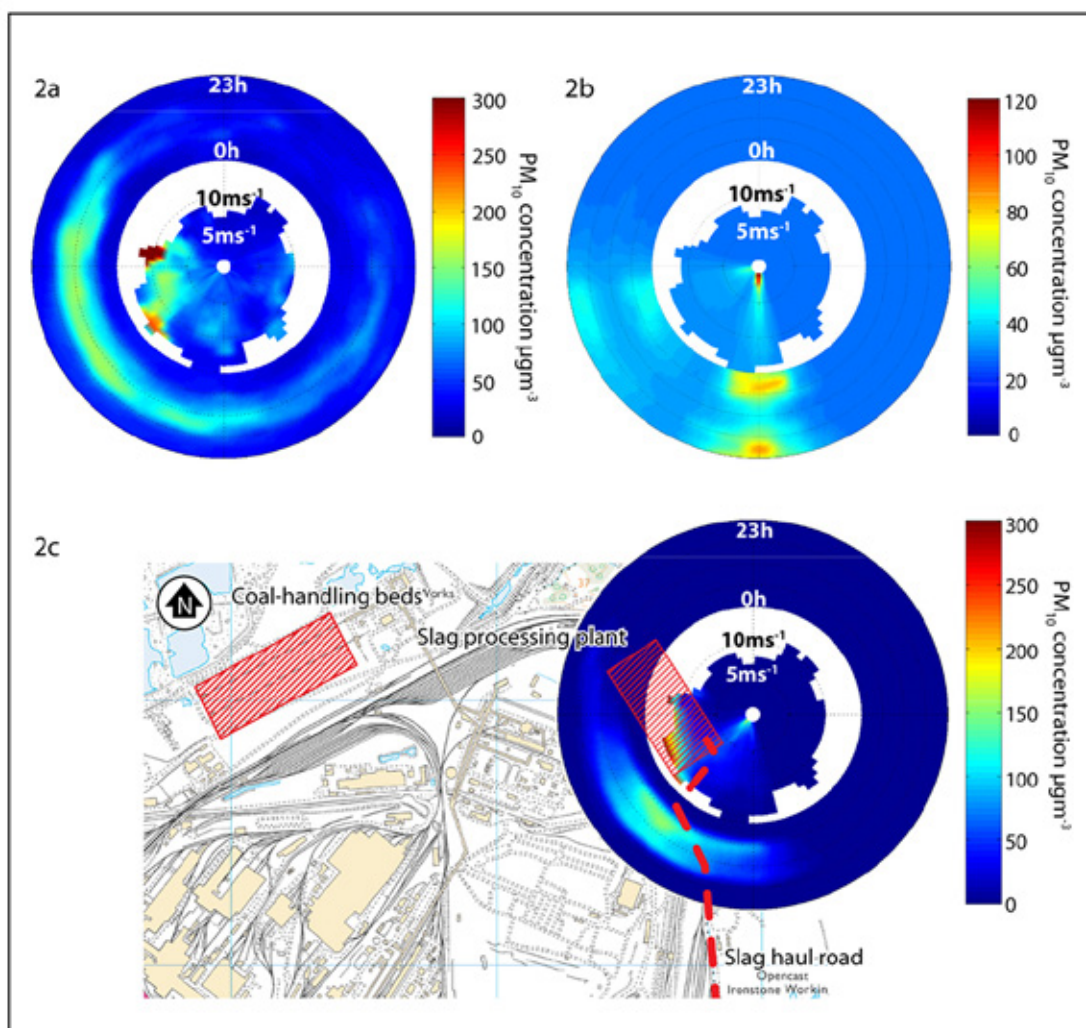


Figure 27: Upper left bivariate polar plot shows how measured ambient PM_{10} concentrations vary with wind speed and direction (inner plot) and with time of day (annular plot). The top right plot shows modelled ambient PM_{10} concentrations, based on an inventory of non-fugitive emissions. A residual plot (lower plot) is based on the difference between measured and modelled ambient concentrations, and highlights wind conditions and times of day that were associated with fugitive source impacts; this information was used to develop a fugitive source inventory (Malby *et al.*, 2013).

The residual plot indicates the locations and timings of steelworks activities that generated fugitive emissions and impacts. For example, the highest particulate residuals ($> 100 \mu\text{g m}^{-3} PM_{10}$) occurred under westerly conditions of high wind speed and were associated with activities involving the handling and transport of coal and slag during working hours. By combining such activity information with generic emission factors, it was possible to develop a fugitive release inventory that took account of the indicated activities of fugitive sources.

