# Sources, Sinks and Levels of Atmospheric Mercury in the UK

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D. S. Lee[1], E. Nemitz[2], D. Fowler[2], P. Hill[2], S. Clegg[1]
and R. D. Kingdon[1]

[1]Defence Evaluation and Research Agency

[2]Centre for Ecology and Hydrology, Edinburgh

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Authorization

Prepared by	Dr D. S. Lee
Title	Technical Team Leader, Atmospheric Processes
Signature	
Date	December 2000
Location	DERA Pyestock

Approved by	Prof. C. W. Wilson
Title	Technical Area Leader, Combustion and Environment
Signature	
Date	December 2000

Authorized by	Dr R. Onions
Title	Business Area Manager, Propulsion and Performance Department
Signature	
Date	December 2000

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Executive summary

This report on '*Sources, Sinks and Levels of Atmospheric Mercury*' in the UK has been compiled by DERA and CEH, Edinburgh, for the DETR, the Scottish Executive, National Assembly for Wales and the DoE Northern Ireland under contract EPG 1/3/157.

A   Background

Mercury (Hg) is a toxic environmental pollutant that can adversely affect human health. It is emitted from a range of sources, natural and man-made. It is a global pollutant and has many unusual chemical and physical properties that make its behaviour difficult to predict with current knowledge.

This report draws together existing global and UK knowledge of Hg, identifying what is known, what is uncertain and what is entirely unknown. Conclusions are drawn on the state of knowledge and the monitoring and assessment required for the UK, particularly with respect to development of an air quality standard.

Mercury is ubiquitous in the atmospheric environment. Its unique characteristics result in this metal being mostly present in the relatively unreactive form of gaseous elemental monovalent mercury (Hg^0). Elemental gaseous mercury has a long atmospheric lifetime (of the order 1 year) and is therefore present throughout the global atmosphere with largest concentrations in the northern latitudes.

Mercury is also present in the atmosphere in the divalent form, either attached to particles (Hg-p) or in inorganic/organic reactive forms (reactive gaseous mercury, RGM).

The forms of Hg that are of principal concern in terms of adverse health effects on humans are the organic methylated forms: monomethylmercury (MMHg) or dimethylmercury (DMHg). These forms of Hg are highly toxic, causing neurotoxicological disorders. Methylation of Hg occurs in animal tissues but also in the environment. Moreover, methylmercury has been detected in air and precipitation, although its sources are uncertain.

B   Current legislation

Mercury is incorporated into the United Nations Economic Commission for Europe Convention on Long-Range Transboundary Air Pollution Heavy Metals Protocol and is also a pollutant listed for consideration under the European Commission's Air Quality Framework Directive (Directive 96/62/EC). It will become incorporated at a future date under a Daughter Directive of the Framework Directive. Thus, Hg will need to be considered within the UK's Air Quality Strategy.

Most countries have not yet set air quality standards for Hg concentrations in air, because the main pathway for Hg to humans is through the food chain and not by inhalation.

C   Data on atmospheric mercury in the UK

C.1   Emissions

- UK emissions of Hg are not well quantified and estimates range from 13 to 36 tonnes yr^{-1}. The speciation of these emissions is not well characterized, no UK measurements being available. This speciation is vital in quantifying budgets, transport and therefore ambient concentrations of mercury.

- An initial speciation of the UK Hg emissions has been made, predicting that 67% is elemental gaseous Hg, 24% reactive gaseous Hg and 9% is particle-bound. More measurements of the speciation from different source categories are needed to obtain a more accurate partitioning. Currently, speciation is not specified within the UK National Atmospheric Emissions Inventory, taking full account of the knowledge of abatement technologies. The toxic methylmercury form is assumed to be some unknown fraction of reactive gaseous mercury.

- Despite the apparent decline in European emissions of Hg over the last decade, there is evidence that emissions outside of Europe have started to increase, increasing Hg ambient concentrations in Europe. These emissions can have a significant effect on the UK budget of deposition and ambient concentrations because of the long lifetime of Hg^0.

- No emissions data on natural sources were available for the UK. An initial quantification from UK measurements and elsewhere has been made and the results suggest that natural emissions may represent a significant fraction of the overall UK emissions. The estimate made here indicates that they are 11% (range 2%–75%) of UK man-made emissions. This estimate is based on flux measurements carried out in the North America and Scandinavia and using UK landcover data.

C.2   Measurement data on concentrations and deposition of mercury in the UK

- Only sporadic measurements of gaseous Hg are available for the UK. Some long-term measurements of Hg-p are available from urban and rural sites.

- A recent study of gaseous and Hg-p close to sources has yielded some data but these measurements are subject to sampling artefacts that limit their interpretation.

- No measurements of reactive gaseous Hg or methylmercury in air or precipitation have been made in the UK.

- There are no reliable measurements of the wet deposition of Hg with which deposition inputs to the UK can be quantified. Analytical techniques with inadequate detection limits were used for early wet deposition measurements.

- Some deposition data for Hg are available with spatial coverage for England and Wales but these data were obtained with a collector type whose collection efficiency is poorly characterized. It is unclear what forms of Hg were collected and how much the collection was influenced by dry deposition. However, from these data, a total deposition of > 17 tonnes Hg yr^{-1} was derived for England and Wales as part of this study, more than 2.5 times larger than current model estimates.

- No dry deposition measurements for any of the forms of atmospheric Hg have been made in the UK; this is one of the critical limiting factors in model formulation and budget analysis.

C.3   Budget estimates

- The UK measurement database for atmospheric Hg is inadequate for the task of defining concentrations, deposition and subsequent exposure. Thus, a UK budget based on measurements cannot be constructed. However, a budget has been provided based upon a modelling study, undertaken specifically for this report but very limited data are available to validate the model results.

- The budget analysis undertaken for this work indicates the following: 25% of the deposition to the UK arises from Northern Hemisphere/global background concentrations; 41% arises from UK sources; 33% arises from other European sources. Of the UK emissions, it is estimated that 68% are exported.

- The DERA model results are in disagreement with the EMEP Meteorological Synthesizing Centre-East modelling, which are disparate in themselves. One EMEP report (Ryaboshapko *et al.*, 1998) suggests that 36% of deposition to the UK is from background sources, 9% from European sources and 55% from UK sources. In the other EMEP report (Ryaboshapko *et al.*, 1999), 60% of UK deposition was calculated to be from background sources, 4% from other European sources and 36% from UK sources.

Table 0-1: Summary of mercury budgets for the UK (in tonnes yr^{-1})

	Ryaboshapko *et al.*, 1998	Ryaboshapko *et al.*, 1999	This study
Reference year	1995	1998	1998
Emission			
Total	19.7	12.4	12.7
to UK	5.0 (25%)	3.2 (26%)	4.1 (32%)
to EMEP region	7.7(39%)	2.6 (21%)	8.6 (68%)
to global pool	7.0(36%)	6.5 (53%)	
Deposition			
Total	9.1	9.0	9.9
from UK sources	5.0 (55%)	3.2 (36%)	4.1 (41%)
from European sources	0.8 (9%)	0.4 (4%)	3.3 (33%)
from global pool & oceans	3.3 (36%)	5.4 (60%)	2.5 (25%)
Ratio of Deposition / Emission	49%	73%	78%

- Although the overall budget estimates of the two modelling scenarios for 1998 are very similar, the contribution of wet and dry deposition of the various forms of Hg (Hg^0, RGM, Hg-p) to the total deposition varies significantly between the two estimates, affecting the spatial pattern of the deposition.

C.4   The relationship between emissions, concentrations and deposition

- Understanding the relationship between emissions and ambient concentrations is severely hampered by a lack of measurements. According to current understanding and the limited UK observations of ambient concentrations, concentrations away from sources are modified by sinks (atmospheric and dry/wet deposition) rather than sources. Closer to sources, emissions are more important.

D   Effects

Inhalation of ambient Hg is not the route by which human health is threatened. The threat to human health is through consumption of contaminated foodstuffs, principally fish, which accumulate Hg in its toxic methylated forms. A better way to minimize effects on human health would be to adopt a 'critical loads' approach to limit the entry of Hg into the food chain, both through deposition to water bodies and agricultural land.

Mercury emissions from dental amalgam fillings constitute a second major source for Hg uptake by man, equalling that of intake through food consumption.

There is evidence that Hg concentrations in some unknown proportion of top-level food chain biota such as eels, herons and otters are close to levels at which toxicological disorders may occur. Mercury concentrations in eels have been found to exceed those stipulated under EU Directive (93/351/EEC).

It does not appear to be appropriate to set an ambient air quality standard for Hg. The limited measurements show that elemental gaseous Hg and Hg-p are at concentrations for which the risks of direct effects on human health are considered negligible.

E   Recommendations

In the following, E.1 represents an overall recommendation for UK air quality policy, based upon our findings given in this report. Therefore, we recommend a way forward to ensure protection of human health and eco-systems from (potentially increasing) deposition of Hg. The recommendations E.2 to E.5 are all of equal importance, based on our current scientific understanding.

Nonetheless, we identify and emphasize that measurements of deposition and ambient concentrations of Hg are the limiting factor in all these recommendations (other than E.3, which is a detailed recommendation for such measurements). This is because one of our basic findings is that the UK has virtually no measurements that can be used to quantify deposition fluxes or validate model results.

E.1   Air quality standards for mercury species

An ambient air quality standard for Hg should not be pursued. It terms of ambient levels, concentrations away from sources are dominated by elemental gaseous Hg, which has an atmospheric lifetime of the order 1 year. This needs to be fed back into formulation of any EU Daughter Directive on atmospheric Hg.

For the protection of human health and ecosystems, a critical loads approach for Hg would provide the best solution.

E.2   Critical loads for mercury

A critical loads methodology should be developed. This is a non-trivial task and further scoping on how such a methodology could be developed may be needed. Essential components of such a study would require: defining the allowable limits of Hg uptake for the UK population (considering the toxicity of the different forms, their uptake, accumulation and excretion); a study of the linkages between deposition, bioaccumulation and dose to at-risk groups; the pathways of Hg deposited to soils, through catchments to biota; the chemical conversion processes in soils, catchments and biota. In addition, the Hg dose experienced by the UK population from dental amalgam emissions and their contribution to methylmercury in the human body should be quantified.

It is pointed out that the current lack of measurement/deposition data will limit our ability to compare actual loadings with defined critical loads (see E.3).

E.3 Defining the UK pollution climatology for mercury

A critical loads approach for Hg cannot currently be used as inputs of Hg are inadequately defined. This requires quantification of wet and dry deposition across the UK by establishment of measurement networks.

In order to develop a measurement strategy, we recommend that in the first instance, a research site is established that would make measurements of wet and dry fluxes of speciated Hg measurements. This would ensure the development of a cost-effective strategy for a future measurement network for Hg species.

Such a site would have the additional advantage of aiding concomitant model development (see E.4), which would itself aid a measurement strategy to be defined.

In a next step, a network measuring speciated Hg concentrations and deposition would be established.

E.4 An improved modelling approach for atmospheric mercury

An improved modelling approach is required in parallel with a measurement strategy. The modelling should utilize the measurements made available from E.3 for model calibration and validation. In addition, the results of the modelling can be used to develop the measurements strategy. The discrepancy between the EMEP-MSC East model results and those from the modelling undertaken for this work is large and unsatisfactory. Moreover, there is an inexplicable difference between assessments in the two EMEP reports. Independent UK modelling has proved vital elsewhere, e.g. in acid deposition modelling, and should be pursued. The modelling approach should be considered carefully in order to account for global and hemispherical background concentrations. In addition, natural/re-emissions should be incorporated, as currently models do not treat this processes in a consistent manner (see E.5 cross-referencing E.3).

E.5 Improvements to the UK emissions inventory for atmospheric mercury

Estimates of UK emissions of Hg from industrial/man-made sources need to be improved. Improvements should include: (i) independent assessment and validation of the emissions reported to the ISR database; (ii) speciation of the emission estimates; (ii) improved spatial disaggregation of emissions from institutional/residential combustion processes, incineration and landfill; (v) usage of actual activity figures (currently held confidentially by the Dti).

In addition, natural emissions/re-emission could represent an important fraction of the UK budget. Fluxes are determined by the production of Hg^0 in water and soils, the rate of which appears to be governed by total Hg available, solar radiation and bacterial activity. Measurements are required to determine source strengths for UK conditions (see E.3). These should be utilized in combination with a literature-based activity to compile a spatially disaggregated inventory of natural/re-emissions for improved modelling purposes (see E.4).

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1 Introduction

1.1 Mercury—chemical and physical characteristics

1.1.1 Mercury (named after the Roman god of merchants and merchandise, it sometimes being known as 'quicksilver') is ubiquitous, being found in all environmental compartments because of its unique chemical and physical characteristics as a metal. The history of mercury (Hg) and its uses goes back at least to Theophrastrus (about 300 B.C.), who mentions its extraction from cinnabar, its most widespread form in the geosphere. Mercury has played an important role in medicine and chemistry; for example, it was instrumental in Priestley's discovery of oxygen.

1.1.2 Mercury has an atomic number of 80, an atomic weight of 200.59, a melting point of -38.87 ºC and a boiling point of 356.58 ºC. These characteristics give it the unique property for a metal of being liquid at most environmental temperatures. Its chemical reactivity is generally low and the liquid metal has a very high surface tension that accounts for its high adsorptive properties to solids, in which it will form very small spheres.

1.1.3 Mercury has seven stable isotopes and four unstable radioactive isotopes. It can exist in three oxidation states: 0, +1 and +2. Mercury exists in the atmosphere mainly as elemental gaseous Hg with an oxidation state of 0 (Hg^0). The +2 oxidation state is also found in the atmosphere (either in the gaseous form or attached to particles) but the +1 state has not been observed in the atmosphere. In water, soil, sediments and biota, most Hg is in the form of Hg salts or organic forms.

1.1.4 The usage of Hg is widespread in industry in processes and incorporation into various products (e.g. batteries, lamps, and thermometers). Moreover, it is still widely used in dentistry as an amalgam for repair of dental cavities and used widely in the pharmaceutical industry. Comprehensive reviews of its usage in the UK have been undertaken by ERM/DOE (1996), WS Atkins (WSAC, 1997) and by EuroChlor (1999). The usage of Hg and Hg-containing products will not be considered further in this report, except in relation to emissions and where relevant to specific chapters.

1.2 Mercury—overview of its behaviour as an atmospheric contaminant

1.2.1 The interest and concern over Hg in the environment arises from the extremely toxic forms in which Hg can occur, namely methyl Hg species. Cinnabar (HgS) is the most widely found natural inorganic form in the earth's crust, whilst Hg^0 dominates the atmospheric form. Inorganic Hg in the environment can be converted by natural biological processes into methylated forms of Hg (MHg). This MHg can then bioaccumulate over a million-fold and concentrate in biota, principally,

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fish (Bloom, 1992).

1.2.2   Methylmercury compounds used include monomethylmercury (CH_3Hg or MMHg) and dimethyl-mercury (($CH_3)_2Hg$). Dimethylmercury (DMHg) is highly volatile, reacts quickly in the atmosphere, and dissociates to form monomethylmercury at neutral or acidic pHs. In contrast, MMHg is stable and bioaccumulates. Methylated forms of Hg are the principal cause of concern from an ecotoxicological standpoint because all forms of Hg can be converted into them. Monomethylmercury can bioaccumulate and magnify in aquatic ecosystems, and it is the most toxic form of Hg.

1.2.3   Much of the early concern over MMHg originated from the tragic consequences of discharges of an acetaldehyde factory into Minamata Bay, Japan. In 1956, the so-called 'Minamata Disease' was recognized and in 1963, a report concluded that the disease was caused by the consumption of shellfish from Minamata Bay. However, the discharges did not cease until 1968. In the late 1960s, MMHg was found in fish from Swedish lakes where there was no discharge of MMHg (Bakir *et al*., 1973). It was subsequently found that methylation of Hg occurred in the sediments of the lake and that this bioaccumulated and biomagnified in the lake biota. In such areas, the Hg can originate from atmospheric deposition or, possibly, mobilization of inorganic Hg from the catchment by acidic inputs from the atmosphere.

1.2.4   More recently, gold mining in Brazil has been a particular cause of potential Hg poisoning in the Amazonian environment (e.g. Akagi *et al*., 1995). Mercury is used as an amalgam for gold extraction and, consequently, large amounts of Hg are lost to watercourses where subsequent methylation, bioaccumulation and biomagnification may take place. Moreover, in the refining process, also carried out locally (gold 'roasting') and often done in the open, large amounts of Hg are released to the atmosphere.

1.2.5   Whilst the above problems have been identified as being regionally specific, they are relevant to the UK and European environment. This is essentially because the atmospheric lifetime of Hg^0 is long; of the order of months to a year. Man-made emissions of mercury arise from fossil fuel combustion, smelting, chlor-alkali plants, incineration and gold mining (Sloss, 1995). Natural sources include soils, vegetation and volcanoes. With the exception of volcanic emissions, natural emissions of Hg occur in the gaseous elemental form, with a small but unquantified contribution from volatile organic forms. In contrast, a fraction of the man-made emissions may be converted into the divalent form immediately after their release, or adsorbed to particles. This fraction depends upon many parameters such as flue gas temperature and composition, and the fractionation ranges from 0–70%, depending on the process.

1.2.6   Since most Hg is emitted in the relatively unreactive Hg^0 form with a long atmospheric lifetime, the scale of the cycling of mercury is global (Rodhe, 1996; Bergan *et al*., 1999). The mixed layer of the oceans represents the largest sink, principally from wet deposition (Mason *et al*., 1994). However, the mixed layer acts only as a temporary reservoir, since elemental Hg, derived from

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reduction of divalent Hg, is thought to be emitted from oceans at a rate equal to that of deposition (Mason *et al.*, 1994). Therefore, the emission, transport and deposition of Hg is a global issue.

1.2.7 This concern is reflected by the incorporation of Hg within the United Nations Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution (UNECE-CLRTAP). A first UNECE-CLRTAP Heavy Metals Protocol was signed at Aarhus, June 1998, which addressed the emissions of cadmium, lead and mercury. Later expansions of the Protocol in scope and re-definition of emissions reductions are likely. In addition, The Air Quality Framework Directive (Directive 96/62/EC) and its Daughter Directives have an impact upon UK air quality policy and the UK's Air Quality Strategy. Mercury is on the list of Directive pollutants and at some point, a Daughter Directive will be introduced. The UNECE-CLRTAP Heavy Metals Protocol will need to be taken into account when Daughter Directives are introduced.

1.2.8 There is an essential link between the UNECE-CLRTAP and the Air Quality Framework Directive in that they both seek to protect human health and ecosystems. The essential difference between Protocols and Directives is that Directives seek to protect human health through ambient air quality standards whilst the Protocols define ecosystem loadings and ambient standards as metrics for protection.

1.2.9 One of the specific issues that this report will address is the main pathways by which humans are exposed to environmental Hg: whether ambient air quality is 'the' issue, or whether uptake via ingestion, and the potential balances of these two routes.

1.2.10 In considering Hg in the atmosphere, it is important to discriminate between its phases and chemical forms, as they have very different properties. Elemental gaseous mercury constitutes the bulk of direct emissions (Sloss, 1995). This form is relatively unreactive, deposits directly to the earth's surface at a very low rate, is very insoluble and is therefore not removed efficiently in precipitation in its 0 oxidation state, and consequently has a long atmospheric residence time. Divalent mercury can be present in the atmosphere in either organic (monomethyl or dimethylmercury) or inorganic forms (e.g. $HgCl_2$). If divalent Hg is in the gaseous phase, it is thought to be rapidly dry deposited, soluble, and effectively wet scavenged, which leads to a short residence time. Divalent Hg may also be attached to particles and originates from direct emissions (a small fraction of the total Hg emission), or from oxidation of gaseous elemental Hg. This oxidation is relatively slow.

1.2.11 Much of the particulate-phase Hg present in the atmosphere is found in the fine sub-micron particle diameter size range and thus has a low deposition velocity and an atmospheric residence time of days, as this material may be scavenged efficiently by precipitation (Rodhe and Grandell, 1981).

1.2.12 From the brief description above, it is clear that the speciation of atmospheric forms is critical to removal rates and transport distance from emission sources.

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1.3   Structure of the report

1.3.1   In our response to the DETR's invitation to tender (EPG 1/3/157) the following three overall requirements were identified:

- the construction of a UK budget for Hg;
- to assess the current knowledge of concentrations of Hg in the atmosphere;
- to assess the current knowledge of concentrations of Hg in the atmosphere in the light of adverse environmental risk.

1.3.2   The DETR stipulated the objectives by which the above should be achieved and these are reiterated below:

- review the knowledge of UK emissions of Hg into the atmosphere;
- assemble all available sources of data on the concentrations of Hg in the atmosphere in the UK;
- review the current state of knowledge on the behaviour of Hg in the environment;
- construct an initial UK budget of Hg;
- analyse the correlation of emissions with atmospheric concentrations of Hg and establish which factors critically govern ambient concentrations of Hg in the atmosphere;
- put the concentrations of Hg in the atmosphere in the UK in the context of known adverse human health effects and other adverse environmental end-points;
- draw conclusions about the gaps in knowledge and analysis that will be necessary to close in order to select and appropriate air quality standard and/or emissions target to protect human health and the environment.

1.3.3   In writing this report, the above objectives were addressed in turn as individual Chapters (2 to 8).

In addition, we draw overall conclusions and provide recommendations in Chapters 9 and 10.

1.4   Nomenclature

1.4.1   In the list below, the nomenclature used in this report is defined:

Hg   total mercury, form(s) unspecified
Hg^0 elemental monovalent gaseous mercury
Hg^{2+} divalent inorganic gaseous mercury
MMHg   monomethyl mercury
DMHg   dimethyl mercury
MHg   total methylmercury
RGM   reactive gaseous mercury (Hg^{2+} + MHg)
TGM   total gaseous mercury (RGM + Hg^0)
Hg-p   reactive divalent mercury bound to particles

2   Emissions of mercury into the atmosphere

Summary

- Four emission inventories for the UK are reviewed here (rescaled for 1998) and predict emissions in the range of 13 to 36 tonnes Hg yr^{-1}. The National Atmospheric Emissions Inventory (NAEI) estimate of 12.9 tonnes Hg yr^{-1} is at the low end of the range.

- More than half of the Hg emissions predicted in the NAEI inventory are taken from the Inventory of Sources and Releases of the Environment Agency of England and Wales and equivalent databases for Scotland and Northern Ireland. As a result, its quality crucially depends on the emissions submitted by the operators of registered Part A industrial processes. An independent approach to estimating these emissions is required.

- An initial speciation of the NAEI emissions has been made here and predicts a distribution of 67% Hg^0, 24% reactive gaseous mercury (RGM) and 9% particulate mercury (Hg-p). Because of the fast deposition rate and short atmospheric lifetime of RGM, high Hg deposition should be expected near sources that emit large fractions of RGM; namely incinerators and coal/oil combustion.

- Improvements to the NAEI estimate of emissions should concentrate on medical and special waste incinerators, landfill sites and the improvement of disaggregation maps.

- The accuracy of the spatial disaggregation is hampered by data confidentiality.

- Emissions from waste incineration have declined because of the introduction of new legislation and also the gradual phase-out of Hg from many products such as batteries. In contrast, incineration and spreading of sewage sludge are sources that are likely to increase.

- The seasonality in activity figures such as fuel combustion and death rates is likely to result in higher emissions in winter than in summer by 10 to 30%. In contrast, natural emissions increase in summer.

- Current UK inventories do not include natural emissions and re-emissions, which could amount to anything between 2 and 75 % of the currently predicted man-made emissions, with 11% (1.4 tonnes yr^{-1}) being the current best estimate. Research to narrow down this range is vital to (i) forecast the effect of emission reductions, (ii) understand the seasonality of the total emission, (iii) fully investigate the relationship between emissions and ambient levels.

2.1   The NAEI gridded UK Hg emissions inventory for 1998

2.1.1   Overview

2.1.1.1   The inventory of man-made UK mercury emissions is compiled on a yearly basis by NETCEN, AEA Technology, Culham, for the UK DETR as part of the National Atmospheric Emissions Inventory (NAEI). These data are subsequently submitted to the UNECE. The trend of the man-made Hg emissions in the UK according to the NAEI is shown in Figure 2.1.

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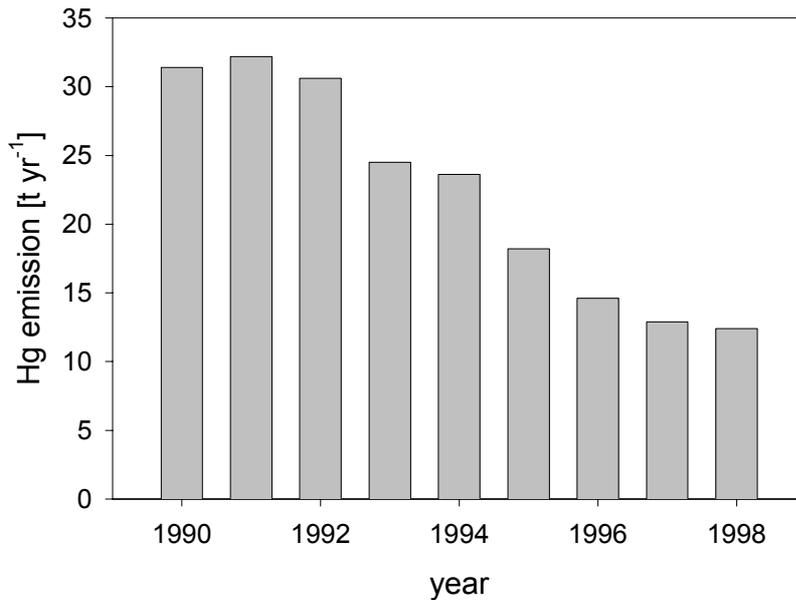
Figure 2-1 Trend of man-made Hg emissions in the UK according to the estimate of the NAEI

2.1.1.2   The UK emissions estimate of Hg emissions has recently been spatially disaggregated (Goodwin *et al*., 2000). This inventory is currently confined to industrial/man-made emissions; natural emissions or re-emissions are not considered. In addition, no speciation is provided for the emissions. This degree of detail is in line with the emissions that are submitted by most countries to the Task Force of Emission Inventories as part of the Convention on Long-Range Transport of Air Pollutants (CLRTAP), but not adequate for an assessment of risk.

2.1.1.3   Natural emissions are estimated to make an important contribution ranging from 20–33% to the global emissions of Hg (Lindqvist, 1991). Budget estimates provided for the CLRTAP account for Hg deposition from the global Hg background, which partly originates from these natural emissions. The country-specific emission inventories used, however, do not include natural emissions. This leads to inconsistencies and an underestimation of the net export of the individual countries.

2.1.2   Summary of the methodology used for the NAEI inventory

2.1.2.1   As stipulated by the EC directive 96/61/EC for Integrated Pollution Prevention and Control (IPPC; EC, 1996), mercury emissions larger than the reporting threshold of 100 g yr^{-1} have to be reported to the Environment Agencies (EA). The EA of England and Wales maintains a digital dataset of reported emissions, the 'Inventory of Sources and Releases' (ISR), formerly known as the 'Chemical Release Inventory' (CRI). The various regional offices of the Scottish Environmental Protection Agency (SEPA) and the Industrial Pollution hold equivalent data and Radiochemical Inspectorate of Northern Ireland as paper copies. The NAEI draws data from these inventories and therefore relies upon the correct reporting by the plant operators.

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2.1.2.2 Additional information on point sources and their geographical location was compiled from various sources, including the 'National Sulphuric Acid Association', the 'Iron and Steel Bureau' and the 'Federation of Burial and Cremation Authorities. Some of these data are confidential and could only be used to calculate national totals, but not to associate emissions with specific sites. A table of 633 point sources covering 75% of the total estimated emissions was compiled. The activities of these point sources are subtracted from the UK totals taken from national statistics of production and energy consumption. For many sources, the remaining emissions are treated as area sources. In other cases, such as clinical incinerators, the total amount of waste incinerated is distributed over the number of identified incinerators, either equally or by registered capacity.

2.1.2.3 Area sources include those emissions that could not be associated with a release point; including all Part B industrial processes, as well as diffuse sources such as domestic heating and agricultural emissions. Emissions from small industrial combustion and production processes (Part B and others) were distributed using employment statistics. Domestic fuel consumption is distributed according to population density, taking account of smoke-controlled areas and landcover. Areas of low population density were assumed not to be connected to the gas supply landlines. Agricultural emissions were distributed using the 'tilled land' landcover class. Emissions from railways and railway supply industry (including space heaters and power generation) were distributed according to a map of rail track kilometres per grid cell. Aircraft emissions below a height of 1000 m were distributed according to airport statistics, location, and extent of the airports.

2.1.3 Emissions predicted by the NAEI

2.1.3.1 A breakdown of the Hg emissions in the UK by source category according to the NAEI and three alternative emissions inventories is provided in Table 2.1. The three main Hg emitters are the metal industry, public power producers as well as waste treatment and disposal. According to the NAEI, 40% of the Hg from the UK is emitted by the 10 major point sources listed in the ISR (Table 2.2). Therefore, significant emission reduction could be achieved by targeting a few plant operators.

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Table 2-1 The breakdown of the Hg emissions for 1998 predicted by the NAEI in comparison with other recent UK emission inventories for mercury (in tonnes yr^{-1})

Name of inventory	NAEI	ERM	Pacyna	CEH
Literature reference	**Goodwin *et al.* (2000)**	**ERM/DoE (1996)**	**Pacyna (1999)**	**Nemitz *et al.* (1999)**
Reference year	**1998**	**1995**	**1995**	**1997**
Source category				
Public power producers	2.4	15.3	7.8	4.1
Institutional / residential combustion	1.1	1.9	1.4	0.4
Waste treatment and disposal (incl. crematoria and waste to energy)	2.2	9.7	-	7.0
Industrial combustion	1.1	1.9	-	2.0
Metal industry	4.4	6.6	0.7	9.5
Chemical processes	1.1	13.7	2.2	1.2
Other production processes (incl. cement, paper, glass etc.)	0.5	2.0	0.6	0.4
Transport	0.0	-		0.0
Natural sources	-	-		1.2
Other sources	0.1	-	7.4	
Total	**12.9**	**51.2**	**20.1**	**25.7**
NAEI estimate for the same year	12.9	18.2	18.2	12.9
Total adjusted for 1998	12.9	36.3	14.2	25.7

Table 2-2 Contribution of the top-ten industrial plants emitting Hg to the total man-made emissions estimated for the UK (data from the ISR)

	Source category	Operator / works	Location	Release tonnes yr^{-1}	Accumulated fraction of total man-made emissions
1	Non-ferrous Metals (Primary lead/zinc)	Britannia Zinc Ltd	Bristol	3.24	25%
2	Chloralkali industry	ICI Chemicals And Polymers Plc	Weston Point	0.77	31%
3	Chloralkali industry	Hays Chemical Distribution Ltd	Sandbach	0.21	32%
4	Power stations	Scottish Power	Longannet	0.18	34%
5	Power stations	National Power plc	Drax	0.17	35%
6	Power stations	National Power plc	West Burton	0.15	36%
7	Iron and Steel	British Steel plc	Scunthorpe	0.12	37%
8	Power stations	PowerGen plc	Ferrybridge C	0.12	38%
9	Power stations	PowerGen plc	Cottam	0.12	39%
10	Chloralkali industry	Rhone-Poulac Chemicals Ltd	Chesterfield	0.11	40%

2.1.3.2   In the NAEI emissions inventory, Britannia Zinc, Bristol, contributes 25% to the estimated national total and accounts for 74% of the emissions from the metal industry.

2.1.3.3   The spatial distribution of the UK Hg emissions predicted by the NAEI is shown in Figure 2.2a, after conversion from a 1 km to 5 km UK OS grid.
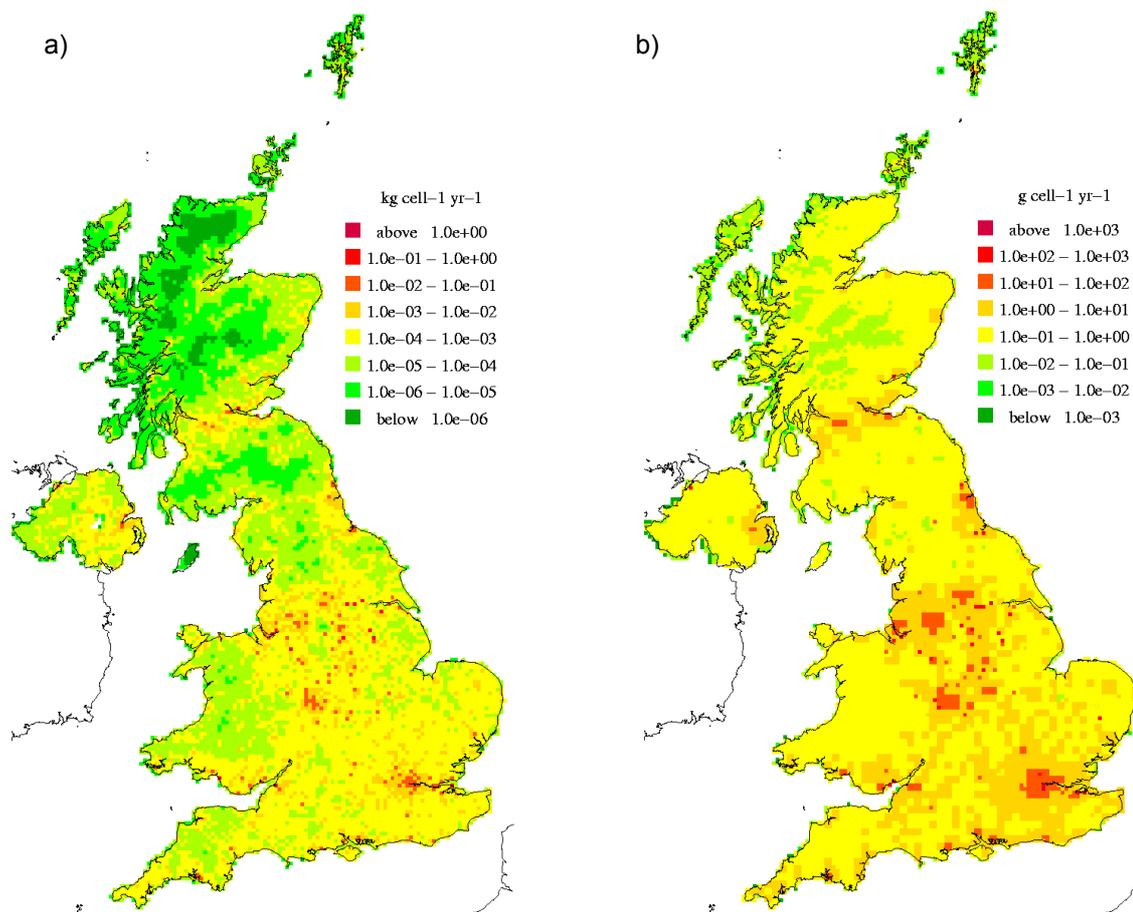
Figure 2-2 Spatial distribution of UK Hg emissions according to (a) the NAEI (Goodwin, 2000) and (b) CEH (Nemitz et al., 1999) both presented on the 5 km OS grid

2.2   Comparison with independent 'expert' inventories

2.2.1   The totals of several recent emission inventories are summarized in Table 2.1. Given the official emission estimates for 1995 and 1997 of 18.2 and 12.9 tonnes yr^{-1}, respectively (Figure 2.1), expert estimates are larger by up to a factor 2.6 than the 'official' figures. Whilst the NAEI and the CEH inventory of Nemitz *et al.* (1999) utilize the ISR, the inventories by Pacyna (pers. comm., 1999) and ERM/DoE (1996) are independent of the data submitted by plant operators and based on generalized emission factors, which tend to lead to higher emissions.

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2.2.2   Particular differences lie between the estimated emissions from coal-fired power plant, with much smaller emissions reported by the UK power generating companies than by independent 'expert' inventories (Pacyna, 1999; ERM/DoE, 1996). This implies that emission factors assumed by the plant operators are much smaller than generalized emission factors, such as published in the EMEP/CORINAIR 'Atmospheric Emission Inventory guidebook' (Richardson, 1999). The difference in the emission from public power between the NAEI and CEH inventories lies primarily in the use of larger emission factors by CEH for those activities that were not covered in the ISR.

2.2.3   Mercury emission from Hg-containing products is a source category that has undergone significant changes over the past 10 years. During the life cycle of, e.g., Hg-containing batteries, barometers, thermometers and fluorescent tubes, Hg may be emitted during production, distribution, use and disposal. WS Atkins (WSAC, 1997) recently reviewed the emission from the use and disposal of these products within the UNECE region and compared their results with an earlier estimate by IVL. Because the study summarizes the consumption and disposal of Hg-containing products for the whole of the Western European UNECE countries together, it does not, in its current form, predict emissions specific to the UK. However, the report assumes that practices of use and disposal do not differ across western Europe, and therefore it is possible to re-scale the results according to the UK population. Table 2.3 shows the UK emissions to air, predicted by this exercise. For breakage and landfill emissions, WSAC (1997) reported separate emission factors for the first year and for years 2 to 10 (of product lifetime). Here, it was assumed that emission occurs over the first 10 years. Given the recent reduction in the use of Hg, for example in batteries, it must be expected that this estimate represents an underestimate of the emission for older equipment disposed of over the past 10 years.

Table 2-3 Mercury emissions in tonnes yr^{-1} from the use and disposal of mercury-containing products, derived from the best estimates provided for the Western European UNECE countries by WSAC (1997)

Product	breakage	landfill	incineration	total
Button cell batteries	0.001	0.020	0.186	0.208
Measuring and control equipment	0.013	0.063	0.133	0.208
Electrical equipment	0.000	0.050	0.106	0.156
Lighting	0.013	0.056	0.119	0.188
Sum	0.027	0.190	0.544	0.760

2.2.4   The emissions in Table 2.4 are based upon the best estimate of the consumption of Hg-containing products in the Western European UNECE countries. WSAC (1997) also provided lower and upper estimates of this consumption. The use of measuring and control equipment is particularly uncertain, with the range spanning an order of magnitude. Unfortunately, the range is only deduced from the range in consumption figures and not from the uncertainty in the emission factors. Although it probably improves upon the older IVL inventory for Eastern European UNECE

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countries, the emission estimates of WSAC (1987) contain little UK-specific information. In particular, emissions originating from the *production* of Hg-containing equipment are not included in their assessment.

2.2.5   A further detailed study of the emission from the production, use and disposal of Hg-containing products was provided as part of the emissions inventory of ERM/DoE (1996) and this is compared with the WSAC and NAEI estimates in Table 2.4. It appears that the NAEI estimate of Hg emissions from industrial and control equipment is higher than the other two estimates.

2.2.6   The disposal of Hg-containing products is only a part of the total Hg disposed of through the waste stream. The breakdown of the Hg emissions arising from waste disposal and incineration (Table 2.4) differs greatly between the NAEI (mainly derived from the ISR) and the ERM inventory, with the ERM predicting much larger emissions from municipal and clinical waste incineration. This is partly explained by the change in legislation for MSW incinerators, which has led to a shutdown of virtually all MSW incinerators by the end of 1996 and the re-opening of new incinerators from 1997. The analysis of the materials disposed of in clinical and industrial incinerators carried out by the ERM appears to be highly detailed, although many open questions remain. In contrast, the operators of crematoria state higher emissions than had been predicted by the ERM.

Table 2-4 Breakdown of the emissions from the use of mercury in products and waste disposal according to ERM/DoE (1996) and Goodwin et al. (2000) in tonnes yr^{-1}

	ERM 1995	WSAC 1997	NAEI 1998
Waste disposal / incineration			
Dental amalgam / incineration	0.32		1.34*
Municipal waste	4.40		0.97*
Sewage sludge	0.12		0.05*
Clinical waste	4.90	0.54$^{\#}$	0.40*
total:	9.74		2.02
Production and use of products			
Batteries	0.01	0.001	0.01
Paints	0.01	no data	no data
Biocides and pesticides	0.01	no data	no data
Industrial and control instruments	no data	0.013	0.25
Electrical equipment	no data	0.000	0.1
Lighting appliances	0.04	0.013	0.02
total:	0.07	0.027	0.38

* taken from ISR database.

$^{\#}$covering Hg-containing equipment listed in Table 2.3 only, which is a combination of MSW, clinical and industrial waste

2.2.7   The only other fully spatially disaggregated emission inventory, apart from the NAEI, is the CEH inventory. This inventory was compiled on 5 km OS grid for the reference year 1997 for the 'Joint Environment Programme' of the main UK power producers (PowerGen, National Power and TXU Europe – formerly Eastern Generation). Compared on 5 km grid, the coarser spatial resolution of

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the CEH inventory (Figure 2.2) is a result of the lower resolution of the underlying population data used by CEH (10 km), compared with the NAEI (1 km).

2.2.8 In general, the spatial structure of the two inventories is very similar, with the CEH inventory predicting slightly larger background emissions (note the logarithmic scale). This is because of the use of larger emission factors for residential and commercial combustion processes, the inclusion of some natural sources, and differences in the spatial disaggregation technique. Owing to the unavailability of employment data for the CEH inventory, more emission categories were disaggregated by population than in the NAEI inventory.

2.2.9 Unlike the NAEI, the CEH inventory also utilizes the replies to 450 questionnaires (with more than 80 useful returns) to the operators of the Hg emitting Part A processes. Through this questionnaire, CEH evaluated emissions, the activity parameters of the plants (which are otherwise kept confidential by the UK Department of Trade and Industry) as well as stack parameters.

2.3 An initial speciated Hg emissions inventory for the UK

2.3.1 The NAEI does not provide information on the speciation of the Hg emitted (elemental gaseous, reactive gaseous, particle-bound, methylated Hg). However, international expert groups have recommended that the member states of the CLRTAP should in future compile speciated emission data in order to improve the estimate of transboundary fluxes of Hg (e.g. WMO, 2000).

2.3.2 At temperatures of over 600°C, all Hg is present in its elemental gaseous form (e.g. Rizeq *et al*., 1994). However, as the flue gas cools, a fraction of the Hg^0 reacts with oxidants in the flue gas or is adsorbed onto particles. The effective speciation of mercury differs between source types and is dependent upon parameters such as boiler type, fuel composition, air pollution control system, and flue gas temperature and composition. For example, in tests carried out by PowerGen on four British coals with a chlorine content between 0.11 and 0.44, 44% showed that the percentage of RGM was higher (over 80 %) for the highest chlorine content coal; similar observations having been made for a range of US coals (Curtis, 1994; Felsvang *et al*., 1994). Some of the coal deposits in the Yorkshire-Nottinghamshire-Derbyshire coal are notably high in chlorine (Lightowlers and Cape, 1988) and therefore a high fraction of RGM would be expected. With the development of measurement techniques for the individual chemical forms of Hg, it has become possible to identify the speciation for selected sources (Table 2.4). Prestbo and Bloom (1995) observed average RGM/TGM ratios of 0.67, 0.23 and 0.71 in the flue gas of the combustion of coal, oil and waste, respectively. Galbreath and Zygarlicke (1996) summarized data on Hg speciation in coal combustion and gasification flue gases. National Power was involved in an unsuccessful 1-year study to determine the fraction of reactive Hg from the flue gas of Eggborough power station (Raymond Wright, pers. comm.).

Table 2-5 Summary of some measurements of Hg speciation from various sources

Source category	Air pollution control system (APCS)	Percent of Hg emitted as				Literature references
		Hg^0	Hg-p	RGM	MHg$^\#$	
Coal fired power plant	none	33	-	67	0.1	averages of data summarized by Galbreath and Zygarlicke (1996)
	FGD	25	-	75		ditto
	ESP	62	-	38		ditto
	ESP and FGD	58	-	42		ditto
Oil fired power plant		77	-	23		Prestbo and Bloom (1995)
Waste incineration		29	-	71		Prestbo and Bloom (1995); Wang *et al*. (1999)
Waste incineration		20	20	60		Bergstrom (1986); Vogg *et al*. (1987); Lindqvist (1986)
Chlor alkali		50-90	10-50	-		Leavander (1987)
Pyrite burning		100				Leavander (1987)
Gasification					> 0.1	

$^\#$It is currently unclear whether MHg emissions observed in some studies are real or an artefact arising from the reaction of Hg^{2+} with acetic acid in collection traps according to the MESA method. Using an alternative trap, Prestbo and Bloom (1995) concluded that flue gas does not contain MHg

2.3.3   These datasets are far from complete. However, as an initial speciation for UK sources, the average speciation estimated for the major source categories by Pacyna (1999), quoted by Ryaboshapko *et al*. (1999), may be used (Table 2.5). Using these estimates in the NAEI inventory, the UK emissions of Hg^0, Hg-p and RGM are 8.4, 1.2 and 3.0 tonnes yr^{-1}, respectively, with a relative distribution over these species of 67% Hg^0, 9% Hg-p and 24% RGM. For comparison, the application to the CEH inventory results in annual emissions of 14.9 tonnes (58%) Hg^0, 2.3 tonnes (9%) Hg-p and 8.5 tonnes (33%) RGM. The higher relative contribution of RGM in the CEH inventory is mainly the result of a larger contribution from waste incineration. The application of this speciation to the CEH inventory is therefore more similar to the prediction by Pacyna (1999) of 53% Hg^0, 13% Hg-p and 35% RGM than the NAEI estimate. A particularly high fraction of reactive gaseous mercury (RGM) is emitted by waste, coal and oil combustion. Since the atmospheric transport distance of RGM is much shorter than that of other Hg species, high Hg deposition must be expected close to these sources.

2.3.4   The speciation by Pacyna (1999) was applied to the basic source categories and redistributed following the methodology used for the NAEI. The spatial structure of the emission of the three components and their contribution to the total mercury emission are presented in Figure 2.3.

2.3.5   Unfortunately, this speciation cannot currently be extended to MHg, which is particularly important from a toxicological point of view. Because of the very low concentrations of this form of Hg, and measurement artefacts associated with sampling of MHg, it is currently not clear whether, and to what extent, MHg is directly emitted by industrial sources and there no emission factors for this species. We are not aware of any disaggregated emissions inventories of MHg.

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Table 2-6 Speciation applied to UK sources and resulting average relative and absolute emissions of elemental gaseous mercury (Hg^0), reactive gaseous mercury (RGM) and particulate mercury (Hg-p)

	Hg^0	Hg-p	RGM
Coal combustion	50%	10%	41%
Oil combustion	51%	10%	39%
Cement production	80%	5%	15%
Non-ferrous metal production	81%	5%	14%
Pig iron production	79%	4%	17%
Caustic soda production	71%	0%	29%
Waste disposal	22%	22%	56%
Other	79%	5%	15%
NAEI inventory			
UK average fractions	67 %	9 %	24 %
UK total emissions	8.4 tonnes yr^{-1}	1.2 tonnes yr^{-1}	3.0 tonnes yr^{-1}
CEH inventory			
UK average fractions	58%	9%	33%
UK total emissions	14.9 tonnes yr^{-1}	2.3 tonnes yr^{-1}	8.5 tonnes yr^{-1}

2.4 Uncertainties in man-made emissions in current UK emission inventories

2.4.1 Data from the NAEI

2.4.1.1 Generally, uncertainties associated with emission estimates such as provided by the NAEI take into account:

- the estimated country total for each source sector;
- the geographical allocation of the emissions;
- the chemical speciation of the emission.

2.4.1.2 While the NAEI has been concerned with providing total UK emissions for individual years (e.g. Salway *et al*., 1997), the disaggregation method, although used in similar form for other primary pollutants, has only been extended recently to Hg (Goodwin *et al*., 2000). A first chemical speciation of UK Hg emissions is made here.

2.4.2 Data from the ISR database

2.4.2.1 More than half of the emissions in both the NAEI and the CEH inventories are derived from the ISR and equivalent databases for Scotland and Northern Ireland and therefore depend on the quality of the data submitted by the plant operators. The ISR contains many gaps and inconsistencies. For example, even some coal-fired power plants are not associated with emission figures. Many of these gaps are obvious and have been complemented in the NAEI and CEH inventories with data from other sources. However, other gaps may not be apparent and some industrial sites may be included in the inventories without emissions.

2.4.2.2   The quality and reliability of the data submitted to the ISR may be expected to vary greatly between operators. Mercury measurements are difficult to carry out, especially in flue gas. Flue gas measurements have shown concentrations to fluctuate by more than an order of magnitude (e.g. Struhs, 1996). It is therefore feasible that emissions are calculated using measurements performed under optimum running conditions and do not account for the actual running conditions.
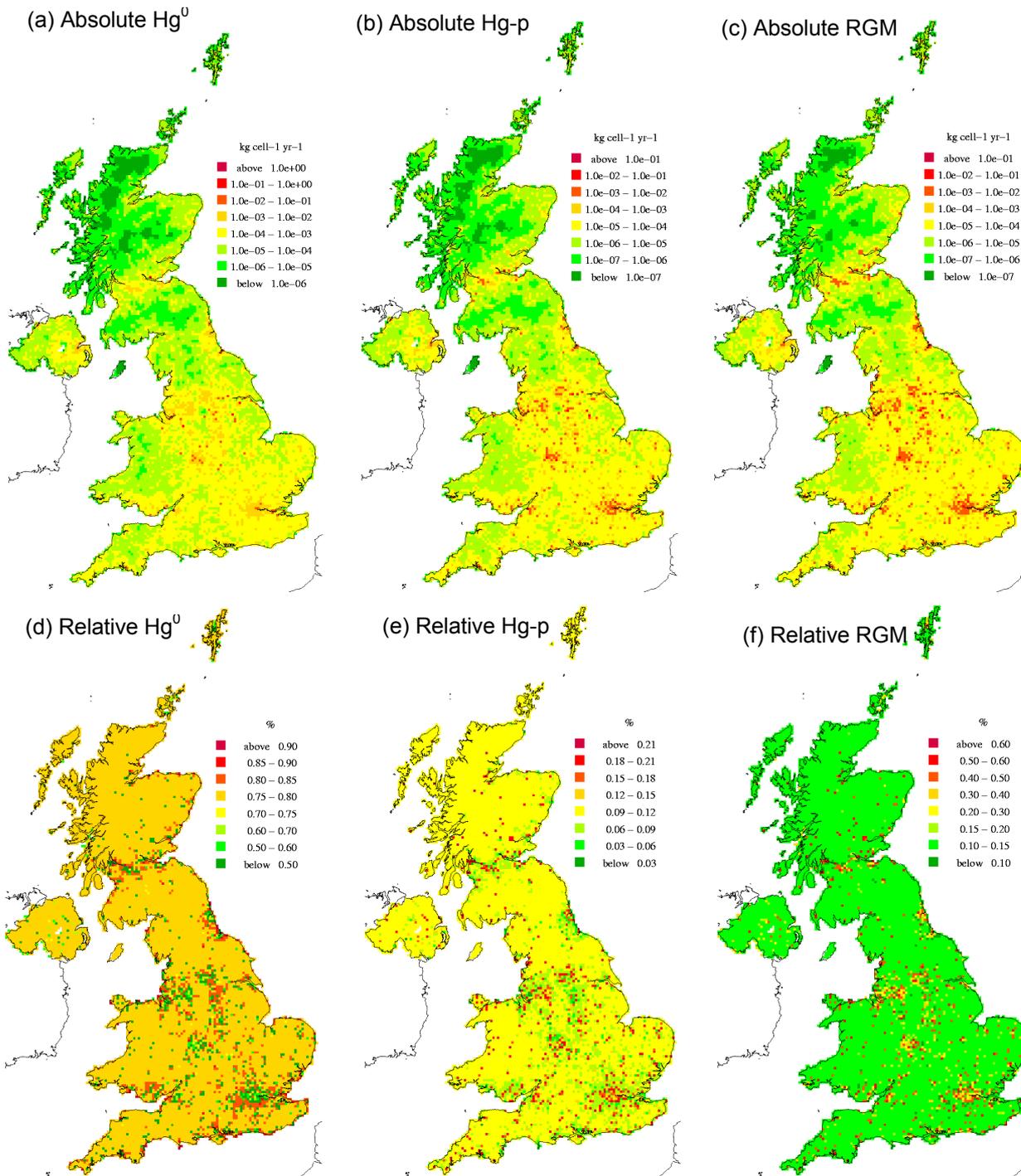
Figure 2-3 Speciation of the UK emission of mercury on 5 km OS grid: (a-c) Emissions of Hg^0, Hg-p and RGM [kg cell^{-1} yr^{-1}], (d-f) contribution of Hg^0, Hg-p and RGM to total emission [percentage]

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2.4.2.3   In addition to improving the quality assurance of the ISR database in general, for modelling pur-poses it would be helpful if stack parameters (height, diameter, temperature, flow rate, and ther-mal strength) could be included into the ISR questionnaire and database.

2.4.2.4   There is a generic problem with data confidentiality. For many processes (including chemical processes), the plant-specific activity figures are held by the Department of Trade and Industry or the relevant UK Trade Associations. However, in many cases the NAEI can only use these data to calculate national totals, which then have to be spatially disaggregated according to publicly available data, such as capacity figures. This leads to a much less accuracy in the distribution of the emissions than could be achieved by using actual plant specific activities. Since abatement technologies differ between plants, errors in the allocation of activities also affect the estimate of the total UK emission.

2.4.2.5   Since Hg is emitted from small, specialized industrial processes such as battery manufacture, an improvement in the estimate of industrial emissions would be made by lowering the reporting threshold of currently 100 g yr^{-1}, which equates to roughly 0.01‰ of the national emissions. In the NAEI the activities (fuel use, production figures) of the identified point sources are subtracted from the national total and the remainder is in general distributed according to employment statis-tics. Emissions are currently reported to the ISR without activity figures, which are often treated as confidential and must therefore be estimated or derived from other sources. The quality of the emissions inventory would be improved if activities had to be reported to the ISR.

2.4.2.6   In Scotland, the information submitted by the operators is on the public register, but they are held by five separate SEPA divisions as paper files. The introduction of an electronic database would assist in ensuring an efficient and reliable transfer of the data to the NAEI.

2.4.3   Public power producers

2.4.3.1   As demonstrated by the mismatch of emissions from public power producers submitted to the ISR and calculated using generalized emission factors (Table 2.1), there is some uncertainty in the emissions especially from coal-fired power stations. Heavy metal emissions from public power producers' plant are studied within the 'Joint Environment Programme' of PowerGen, Na-tional Power and TXU (Europe) - formerly Eastern Generation. Extensive heavy metal sampling has been carried out downwind of UK coal-fired power plants (Mike Jenkins, PowerGen, pers. comm.), although Hg analysis had to be abandoned because of analytical difficulties. In addition, the power generating companies can derive Hg emissions by mass balance from the Hg content in fuels, fuel residuals and filter media. Nevertheless, as with any operator who submits data to the ISR, the emissions are difficult to validate.

2.4.3.2 There is some evidence that generalized emission factors have overestimated emissions from coal-fired power stations in the past, at least relative to other sources: (i) no elevated Hg concentrations of TGM could be observed in the plume of Didcot A by Lee *et al*. (1998a), and (ii) in the early 1990s, global Hg concentrations declined more rapidly than the use of coal, emphasising the importance of the reduction in sources other than coal combustion (Slemr and Scheel, 1998).