The fugitive emissions estimates were incorporated in a dispersion model and the resulting predicted concentrations were broadly in agreement with the inferred residuals. This suggests that the emission factors were broadly correct and may therefore be used to determine the contributions of fugitive sources to exceedences. The 'residuals' method may also be used to track the effectiveness of regulatory measures to control fugitive emissions.

9.2.3 Uncertainties

Ropkins *et al.* (2009) suggested that the high uncertainties associated with modelling in micro-environments where turbulent dispersion processes and/or non-traffic inputs are significant may have restricted more widespread use of inverse modelling procedures within urban environments. Simple dilution scaling approaches may ignore localised sources of turbulence, such as vehicle movements or local heat sources, although parameterisations of these could be attempted. Smit *et al.* (2010) suggest that using average values from several measurement sites along a road, or from different points on the network, would provide higher confidence in estimated factors depending on available measurement sites. Spatial variation of emissions along a road link would, however, need to be taken into account.

The acknowledgement and proper representation of inherent uncertainties within all model parameterisations will be important if error estimates in derived emissions factors are to be accurately obtained. These could be taken into account using Bayesian methods which combine top-down and bottom-up emission estimates within a probabilistic framework as suggested in Keats *et al.* (2007). However, such approaches often propagate errors, using a large number of model runs based on Monte-Carlo sampling which also has a significant impact on computational cost. For the types of semi-empirical models commonly used at the local scale however, this could be feasible, since model runs are fairly computationally inexpensive. Reliable background meteorological measurements and estimates of uncertainties within the model input data would seem to be a necessary requirement of the use of inverse modelling techniques at the local scale for the estimation of emission factors and their error bounds. It is not yet common practice to include the propagation of uncertainties in pollution dispersion models. As the specification of model uncertainties becomes more common, the scope of inverse modelling techniques should improve.

9.3 Regional-scale emissions

At the regional scale, inverse modelling tends to be based on two approaches: (i) time-dependent Eulerian grid-based solutions of reaction–advection–diffusion equations describing the transport and chemical transformation of pollution from a range of sources; and (ii) backwards Lagrangian trajectory models. Both use regional-scale weather predictions as inputs and in both cases the models are fairly computationally demanding.

9.3.1 Eulerian-based approaches

For grid-based models, the simplest inverse modelling approach uses least squares error minimisation. For example, source emission factors can be adjusted in order to minimise the error between the Eulerian grid model prediction and measured concentrations at specified measurement sites. Mulholland and Seinfeld (1995) used such an approach to estimate the spatial and temporal distribution of CO sources in the South Coast Air Basin of California. A three-day intensive series of measurements was conducted at 30 sites, including detailed meteorological measurements. It was demonstrated that adjustment of the temporal, and to a lesser extent the spatial, profiles of mobile and stationary source emissions gave the best improvements, highlighting the need for emission inventories which accurately reflect diurnal variations in sources. Seasonal adjustments were made to the US national ammonia emissions inventory in Gilliland *et al.* (2006) using a Kalman filter-based inverse model based on the Eulerian CMAQ (Community Multiscale Air Quality) model and national

measurements of ammonium ion (NH_4^+) atmospheric aerosol and wet deposition data. They showed that accurately dealing with time lags becomes important when making adjustments to temporal profiles for long-range models. In these types of studies the air pollution model has to be driven by a three-dimensional wind field which, for example in Gilliland *et al.* (2006), was obtained using the Fifth Generation Penn State/National Centre for Atmospheric Research MM5 model. Uncertainties in wind fields and their impact on the derived emission inventories were not fully assessed in these studies making it difficult to assess errors in the adjusted emissions factors.

Adjoint approaches are also commonly used for problems involving 3-dimensional transport and chemical transformations since the relationship between emissions and measured concentrations is likely to be non-linear, making simple least squared fitting approaches less applicable. Adjoint approaches make use of the gradient of a 'cost function' describing the error between modelled and measured concentrations with respect to the surface emissions fluxes. The direct-adjoint model cycle is iterated, adjusting emissions until a minimal cost value is obtained (Pison *et al.*, 2006).

Henze *et al.* (2009) used $\text{PM}_{2.5}$ measurements within an adjoint model of the GEOS-Chem chemical transport model to constrain emissions of NH_3 for the US region, again finding that seasonal and temporal adjustments to the US national inventory were required to best fit the measured data. Quelo *et al.* (2005) used an adjoint model based on Polair3D to adjust a NO_x emissions inventory in order to improve agreement between the modelled and measured O_3 , NO and NO_2 concentrations in the region of Lille, France. Adjustments in the diurnal factors for NO emissions, particularly the morning rush hour emissions (see Figure 28) gave significant improvements in the agreement between modelled and measured concentrations. In this work, the robustness of the derived factors is addressed using sensitivity analysis which takes into account the many uncertainties that exist within the model parameterisations, such as the prior emissions estimates, meteorological conditions, vertical mixing parameters, etc.