2.4.4 Incineration

2.4.4.1 Emissions from incinerators are highly dependent upon what is burnt and the use of generalized emission factors leads to highly inaccurate results. For incineration of hospital waste, for example, Richardson (1999) reported emission factors between 1 and 5 g Hg per tonne waste burnt, which is probably much larger for small onsite facilities without abatement technology, and highly dependent on the waste composition. Currently, the list of incineration facilities reporting to the ISR appears to be incomplete. Whilst detailed information is available on the throughput of crematoria from the 'Federation of Burial and Cremation Authorities', no information is available on the exact activities of clinical incinerators. In the absence of accurate disposal statistics of clinical waste, the current NAEI methodology distributes total UK emissions equally over the identified clinical incinerators, regardless of the actual throughput or size of the associated hospital (J. Goodwin, pers. comm.).

2.4.4.2 A change in the legislation for municipal waste incinerators led to a shutdown of most incinerators in 1996, while incinerators that are more modern have re-opened.

2.4.5 Production and use of products

2.4.5.1 Although WSAC (1997) and ERM/DoE (1996) have provided detailed estimates of Hg emissions arising from the use and disposal of certain Hg-containing products, less information is available on Hg emissions during the production process of these products. ERM/DoE (1996) estimated that in 1994, the quantity of Hg contained in thermometers and sphymomanometers purchased annually for the NHS alone was approximately 1 tonne and 10.2 tonnes, respectively. In contrast, WSAC (1997) estimated that measurement and control equipment disposed of in the mid 1990s contained only approximately 1.5 tonnes yr^{-1}. However, it is even less certain, which fraction of the apparatus in manufactured in the UK and how much Hg is released to the atmosphere during the manufacturing process. Because of the rapid changes in the Hg contents of products over the past 10 years it is currently unclear how many older products are still in use, currently enter the waste stream, and how old spillages and the storage of old equipment on landfill sites affect the current emissions.

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2.4.5.2   It is likely that Hg is emitted from many small industrial applications and accidents not considered by the ISR or that fall into any of the main source categories.

2.4.6   Domestic combustion

2.4.6.1   Generalized disaggregation approaches are often used uniformly for the country, not accounting for local differences. For example, the disaggregation of residential combustion emissions assumes that boiler types in the north and the south of the country are distributed according to the same general patterns. Domestic heating activities are currently disaggregated according to population density statistics. In this approach, the presence of gas landlines is inferred from the population density. Improved aggregation maps are clearly required to improve the distribution of domestic burning of gas and solid fuels.

2.4.7   Landfill sites

2.4.7.1   Emissions from landfill sites are not currently considered in the CEH and NAEI inventories. The amount of municipal solid waste (MSW) taken to landfill sites amounts to 18.7 Mt yr^{-1} for England and Wales (Martin, 1997) and to 2.6 Mt yr^{-1} for Scotland (estimated from SEPA, pers. comm.). Mercury emissions from MSW landfill sites were measured by Lindberg and Price (1999), who derived an emission factor of 0.7 mg Hg (t waste)$^{-1}$. Assuming practices similar to those in the US, UK national emissions from landfill sites would be of the order of 15 kg yr^{-1}, about 0.15% of the national total. From data presented by WSAC (1997), it may be estimated that the Hg input into UK landfill sites originating from the Hg-containing products listed in Table 2.3 amounts to approximately 4.3 tonnes Hg yr^{-1}. Using the WSAC (1997) emissions factor, this would result in an annual Hg emission of 190 kg yr^{-1}, approximately 1.5% of the NAEI estimate. In addition, MSW only amounts to about 15% of all waste disposed by landfill (EA, pers. comm.). ERM/DoE (1996) estimated an additional discharge of nearly 37 tonnes Hg yr^{-1} to landfill from non-domestic sources, more than the amount contained in MSW. This waste originates primarily from the chlor-alkali production (22.8 tonnes yr^{-1}), primary lead and zinc smelting (10.2 tonnes yr^{-1}) and coal-fired power stations (3.4 tonnes yr^{-1}). The precise nature of disposal of these special wastes varies greatly between processes and more investigations are required to estimate the importance of this source. As a first estimate, the additional landfill material may cause an emission of at least 25 kg yr^{-1}, whilst the application of the WSAC emission factors would result in an annual contribution of 2.2 tonnes Hg yr^{-1} (17% of the NAEI total). Although the emission factors used by WSAC appear to be large, more research is required to quantify Hg emissions from landfill sites.

2.4.7.2   Since landfill and sewage gas contain high concentrations of methane, they may also be a major source of the toxicologically important MHg (e.g. Feldmann and Hirner, 1995).

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2.4.8 Budget considerations

2.4.8.1 In the 1970s and 1980s, TGM concentrations in the N hemisphere were still increasing. More recently in Europe, concentrations of Hg have decreased by about 45% (0.17 ng m^{-3} yr^{-1}) between 1990 and 1996 (Slemr *et al*., 1995; Pacyna and Berg, 1996; Slemr and Scheel, 1998). This decrease is stronger than the reduction in coal consumption (Slemr and Scheel, 1998). Therefore, in order to reconcile this observation with current Hg emission inventories, it must be assumed that the contribution of man-made relative to natural sources has been underestimated and/or emissions from other sources (waste incineration etc.) have been underestimated.

2.5 Natural emissions and re-emission of mercury

2.5.1 Introduction

2.5.1.1 The current official UK Hg emissions inventory only considers industrial/man-made emissions. There is increasing evidence that the emissions from natural media such as soils, vegetation and water bodies contribute significantly to the overall Hg budget. These emissions are often divided into 'natural emissions', which would occur without industrial activities; and 're-emissions' which arise from Hg that has entered soils and water bodies from atmospheric or direct inputs from industrial activities. Although this distinction is sensible for the assessment of human influences on the Hg budget, measurements cannot discriminate between the two processes. Mercury may be deposited to plants and soils but it can also be emitted. This bi-directional flux is similar to that of other pollutants (e.g. CO_2, NH_3). Emissions of gaseous Hg from natural media originate from surface gas concentrations (χ_s) in equilibrium with dissolved Hg^0 in water, soil water or leaf surfaces. Approximately 5 to 10 % of the dissolved Hg is in the elemental form (Fitzgerald and Mason, 1996) and the formation of dissolved Hg^0 from its divalent and organic forms in natural waters is promoted by solar radiation and bacterial activity (e.g. Figure 2.4; Carpi and Lindberg, 1997; Gardfeldt *et al*., 2001). The direction of the resultant flux depends upon the comparative magnitude of χ_s and the air concentration, χ_a (Kim *et al*., 1995; Hanson *et al*., 1995). This Hg exchange could helpfully be modelled by a compensation point approach similar to carbon dioxide and ammonia (e.g. Sutton *et al*., 1995), but so far has not.

2.5.1.2 Natural emissions are constrained to the volatile species Hg^0 and MHg, but Hg^0 is expected to completely dominate the emissions (Lindberg *et al*., 1995, 1998).

2.5.1.3 Globally, natural emissions are assumed to be approximately 20–33% of emissions (e.g. Lindqvist, 1991). Without an accurate estimate of these natural emissions and re-emissions in the UK, the ratio of natural to man-made emissions is unknown and the relative emission reduction from emission control strategies cannot be predicted.

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2.5.1.4   Natural emissions and re-emissions may be estimated (i) by measuring exchange fluxes directly; (ii) by analysing the variation of concentrations with respect to meteorological control parameters and (iii) by estimating preindustrial concentrations and depositions of Hg.

2.5.2   Direct measurements of Hg exchange fluxes

2.5.2.1   Direct measurements of the surface/atmosphere exchange fluxes of Hg for vegetation types, soils and water surfaces provides the most accurate means to quantify natural emissions. Unfortunately, there is a complete lack of direct flux measurements in the UK and results have to be adopted from measurements in North America and Scandinavia. Currently, no UK research group carries out Hg flux measurements.

a) Emissions from soils

2.5.2.2   There are few data on Hg concentrations in UK soils. In the area of Mansfield, Nottinghamshire, Hg concentrations range from 20 to 594 ppb with an average of 93 ppb (Barry Smith, BGS, pers. comm.), while Angelone and Bini (1992) reported mean concentrations of 250 and 120 ppb for England and Scotland, respectively. Using a preliminary relationship between soil Hg concentration and Hg^0 emission derived from Rasmussen et al. (1998), this may result in emissions of 28 to 500 ng m^{-2} day^{-1} (average 100). However, Hg^0 emissions from soils are strongly controlled by soil temperature and solar radiation (Figure 2.4; Kim et al., 1995; Carpi and Lindberg, 1998), and the summer data by Rasmussen et al. (1998) may not be representative for the calculation of an annual mean.

2.5.2.3   Extrapolated to the land surface of the UK, a value of 100 ng m^{-2} day^{-1} would lead to 9 tonnes yr^{-1} for the UK, about 2/3 of the man-made emissions. It is uncertain how much of this emission would penetrate plant canopies. Therefore, a more realistic estimate of Hg emission from soils may be obtained by multiplying typical emission fluxes by half the area of tilled land, leading to a yearly contribution of about 1.0 tonnes yr^{-1}.
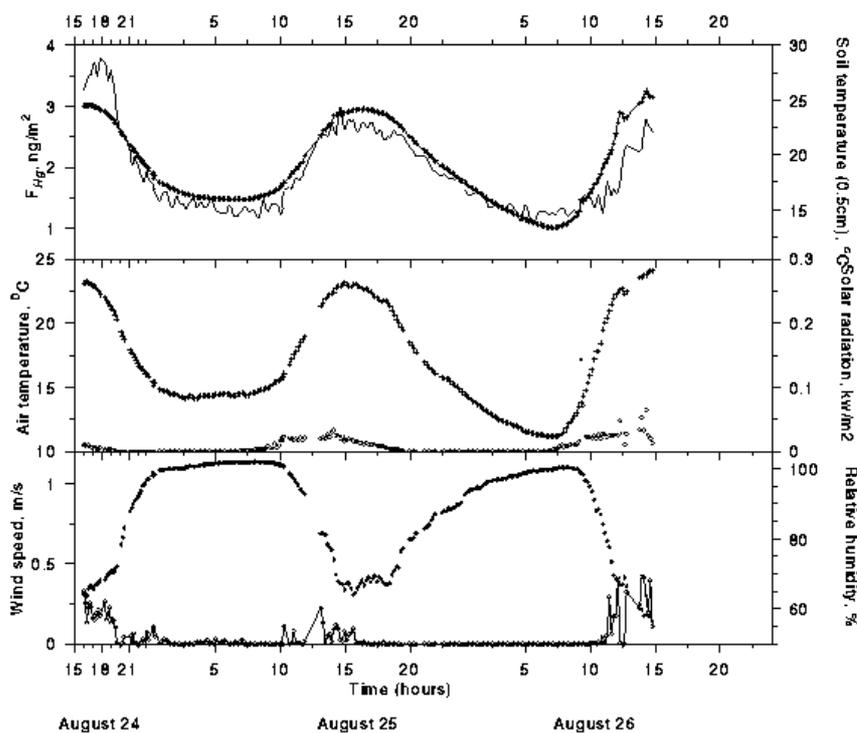
Figure 2-4 Mercury emission from soil with a Hg content of in relation to meteorological variables (from Boudala et al., 2000) --- Mercury flux; -+- soil temperature (0.5 cm); +++ air temperature; ooo solar radiation; -o- wind speed; ●●● relative humidity

b) Emissions from vegetation

2.5.2.4   Based on measurements (Lindberg *et al*., 1992) as well as landcover data (Barr *et al*., 1993), it may be estimated that UK forests may emit some 0.12 tonnes Hg yr^{-1}, about 0.9 % of the NAEI total. Correlations of Hg concentrations in roots, but also in shoots, with soil Hg demonstrate that uptake from soil is a significant route of Hg into vegetation (Cocking *et al*., 1995). Therefore, the re-emission from vegetation is not only related to the previous deposition to the vegetation but also to the Hg content of the soil.

c) Emissions from water bodies

2.5.2.5   Although it is widely accepted that rivers transport large amounts of Hg as a result of industrial discharges, there is little information on Hg re-emission from rivers. In a recent study Bahlman (1997) estimated that the Elbe River in Northern Germany may emit between 100 and 500 kg Hg yr^{-1}, while the only direct measurements of fluxes above river water (Poissant and Casimir, 1996) indicated smaller fluxes of 25 ng m^{-2} day^{-1}.

2.5.2.6   Emission rates of Hg^0 from lakes reported in the literature range from 15 to 200 ng m^{-2} day^{-1} (e.g. Lindberg *et al*., 1995; Gardfeldt *et al*., 2001). Given a coverage of surface freshwaters in the UK of 3200 km^2, this equates to a yearly Hg emission of 0.02 to 0.24 t, up to about 2% of the man-made emissions estimated by the NAEI.

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2.5.2.7   Emissions from the Northern Atlantic are estimated as about 350 ng m^{-2} day^{-1} (Mason and Fitz-gerald, 1996), whilst emissions of 10–140 ng m^{-2} day^{-1} have been reported for estuaries which appear to be correlated to the Hg concentration of the water (Cossa *et al*., 1996).

2.5.2.8   The emission potential of water bodies depends upon the concentration of dissolved gaseous mercury (DGM). Average concentrations of total dissolved Hg in UK estuaries range from 0.6 (Tamar) and 1.2 (Thames) to 2.2 ng l^{-1} (Forth) (e.g. MAFF, 1991; Tang, 1994). The Environment Agency monitors the total Hg concentration in water and sediments downstream of industrial sewage discharge points which receive effluent from a trader that is consented to discharge mercury. In addition to these sites, Hg concentrations are monitored at additional sites (mainly at the bottom of catchments) as part of the National Network (Figure 2.5). Since data on DGM are scarce, however, the emission potential cannot easily be estimated.
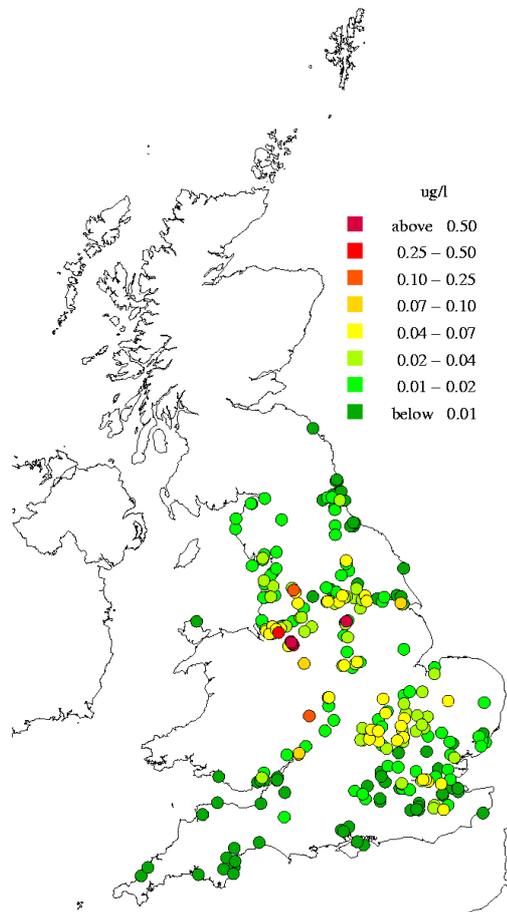
Figure 2-5 Average Hg concentration [μg l^{-1}] in UK freshwaters for 1998 (source: Copyright © Environment Agency of England and Wales)

d) Emissions from naturally and industrially contaminated Hg enriched areas

2.5.2.9 Natural emission and re-emission are largest for substrates enriched in Hg. Gustin *et al.* (1999) showed a map with a belt of productive deposits that stretches from Europe into the south-west of England, but the British Geological Survey could not verify its existence (T. B. Colman, BGS, pers. comm.). More investigations are also required to investigate whether areas of the UK are enriched from industrial contamination, for example through contaminated mill tailings. Leake *et al.* (1993) mentioned the probability of an accident involving amalgamation barrels at the Gwyn-fynydd mine and ore treatment works (Snowdonia, Wales) in 1935. Indications for this accident include the frequent occurrence of amalgams, which were also found in the Kildonan Burn in NE Scotland. In the same study, Hg of natural origin was found in gold from the rivers Afon Wen (Snowdownia, Wales) and Callichar Burn (Perthshire, Scotland) as well as in the Lack area (N. Ireland).

e) Summary of natural emissions and re-emission

2.5.2.10 From these estimates (summary provided in Table 2.6), it is likely that the natural emissions and re-emission probably lie somewhere in the region of 5–40% of the man-made emissions. Both direct UK measurements and investigations into the mechanistic controls of Hg volatilization are urgently required (a) to narrow down this range and (b) to develop an understanding that allow natural emissions to be mapped.

Table 2-7 Preliminary summary of natural emissions and re-emissions

Source category	Area of coverage [km^2]	Min estimate [t yr^{-1}]	Max estimate [t yr^{-1}]	Best estimate [t yr^{-1}]
Coniferous forests	14,300	0.01	0.08	0.04
Deciduous forests	13,200	0.01	0.18	0.09
Fresh waters	3,200	0.02	0.24	0.10
Tidal waters and estuaries	7,700	0.02	0.58	0.20
Soils	tilled: 51,300	0.2	9.0	1.0
Areas geologically enriched in Hg	no data			
Contaminated land	no data			
Total 'natural' as percentage of man-made total estimated by NAEI:		> 0. 26	10.1	1.4
		2 %	78 %	11 %

2.5.3 Hg emissions estimated from variations in air concentrations

2.5.3.1 Diurnal changes in air concentrations of trace gases can sometimes be indicative of a diurnal signal in surface emissions, e.g. as is the case for radon. From diurnal changes in air concentrations of TGM observed at one site, Lee *et al.* (1998a) derived a surface emission rate of 7 ng m^{-2} night^{-1}, which may be scaled up to the UK to give 1.3 tonnes yr^{-1}, 10% of the NAEI total. If day-

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time fluxes are one order of magnitude larger than night-time fluxes, because of the effects of solar radiation and temperature, the surface emission would equate to 6 tonnes yr^{-1} or 50%. Such a scaling assumes that the surface source strength would be uniform across all land surfaces, which is certainly unlikely to be the case, but nonetheless provide an indicative order of magnitude estimate.

2.5.4 Historical levels of Hg concentrations and deposition

2.5.4.1 One approach to distinguish between natural background emissions and re-emission is the identification of Hg concentrations and deposition prior to industrialization and to derive the associated emissions by mass balance. Early estimates of the global annual emissions derived from ice core and global ice and snow samples were as large as 190,000 tonnes yr^{-1}, while more recent estimates based on lake sediment cores range from 1,600 to 3,000 tonnes yr^{-1} (Allan, 1999).

2.5.4.2 From sediment records of high-latitude lakes in Canada, Lockhart *et al*. (1995) derived that current deposition rates are 1.2–2 times larger than historical rates, with maximum enrichment factors of 7. Current fluxes ranged from 3.8–28.4 μg m^{-2} yr^{-1}, while historic fluxes ranged from 0.7–14.5 μg m^{-2} yr^{-1}. Similar results were obtained from peat records, which indicate a preindustrial deposition of 10 μg m^{-2} yr^{-1} and a current deposition of 25 μg m^{-2} yr^{-1} (Benoit *et al*., 1998). The measurements indicate a high variability in natural sources and that many remote areas in N. Canada and the Hudson Bay derive Hg primarily from geological or other natural sources. However, Mason *et al*. (1994) concluded that man-made emissions have tripled the concentration of Hg in air and in the surface ocean. Correcting sediment data for contributions from catchments and vertical transport, Meili (1995) derived preindustrial deposition rates in temperate and boreal zones of 1–5 μg m^{-2} yr^{-1}. Assuming steady state conditions, this would imply a natural emission of 314 ng m^{-2} day^{-1}. Since the Hg pool stored in biota, soil and water bodies has increased from the deposition of industrially-derived Hg, it is likely that current re-emissions are considerably higher than preindustrial natural emissions.

2.5.4.3 Recently, the DETR commissioned The Environmental Change Research Centre of University College London, to examine lake sediment cores from around the UK for historical changes in Hg accumulation (Rose, pers. comm.). Although the data analyses and interpretation are incomplete, at the time of writing, some preliminary observations can be made. The rise in concentrations at most sites are consistent with what is known about global/northern hemispheric time trends of coal consumption over the last 100 years: peak concentrations are shown at some sites corresponding to the period approximately 1950 to 1970. The most remarkable observation is that Hg concentrations in sediments appears to fall into the upper range of observations for Europe.

2.6   Temporal variations and trends in emissions

2.6.1   Temporal variations

2.6.1.1   Temporal variations in Hg emissions are linked to temporal patterns in activities (for industrial sources) and changes in parameters that control evasion (for natural emission and re-emission). Seasonal patterns of selected industrial activities are exemplified in Figure 2.6. Several important activity patterns show a clear seasonality with colder temperatures in winter leading to higher mortality rates and an increased consumption of coal, oil and gas. In contrast, cement production is related to building activities, which are reduced during winter. Other production figures such as of the steel and chloroalkali industry show a significant month-to-month variability with changes of up to 40%, which is driven by the dynamics of the market and does not follow a seasonal pattern. In addition to this seasonal variation, many human activities, including residential heating and many production processes, follow a clear diurnal pattern.

2.6.1.2   Mercury concentration measurements consistently show the largest values in winter (Section 3), which is consistent with the seasonality in man-made sources. However, there are alternative explanations: during winter the boundary-layer height is, on average, lower than in summer so that the same amount of Hg is confined to a shallower layer. The chemical behaviour of atmospheric Hg adds to this effect: higher oxidant concentrations in summer lead to an increased deposition of TGM via the transformation into fast-depositing RGM. This is confirmed by the seasonality of RGM concentrations, which show summer maxima (Sommar *et al*., 1999).

2.6.1.3   Natural Hg emissions and re-emission from soils and water surfaces are governed by available solar radiation and temperature (see Section 2.5), and are therefore expected to be largest in summer and during daytime.

2.6.1.4   In summary, industrial Hg emissions may be expected to be 10–30% larger in winter than in summer. A better quantification of the natural emissions is needed to estimate the variation of the total Hg emission.

2.6.2   Future trends in emissions

2.6.2.1   Mitchell *et al*. (1992) speculated that with the 1998 ban on disposal of sewage sludge at sea, the incineration of sewage sludge is likely to become an increasingly important source of heavy metals. Alternatively, sewage sludge application to land would increase Hg^0 emissions by 1 to 2 orders of magnitude (Carpi and Lindberg, 1997), although significantly higher Hg concentrations in UK soils amended with sewage sludge compared with untreated soils could not be observed (DoE, 1993).

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2.6.2.2   Mercury consumption for a number of products is gradually being reduced or even phased out. For example, with the introduction of the EU Directive 91/157/EEC, the Hg content of standard batteries has been negligible since 1993, while current emissions originate from special purpose button cells (WSAC, 1997). Substitutes for Hg are also being introduced for thermometers, barometers, sphygmomanometers and lighting equipment. It is therefore expected that emissions from the production and use of these instruments will decrease further, although many existing instruments will continue to be in use and changes in acquisition will only slowly propagate to the waste stream.

2.6.2.3   As mentioned before, TGM concentrations have consistently increased in the 1970s and 1980s, while they declined between 1990 and 1997. However, there is some indication that global TGM concentrations have started to increase again since 1997. While the decline in the early 1990s is consistent with the restructuring of the former Soviet Union, the latest increase is thought to be because of increased coal combustion of Hg-rich coals in the Far East and mainly in China (F. Slemr, pers. comm.). Given the scale of transport of Hg^0, such an explanation is quite plausible.
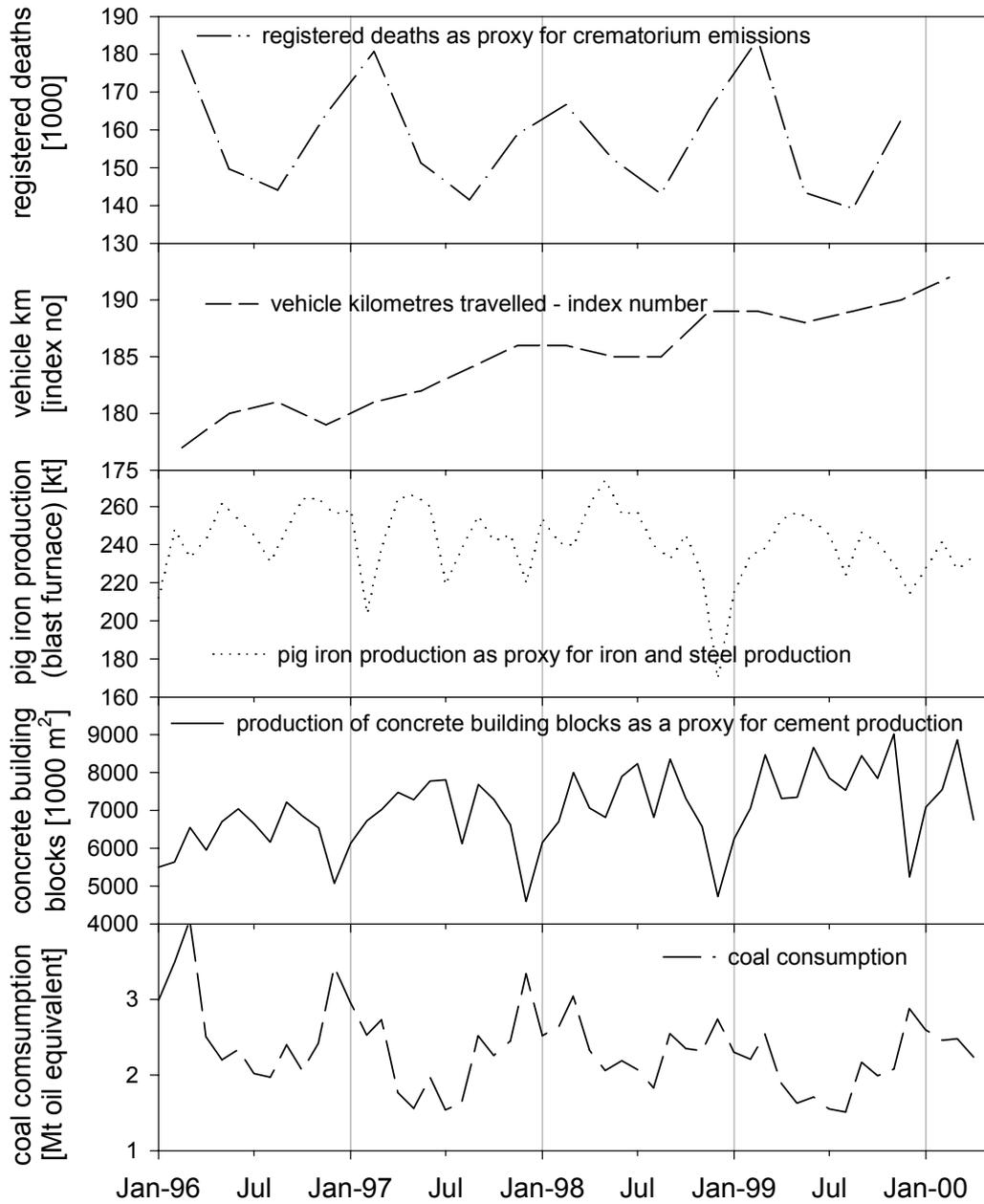
Figure 2-6 Seasonal patterns of selected activity parameters (source: Crown Copyright 2000 - © National Statistics)

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3 Mercury in the atmosphere of the UK

Summary

- The UK has limited data on atmospheric Hg: a one-year study of total gaseous Hg in a rural area and some urban and rural long-term measurements of Hg-p. Also available are some very limited measurements of total gaseous Hg, close to sources.
- The measurements of Hg-p close to sources are prone to sampling artefacts from reactive gaseous Hg that render them unreliable, until speciated measurements are made.
- Measurements of total gaseous Hg made close to sources are also prone to sampling artefacts from reactive gaseous Hg that limits their interpretation.
- Measurements of total gaseous Hg away from sources represent a good measurement of elemental gaseous Hg and the sampling artefact should be small, of the order 1–10%.
- UK measurements of the wet deposition of Hg have either been performed using unsuitable analytical techniques or with a collector type whose dry deposition collection efficiency is poorly characterized. Although a wet deposition field has been estimated from this network as part of this study, there are major uncertainties involved because of the aforementioned sampling uncertainties.
- The UK has no measurements of reactive gaseous Hg, nor methyl Hg in air or precipitation.
- The UK has no measurement data with which dry deposition inputs of Hg can be calculated.
- The long-term measurements of rural Hg-p show a step-change in concentrations with a change in analytical technique.
- There is some evidence of 'hot-spots' of enhanced ambient Hg concentrations but the form that the Hg takes is unknown.
- The rural measurements of total gaseous Hg are generally consistent with other European measurements.
- There is evidence from long-term measurements of total gaseous Hg in Germany that levels declined from 1990 to 1997 but have thereafter increased.
- The UK is in a very poor position to assess exposure of humans to ambient Hg levels or derive bioaccumulation factors because of poorly characterized deposition loads.
- Given the route of exposure of humans to Hg through the food chain, rather than ambient concentrations, it is recommended that more emphasis is made in the future on assessing deposition than exposure to ambient levels.

3.1 Measurement techniques for atmospheric mercury

3.1.1 Measurements of Hg have been limited in previous years by measurement technology. Gas-phase measurements prior to the availability of a commercial instrument capable of measuring ambient concentrations were difficult and/or laborious. Most Hg measurements made in the UK have been with particle samplers (either hi-volume or low-volume samplers, depending on the time resolution required and the sensitivity of the analytical technique employed). In the last few years commercial equipment has become available for the automatic detection of total gaseous Hg (TGM) and more recently, reactive gaseous Hg (RGM).

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3.1.2   Particulate measurements

3.1.2.1   Measurements of particulate-phase Hg (Hg-p) are usually made by drawing air through a sampling medium such a filter paper. Such measurements should be viewed with some caution as they may suffer from positive and negative artefacts. Given that we now know that Hg exists in three dominant forms in the atmosphere—Hg^0, Hg-p and RGM—it is possible to speculate on what the artefacts might be qualitatively, but not quantitatively. Moreover, methylated forms of Hg (monomethyl and dimethyl forms) have also been detected in the atmosphere at pg m^{-3} levels (Brosset and Lord, 1995), although the atmospheric lifetime of DMHg is likely to be extremely short because of its rapid reaction with OH (Niki *et al.*, 1983).

3.1.2.2   Elemental Hg is unlikely to be an artefact in Hg-p measurements because of its low reactivity and apparent low affinity for surface adsorption (other than to gold). Reactive gaseous Hg is, however, a potential positive measurement artefact on TGM and Hg-p, according to our limited understanding of ambient concentrations and its behaviour. From the limited data, it appears that RGM occurs at concentrations similar to those of Hg-p but it is likely to be more spatially variable, especially close to sources. It is commonly assumed that RGM behaves much like HNO_3 or HCl and has a zero or near-zero surface resistance. Thus, it can be inferred from this assumption that it is highly likely to stick to surfaces such as the filter medium of a particulate sampler. Equally, it might well revolatilize resulting in a negative artefact if any RGM has been adsorbed to particles in the ambient atmosphere.

3.1.2.3   Thus, any measurements made by conventional particulate sampling techniques will be prone to unquantified artefacts, particularly near sources of RGM. It is likely that rural measurements will be much less prone to such an artefact, given the differences in concentrations of RGM and Hg^0, and the likely rapid rate of removal by wet and dry deposition of RGM. The contribution of any positive or negative artefacts remains uncertain as other measurements have shown that RGM may exceed Hg-p concentrations (Guentzel *et al.*, 1996; Bloom *et al.*, 1996).

3.1.3   Gaseous-phase measurements

3.1.4   Measurements of Hg^0 have mostly been made using gold traps as an adsorbent. The measurement is strictly one of total gaseous mercury (TGM) as elemental Hg cannot be discriminated from other forms of gaseous Hg. However, other measurements of RGM and methylated Hg consistently suggest that TGM is dominated by Hg^0 as RGM/MHg are at concentrations approximately one order of magnitude lower than Hg^0, away from sources (Stratton and Lindberg, 1995). Closer to sources, the picture may not be quite so clear-cut.

3.1.5   The recent development of a commercially-available reliable instrument for TGM measurements has made a large impact on the global measurements database. The Tekran vapour phase in-

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strument measures TGM and, as described above, is an operationally defined measurement of Hg^0 and RGM, combined. This instrument has allowed many high-quality measurement and monitoring activities to be undertaken, including flux measurements. The instrument has two channels which trap vapour-phase Hg onto gold adsorbents. The two adsorbent cartridges thermally desorb alternately, after which Hg is detected using cold vapour atomic fluorescence spectrometry (CVAFS), enabling a time resolution down to 5 minutes. This instrument has been used successfully at a number of locations around the world and has been found to give comparable results to other methods (Ebinghaus *et al*., 1996). The limit of detection of the measurements made with this instrument is approximately < 0.1 ng m^{-3}.

3.1.6   The capability of the Tekran has recently been extended with an add-on unit that measures RGM using a denuder. In addition, a particulate measurement device can be added between the RGM denuder and the gold traps. The detection limits are not specified in the current Tekran web-site literature but graphs are shown that indicate the sensitivity of the RGM unit to be around 10 pg m^{-3}. These add-on units to the Tekran give a powerful (but expensive) measurement capability that should be free of artefacts and allows a good speciation of ambient measurements.

3.2   Concentrations of mercury in the European atmosphere

3.2.1   Elemental gaseous mercury/TGM

3.2.1.1   A number of measurement campaigns of TGM have been conducted in Europe, principally in Germany, Sweden and at Mace Head in western Ireland. Long-term measurements of TGM have been made since 1990 at the summit of the Wank mountain in Bavaria (1,780 m a.s.l.). In this section, some of the available measurements are reviewed. This review is not intended to be exhaustive but to draw out some of the main features of the observations of Hg^0/TGM over Europe.

3.2.1.2   The measurements of TGM made at the summit of the Wank mountain are invaluable as they represent the only long-term European data set. These measurements were initiated as a result of earlier findings of the IfU (Fraunhofer-Institut für Atmosphärische Umweltforschung) group's study of hemispheric differences and global increases in atmospheric concentrations of TGM between 1977 and 1990 (e.g. Seiler *et al*., 1980; Slemr *et al*., 1981, 1985; Slemr and Langer, 1992). The long-term measurements have been reported by Slemr *et al*. (1995) and Slemr and Scheel (1998). Slemr and Scheel (1998) report the measurements from Wank until 1997, which show a decline of approximately 7% per year. This decline was consistent with TGM measurements made over a period of 5 years in southern Norway by Pacyna and Berg (1996). In both cases, the explanation offered for the observed decline was the major industrial restructuring of central and eastern Europe.

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3.2.1.3   Whilst the decline in European concentrations is encouraging, it is far from clear that the situation with regard to atmospheric loading is improving. The study of Slemr and Scheel (1998) pointed out that emissions estimates could not be reconciled from their measurements and that the balance of man-made to natural emissions was still an open question. More importantly, Slemr (2000) reported that since 1996, the concentrations of TGM at Wank have subsequently *increased*. The explanation offered was that whilst industrial restructuring in central and eastern Europe resulted in a dramatic decline in concentrations between 1990 and 1996, the increased coal burning in the Far East has increased the background Northern Hemisphere concentrations of Hg^0, contributing significantly to the rise in concentrations of TGM measured at the Wank summit site. This explanation, whilst not verified, seems plausible as coal burning and other Hg-releasing industrial activities in Europe have not increased but rather decreased.

3.2.1.4   Two major comparisons of measurement techniques for TGM have been made: an early campaign in 1991/93, during which measurements were made at Mace Head on the west coast of Ireland and an industrialized region of Germany (Leipzig/Halle/Bitterfeld) (Ebinghaus *et al*., 1995). This earlier study of showed a mean concentration for TGM of 2.1 ng m^{-3} (for a limited measurement period of approximately 10 days in Oct. 1991 and Nov. 1992), whereas the concentrations measured in the industrial region of the former East Germany were 8.2 ng m^{-3} (Ebinghaus *et al*., 1995). A later campaign looked at concentrations along a transect of four sites going from south to north: Neuglobsow (FRG), Zingst (FRG), Rörvik (Sw) and Aspvreten (Sw) (Schmolke *et al*., 1999). A coherent gradient of mean concentrations of 1.93, 1.78, 1.53 and 1.54 ng m^{-3} was found.

3.2.1.5   Recently, it has been shown (Munthe, pers. comm. 2000) that concentrations of TGM at Mace Head appear to be slightly higher than those observed at Aspvreten in southern Sweden, an observation for which no satisfactory explanation has yet been found.

3.2.1.6   The well-mixed nature of Hg^0 in the European atmosphere (using TGM measurements) has been demonstrated recently by Ebinghaus and Slemr (2000) who found during a flight campaign that TGM was evenly distributed over a horizontal distance of 400 km and that concentrations in the free troposphere (2,500 m) were only 8% lower than those in the boundary layer (900 m). The earlier measurements of Seiler *et al.* (1980) show that similar concentrations are maintained in the upper troposphere and lower stratosphere (8–10 km, on a flight from Cologne to Canada, and then across the hemispheres to Chile).

3.2.2 Reactive gaseous mercury

3.2.2.1 There are very few measurements of RGM in comparison to TGM. Some measurements have been made in Europe, whilst the bulk of the available data originates from North America. Some early measurements were made in Europe by Brosset (1987) but the bulk of the European data originate from the European RTD Programme '*Mercury Species Over Europe—MOE*', which has now finished. Sommar *et al*. (1999) report the development and application of a system to measure RGM and DGM (divalent gaseous mercury). RGM is discriminated from DGM based on the amount of Hg^{II} in the aqueous phase, where DGM is usually slightly greater in concentration than RGM. The measurements showed that DGM was present at the ppq (parts per quillion, 10^{15}) level, of the order 1–10 ppq at a variety of sites, some of which were close to urban centres, some rural. Despite the very low concentrations measured, the importance of DGM/RGM to deposition levels was emphasized because of its rapid rate of dry deposition and high precipitation scavenging ratio, compared with those for Hg^0.

3.2.2.2 It is evident that the European database for RGM/DGM is rather sparse. Moreover, no data exist for the UK. Given that RGM has been shown in this study to potentially play a significant role in UK deposition (Section 5), it is important that this situation should be rectified.

3.2.3 Methyl mercury

3.2.3.1 In this section, MHg—a divalent form of mercury often incorporated into the term 'RGM'—has been particularly identified because of its toxicity. Only a few measurements of MHg have been made. Early measurements of Slemr *et al*. (1981) suggested that DMHg was up to 30% of TGM over continental Europe. Later measurements subsequently showed that this estimate was too high, monomethyl Hg being only a few percent of TGM in continental air (Slemr *et al*., 1985). However, the measurements of Bloom and Fitzgerald (1988) in the US showed that only 0.7% of TGM was MHg, being found at concentrations of 10 pg m^{-3} and less.

3.2.3.2 Methylated Hg has been found in precipitation (Bloom and Watras, 1989; Munthe and Iverfeldt, 1993; Brosset and Lord, 1995) but its source is unknown. Combustion processes do not apparently emit MHg (Prestbo and Bloom, 1994) so that other mechanisms or sources are required to explain its presence in air and precipitation. In a laboratory study, Hall *et al*. (1995) looked at the possibility of methyl iodide (CH_3I) and dimethyl sulphide (DMS) as being atmospheric methylating agents and found that CH_3I could produce MHg but DMS did not, in agreement with the later study of Tokos *et al*. (1998). However, the rate of methylation from CH_3I was so low that this reaction could not explain atmospheric MHg. Baldi *et al*. (1995) have suggested that MHg may be degassed from anaerobic H_2S-rich environments and that this may be of importance in biogeochemical cycling but no attempt was made to quantify its importance.

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3.2.3.3   Other measurements of MHg in precipitation have been made in the Chesapeake Bay area of the eastern US (Mason *et al*., 1997a, 1997b) and southern Sweden (Munthe *et al*., 1995a, 1995b). Concentrations were found to be low: being approximately 0.4% of the Hg in precipitation at Chesapeake Bay (Mason *et al*., 1997a) and showing no urban enhancement (Mason *et al*., 1997b). Concentrations of MHg in southern Sweden were of the order 0.2–0.5 ng/L but were a higher fraction of the total, being of the order 2–5% of total Hg in precipitation (Munthe *et al*., 1995a).

3.2.3.4   In contrast to the very low fractions of MHg to TGM in air, from a very limited number of samples in the US and Sweden, MHg was found to be 0.1–6% of Hg in precipitation (Munthe *et al*., 1995a). This is partly explicable from the fact that the species that will be removed in precipitation are divalent inorganic and organic forms of Hg (i.e. Hg-p and RGM), not Hg^0. These divalent forms are of the order 5–10% of total atmospheric Hg. However, this does not explain the source of the MHg in precipitation.

3.2.3.5   Reconciling the source of MHg appears to be important. Hultberg *et al*. (1994; 1995) concluded that deposition of MHg was an important contributor to the MHg budgets of freshwater lakes in southern Sweden.

3.2.3.6   In conclusion, it is worth noting that there are no measurements of MHg in either air or precipitation in the UK, to our knowledge.

3.3   Concentrations of mercury in the UK atmosphere

3.3.1   Overview

3.3.1.1   There is a paucity of data on concentrations of Hg in the UK atmosphere. This is partly a result of the historical difficulties involved with making measurements of Hg^0, the predominant component. However, there exists some long-term data on Hg-p from a number of rural and urban sites in the UK between approximately the late 1970s and the early 1990s (Lee *et al*., 1994). In addition, some TGM measurements made over a period of approximately 1 year are available from a rural site in central southern England (Lee *et al*., 1998a).

3.3.1.2   Recently, measurements of Hg-p were attempted near industrial plant but analytical problems were experienced such that no data were generated (Maggs, pers. comm., 1999). However, some measurements of TGM have been made, which are summarized in Section 3.3.3.

3.3.1.3   Wet deposition data of Hg are more problematic, there being very few measurements. What measurements there are and experience in attempting to measure Hg is described in Section 3.3.5.

3.3.2 Particle-phase measurements

3.3.2.1 Measurements of Hg-p have been made at both rural and urban sites in the UK since the early 1970s. The rural sites include: Wraymires in the Lake District in the north west of England; Chilton in central southern England; and Styrrup, a rural part of the east Midlands of England. However, this latter site is surrounded by many large towns and cities and lies to close to an area in which much of the country's generating capacity from large coal-fired power stations are situated. The urban sites include four in the Greater Manchester conurbation (Manchester Rusholme, Manchester Bradford, Altrincham and Flixton), Walsall and Brent. The sampling and analysis methods have been described in detail by Lee *et al.* (1994).

3.3.2.2 The long-term measurements of particle phase Hg at rural sites are presented in Figure 3.1 and at the urban sites in Figure 3.2.

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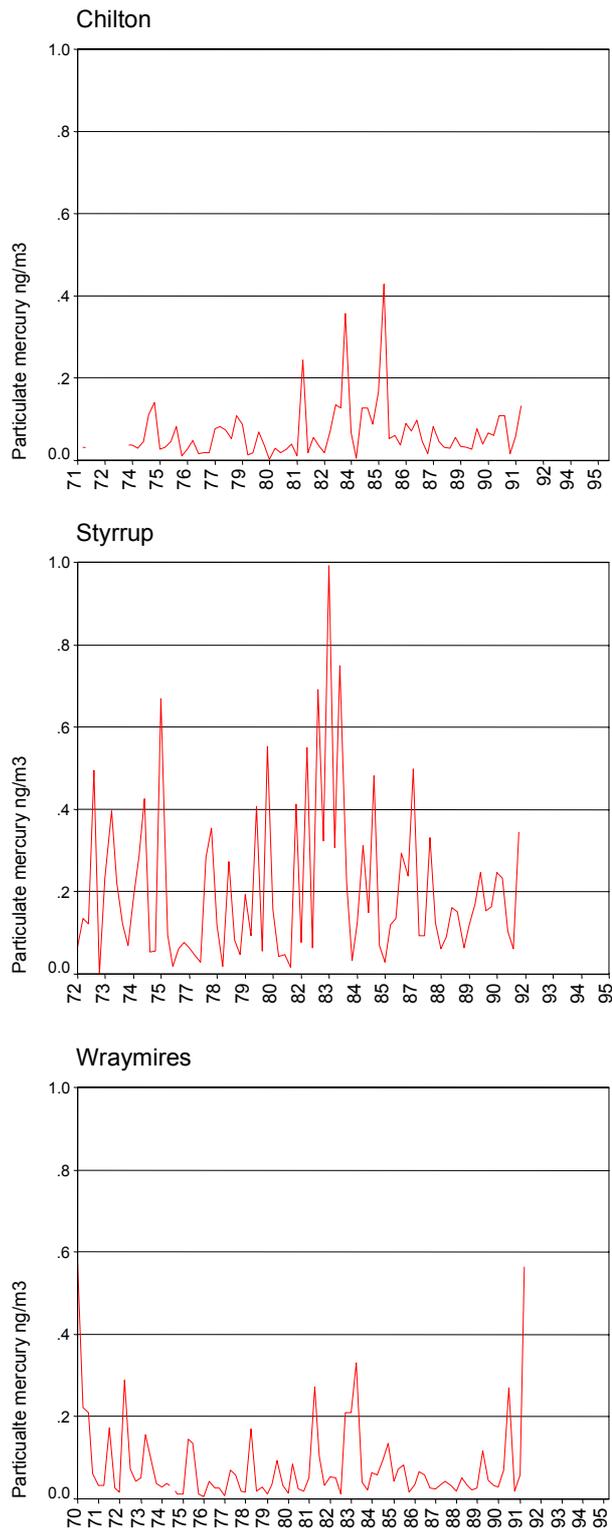
Figure 3-1 Long-term measurements of particulate phase mercury at three UK rural sites, Chilton, Styrrup and Wray-mires

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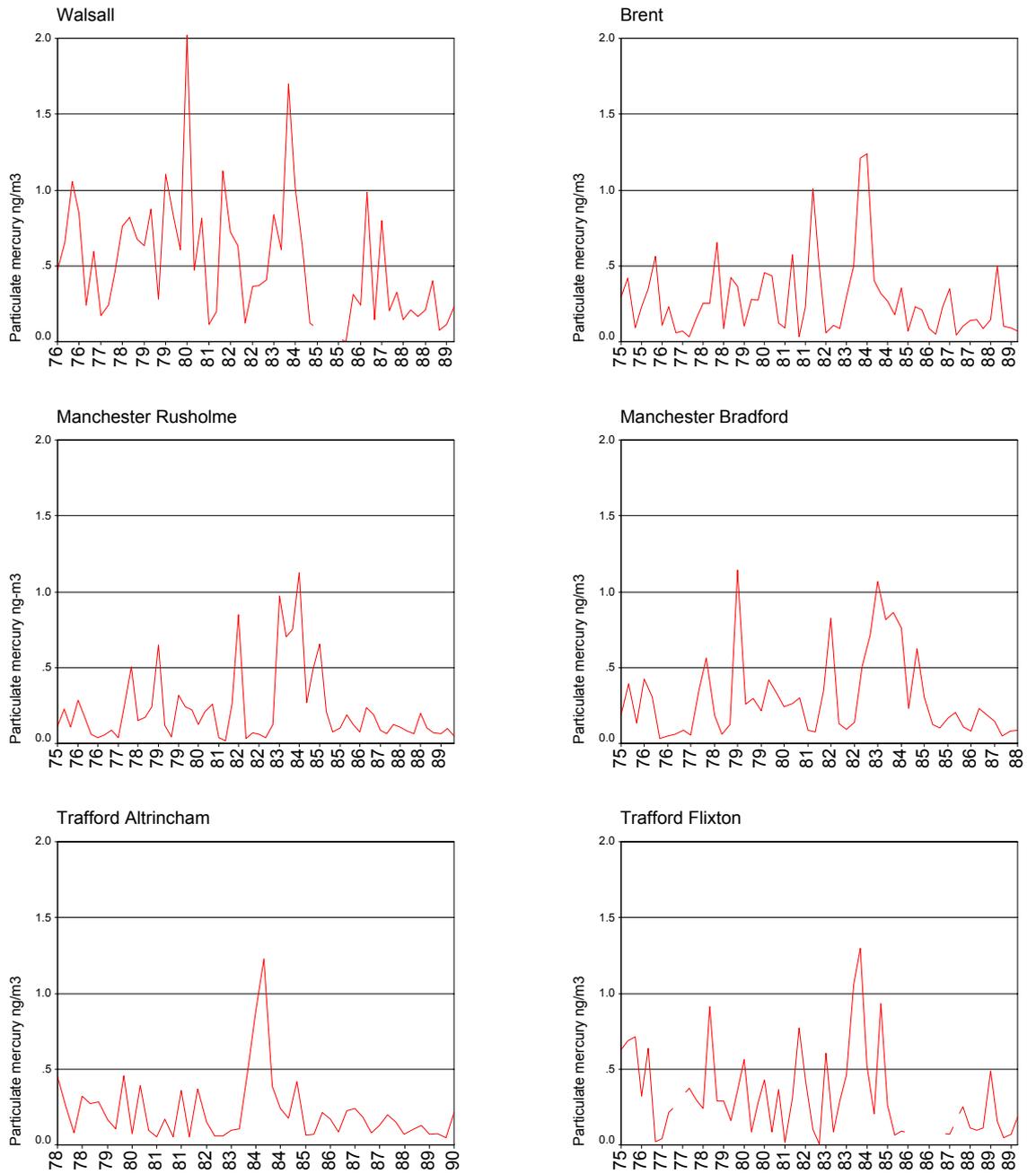
Figure 3-2 Long-term measurements of particulate phase Hg at six urban sites (Lee et al., 1994)

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3.3.3 Gas-phase measurements

3.3.4 Gas-phase measurements of Hg have been made at a rural site in central southern England (Harwell) by Lee *et al.* (1998a) using a Tekran vapour phase instrument (see Figure 3.3). This instrument measures total gaseous mercury (TGM) and as such, is an operationally defined measurement of elemental gaseous Hg and reactive gaseous Hg, combined.

3.3.4.1 The measurements were made over a period of approximately a year. The average concentration was 1.68 ng m^{-3} with a maximum hourly mean concentration of 20.5 ng m^{-3} and a minimum of 0.26 ng m^{-3}. An analysis of the data by wind sector was made (see Figure 3.4) that showed almost uniform concentrations with a background of approximately 1.5 ng m^{-3}. Enhancements were shown in easterly and westerly winds. The explanation offered for these enhancements was the location of an industrial smelting plant to the west and higher concentrations originating from central and eastern Europe possibly explaining the enhancement to the east (Lee *et al.*, 1998a).
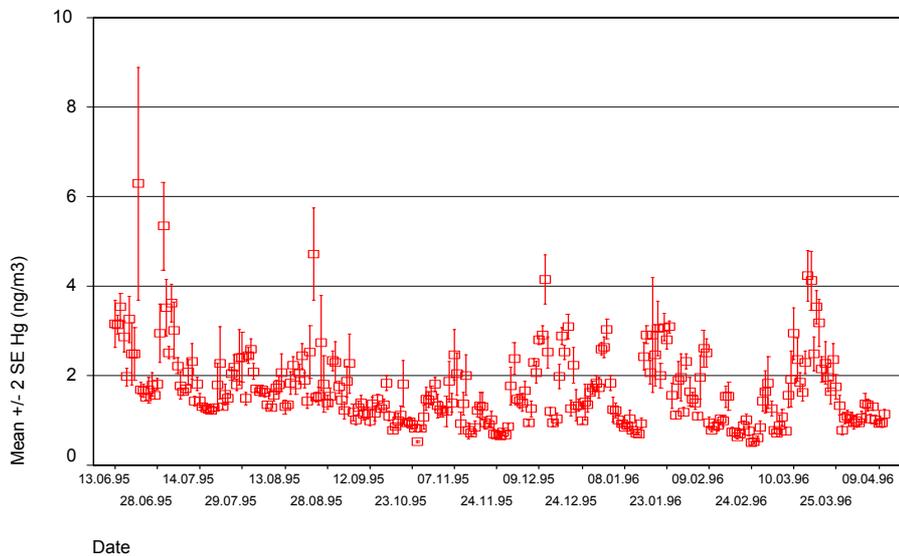
Figure 3-3 Daily mean concentrations (+/- 2 SE) TGM concentrations at Harwell (Lee et al., 1998a)

3.3.4.2 Other interesting features of the data were the apparent lack of correlation with peaks of SO$_2$ from a nearby coal-fired power station, and the apparent surface emission, as shown by the diurnal variability of the data.
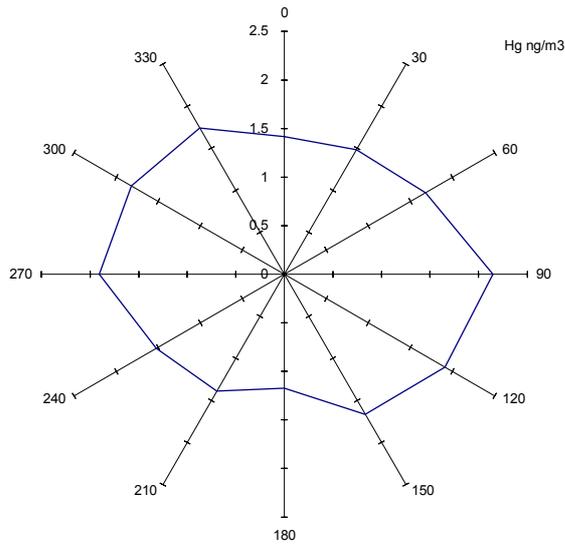
Figure 3-4 Sector plot of TGM at Harwell (Lee et al., 1998a)

3.3.4.3   Very recently, TGM measurements, also using a Tekran vapour analyser, have been made at the CEH Edinburgh air quality monitoring site, 10 km south of Edinburgh, Scotland. The first 9 days of continuous measurements (Figure 3.5) average 1.6 ng m^{-3} and confirm a UK background concentration of TGM of approximately 1.5 ng m^{-3}.
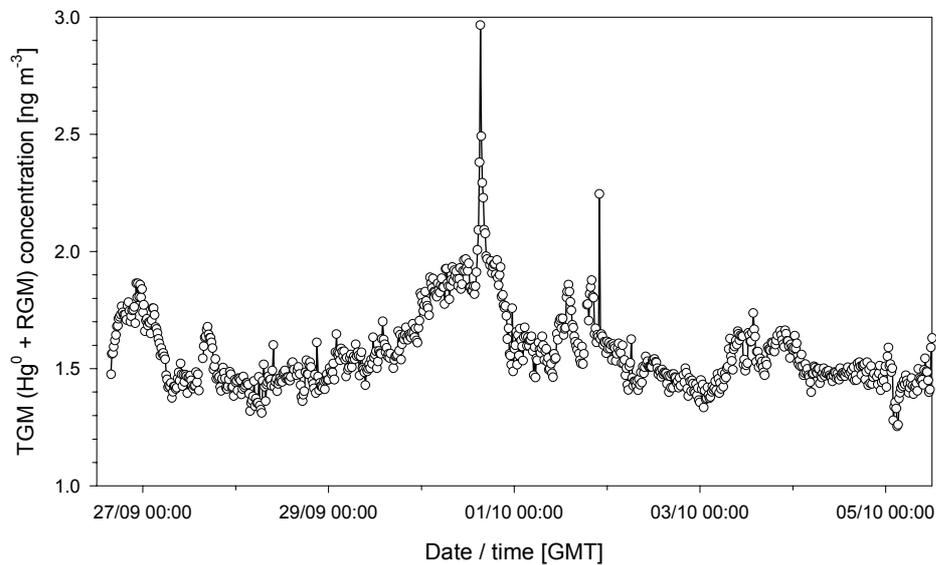
Figure 3-5 Quarter-hourly averages of TGM concentrations at CEH Edinburgh (unpublished data)

3.3.4.4   The clear structure in the data with concentration peaks of up to 3 ng m^{-3} has been found to be significantly (P=0.05) and positively correlated with NO_x concentrations indicating some similarity of the sources. The correlation with SO_2 is more complex with several populations within the

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dataset showing a high correlation between TGM and SO_2. It appears that TGM/SO_2 ratios differ between local point sources such as the petrochemical industrial complex at Grangemouth. However, the dataset is currently too limited to draw any firm conclusions.