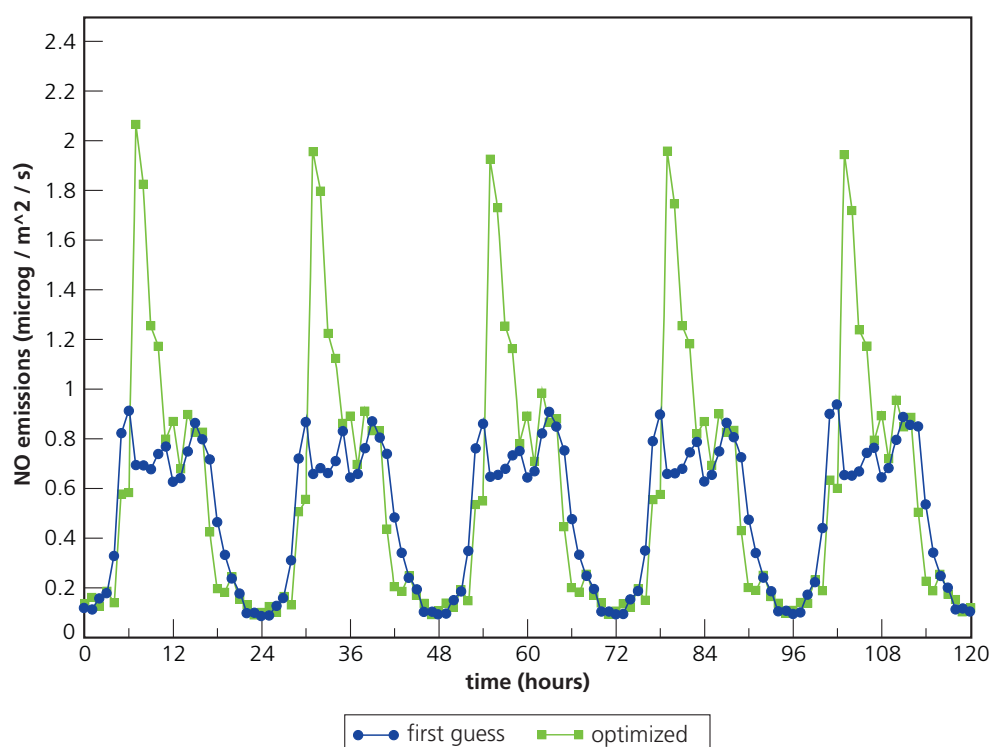


Figure 28: Daily distribution of NO emission for the period 11-15 May. Reference and optimised parameters (Quelo *et al.*, 2005).

Adjustments to NO_x, speciated VOC and CO inventories for the Atlanta, Georgia, metropolitan area were made using a similar data assimilation approach in (Mendoza-Dominguez and Russell, 2001). In this case, the VOC inventory was subject to the largest adjustments, particularly for rural locations. Availability of measurement sites, especially in rural areas, was found to affect errors in this case. Pison *et al.* (2006; 2007) developed a data kriging approach to deal with measurement sparsity which uses optimal interpolation to merge measurements and model results. The approach was used to improve surface NO_x emission factors within the Paris region based on interpolated measurements.

9.3.2 Lagrangian-based approaches

In the UK, the Lagrangian-based Numerical Atmospheric Dispersion Modelling Environment (NAME) model has typically been used for inverse modelling applications at the regional scale. NAME simulates particle trajectories driven by wind fields derived from the Met Office's Unified Model, and estimates turbulence parameters using fits to observational data. In a Defra-funded project, ammonia emission maps for a 100 km domain surrounding the Auchencorth Moss monitoring supersite were derived through inverse modelling based on backwards NAME trajectory calculations, and an iterative best fit technique for emissions estimates based on simulated annealing. The results were compared with those derived from the NAEI (Manning, 2009). High temporal resolution gaseous measurements of NH₃, hydrogen chloride (HCl), HNO₃ and nitrous acid (HNO₂) from Auchencorth Moss during 2007 were used taking into account an estimated background concentration. Both similarities and differences between the NAEI emissions and those estimated by Manning were found, with differences exceeding a factor of two in some cases. Both distant sources and uncertainties within the simulated wind fields contributed to potential errors in the emissions derived using the inverse model. The emissions were assumed to be constant in time and geographically static across the one-year period, whilst other studies have shown strong seasonal dependencies of ammonia emissions. The study does, however, show the potential of such approaches for application within the UK and could be extended to look at seasonal and spatial variability in emissions.