3.3.4.5   Nevertheless, the wind sector dependence of this limited dataset already indicates much higher average concentrations (up to 2 ng m^{-3}) observed for urban wind directions (Figure 3.6).
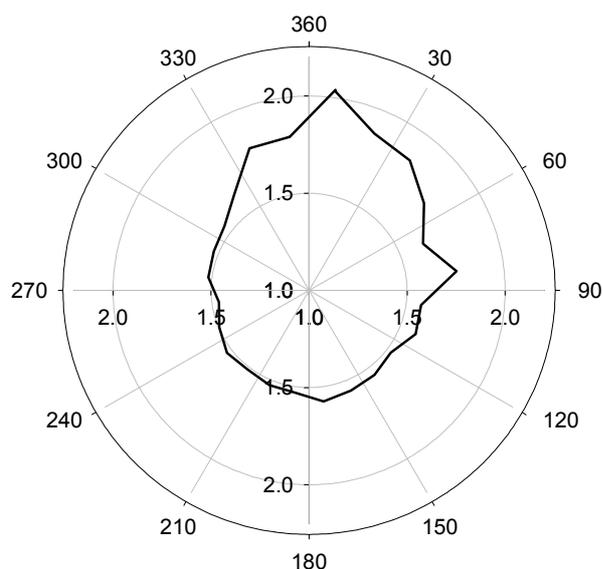
Figure 3-6 Sector plot of TGM at CEH Edinburgh (unpublished data)

3.3.5   Wet deposition of mercury

3.3.5.1   Trace elements in air and rain were measured at a number of rural locations in the early 1970s (Pierson *et al*., 1973, 1974), three sites of which (Chilton, Styrrup and Wraymires) have been continued to the present day (e.g. Cawse *et al*., 1995; Lee *et al*., 1998b). However, measurements of concentrations in precipitation were rather limited and are no longer made. Unfortunately, the early data that do exist for Hg in precipitation all report 'less than' values (e.g. Cawse, 1974) such that this network never produced any useable data on Hg in precipitation.

3.3.5.2   With the Hague Declaration of the Protection of the North Sea in 1990, a further network was set up that measured, amongst other things, metals in air and precipitation, initially at four sites from 1986. Data from 1986 to 1991 were reported by Playford *et al*. (1995) and included Hg-p measurements and Hg in precipitation. Data on Hg concentrations in rain are given in summary tables in the report but on close inspection of the detailed data in the appendices, a large proportion (of the order 75%) of the data are 'less than' values. This renders the data unusable for assessment of wet deposition of Hg from these sites. Mercury is currently only measured at one site (Chilton) but the data are still rather uncertain because of constraints in detection limits (Playford, pers.

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comm., 2000). These data have been rejected by the EMEP Chemical Co-ordinating Centre because of these problems.

3.3.5.3 More recently, the Ministry of Agriculture, Fisheries and Food commissioned a study of heavy metal inputs to agriculture in England and Wales (Alloway *et al*., 1998). Measurements of Hg concentrations in precipitation were made using dust deposition gauges (inverted frisbee samplers) rather than standard wet-only or bulk precipitation collectors. The aerodynamic properties of these gauges are designed to maximize the capture efficiency for large aerosol particles (e.g. Vallack, 1995), but it is highly uncertain how the dry deposition to these samplers compares with the deposition to vegetation.

3.3.5.4 By convention, normal 'bulk' precipitation samplers aim to minimize dry deposition of both particles and gases such that the use of dust deposition gauges to measure wet and dry deposition gives an unquantifiable artefact to wet deposition inputs.

3.3.5.5 Despite these difficulties, deposition estimates have been made by multiplying the Hg concentration in precipitation by the 30-year long-term rainfall field. This simple multiplication of concentration and precipitation is inadequate for representing deposition at higher elevations where the orographic enhancement of precipitation and wet deposition by the seeder-feeder process occurs (Fowler *et al*., 1988). A simple procedure to account for this is normally used to enhance the measurements to account for additional scavenging of high concentrations of solutes and particles captured in cap-cloud (Dore *et al*., 1992). The unenhanced measurements indicate deposition rates, as mapped by the Alloway *et al*. (1998), of the order 0.5–1.0 g ha^{-1} yr^{-1} to much of lowland England. In higher rainfall areas, deposition rates increased to of the order 1.5–2.0 kg ha^{-1} yr^{-1}.

3.3.5.6 In order to provide an improved map of Hg deposition, the deposition data given by Alloway *et al*. (1998) have been converted into precipitation-weighted air concentrations at the measurement sites, using precipitation scavenging coefficients from the literature. The concentration field is expected to be smoother than the deposition field, which is additionally affected by factors such as rainfall, land-cover type and topography. Therefore, the interpolation was carried out on the concentrations. From the air concentration field, the deposition map is derived, taking into account the precipitation field and including the seeder-feeder effect according to Smith and Fowler (2000). The same enhancement factor as is used as for sulphate and nitrate particles was used, on the basis that Hg-p is likely to have a similar size distribution and thus, the same empirical enhancement factor is appropriate. The improved map (Figure 3.7) shows a much higher spatial variability than the map derived directly by interpolation of the measured deposition, with elevated deposition in the Welsh uplands and the Pennines.

(a) Deposition using
all data

(b) Deposition after removal of two
data points
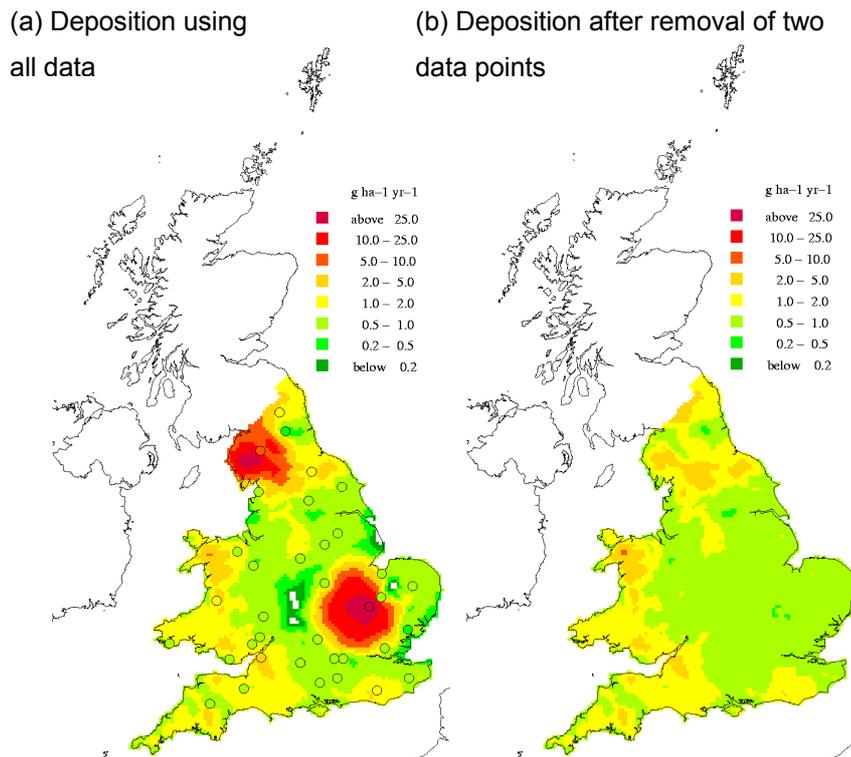
Figure 3-7 (a) Deposition of Hg derived from the dust deposition collector network, taking into account seeder-feeder effects. (b) deposition derived from the dust collector data after removal of the two highest concentrations measured (data from Alloway et al., 1998)

3.3.5.7   The comparison between measured deposition and the total Hg deposition predicted for the measurement sites by two different atmospheric transport models is shown in Figure 3.8. The agreement is very poor, with the dust gauges measuring a much larger deposition than predicted by the models. This highlights the uncertainties currently associated with deposition estimates. It is unclear whether the discrepancies are caused by:

-    the capture of locally resuspended Hg containing soil particles in the dust collectors;

-    underestimation of the emissions (e.g. because the lack of data on natural emissions);

-    spatial variations that lead to the measurement points being unrepresentative for the deposition averaged over a 20 or 50 km grid cell.
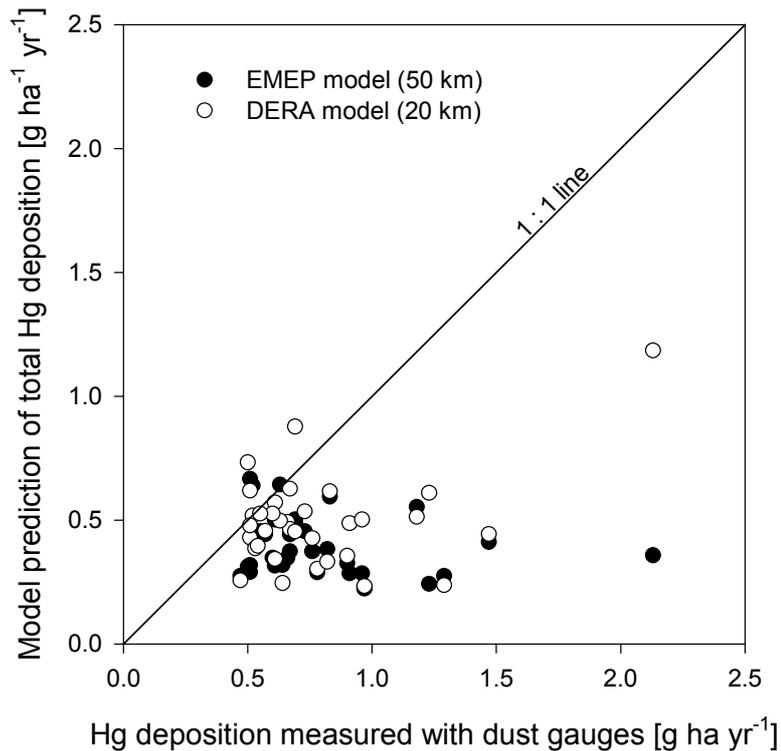
Figure 3-8 Comparison between the total deposition modelled with two different transport and deposition models and the deposition measured with the dust collectors

3.3.6   Spatial and temporal variability of mercury

Spatial variability

3.3.6.1   Other than the modified wet deposition maps, shown in Figure 3.7, which have large uncertainties because of the sampling technique, there are no data with which the spatial variability of any Hg species can be represented. The only comment that can be made is that Hg-p concentrations are generally higher in urban areas and close to large combustion sources, in comparison with rural areas, but that a measurement artefact from RGM cannot be ruled out. Furthermore, measurements of TGM appear to be higher closer to sources but, again, this may be partially the result of RGM measurement artefacts.

Long-term trends of gases and particulates

3.3.6.2   Long-term trends of Hg-p are available from the 3 UK rural sites and the 6 urban sites, covering approximately 1970–1990. No long-term data are available for Hg^0.

3.3.6.3   The time trends of the rural Hg-p data are difficult to interpret. Linear regression lines are not appropriate as has been discussed elsewhere for these data (Lee *et al*., 1994). The data do not indicate a linear trend, with significantly higher concentrations being observed in the early 1980s. Taking the more recent rural data between 1986 and 1991, the mean concentrations of Hg-p were 0.06 ng m^{-3} at Chilton, 0.18 ng m^{-3} at Styrrup and 0.05 ng m^{-3} at Wraymires. The concentrations at the urban sites over the same period were: 0.16, 0.11, 0.13, 0.14 and 0.16 ng m^{-3} at Brent, Manchester Rusholme, Manchester Bradford, Altrincham and Flixton, respectively. The overall temporal variability shows some similarity at both the rural and urban sites. The 'rural' site Styrrup shows a mean concentration over this period similar to the urban sites but this is consistent with its proximity to large combustion sources.

3.3.6.4   Local source effects are apparent in the long-term Hg-p measurements, urban values being approximately 2–3 times the truly rural measurements (Wraymires and Chilton). This order of urban enhancement is consistent with that of other trace metals (Lee *et al*., 1994) and other comparisons of rural and urban Hg-p data (Burke and Keeler, 1996).

3.3.6.5   If these data are representative of Hg-p in the atmosphere, then the TGM measurements at the Harwell site imply that Hg-p concentrations contribute approximately 4% of the Hg content (all fractions) of the atmosphere in rural areas. This small contribution of Hg-p to total atmospheric Hg is consistent with other observations of the phase partitioning of Hg (EPMAP, 1994; Burke and Keeler, 1996; Bloom *et al*., 1996).

Seasonal variability

3.3.6.6   It is possible to consider seasonal variability of the long-term particulate phase measurements from the rural and urban sites. These data provide coverage of enough seasons to provide robust patterns.

3.3.6.7   The seasonal variability of the rural data is shown in Figure 3.9 and the urban data in Figure 3.10 as boxplots. The rural data show a consistent seasonal pattern between the sites with higher concentrations in winter than in summer (quarters 1 and 4[1]). The urban sites show some similarities and dissimilarities. High winter concentrations prevail at the two Manchester sites, Trafford–Flixton and Trafford–Altrincham (marginally so) but Walsall and Brent exhibit different behaviour. A smelter was near Walsall so that this source may have made an impact on seasonality: cer-

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[1] Quarter 1=Jan.–March, 2=April–June, 3=July–Sept., 4=Oct.–Dec.

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tainly, the concentrations were higher than at any other site. Brent shows anomalous behaviour in quarter 2 but otherwise resembles the seasonal pattern found the rural sites. This similarity in temporal patterns provides some subjective evidence that the seasonality is not the product of an RGM measurement artefact, as RGM is not expected to be a significant component of the background air at the rural sites, particularly Windermere.

3.3.6.8   The seasonal variability probably has its source in two major factors: fuel and energy consumption tend to be higher in winter months leading to greater emissions and winter-time inversions both may exacerbate this pattern. The overall pattern is consistent with a range of metal particles in the atmosphere at both urban and rural sites (Salmon *et al*., 1978; Lee *et al*., 1994) and natural [210]Pb (Peirson *et al*., 1966).
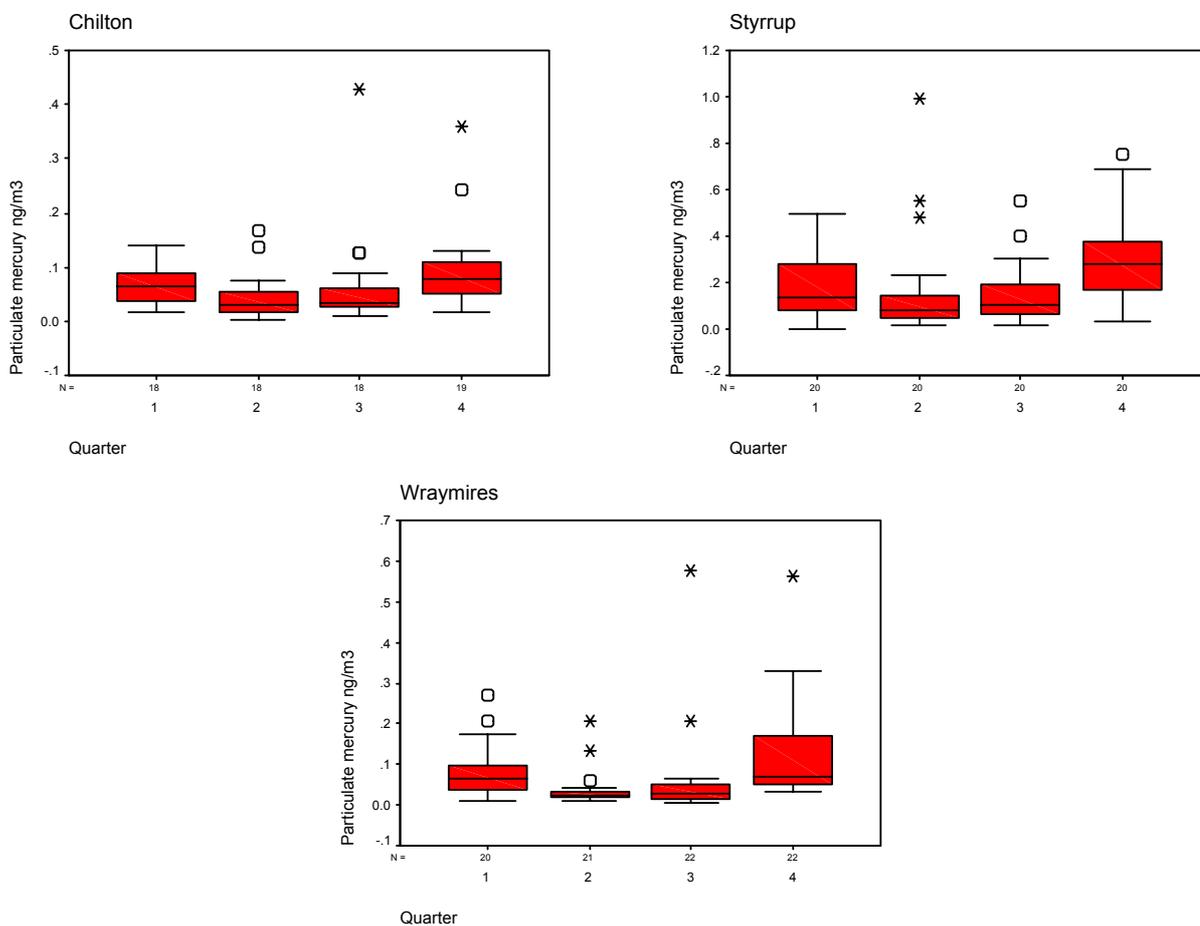
Figure 3-9 Boxplots of the rural particulate phase Hg data illustrating the seasonal behaviour of Hg at these sites
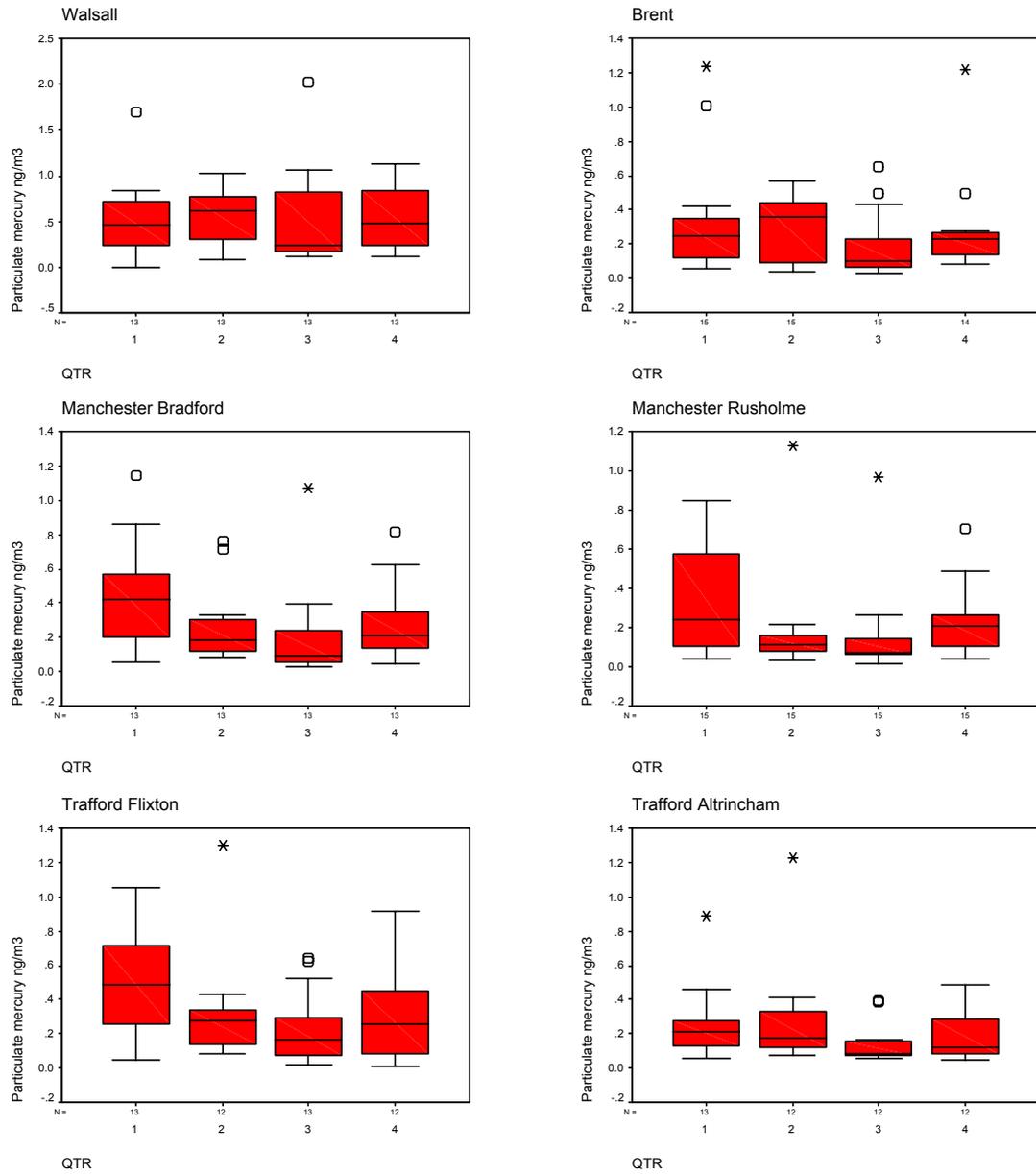
Figure 3-10 Boxplots of the urban particulate phase Hg data illustrating the seasonal behaviour of Hg at these sites (re-analysis of data from Lee et al., 1994)

Diurnal variability

3.3.6.9   Diurnal data are only available for the TGM measurements made at Harwell (Lee *et al*., 1998a). A clear diurnal signal in the data was found that was stronger in the winter than in the summer, with higher concentrations being found at night. This was suggested to be indicative of a surface source accumulating under stable nocturnal boundary layers. Corroborative evidence for this was the high correlation with ethane, which is known to have a surface source. The diurnal behaviour of TGM is shown in Figure 3.11. Between the hours of 10:00 and 15:00 there was a smaller peak in concentrations. It could be that this represents a partial offset of the apparent diurnal cycle from an increase in daytime surface emission rates. The signal shown in Figure 3.11 is robust, being made up of approximately 270 hourly measurements. However, the interpretation of these data can only be confirmed by direct flux measurements.
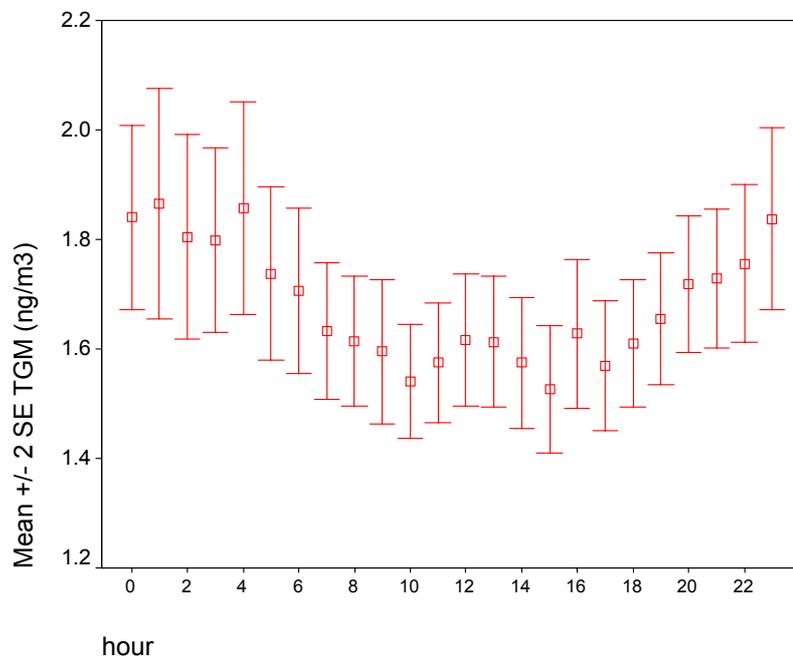
Figure 3-11 Diurnal variability of TGM at Harwell (Lee et al., 1998a)

3.3.7   Evidence for 'hot-spots'

3.3.7.1   The evidence for 'hot-spots' close to known sources or in urban areas is rather limited. The DETR recently commissioned a network of particulate measurements to be made close to known sources (R. Maggs, Stanger, pers. comm., 1999). However, as mentioned, difficulties in the analytical method have, so far, resulted in a nil data return. This should be rectified in the near future. However, even if ratified data become available, it is important to point out that it is unclear as to what they represent: other limited measurements indicate that RGM may be of the same magnitude as Hg-p and that RGM may be a positive sampling artefact in particulate measurements.

The 'Partisol' samplers used will be prone to this artefact. In the absence of carefully speciated measurements, any urban or near-to-source measurements will probably best represent RGM+Hg-p. However, these forms have rather different atmospheric behaviour in terms of deposition and transport distances.

3.3.7.2   Stanger have also made some limited measurements of TGM between approximately March and June 2000, on a weekly basis at 5 of the industrial sites: British Steel, Rotherham; Castle Cement, Wrexham; Sutton Coldfield Crematorium; and ICI chloralkali plant, Runcorn. Boxplots of the data from the first 4 sites are shown in Figure 3.12 and in the latter in Figure 3.13
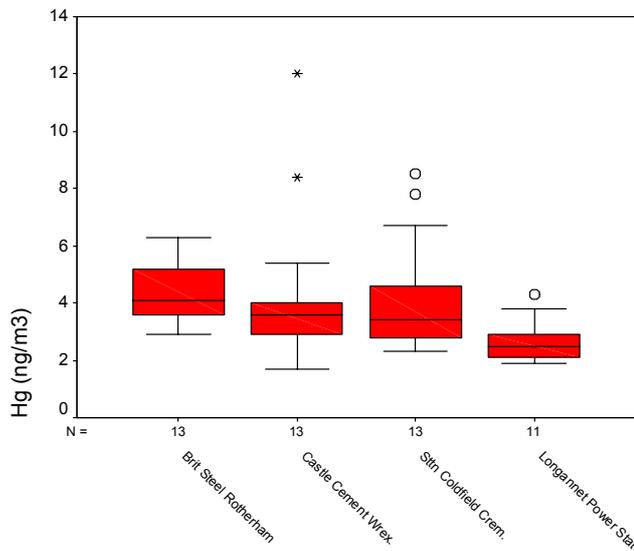
Figure 3-12 TGM near four industrial sites (data courtesy of R. Maggs, Stanger, pers. comm., 2000)
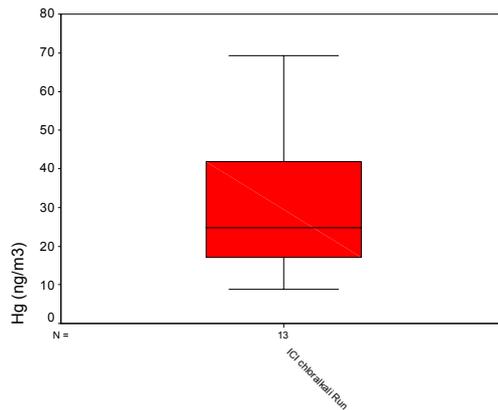
Figure 3-13 TGM near a chloralkali plant (data courtesy of R. Maggs, Stanger, pers. comm., 2000)

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3.3.7.3   From Figures 3.12 and 3.13, it is clear that the TGM measurements show a clear enhancement over the rural TGM data from Harwell. Although the data are limited, the data from the sites in Figure 3.12 show an enhancement of approximately ×2 over the rural TGM data, and the data shown in Figure 3.13 taken from the vicinity of a chloralkali works show an enhancement of ×17. Again, caution must be applied in interpreting these measurements as close to such sources, the contribution of RGM to TGM may be significant.

3.3.7.4   Some corroboration to 'hotspots' of RGM existing can be drawn from a model simulation of surface concentrations of RGM. In Section 5, a UK model for atmospheric Hg is described and 20 km average surface concentrations of RGM are represented below in Figure 3.14.
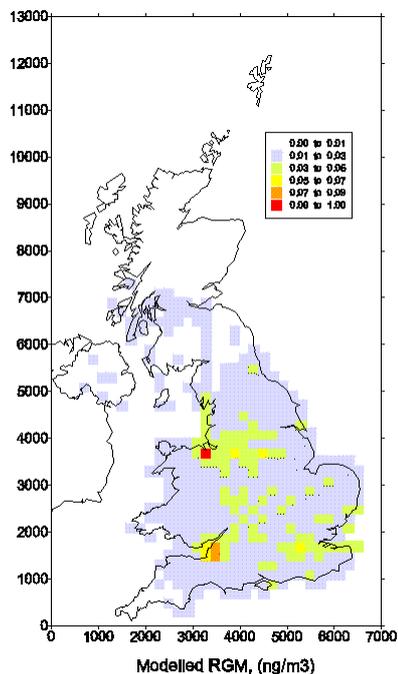
Figure 3-14 20 km average modelled concentrations of RGM (ng m^{-3})

3.3.7.5   Some caveats must be given with regard to the modelled RGM concentrations shown above: there are significant uncertainties in many of the model parameters and the input data. Moreover, the concentrations shown represent averages of the 20 km × 20 km grid squares and closer to sources, such as for the measurements shown in Figures 3.12 and 3.13, the concentrations would be expected to be much higher. Nonetheless, the modelled concentrations do show some evidence of 'hot-spots' of RGM that may contribute significantly to TGM and a close correlation with the location of point sources in the emissions inventory is evident.

3.3.7.6   Further evidence for Hg 'hot-spots' exist from limited non-UK data. Figure 3.15 shows 3 sets of measurements taken from the Tekran web-site, illustrating the range of concentrations that may be encountered in different environments.

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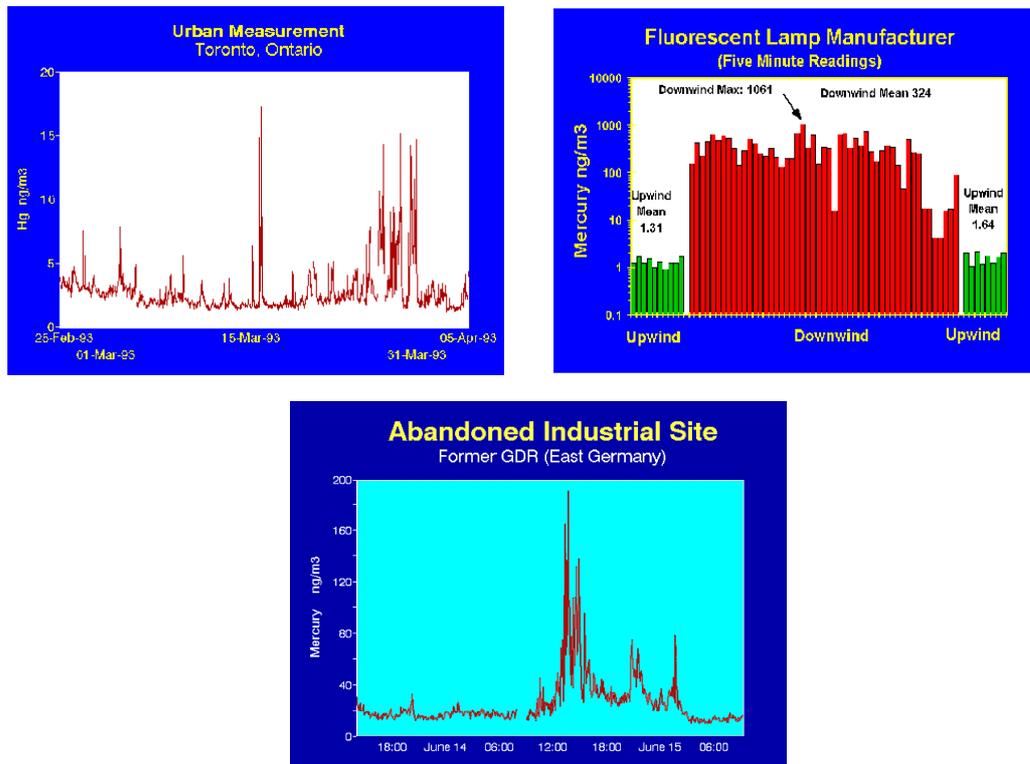
Figure 3-15 Examples of measurements close to sources (data source: Tekran web-site)

3.3.7.7   It is not suggested that these data may be typical of conditions in the UK but do show that en-
hancements close to industrial sources and in an urban centre have been shown.

3.3.7.8   In terms of UK measurements of Hg-p, the urban Hg-p data show a clear enhancement over
concurrent measurements at the rural sites Chilton and Wraymires. The semi-rural site, Styrrup,
showed intermediate concentrations. Near a smelter in Walsall, concentrations of Hg-p were
highest.

3.3.7.9   There have been no measurements of Hg^0 or RGM in urban areas. Some enhancement is possi-
ble (see e.g., Figure 3.12), particularly close to known sources but this remains unquantified. The
only interesting anomaly are the TGM measurements made at Harwell, where no enhancement
of TGM could be seen when the wind was from the direction of a large power station (Didcot) and
yet SO_2 concentrations were clearly high. However, this could simply be explained by the plant
burning low-Hg coal and that it did not represent a significant source.

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3.4 Adequacy of the current database for atmospheric mercury measurements in the UK

3.4.1 In this chapter, the UK database of Hg measurements in all phases has been reviewed. Whilst the long-term measurements of Hg-p at rural and urban sites are invaluable, there are some problems. There are no *urban background particulate measurements* available since 1990. Although a measurement programme is underway near sources, at the time of writing there have been significant analytical problems that may make these data unverifiable. The outcome of further investigations on QA/QC is awaited (Maggs, pers. comm. 2000).

3.4.2 Regardless of the problems encountered with the analysis of samples from the new DETR network, there are significant uncertainties over what the measurements may represent. If these measurements are made close to sources of RGM, then it is likely that a large proportion of the signal may be RGM rather than Hg-p. Reactive gaseous Hg will have a very different atmospheric behaviour to Hg-p in terms of transport distance and deposition.

3.4.3 The *rural particulate measurements* are unlikely to suffer from the same sampling artefacts but it remains that no speciated measurements of RGM and Hg-p have been made with which these measurements may be compared. Moreover, since a change in analysis method in 1992, there are uncertainties over the rural Hg-p data collected by AEA Technology as there appears to have been a step-change increase in concentrations at all three sites. This requires investigation and verification of the later results (see Figure 3.16).

3.4.4 No measurements of *reactive gaseous mercury* have been made in the UK, to our knowledge.

3.4.5 *The measurements of elemental gaseous mercury* are limited to a set of measurements made between 1995 and 1996 of TGM at Harwell and recent ones measured by CEH (Nemitz, pers. comm.). These data were highly temporally resolved and represent the only rural datasets currently available. The concentrations measured showed some interesting features in terms of possible sources, diurnal variability and consistency with other measurements made outside the UK. Nonetheless, this is a very limited measurement database for the UK and no urban measurements have been made. Limited measurements have been made close to sources which show enhancements in TGM over the rural Harwell measurements but again, the contribution of RGM is unknown.

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3.4.6   No long-term nor reliable *wet deposition measurements* of Hg with standard collectors are available. The measurements available from the MAFF network have uncertainties because of the sampling method. The dust deposit gauges were originally designed to maximize the dry collection efficiency for super-micron particles. Usually, wet deposition is measured with bulk precipitation samplers, which have a low collection efficiency for dry deposited particles, whilst an estimate of the dry deposition is made from aerosol concentrations in combination with a knowledge of surface characteristics. Consequently, it is currently unclear how to interpret the results from the dust gauge collector network.

3.4.7   There is limited evidence for *'hot-spots'*. The only available Hg-p measurements are those made between 1972 and 1989. As mentioned, more data on Hg-p near sources may become available shortly if analytical problems are overcome but, based on measurements made elsewhere on Hg-p and RGM, these measurements may suffer from significant sampling artefacts from RGM.
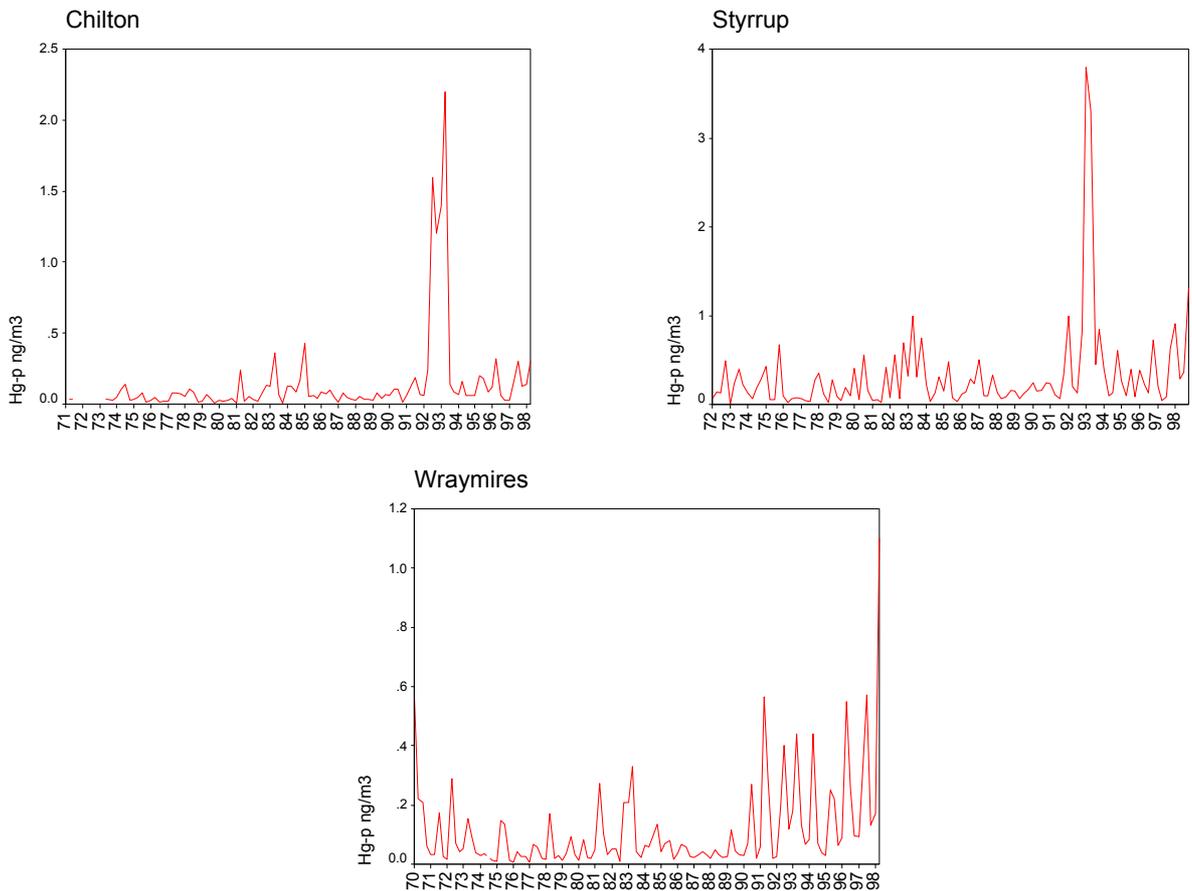
Figure 3-16 Rural long-term Hg-p data showing step changes in concentrations (approximately 1991 on) after a change in analytical technique

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4 The behaviour of mercury in the environment

Summary

- Mercury is a global pollutant. The disparate time scales of Hg species can be summarised as being: elemental gaseous Hg ~1 year; particulate Hg ~days; and reactive gaseous Hg ~hours to days. Particulate Hg arises from direct emissions and atmospheric transformation, thus deposition of this form can have its emission source thousands of kilometres distant because of the very low transformation rate from elemental gaseous Hg to particulate Hg.
- Global cycles have been formulated as budgets. These budgets illustrate the importance of natural emissions, re-emission and the mixed layer of oceans as a large temporary reservoir.
- The oceanic reservoir of Hg is thought to arise from deposition rather than freshwater inputs from run-off etc. The subsequent transformation of divalent Hg to elemental Hg and its emission has only been estimated, not measured.
- Most 'natural' emissions are thought to be the result of previously deposited Hg, similar mechanisms to those in oceans being present that result in reduction of divalent to monovalent Hg. This mechanism, whilst being unidentified, is driven by temperature and solar radiation. Recent data suggest that evapotranspiration is a significant global source of Hg.
- Atmospheric transformation of elemental gaseous Hg to divalent gaseous/particulate Hg proceeds at a relatively slow rate. Chemical mechanisms have been identified and rate constants determined but knowledge is incomplete.
- Elemental gaseous Hg dry deposits at a relatively slow rate but because atmospheric transformation is also slow, it is also important as a removal mechanism. Dry deposition of particulate and reactive gaseous Hg is thought to proceed at a much faster rate although rates are not well characterised for any of the Hg species.
- Wet deposition is an important removal pathway for particulate Hg and reactive gaseous Hg. Elemental gaseous Hg is not directly washed out.
- Atmospheric transport models have been constructed for Hg. The disparate time-scales present a number of problems including spatial and temporal scales, and boundary conditions. Model improvements are required to further understanding of regional and global cycles.

4.1 Environmental compartments and global cycles

4.1.1 Mercury is a naturally occurring metal in all environmental compartments because of its presence and ubiquity in the lithosphere and hydrosphere. Because of its unique characteristics amongst environmental metals, elemental Hg is readily volatilized from water and soil compartments to the atmosphere. Once volatilized, it may undergo atmospheric transformation to the divalent form and subsequently be deposited. Once deposited, it may undergo transformation back to the elemental form and subsequently be revolatilized. Indeed, it is a metal with very few sinks. The only permanent sinks of Hg are thought to be lake and deep oceanic sediments (Nriagu, 1979).

4.1.2 There have been several attempts to summarize and analyse the global cycle of Hg (Nriagu, 1979; Lindqvist and Rodhe 1985; Nriagu and Pacyna, 1988; Nriagu, 1989; Fitzgerald 1989; Lindqvist *et al*., 1991; Mason *et al*., 1994; Hudson *et al*., 1995; Fitzgerald and Mason, 1996). However, the most recent global cycle analyses have been based on that of Mason *et al*. (1994).

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4.1.3   The present-day global cycle of Hg is illustrated in Figure 4.1. One of the important points of this cycle is the role of the oceans. Land is the predominant sink at 5,000 tones yr^{-1}, 60% of this coming from globally cycled Hg and 40% from local and regional deposition, and the oceans the smaller at 2,000 tonnes yr^{-1} (from the atmosphere). However, the oceanic reservoir at 10,800 tonnes is over 1.5 times the size of the global atmospheric burden (7,000 tonnes). The oceanic input from run-off is rather small, at 200 tonnes yr^{-1} and thought to be in balance with deep sediment accumulation, or effective loss from the cycle.

4.1.4   In contrast, the overall fluxes proposed by Mason *et al*. for preindustrial times are much smaller (see Figure 4.2). By implication, Mason *et al*.'s budget suggests that Hg accumulates in the surface mixed layer of the oceans but not the land surfaces as the natural emission term is the same. However, this is not in accord with recent understanding that deposited Hg from man-made emissions will re-volatilize. It may be argued that this 'recycling' is subsumed within the whole budget but this requires to be separated out in future studies to advance understanding.
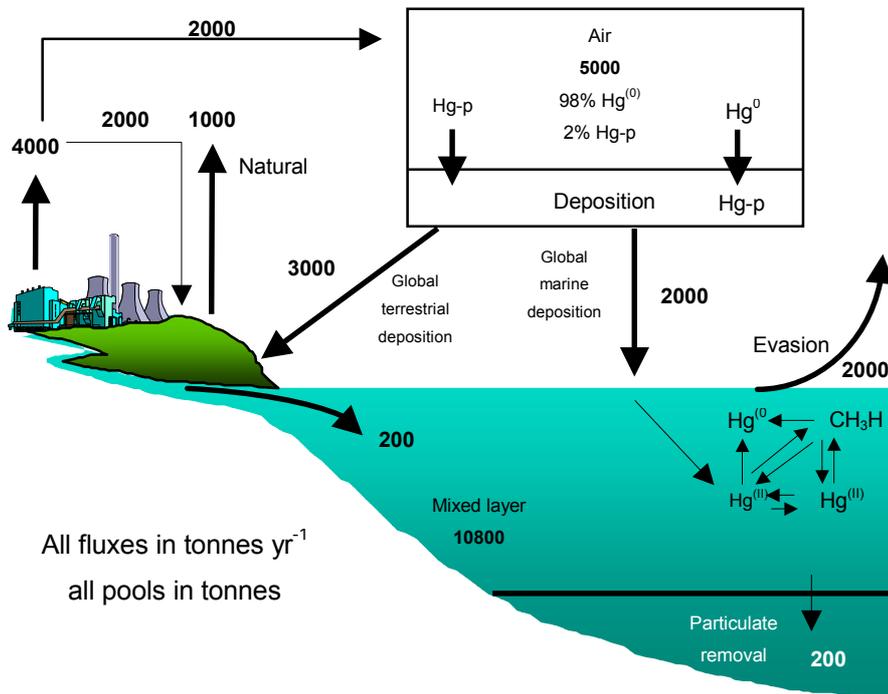
Figure 4-1 The present-day global mercury cycle, from Mason et al. (1994)
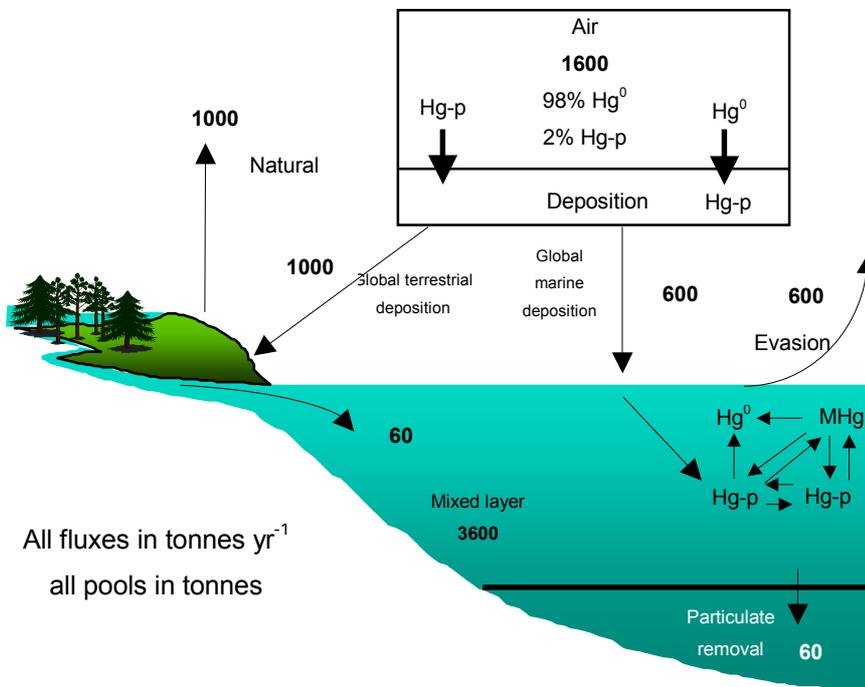
Figure 4-2 The preindustrial mercury cycle, from Mason et al. (1994)

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4.1.5   One of the major assumptions in Mason *et al*.'s (1994) study is that the atmosphere and ocean are in rapid equilibrium. That this is so, is not clear. Despite this assumption, the implications of Mason's study for regional pollution control are important. If the turn-over times suggested by Mason are correct — 1 year for the atmosphere and 3.5 years for ocean to atmosphere — then if all man-made emissions ceased instantaneously, it would take of the order 15–20 years to re-move the atmospheric burden, since it will be replaced and recycled by previously deposited Hg to land and ocean surfaces. Within such time-scales, there is obviously much opportunity for bio-logical methylation and bioaccumulation to continue. These conclusions are inevitably rather un-certain quantitatively but qualitatively, quite clear.

4.1.6   The global cycle analyses cannot be improved further until 0D and 1D modelling is abandoned in favour of more sophisticated approaches using 2D or 3D studies with coupled ocean models.

4.2   Environmental pathways

4.2.1   Environmental pathways—introduction

4.2.1.1   Having outlined the status of understanding of global cycling, particular pathways are now con-sidered by which Hg finds its way into the biosphere and bioaccumulates. Ultimately, this is how Hg causes damage to man and ecosystems. The form that is harmful to man (reviewed in more detail in Chapter 7) is the methylated form of Hg. In this section, the pathways are reviewed.

4.2.2   Natural emissions—land and waters

4.2.2.1   Natural emissions of Hg have been reviewed in the context of the UK. Here, more global aspects are considered. The global budgets presented by Mason *et al*. (1994) for present-day and prein-dustrial times clearly show the potential importance of natural emissions and re-emissions. This terminology and distinction represents a difficulty: whether an emission is the result of a natural process or simply a processing of previously deposited Hg is difficult to establish. However, it is clear that whatever the source, the emission from terrestrial and aquatic/marine surfaces is Hg^0.

4.2.2.2   Fluxes of Hg have been found to be bi-directional for plant canopies, showing both deposition (Lindberg *et al*., 1992) and emission (Hanson *et al*., 1995). Similarly to other trace gases, such as ammonia, a 'compensation point' has been formulated to explain these bi-directional fluxes (Xu *et al*., 1999). For two forest canopies characterized, Lindberg *et al*. (1998) found that fluxes of Hg were dominated by emissions. The controlling parameters were temperature, solar radiation and atmospheric turbulence. Lindberg *et al*. (1998), using micrometeorological techniques, were able to show that plant canopies appear to emit Hg^0 through evapotranspiration. This was an impor-tant finding as previously, most measurements had been limited to chamber experiments that have obvious limitations of scale and disruption of the system. Lindberg *et al*. (1998) also inferred

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that the fluxes arose from previously deposited Hg, rather than naturally occurring Hg in the soils. This is certainly plausible as previous studies have identified that deposited Hg^{II} can be photore-duced to Hg^0, a mechanism that has also been shown to operate for natural waters (Xiao *et al.*, 1995) and soils (Carpi and Lindberg, 1997; 1998). In a simple scaling exercise, Lindberg *et al.* (1998) hypothesized that the re-emission of Hg could be much larger than previously thought, or implied by Mason *et al.*'s (1994) global budget.

4.2.2.3   Given that micrometeorological techniques have now been established to make Hg flux meas-urements (e.g. Kim *et al.*, 1995; Meyers *et al.*, 1996), it would be of value to make such meas-urements over other surfaces and forests. If evapotranspiration represents an important flux, as shown by Lindberg *et al.* (1998), it could be that the re-emission of Hg for the UK are much larger than those suggested in Chapter 2.

4.2.2.4   The global budget of Mason *et al.* (1994) emphasizes the role of oceans in the global Hg cycle. Whilst Hg^0 is found throughout the ocean water column, a significant fraction is in the mixed layer and that the concentrations present and estimated fluxes cannot be sustained simply by mixing in of deeper layer water (Mason and Fitzgerald, 1996). This implies the production of Hg^0 in the mixed layer (Mason and Fitzgerald, 1993). Various possibilities for this cycling have been sug-gested, based upon speciated measurements in the ocean mixed layer (Mason and Fitzgerald, 1996). Only a small proportion is thought to be removed to sediments in the oceans (Mason *et al.*, 1994).

4.2.2.5   The implications of the global budget analysis of Mason *et al.* (1994) are important: if deposition represents the largest input to the oceans, then the oceans have the capacity to recycle the de-posited Hg^{II} into Hg^0 with its subsequent evasion. It is worth pointing out that the evasion fluxes remain rather speculative, currently being based on the frequently-used model of Liss (1983) of sea-air transfer. Measurements of evasion rates, although difficult, would be invaluable.

4.2.2.6   If such budgetary estimates are correct, then evasion from the oceans represents an important part of the atmospheric cycle and should be incorporated into models. Currently, oceans are not considered properly because no atmospheric transport model considers the full biogeochemical cycle. A first simple attempt should be made to estimate global oceanic fluxes on a 2D basis, as has been done for other trace gases, e.g. ammonia (Bouwman *et al.*, 1997).

4.2.3   Atmospheric pathways and processes — 1. Atmospheric chemistry

4.2.3.1   Atmospheric chemistry and dry deposition are the main sinks for Hg^0, both being of importance as although dry deposition rates are rather small, overall conversion of Hg^0 to Hg^{II} is also small, being of the order 0.01% hr^{-1} (Bergan *et al.*, 1999; Pai *et al.*, 1997). These two small loss rates conspire to give Hg^0 a long atmospheric lifetime of the order of months to an upper limit of ~2

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years according to current understanding. Thus, it is important to characterize both loss pathways. Atmospheric chemistry is dealt with in this section and dry deposition in the subsequent (Section 4.2.4).

4.2.3.2   The atmospheric chemistry of Hg, despite having been discussed in the literature for some considerable time, is not well known. As has been outlined previously, the largest fraction of the emissions is Hg^0, the smaller fractions being Hg-p or RGM, both being divalent Hg species. Divalent Hg attached to particles will typically have a lifetime of hours to days, much like sulphate aerosol. RGM–a gas phase divalent Hg species–is thought to be readily dry deposited and washed out by precipitation, again resulting in a short atmospheric lifetime. Thus, the main point of interest in the atmospheric chemistry of Hg is its oxidation of Hg^0 to Hg^{II}, the latter being in the gaseous or particulate phase, and possible reduction reactions returning Hg^{II} to Hg^0.

4.2.3.3   The atmospheric chemistry of Hg has been reviewed recently by Lin and Pehkonen (1999) and they discuss transformations in the gaseous and aqueous phases—heterogeneous reactions have been discussed but not well quantified (Seigneur *et al.*, 1998). Lin and Pehkonen (1999) summarize the known reactions as follows:

–   aqueous phase oxidation of Hg^0 by ozone (O_3), hydroxyl radicals (OH) and by chlorine ($HOCl/OCl^-$);
–   aqueous phase reduction by sulfite (SO_3^-) and hydroperoxy radicals (HO_2);
–   gas phase oxidation by O_3, NO_3, Cl_2 and by hydrogen peroxide (H_2O_2).

4.2.3.4   **Aqueous phase oxidation** of Hg^0 by O_3 was investigated by Munthe (1992) who found the reaction to be independent of pH (5.2 and 6.2) and temperature (5–35ºC). Ozone is a ubiquitous oxidant in the troposphere present at concentrations of ~30–100 ppb, depending upon time, location and height. Aqueous phase oxidation of Hg^0 by OH was investigated by Lin and Pehkonen (1997): OH is also an oxidant present during the day. Hydroxyl radicals are present in the aqueous phase from scavenging of gaseous OH or from in-cloud production from, e.g. H_2O_2, nitric and nitrous acids. The oxidation of Hg^0 by chlorine ($HOCl/Cl^-$) in the aqueous phase was investigated by Lin and Pehkonen (1998b). Reactive chlorine is prevalent in the marine atmosphere, being produced from sea-salt aerosol. Chlorine is a night-time oxidant as Cl_2 and HOCl are readily photolysed during the day. The $Cl^-_{(aq)}$ arises from scavenging of $Cl_{2(g)}$.