Polson *et al.* (2011) used the approach described in (Manning, 2009) to derive total UK and spatial disaggregated emissions estimates for CO, CO₂, CH₄, nitrous oxide (N₂O), HFC-134a, HCFC-141b, HCFC-142b and HCFC-22. In this case, measured data were obtained using an aircraft circumnavigating the UK and hence backwards trajectories were released from along the observation flight path. The modelled overall UK CO flux and spatial apportionment were found to be in remarkably good agreement with the UK NAEI inventory. Total and apportioned CO₂ emissions were also found to be close to the NAEI values but significantly larger values were estimated via the inverse modelling for N₂O and CH₄ emissions than those in the NAEI. Uncertainties in the estimated values were based on the variation between measurements taken during different aircraft flights and sources of uncertainty in the inverse model such as those arising from meteorology and transport parameterisations within NAME. The largest uncertainties were estimated for CH₄ and N₂O since the quality of measured data for these species tended to vary significantly between flights.

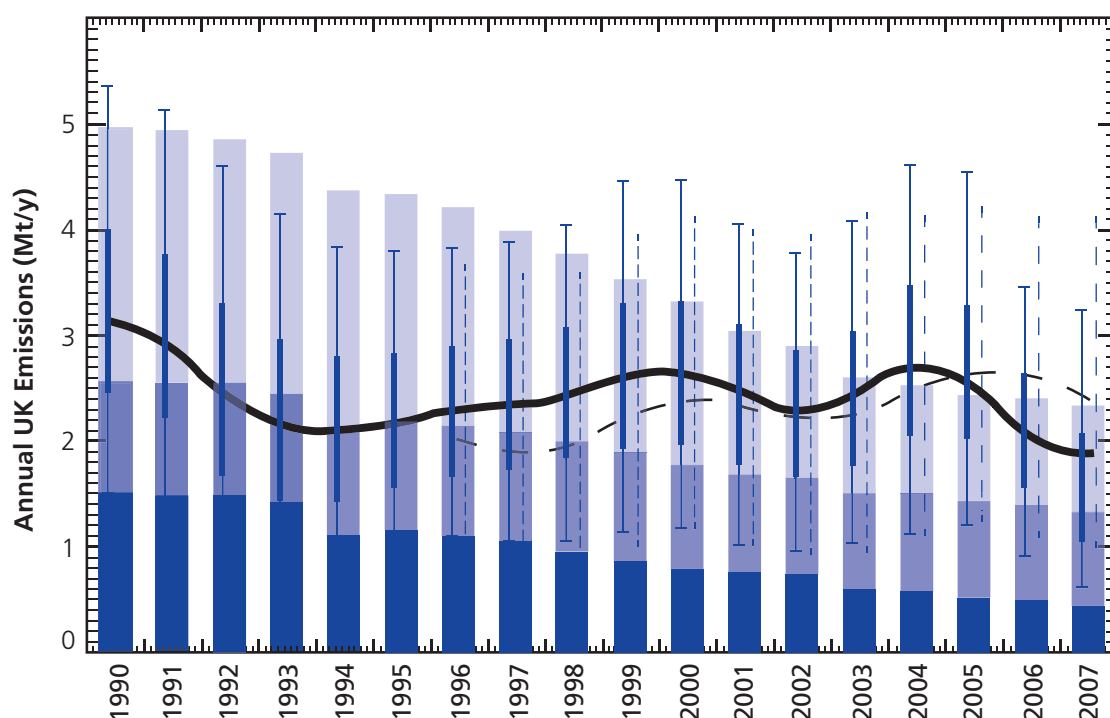


Figure 29: UK emission estimates for CH₄ based on NAME inversion (solid line is with ERA Interim meteorology and dashed line with UK met office meteorology). Uncertainty bars show median, 5th, 25th, 75th, 95th percentiles) and UNFCCC inventory. Cumulative columns from bottom: energy, industry (very small), agriculture, waste (Manning *et al.*, 2011).