4.2.3.5   **Aqueous phase reduction** of Hg^{II} by sulphite may also occur (Munthe *et al.*, 1991). As Lin and Pehkonen (1999) point out, it is important to know the speciation of Hg^{II} in this proposed reaction as the reduction is species-specific: the example given is that $HgSO_3$ is unstable, whereas $Hg(SO_3)_2^{2-}$ is rather stable (Munthe, 1994). Photo-reduction of Hg^{II} is also species-specific (Lin and Pehkonen, 1999). In contrast, reduction of Hg^{II} by HO_2 is not species-specific (Lin and Pehkonen, 1998a).

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4.2.3.6 **Gas phase oxidation** of Hg^0 by O_3 was initially thought to be the primary route of oxidation and several workers estimated rate constants from some rather old work (P'yankov, 1949), yielding estimations of the order 4–5×10^{-18} cm^3 $molecules^{-1}$ s^{-1}. More recently, the rate constant has been measured by Iverfeldt and Lindqvist (1986) and Hall (1995) who reported rate constants of 1.7×10^{-18} cm^3 $molecules^{-1}$ s^{-1} and 3×10^{-19} cm^3 $molecules^{-1}$ s^{-1}, respectively. Hall (1995) also noted the positive effect of sunlight irradiation on the rate. Sommar *et al.* (1997) report gas phase oxidation of Hg^0 by NO_3 but noted that because of statistical error, the rate may be insignificant or zero. Oxidation by H_2O_2 was investigated by Tokos *et al.* (1998), yielding a rather small rate constant; 8.5×10^{-19} cm^3 $molecules^{-1}$ s^{-1}.

4.2.3.7 Several chemical modelling efforts have been undertaken to understand the relative roles and importance of the reactions outlined above; e.g. Munthe (1992, 1994), Seigneur *et al.* (1994), Pleijel and Munthe (1995a,b), Lin and Pehkonen (1998a,b). From these studies, it is clear that gas phase oxidation of Hg^0 by $O_{3(g)}$ contributes a large fraction of the Hg^{II} found in cloud water. However, these models do not include transport processes so that the overall balance of importance has not been studied.

4.2.3.8 In their review, Lin and Pehkonen (1999) point out that whilst much progress has been made in the last decade in understanding the atmospheric chemistry of Hg, there are unidentified gas phase transformation pathways, the rate constants are rather uncertain and the significance and role of heterogeneous reactions on particles is unknown. An example of the evidence for unknown atmospheric pathways is the depletion of TGM in the Arctic during polar sunrise (Schroeder *et al.*, 1998). Nevertheless, it is clear that there is sufficient understanding of the chemistry to start to investigate the importance of processes in chemical transport models, e.g. Petersen *et al.* (1995, 1998, 2000), but that these have not yet been fully explored (see Section 4.3).

4.2.4 Atmospheric pathways and processes — 2. Dry deposition

4.2.4.1 Initial measurements of Hg surface/atmosphere exchange fluxes indicated moderate deposition rates in the range of 0.1 to 1 mm s^{-1} (e.g. Lindberg *et al.*, 1992). Most Hg gas monitors used for flux measurements measure total gaseous mercury (Hg^0 + RGM). Recently, with the availability of denuder based speciation units, a more detailed picture has evolved: dry deposition rates differ greatly between the mercury species.

4.2.4.2 The dry deposition velocity of a gaseous pollutant (V_{dg}) is governed by three factors: turbulent diffusive transport in the atmosphere, molecular diffusive transport through the quasi-laminar sublayer at the ground surface and uptake by the surface or vegetation. Since gaseous Hg^0 is relatively inert, it is likely that Hg^0 does not to deposit at all or with a V_{dg} of less than 0.3 mm s^{-1}. Owing to the high background concentration of Hg^0 in the UK of typically 1.7 ng m^{-3} (Lee *et al.*,

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1998a), the total deposition of Hg is very sensitive to this value. Given the wide range of values of $V_{dg}(Hg^0)$ used in the literature, the contribution of Hg^0 dry deposition to the UK total may range from 0% to 50% of TGM + Hg-p.

4.2.4.3   Reactive gaseous mercury (RGM), expected to represent mainly $HgCl_2$, is assumed to be readily taken up by vegetation surfaces and deposit rapidly, with a deposition velocity (V_d) that approaches the maximum rate possible by turbulence (V_{max}), similar to the atmospheric acids HNO_3 and HCl. The ratio of the molecular diffusivity of $HgCl_2$ and HNO_3 may be estimated from the square roots of their molecular weights (Wesley *et al*., 1989) as about 0.5. Consequently, the transport resistance through the quasi-laminar sublayer is about 75% larger than for HNO_3 (Garland, 1977), leading to an average deposition rate of about 2/3 the value for HNO_3. This effect does not appear to be accounted for in any of the modelling approaches.

4.2.4.4   The deposition velocity of particles (V_{dp}) is determined by both turbulence and the microphysical properties of the absorbing surface. For example, deposition velocities are much larger for forests than for smooth vegetation. In addition, V_{dp} is a strong function of particle size (Slinn, 1982). Milford and Davidson (1985) compiled size-spectra of trace metals and inferred a mass median diameter (MMD) of 0.61 μm for Hg bound to particles, while Keeler *et al*. (1995) observed an overall MMD of 0.80 μm, originating from a bi-modal distribution centred around 0.68 and 3.8 μm. The coarse mode Hg-p was correlated with the total aerosol mass and probably represents adsorption of gaseous Hg^0 onto existing particles. With V_{dp} increasing more than linearly with particle size, the dry deposition flux of the coarse mode was estimated to be 4–5 times the fine Hg-p flux. Deposition rates of particles in this size range are of the order 1 to 3 mm s^{-1} above short vegetation and 5 to 10 mm s^{-1} to forest.

4.2.4.5   It should be noted that the size distribution of Hg-p changes as the aerosol ages from its point of release, as a result of formation of secondary aerosol, evaporation of volatile constituents such as ammonium salts and certain organic compounds, cloud processing and the rapid deposition of large particles. Accounting for this secondary effect would require the incorporation of source specific size spectra into emission inventories and aerosol dynamics into transport models.

4.2.5   Atmospheric pathways and processes — 3. Wet deposition

4.2.5.1   It is generally accepted that gaseous elemental mercury (Hg^0) is not wet deposited. This is concluded from the known physical properties of Hg^0 but it also inferred from the long atmospheric lifetime of Hg^0. Instead, for Hg^0 the main atmospheric deposition process is probably the aqueous oxidation by ozone followed by an in-droplet adsorption primarily onto soot particles (Munthe 1992; Petersen *et al*., 1995), generating a strong non-linearity between emissions and deposition through the influence by secondary pollutants such as ozone and soot (Ebinghaus *et al*., 1999b).

4.2.5.2 Often wet deposition is parameterized through the precipitation rate and the washout ratio, which is the ratio of the Hg concentration (on volume basis) in rainwater divided by the Hg concentration (on volume basis) in air. Often the washout ratio for Hg-p is taken as equal to the value for sulphate (700,000; Iversen *et al.*, 1991; Petersen *et al.*, 1995), while for RGM a value of 1,400,000 has been suggested by analogy with HNO_3 (Jonsen and Berge, 1995).

4.2.5.3 The washout coefficient for individual Hg species is difficult to measure because, once in water, the original chemical form cannot be established. Figure 4.3 summarizes washout ratios derived for particulate mercury as the ratio of Hg-p in air divided by Hg concentration in precipitation. As RGM also contributes to the Hg in solution, this value must be expected to represent an upper estimate.
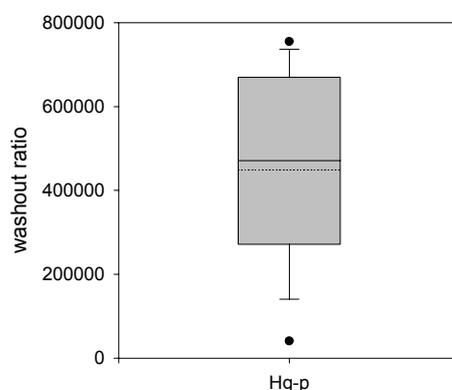
Figure 4-3. Boxplot of washout ratios of mercury derived from simultaneous measurements of Hg-p concentrations in air and Hg concentration in rain (data compiled from Guentzel et al., 1995; Lamborg et al., 1995; Scherbatskoy et al., 1997)

4.2.5.4 As mentioned before, rain water concentrations are enhanced by the seeder-feeder effect at high elevation sites (e.g. Smith and Fowler, 2000). There are no direct measurements of this orographic enhancement on Hg deposition. Evans and Hutchinson (1996) transplanted various bioindicators from lowland to hill-top sites and found that Hg concentrations in mosses increased by up to a factor of 2. Unfortunately, the authors did not compare the amount of precipitation at the various sites. It is highly likely that the increase in deposition at the summit is not entirely due to cloud deposition, as stated by the authors, but that it is also a consequence of the orographic enhancement of precipitation.

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4.3 Atmospheric transport modelling of mercury

4.3.1 Current status of mercury modelling

4.3.1.1 Atmospheric transport modelling of Hg is not well developed. Petersen (1996; 1998) has recently reviewed the models that have been used for heavy metals within Europe. Only five models have been developed that account for spatial patterns of deposition of Hg within Europe. These are:

1. a version of the Dutch (TNO/RIVM) TREND model (Van Jaarsveld *et al*., 1986) applied to the North Sea (Warmenhoven *et al*., 1989; Baart and Diederen, 1991);
2. the EMEP MSC-EAST hemispherical model (Galperin *et al*., 1995, 1996);
3. the EMEP MSC-EAST regional Eulerian model (Ryaboshapko *et al*., 1998, 1999);
4. a version of the EMEP MSC-WEST single layer acid deposition model adapted by GKSS for Hg (Petersen *et al*., 1995);
5. and an Eulerian model of Europe developed by GKSS (Petersen *et al*., 1998, 2000)

4.3.1.2 Of these models, the GKSS Eulerian model is the most well developed being a full tropospheric model (to 10 km) and having a comprehensive Hg chemistry module (Petersen *et al*., 1998). The chemistry module is a condensed mechanism based upon the more comprehensive chemistry module of Pleijel and Munthe (1995b). The EMEP MSC-East Eulerian Model has a much simpler chemical scheme and covers only the planetary boundary layer (PBL) and the lowermost few hundred metres of the free troposphere (Ryaboshapko *et al*., 1998, 1999); in essence, it can be regarded as a PBL model. The EMEP MSC-East modelling activity is of particular relevance to the UK as it is the model used for UNECE analyses and policy negotiations. Ryaboshapko *et al*. (1998) gave a description of the model and some comparisons with observations. However, the validation exercise was not comprehensive although Ryaboshapko *et al*. (1998) claimed that "*Calculation results are in a satisfactory agreement with measurement data available…*". Whilst very few measurements are available, they were hardly utilized by Ryaboshapko *et al*. (1998).

4.3.1.3 Regional scale modelling of North America has been described by Pai *et al*. (1997; 1999). The only global 3D modelling effort that has been undertaken is that of Bergan *et al*. (1999). This approach was an important first step but the parameterization of emissions, chemistry and deposition was rudimentary.

4.3.2   Atmospheric mercury modelling—key uncertainties and scope for improvements

4.3.2.1   The problems associated with modelling Hg in Europe can be summarized according the following: problems with input data; problems with spatial and temporal frameworks; problems with validation data. These are dealt with in turn, below.

4.3.2.2   **Problems with input data**. Here, 'input data' is deemed to cover both data and parameterizations as these rely, ultimately, on empirical data or measurements. Emissions data are essential input in any modelling study. The emissions data used are almost universally poor in quality. The UK and European situation has been reviewed in Chapter 2 with regard to emissions. Only limited spatially disaggregated data are available and these are for 10 years ago (Berdowski *et al*., 1997). In order to update these data, Ryaboshapko *et al*., (1999) describe a number of approaches they have taken to utilize these and other country data and combined them with an independent estimate of Pacyna (2000) whose estimation is described in Chapter 2. So-called 'natural emissions' are in themselves, a huge uncertainty (see Section 4.2.2).

4.3.2.3   The data on which parameterizations in the models are built are rather sparse. The wet removal rates are usually based on the assumption of Hg-p behaving rather like sulphate or nitrate particles, a reasonable assumption based on current knowledge. The dry deposition rates are likewise based on little more than conjecture. Only a few speciated mercury flux data are available. Most model studies assume Hg^0 not to be deposited, or deposited at a very low rate, based upon its low solubility. Reactive gaseous Hg is usually assumed to behave like HCl or HNO_3, i.e. with a zero surface resistance: however, as outlined in Section 4.2.4, r_b may be higher than for these acids. Particulate-phase Hg is assumed to behave much like submicron sized sulphate and nitrate particles. A summary of assumptions is given in Table 4.1 below.

Table 4-1 Overview of dry deposition velocities (cm s^{-1}, unless otherwise specified) used in atmospheric models. Notes: [a]*, day/night;* [b]*, dry/wet;* [c]*, forest only*

Hg speciation	Petersen *et al*. (1995)	Bergan *et al*. (1999)	Pai *et al*. (1997, 1999)	Galperin and Sofiev (1995)	Petersen *et al*. (2000)
Hg^0	0.0	0.0	0.0	0.01/0.03[b]	0.001–0.03[c]
Hg-p	0.2	0.3/0.15[a]	as SO_4	0.1	not given
RGM	4.0	n.a.	$r_c=0$	0.5/1–2	not given

4.3.2.4   The chemistry of atmospheric Hg has been reviewed in Section 4.2.3. In terms of current models, the GKSS Eulerian model (Petersen *et al*., 1998) is clearly the most sophisticated for a long-range transport model, and the EMEP MSC-East Eulerian model described by Ryaboshapko *et al*., (1998) much more rudimentary. It is clear that the mechanisms and rate coefficients are uncertain and poorly characterized. In contrast, the chemical scheme of Bergan *et al*. (1999) in their global study is highly simplified to a simple conversion rate.

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4.3.2.5   In terms of improvements to the models in this area, input data urgently need to be improved: e.g. measurement of reaction rates, better estimations of emissions, flux studies. However, there is considerable scope for improvement in some of the models in terms of completeness of chemistry and physical parameterizations. However, perhaps most critical to better input data and parameterizations is an improved understanding of the flux behaviour of Hg species.

4.3.2.6   **Problems with spatial and temporal frameworks**. One of the key problems with regional modelling of the Hg is the very different lifetimes of the species involved. Elemental gaseous Hg has a lifetime of the order of 1 year (Bergan *et al*., 1999); RGM, if it behaves similarly to HCl and HNO$_3$, will have a lifetime (in the PBL) of about 1–2 days. Particulate-phase Hg will behave similarly to sulphate particles and have a lifetime of typically up to 10 days.

4.3.2.7   From the above summary of lifetimes, it is clear that RGM and Hg-p are ideal for treatment within a regional-scale model of northern Europe. However, Hg^0 with a lifetime of ~1 year requires treatment within a hemispherical or global model to adequately represent its transport, and thus lifetime. When such long-lived species are treated in regional-scale models, boundary conditions and initializations become a significant issue. In essence, the parameterization of Hg sources, sinks, transport and transformations in a regional-scale model becomes a perturbation problem. In other words, the boundary conditions and initializations have a large overall effect on the modelled system. Under such circumstances, the effect of changes in emissions within the regional domain may have a relatively small effect, compared with other systems e.g. SO$_2$/NO$_x$, and cannot be modelled with a high degree of confidence.

4.3.2.8   To take the example of the most sophisticated and well developed regional-scale model of Hg, the GKSS Eulerian model (Petersen *et al*., 1998, 2000), this model is a full troposphere model so that the vertical domain is adequately treated. The Hg chemistry, as mentioned above, is comprehensive. However, boundary conditions of elemental gaseous Hg were fixed at 1.5 ng m^{-3} whereas the modelled surface concentrations for February 1998 were in the range of approximately 1.5 to 2.3 ng m^{-3} (Petersen *et al*., 2000). Moreover, concentrations of O$_3$, SO$_2$ and soot that 'drive' the chemistry were fixed boundary conditions, i.e. there was no linkage to a conventional tropospheric NO$_x$–O$_3$–CH$_4$–CO–HO$_x$ oxidation scheme nor emissions of precursors.

4.3.2.9   In contrast, the global model of Bergan *et al.* (1999) was highly simplified. A fixed conversion rate of Hg^0 to Hg-p was specified (approximately 0.011% hr^{-1}) and RGM was effectively ignored.

4.3.2.10   Common to all the aforementioned studies is a lack of treatment of the long-term accumulation of Hg in the atmosphere, hydrosphere, pedosphere and biosphere. Re-emissions are treated simply: long-term accumulations, reservoirs and sinks have only been modelled in 0D or 1D models (e.g. Mason *et al*., 1994; Hudson *et al*., 1995). Such long-term biogeochemical cycling is impor-

tant when considering a pollutant that has long-term reversible reservoirs such as Hg in the surface oceans that may have a large influence on the background atmospheric concentrations. Long-term cycles that occur on the global scale are ideally treated in 2D global model studies (e.g. Hough and Derwent, 1990).

4.3.2.11 Such a long-term study would be valuable in setting boundary conditions for a 3D global model study. It is critical to understand the effect of global background concentrations on regional scale pollution control with long-lived species such as elemental gaseous Hg. The subsequent step-wise improvement would then be to nest a regional scale model (such as that of Petersen *et al.*, 1998), fully interactive within a global scale model. This is the only way that regional changes in Hg emissions can be more reliably modelled.

4.3.2.12 **Problems with validation data**. A key problem in understanding the performance of models is validation data. There are only a few measurements of the various species of Hg in the UK. To recall from Chapter 3: a one year study of TGM at a rural site; some older urban measurements of Hg-p; some long-term measurements of rural Hg-p at three rural sites. A study is underway of Hg-p at sites close to potential sources but these measurements, if they become available, are likely to suffer from a sampling artefact of unknown magnitude from RGM. The older urban measurements are also likely to suffer from this problem. The rural particulate measurements appear to have a step change from a change-over in analysis method in 1991 that is, as yet, unresolved. There are no reliable wet deposition measurements in the UK.

4.3.2.13 In short, the UK is in a very poor state for measurements of atmospheric Hg. What is needed is a complete set of speciated measurements at least one site, along with wet and dry fluxes. Such a site would help to improve our process-based knowledge and concomitantly aid model improvement for assessment of the effects of emission changes.

4.3.2.14 There are other European (and other) measurements of TGM, Hg-p and wet deposition fluxes that, if carefully used, would be useful in model validation.

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5   An initial UK budget for atmospheric mercury

Summary

- Two UK deposition budgets are available: one from work undertaken at the EMEP Meteorological Synthesising Centre East; the other from modelling work undertaken for this report. In addition, a wet deposition estimate of Hg is available from a modification of existing measurements but these are rather uncertain because of the unconventional measurement technique used.

- The EMEP MSC-E results differ greatly between two major reports. For example, the earlier 1998 report indicates that 34% of UK deposition arises from 'natural emissions' within the EMEP domain and background global concentrations. In the later 2000 report, approximately 60% of UK deposition arises from the same sources. The causes of these differences are not apparent.

- An independent estimate of wet deposition has been made using UK measurements. This gives a wet deposition estimate of 17.1 tonnes yr^{-1}, approximately twice that of the EMEP MSC-E modelling and the modelling undertaken here. This may partially arise from the usage of 'dust deposit' gauges that are deliberately designed to maximize particle dry deposition, a measurement conventionally minimized in wet deposition measurements. The characteristics of the dry deposition capture rate are unknown in comparison with the real landscape.

- Modelling undertaken for this work using a simplified approach in a long-term Lagrangian trajectory model has yielded useful results for comparison to the EMEP MSC-E results. A similar total UK deposition is modelled: 9.878 tonnes yr^{-1} from this work and 9.075 tonnes yr^{-1} from the EMEP MSC-E (1998) work. However, in terms of speciation and attribution, the results are rather different.

- The EMEP MSC-E (1998) work implies an import of Hg deposition to the UK from European land sources of 9%, cf 34% this work; the EMEP MSC-E (1998) work implies a contribution from Northern Hemisphere concentrations and oceans to the UK deposition budget of 36%, cf 25% this work.

- In terms of speciation, this work has shown a large fraction of the UK deposition budget arises from reactive gaseous Hg (65%) and that the deposition of this form of Hg is rather sensitive to the emissions speciation profile assumed.

- The modelling work presented here is discussed and it is concluded that within the constraints of the simple approach taken, the representation of what measurements are available and known wet deposition patterns is adequate. However, the gross simplification of some of the processes disallow more complex questions to be posed and the importance of some processes to be investigated. An improved approach is suggested.

- Critical in improving the modelling is a concomitant improvement in the measurement database–for both ambient measurements and fluxes–for the UK, which at present, is inadequate.

5.1   Introduction

5.1.1   Atmospheric budgets depend upon the processes included in the emission and deposition estimate. For example, if the aim of a study is to define country-to-country transport matrices, locally re-suspended large soil particles should be ignored as they are transported over a few kilometres at most. Natural emissions should be considered in a budget estimate of the contribution by industrial impacts.

5.1.2   Owing to a lack of measurement data, there are no estimates of natural emissions of Hg for the UK, whilst the estimate of man-made emissions is somewhat incomplete and rather uncertain as

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it is largely based on emission figures submitted by the industrial plant operators that have not been validated (see Chapter 2).

5.2   The global mercury budget

5.2.1   The current perception of the global Hg budget has been already shown in Figure 4.1 and contrasted with the preindustrial Hg cycle as derived from historical records. In preindustrial times (Figure 4.2) natural emissions from the land of 1,000 tonnes yr^{-1} were balanced by the global terrestrial deposition, while the marine evaporation and deposition also formed a steady state exchange of 600 tonnes yr^{-1}. This led to 5,000 tonnes Hg contained in the atmosphere.

5.2.2   Current global emissions are estimated to be around 7,000 tonnes yr^{-1}, with 57% from man-made sources, 14% from land based natural sources and 28% re-emission from seawater. Of the man-made emission 50% is expected to be locally and regionally deposited, while the other 50% contributes to the atmospheric pool of the long-lived Hg^0, which has increased to 5,000 t. This implies that 43% of the recycled Hg is not treated in emissions inventories of man-made sources.

5.2.3   The total deposition to land is expected to be about 5,000 tonnes yr^{-1}, with 40% originating from local and regional sources and the majority derived from the atmospheric Hg pool.

5.3   The EMEP MSC-E budget for the UK

5.3.1   Mercury is one of the three toxic metals treated by the Convention for Long-Range Transport of Air Pollutants (CLRTAP; UNECE, 1998). The Convention has set up Task Forces for emission inventories and critical loads mapping under the EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe). Modelling activities for heavy metals and persistent organic pollutants are carried out by the Meteorological Synthesizing Centre East, while the Chemical Co-ordination Centre (CCC) compiles datasets of concentrations and wet deposition measurements across the EMEP domain.

5.3.2   The EMEP MSC-E long-range transport model uses the official emission inventories submitted by the member states of the Convention, whilst independent expert estimates (e.g. Berdowski *et al*., 1997; Pacyna, 1999) are used for comparison.

5.3.3   Figure 5.1 shows the surface concentration and deposition calculated with the Eulerian multi-layer EMEP MSC-E model using the official estimates for the whole EMEP domain (Ilyin *et al*., 2000). Figure 5.2 shows a breakdown of the UK deposition derived by EMEP MSC-E by species and Figure 5.3 shows attribution by UK and non-UK sources for wet and dry deposition.

5.3.3.1   In the current version of the EMEP MSC-E model, Hg boundary concentrations for the EMEP domain are prescribed as 1.77, 1.07, 1.70 and 1.50 ng m^{-3} for Atlantic (W), Arctic (N), African (S) and Asian (E) wind directions, respectively. The background air Hg concentration is assumed to

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be independent of height and the ratio Hg-p/Hg^0 is 150.
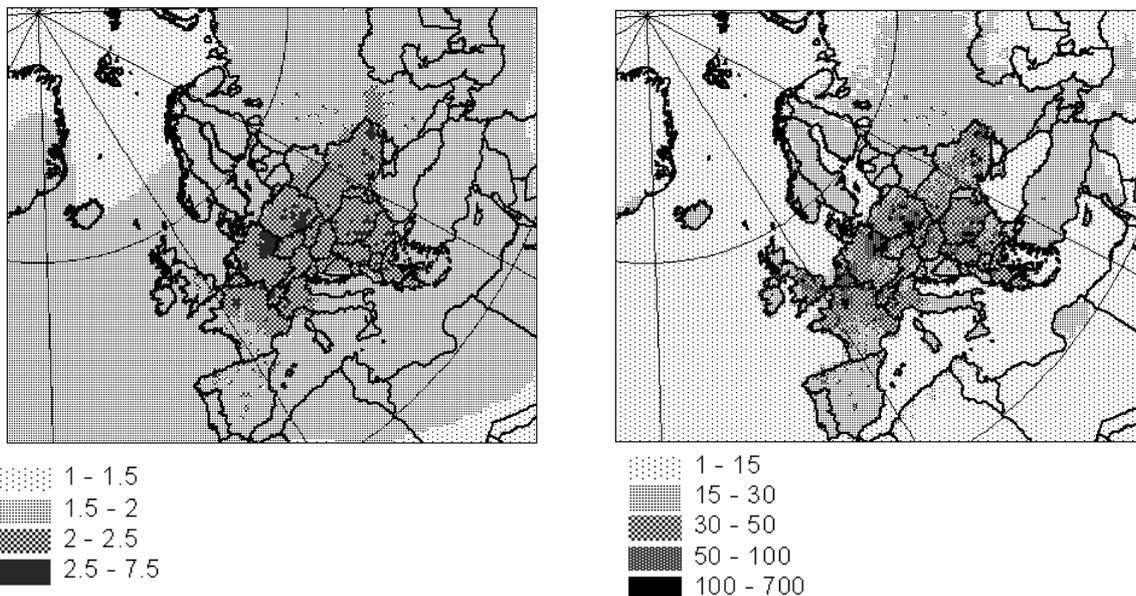
Figure 5-1 EMEP results: (a) Hg concentration in surface layer [ng m^{-3}] and (b) Hg deposition [g km^{-2} yr^{-1}] (from Ilyin et al., 2000)
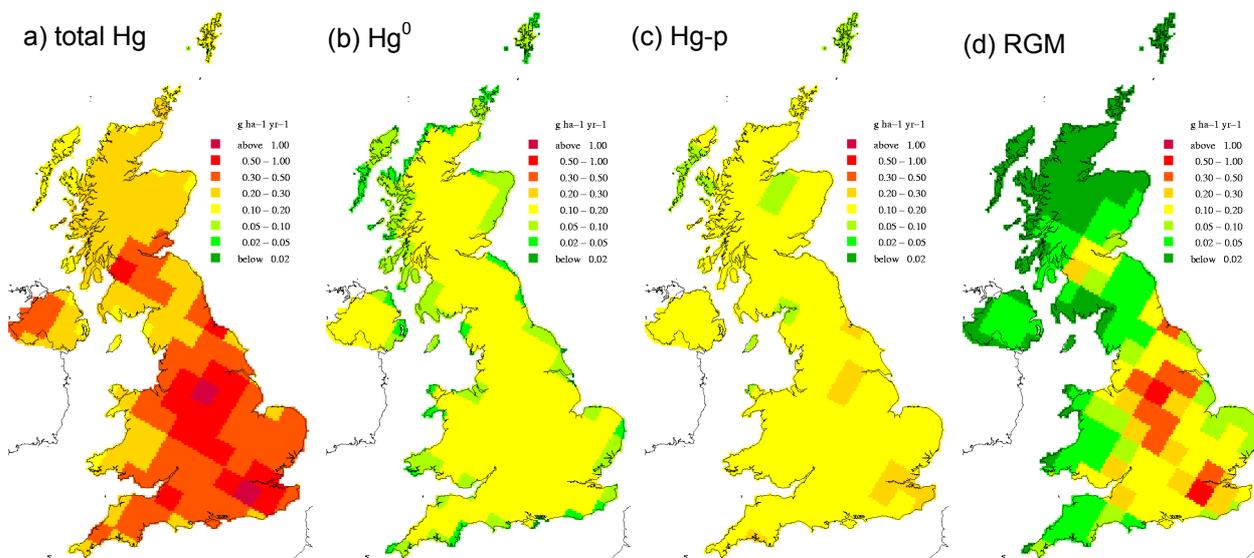
Figure 5-2 EMEP results of the UK deposition of total, elemental gaseous mercury, reactive gaseous mercury, and mercury bound to particles, partly divided into UK and non-UK sources