DECC has supported high frequency continuous observations of over 20 greenhouse gases and ozone-depleting substances at Mace Head, Ireland, with a view to evaluating the accuracy and completeness of the UK NAEI/GHGI (Greenhouse Gas Inventory) through inverse modelling. The technique was first developed in Manning *et al.* (2003) and further developed using backwards NAME trajectories to infer the spatial distribution and trends with time of a range of trace gas emissions across north-west Europe from 1995 until June 2009 (Manning *et al.*, 2011). An example of the time series for CH₄ is shown in Figure 29. For the trace gases CO and N₂O, close agreement was found between the absolute magnitudes and spatial distributions of the inferred emissions and EMEP and the NAEI inventories respectively. Close agreement was also found in the trends with time since 1990. However, for methane there were significant discrepancies in both absolute magnitudes and trends with the UK GHGI, whereas there was close agreement for Germany, Netherlands and Ireland, pointing to possible errors within bottom-up inventories for the UK. This disagreement is of some policy concern to DECC and has focused attention on landfill and coal mine emissions and their possible overestimation during the early years of the 1990s. DECC has extended this inversion work by increasing the number of high frequency continuous observations sites, so that a more accurate spatial resolution can be achieved within the UK with the aim of increasing accuracy for the devolved administrations. Increasing the spatial resolution of measurements is likely to improve estimates of emissions trends based on inversion approaches.

9.4 Summary points

9.4.1 Strengths

- A wide range of inverse modelling approaches has been developed for emissions estimations across wide spatial and temporal scales.
- Models continue to develop in sophistication and increasingly methods exist to carry out inverse modelling at a range of scales.
- There is the potential to provide a better understanding of temporal or seasonal trends in emissions, for example, for:
 - point source emissions factors using targeted local measurements for specific source types. This has already been demonstrated in the case of ammonia;
 - long-term trends in greenhouse gas emissions by exploiting an increase in the number of high frequency long-term observation sites;
 - seasonal variations in regional ammonia emissions by the use of existing supersite measurements and regional-scale models; and
 - real world traffic emissions by exploiting existing urban networks where both roadside and urban background measurements are already available.
- Models can be used to account for well-characterised sources, leaving a “residual” signal that can help quantify and characterise poorly defined sources such as fugitive emissions.

9.4.2 Weaknesses

- Measurement sparsity. For isolated point sources it is suggested that four concentration measurements may be sufficient to estimate source strength and location if no significant local flow disturbances are present. For complex urban air shed or regional applications however, as many as 30 monitoring sites have been used in the past, which may prohibit the effective use of inverse methods based on 3-dimensional Eulerian grid-based models in the near future. For urban areas, background and roadside sites exist in many cities but local meteorological measurements are often not available and the background signal is likely to be spatially variable. The spatial variability in both emissions and local flow patterns in urban areas will also add to inherent uncertainties in the approach. In the short term the use of inverse modelling for urban areas may be restricted to assessing relative emissions trends (such as diurnal variability) rather than for deriving vehicle-specific emission factors.
- The treatment of uncertainties. The propagation of uncertainties within air quality models has only been addressed by a small number of studies but is critical to the estimation of uncertainty in emission factors derived from inverse modelling.
- Computational costs. The use of Bayesian techniques would seem to be a useful way forward but carries with it the added computational cost of performing large numbers of model runs.

9.4.3 Conclusions and recommendations

- It is likely that inverse Gaussian/semi-empirical models or backwards Lagrangian trajectory models will be the easiest techniques to exploit in the near term, particularly for non-reacting tracers. Useful application to both point source emission estimates (e.g. for local ammonia sources) and regional tracer emissions has already been demonstrated. A key useful outcome from inversion studies so far appears to be to identify problems with estimates of diurnal and or seasonal variability. At the moment, the use of adjoint methods based on complex 3-dimensional Eulerian reactive dispersion models may require too high a density of measurements and contain too many inherent model uncertainties to be immediately useful. As models become more sophisticated and the treatment of model uncertainties becomes more widespread, such approaches could provide insight into both the spatial and temporal variability in urban to regional scale emissions.
- Important factors to be addressed for the effective application of inverse techniques include the following:
 - Suitable meteorological reference data and uncertainties need to be provided since for local-scale studies, on-site measurements have been shown to improve accuracy compared to using estimates for turbulence parameterisations.
 - In order to provide estimates of errors for derived emission factors using inverse modelling, it is important to include estimates for all uncertainties within the model used for the inversion, e.g. in meteorological data, measurements, chemical and deposition rates, etc. This issue has not been fully addressed in many previous studies.
 - Model complexity. The model used needs to adequately represent the key physical factors affecting flow and dispersion in the environment being considered, whilst running in reasonable computational time. This requirement is very challenging.
 - Background data. Adequate account needs to be taken of background data and any other source categories which are not part of the inversion process. For regional pollutants with a large number of source categories this can be difficult. However, at the local scale, estimates of the increment above background may be achievable using current network data or a low number of measurements.
 - Speciation. For detailed chemical speciation or source apportionment, inverse modelling may need to be coupled with receptor modelling techniques.

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