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(a) UK sources   (b) non-UK   (c) wet   (d) dry
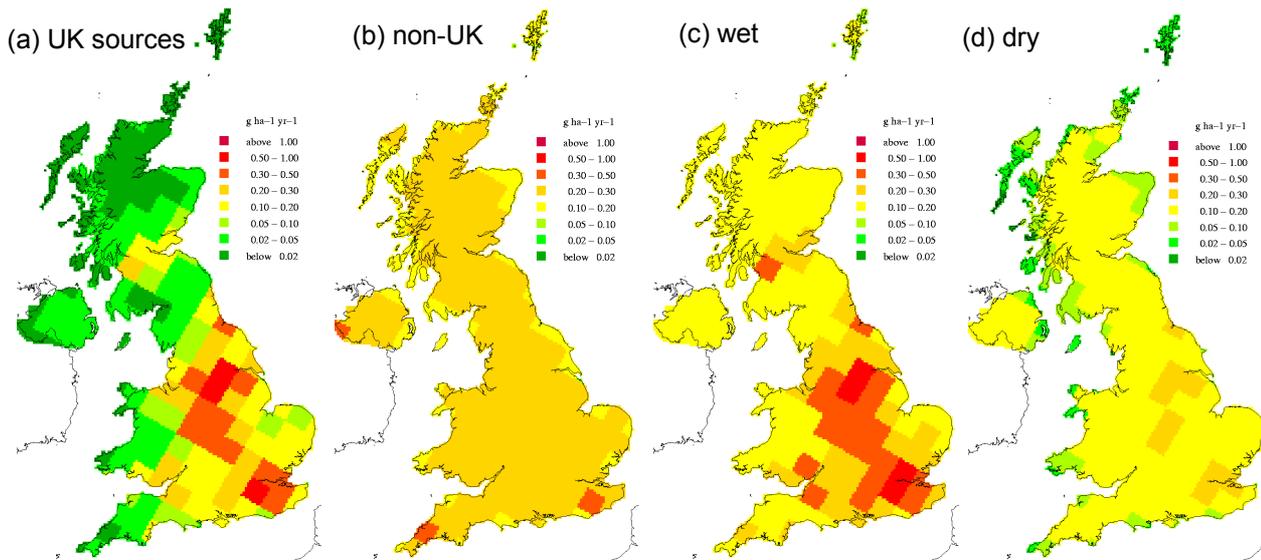
Figure 5-3 Hg deposition in the UK originating from (a) UK sources and (b) non-UK sources according to the EMEP results, 1998. (c) Wet deposition and (d) dry deposition of mercury according to the EMEP results, 1998

5.3.4   The breakdown of the fate of the UK emissions and the origin of the Hg deposited to the UK (Figure 5.4 and Table 5.1) demonstrates that, according to EMEP MSC-E, only a quarter of the UK emissions are deposited within the UK, contributing 36% to the total deposition. Because of the high background concentrations compared with the man-made emissions in the UK and the geographical position of the British Isles, the contribution of Hg from outside the EMEP domain (indeterminate origin) to the UK deposition is very important (60%; Figure 5.4b). This import is mainly arises from the long-range transport of Hg^0 and Hg-p, which show a very homogeneous deposition pattern (Figure 5.1b, c). The deposition of RGM is much more closely linked to the source regions (Figure 5.1d) and dominates the deposition from UK sources. The wet deposition field (Figure 5.3c) is closely linked to the deposition of RGM as this is readily scavenged, while the dry deposition field is smoothed out by the contribution through the more equally distributed Hg^0.
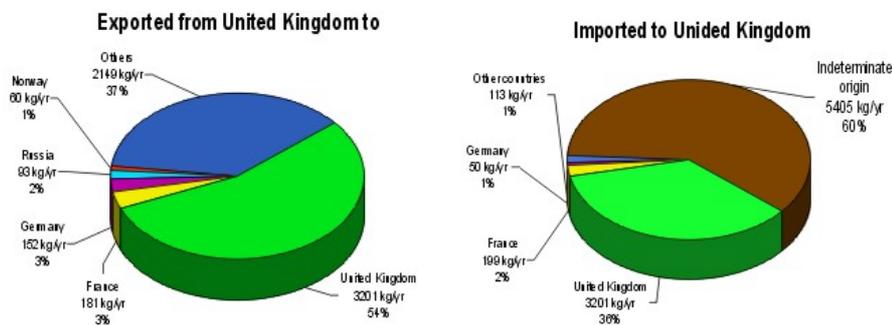
Figure 5-4 Breakdowns of (a) UK export to EMEP region and (b) import of atmospheric mercury according to EMEP model results (from Ilyin et al., 2000)

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Table 5-1 The EMEP mercury budget for the UK for 1998 (Ilyin et al., 2000).

Allocation	total Hg
Emission	12.4 tonnes yr^{-1}
exported	74%
deposited within the UK	26%
Deposition	9.0 tonnes yr^{-1}
from UK sources	36%
from global Hg pool	60%
from France	2%
from Germany	1%
from other member states of CLRTAP	1%

5.3.5   Thus, while the occurrence of deposition 'hot-spots' is the result of local deposition of RGM and may therefore be controlled by emission reductions, the response of the *total* UK deposition to reductions in UK emission is strongly non-linear. This severely limits the potential for deposition reduction through national and even European emission control.

5.3.6   Although the UK is predicted to be a net exporter of total Hg, the budget estimates of the individual Hg components need to be differentiated (Table 5.2). For Hg^0, the deposition to the UK is only 1/3 of the emissions and most of the Hg^0 emitted by the UK is added to the global atmospheric Hg pool. For RGM, deposition and emission is roughly in balance, emphasising the short transport distance of this fast depositing species. For Hg-p, the deposition exceeds the emission by more than a factor of two. This is partly because of imports from continental Europe, but mainly mediated by the chemical conversion of Hg^0 both from the global atmospheric Hg pool and from UK sources into Hg-p.

Table 5-2 The speciated mercury budget for the UK for 1998 (tonnes Hg yr^{-1})

Allocation	total Hg	Hg^0	Hg-p	RGM
Emission	12.4	8.4	1.2	3.0
Deposition	9.0	3.0	2.6	3.5
Deposition as fraction of emission	73 %	36 %	220 %	120 %

5.3.7   Uncertainties in the EMEP budget

5.3.7.1   The remote concentration and wet deposition measurements of Hg currently available within Europe are of limited value for the comparison with model results. This is because of the poor spatial coverage of the measurement stations and inadequate chemical procedures leading to many values being reported below the detection limits. In fact, the data from rural UK monitoring sites archived by the CCC (East Ruston, Staxton Wold and Banchory, 1989-1992) were rejected by the internal QA/QC procedures. By comparison, for Pb and Cd the measurement database is more extensive and more reliable. These measurements are more in line with the modelling results based on much higher expert emission estimates than with the lower official emissions. This

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suggests that, on average, the emission estimates submitted by the member states of the convention are underestimates. This could imply that the higher UK Hg emission estimate of Pacyna (1999) is more realistic than the NAEI estimate, which is (in part) based upon the emission figures submitted by the industrial plant operators to the ISR.

5.3.7.2   Except for some re-emission from sea, natural emissions and re-emissions are not considered by EMEP.

5.3.7.3   The speciation of Hg emissions is currently superimposed onto the official emission estimates by the CCC. For a more realistic approach it is necessary that many more measurements of the speciation from a range of source types are carried out so that the member states of the convention submit speciated emissions derived with the best knowledge of the industrial plants operating. Alternatively, as an initial improvement, emissions should be speciated by industrial process, based upon measurements.

5.3.7.4   The wet deposition field as predicted by the EMEP MSC-E model (Figure 5.3c) shows a better correlation with the source regions than with the patterns of rainfall and topography. This is in contrast to the deposition map derived from the dust collector network (Figure 3.7) and wet deposition of other pollutants (e.g. sulphate and nitrate; RGAR, 1997) and suggests that precipitation may not correctly be reproduced by the weather prediction module of the EMEP MSC-E model. However, this partly arises because of the inadequate scale representation of the EMEP MSC-E model for the UK. The EMEP MSC-W 50 km × 50 km acid deposition models also share this problem of misallocating the deposition of S and N species as independently demonstrated by Lee and Kingdon (2000b). Moreover, the EMEP MSC-E model does not include seeder-feeder effects and will therefore underestimate the deposition to sensitive upland ecosystems.

5.3.7.5   The fraction of Hg deposition derived from long-range transport of Hg^0, at an estimated 60%, is very important. Since dry deposition is the only direct pathway for Hg^0 deposition, the choice of the dry deposition velocity used is critical. Although it is generally accepted that this deposition velocity is very small, the relative error associated with the values currently used is very large and the deposition budgets rather sensitive to this parameterization. More measurements of Hg^0 deposition are urgently needed, while most old studies have measured total gaseous mercury (TGM = Hg^0 + RGM), which can be affected by the fast deposition of RGM.

5.3.7.6   A significant proportion of this deposition of Hg^0 is mediated by oxidation to more reactive forms of Hg. Therefore, the deposition is very sensitive to the oxidation rates used in the description of the poorly understood and insufficiently quantified Hg chemistry.

5.3.7.7   One particularly significant issue is the large difference between the results of Ryaboshapko *et al*. (1998) and Ilyin *et al*. (2000). Taking the summary of Ilyin *et al*. (2000) and comparing these with

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the results of Ryaboshapko for the UK deposition budget for the UK, large discrepancies are noted: these two sets of results are given in Table 5.3 below.

Table 5-3 EMEP deposition budgets for the UK for 1995 and 1998 (tonnes yr^{-1})

Origin of deposition to the UK	Ryaboshapko *et al.* (1998) estimation	Ilyin *et al.* (2000) estimation
United Kingdom	5.007	3.201
France	0.221	0.199
Germany	0.219	0.050
Other countries	0.321	0.113
Indeterminate origin[†]	3.307	5.405
Total	9.075	8.968

[†]Includes 'natural' emissions within EMEP modelling domain and contribution of background concentrations (boundary conditions).

5.3.7.8 Much of the discrepancy evidently has its origin in the allocation of deposition from sources of 'indeterminate origin', however, the cause or reasoning behind this is not immediately obvious from the two reports.

5.4 Comparison with other emission/deposition estimates

5.4.1 The atmospheric Hg budget depends critically on estimates of emission and deposition. While emission estimates are compared in Table 2.1, even fewer data are available for deposition estimates to the UK. For England & Wales a deposition estimate may be derived from the results of the dust collector network by Alloway *et al.* (1998) presented in Figure 3.7. At 45.2 tonnes yr^{-1} these measurements indicate a much larger deposition of Hg than the EMEP MSC-E model output (Table 5.3). Two very high values in the deposition data of Alloway *et al.* (1998) may be the result of localized contamination or point sources and bias the overall results. Omitting these two measurements in the calculation leads to a reduced total of 17.1 tonnes yr^{-1} which is in better agreement with implied modelled deposition but is still 2.7 times greater than the equivalent EMEP MSC-E value of 6.4 tonnes yr^{-1} (note that the wet deposition measurements are available for England and Wales only, not Scotland and Northern Ireland and hence this value of 6.4 tonnes Hg yr^{-1} represents England and Wales).

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Table 5-4 Comparison of Hg deposition estimates to the area of England and Wales

Method of estimate	Deposition [t yr^{-1}]	Fraction of NAEI emissions of E&W	Fraction of CEH emissions of E&W
EMEP model output	6.4	55 %	29 %
Dust gauge network	45.2	390 %	200 %
Dust gauge network – largest two values removed	17.1	150 %	76 %

5.4.2   It is important to note that the EMEP MSC-E modelled deposition field and that measured would not necessarily be expected to be identical. The deposition measurements identify the overall burden from all sources, including industrial sources, natural sources and re-emission, some of which are not included in the emission inventories upon which the EMEP model is based. The dust gauges measure the total deposition (wet and dry), but deposition rates to the collectors are not necessarily the same as, or even proportional to, the deposition to the landscape as collection properties for Hg-p and RGM are unknown (cf. Section 3.3.6.3). For Hg, the particle bound-phase constitutes only a minor fraction to the total concentration, and this artefact is likely to be less important than for other metals. However, there might be some contamination through locally re-suspended large soil derived particles. This is also supported by the results for other metals (e.g. lead and cadmium), for which the discrepancy between measurements and model results is even more pronounced – despite the absence of natural sources for these metals.

5.5   A new formulation and sensitivity analysis of the UK mercury budget

5.5.1   Model description

5.5.1.1   For this study, an existing regional long-range transport model was modified to incorporate a simple representation of the atmospheric Hg cycle. The purpose of the study was not to represent a detailed description of the atmospheric chemistry of the Hg cycle but rather to use a highly simplified approach similar to that of Bergan *et al*. (1999) to study the sensitivity of the UK deposition budget to speciation of emissions between the different forms, i.e. Hg^0, RGM and Hg-p.

5.5.1.2   The Hg model was based upon the DERA regional long-term receptor-oriented trajectory model, RCTM (Regional Chemistry Trajectory Model). The model has been described by Lee and Kingdon (2000a) and is a development over previous UK and European trajectory models (e.g. Derwent *et al*., 1988; Lee *et al*., 2000b).

5.5.1.3   The modelling approach remains a receptor-oriented long-term (annual) Lagrangian trajectory model that can be operated in single or multi-layered modes. The model is of the usual form widely used for such trajectory models:

$$\frac{dc_i}{dt} = E_i + R_i(c_j) - v_{g_i}c_i \Big/ h - \Lambda_i c_i \qquad (1)$$

where:

c_I	concentration of species i;
E_I	emission rate of species i;
$R_i(c_j)$	rate of change of species i as a result of the chemical reactions of itself and other species j;
v_{gi}	dry deposition velocity of species i in the lowest box;
h	depth of the lowest box;
Λ_I	washout (wet deposition) coefficient of species i.

5.5.1.4 The development of the chemical composition of the air parcel is solved using a quasi-implicit variable timestep solver. A climatological approach was taken in estimating annual average concentrations and deposition. Precipitation data across the EMEP domain were taken from a global long-term average data set with a resolution of 0.5º latitude × 0.5º longitude (Legates and Willmott, 1990) regridded to 50 × 50 km. For the UK, the Meteorological Office 5 km long-term rainfall field was used, modified to account for directional seeder-feeder enhancement using the method of Lee *et al*. (2000c). In the Lagrangian approach adopted, air parcels travel along straight-line trajectories at intervals of 15º to each receptor at a geostrophic wind speed of 7.5 m s^{-1} (Jones 1981). The contribution of each trajectory arriving at a receptor is then weighted by long-term directional precipitation data from the nearest meteorological station, taken from the ISMCS (1995) database.

5.5.1.5 The model can be used in single, 5, or 10-layer modes. When used in 5 or 10-layer modes, the vertical diffusion of species is described by the *K*-theory diffusion equation, based upon Monin-Obukhov similarity theory (e.g. Stull, 1988; Seinfeld, 1988).

5.5.1.6 Specific modifications were made to the model to incorporate the treatment of Hg. European emissions were taken from gridded data from Berdowski *et al*. (1997), and UK gridded emissions from Nemitz *et al*. (1999). The speciation of the emissions is not well characterized (Section 2) so in order to test the sensitivity of the UK budget to this, a facility was devised whereby the emissions could be repartitioned in given proportions between Hg^0, RGM and Hg-p as fractions of the totals for UK and (other) European high and low-level sources.

5.5.1.7 Dry deposition of Hg species was calculated using a very simple approach of prescribed single deposition velocities for each Hg species to all surface types. The view was taken that the dry deposition of Hg species is insufficiently well understood to prescribe r_c values, as is necessary when using a 'multiple resistance' approach in the model. Wet deposition is represented by a simple loss (or washout) coefficient for the relevant species, based upon observations of the ratio of the species in air and rain, usually specific to a given precipitation amount. The wet deposition scheme is a modified form of Lee *et al*.'s (2000c) formulation that accounts for seeder-feeder enhancement of wet deposition in a mechanistic manner, considering the directionality of both precipitation and the seeder-feeder mechanism but at a resolution of 5 km. Wet deposition scaveng-

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ing factors, as discussed in Section 4.2.5, are not well known. The principle assumption for chemical conversion of Hg^0 is that when it is converted to the divalent form, it attaches to existing particles. Therefore, it is reasonable to use washout factors applicable to sulphate and nitrate particles. For RGM, the assumption is that it will have similar characteristics to HNO_3 and will be washed out rather readily by in-cloud and sub-cloud scavenging. Thus, a washout factor utilized for HNO_3 was applied to RGM. Elemental gaseous Hg was assumed not to be removed (in this form) by precipitation. The wet and dry removal factors are summarized in Table 5.5.

Table 5-5 Removal parameters for Hg species in RCTM model

Hg species	Dry deposition velocity (m s^{-1})	Washout (s^{-1})
Hg^0	1.55×10^{-4}	0
RGM	4.0×10^{-2}	9.0×10^{-6}
Hg-p	1.5×10^{-3}	1.3×10^{-5}

5.5.1.8   For regional-scale modelling, boundary conditions of some Hg species are a significant issue. This is the case for Hg-p and Hg^0 but not for RGM, as parameterized, as its lifetime is rather short. The boundary conditions were taken from Ryaboshapko *et al*. (1998) of 1.5 ng m^{-3} Hg^0 and 0.01 ng m^{-3} Hg-p. Trajectories were initialized at the edge of the EMEP grid with these values, after which the normal evolution of the air parcel in terms of emission, deposition and transformation subsequently controls the air concentrations.

5.5.1.9   The chemistry of Hg was represented as a simple rate conversion of 0.01% per hour as representing an overall conversion of Hg^0 to Hg^{II} (p) via homogeneous and heterogeneous processes. Whilst a gross simplification, this is similar to the parameterization of SO_2 to SO_4 in most simple acid deposition models, whereas in actuality, S^{IV} to S^{VI} oxidation is a similarly complex process controlled by homogeneous and heterogeneous processes. Bergan *et al*. (1999) took a similar approach in their global Hg study and the rate conversion of 0.01% hr^{-1} is consistent with their modelling studies and the estimations of Pai *et al*. (1997).

5.5.2 The modelled UK mercury budget using RCTM—Results

5.5.2.1 Deposition budgets for the UK are given in Table 5.6. All simulations were made using the UK-scale model operating at a resolution of 20 km × 20 km with 10 vertical layers.

Table 5-6 Deposition budgets of speciated Hg from RCTM (all units in tonnes yr^{-1})

Deposited form of Hg	Base case	Totals wet & dry	Zero initialized trajectories	Totals wet & dry	European sources only	Totals wet & dry
dry Hg^0	1.978		0.184		0.131	
wet Hg^0	0.000	1.978	0.000	0.184	0.000	0.131
dry RGM	5.489		5.489		2.295	
wet RGM	0.884	6.373	0.884	6.373	0.423	2.718
dry Hg-p	0.136		0.108		0.052	
wet Hg-p	1.390	1.526	0.706	0.814	0.418	0.470
Total	**9.878**		**7.372**		**3.319**	

5.5.2.2 In the 'base case', all emissions from the UK and European sources are accounted for, along with initializations of the trajectories to represent boundary conditions to the EMEP modelling domain. This gives a total UK deposition of 9.9 tonnes yr^{-1}. In order to quantify the contribution of the Northern Hemisphere background to UK deposition, a simulation was made in which the boundary conditions were set to zero, giving a total UK deposition of 7.4 tonnes yr^{-1}. The European sources were quantified by setting the UK emissions to zero and subtracting the deposition from background conditions, resulting in a UK deposition of 3.3 tonnes yr^{-1}.

5.5.2.3 By differencing, a Northern Hemisphere background contribution to UK deposition of 2.5 tonnes yr^{-1} is implied. This was confirmed by an independent explicit run with no emissions and only trajectory initializations. The UK contribution to itself was calculated to be 4.1 tonnes yr^{-1}.

5.5.2.4 Two further simulations were made to test the model sensitivity to the speciation of UK emissions. In the base case, UK emissions totalling 12.7 tonnes yr^{-1} were used. In the two sensitivity studies, the same UK total emissions were used but partitioned differently between Hg^0, RGM and Hg-p. In all simulations, the other European sources were held constant, also with constant speciation. The emissions used are given in Table 5.7 and the results of these sensitivity studies given in Table 5.8.

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Table 5-7 Emissions used in UK deposition budgets sensitivity studies to speciation of Hg (tonnes yr^{-1})

Deposited form of Hg	Emissions	Fractionation of low and high UK sources %	Low Hg^0 scenario	Fractionation of low and high UK sources %	High Hg^0 scenario	Fractionation of low and high UK sources %
low-level Hg^0	2.2	65	1.02	30	2.72	80
low-level RGM	0.8	23	1.70	50	0.51	15
low-level Hg-p	0.4	12	0.68	20	0.17	5
high-level Hg^0	6.2	67	2.80	30	7.44	80
high-level RGM	2.3	25	4.70	50	1.40	15
high-level Hg-p	0.8	8	1.90	20	0.47	5

Table 5-8 Sensitivity studies of UK deposition budgets of speciated Hg from RCTM (all units in tonnes yr^{-1})

Deposited form of Hg	Low Hg^0 scenario	Totals wet & dry	High Hg^0 scenario	Totals wet & dry
dry Hg^0	1.949		1.989	
wet Hg^0	0.000	1.949	0.000	1.989
dry RGM	8.894		4.236	
wet RGM	1.373	10.267	0.703	4.939
dry Hg-p	0.198		0.110	
wet Hg-p	1.725	1.923	1.258	1.368
Total	**14.139**		**8.297**	

5.5.2.5　Evidently, in the 'low Hg^0' scenario the increased amount of RGM relative to other species results in a higher total UK deposition by approximately 43%. Conversely, in the 'high Hg^0' scenario, the reduced amount of RGM results in a smaller UK total deposition by 16% (relative to the base case).

5.5.2.6　The spatial distributions of modelled Hg^0 and wet deposited Hg are shown in Figure 5.5.
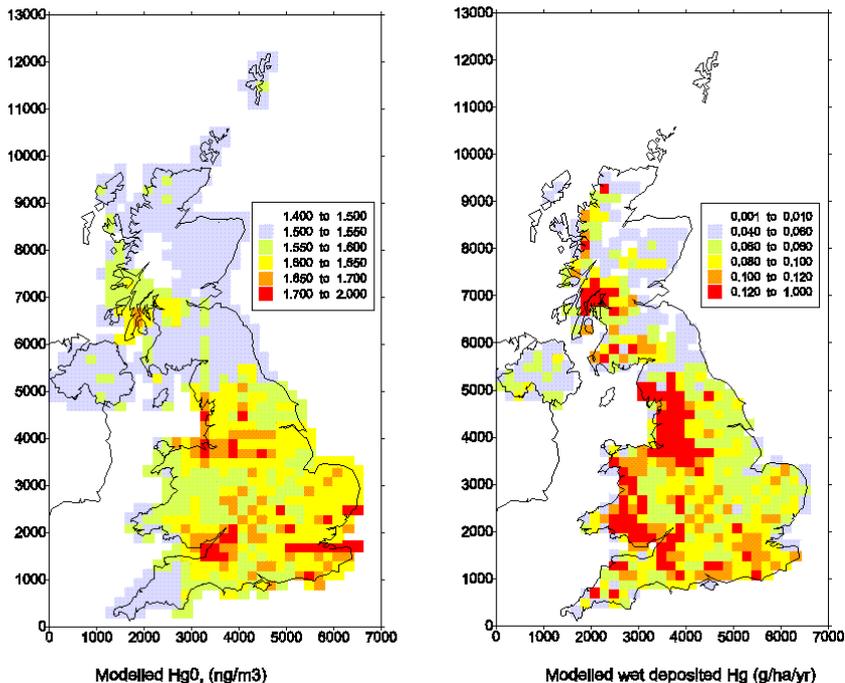
Figure 5-5 Modelled Hg^0 and wet deposited Hg (all species) for the UK using RCTM

5.5.2.7   It is of interest to examine the proportions of wet deposition that arise from the different Hg species: the proportions of RGM and Hg-p that make up the contributions to an individual 20 km × 20 km square are shown in Figures 5.6a and b, respectively.
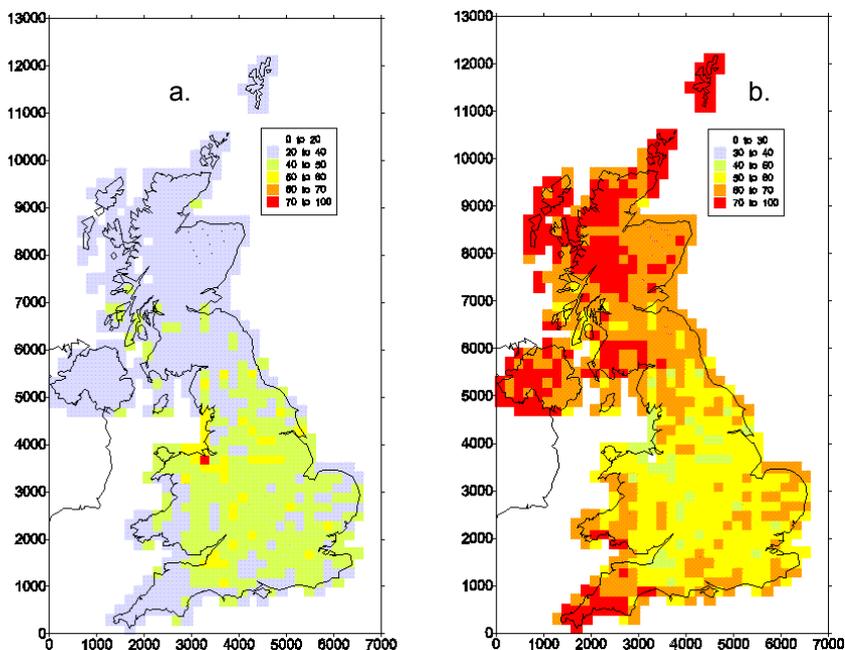
Figure 5-6   Proportions of wet deposited RGM (a) and Hg-p (b) to grid squares in RCTM base case

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5.5.2.8   It is also possible to run RCTM in 'EMEP mode', calculating for 50 km grid square receptors across the EMEP modelling domain area (land surfaces, the Baltic and North Seas). For comparison with the RCTM UK-scale and the EMEP MSC-E results, a simulation was run using the 5-layer model. The concentrations of Hg^0 and wet deposited (all species) Hg are shown in Figures 5.7a and b, respectively. The results are comparable with the UK-scale modelling as although the Berdowski *et al*. (1997) inventory for 1990 was used on the EMEP-scale, giving a total emission of 25.6 tonnes yr^{-1}, the inventory was scaled to current estimations of the total European emissions.

Figure 5-7 RCTM modelled Hg[0] (a), ng m^{-3}, and wet deposited Hg, all species (b), g ha^{-1} yr^{-1}, base case, EMEP 50 km receptors

Modelled Hg0 using Berdowski et al. (1997) inventory with RCTM 5-layer model

Modelled total wet deposited Hg using Berdowski et al. (1997) inventory with RCTM 5-layer model

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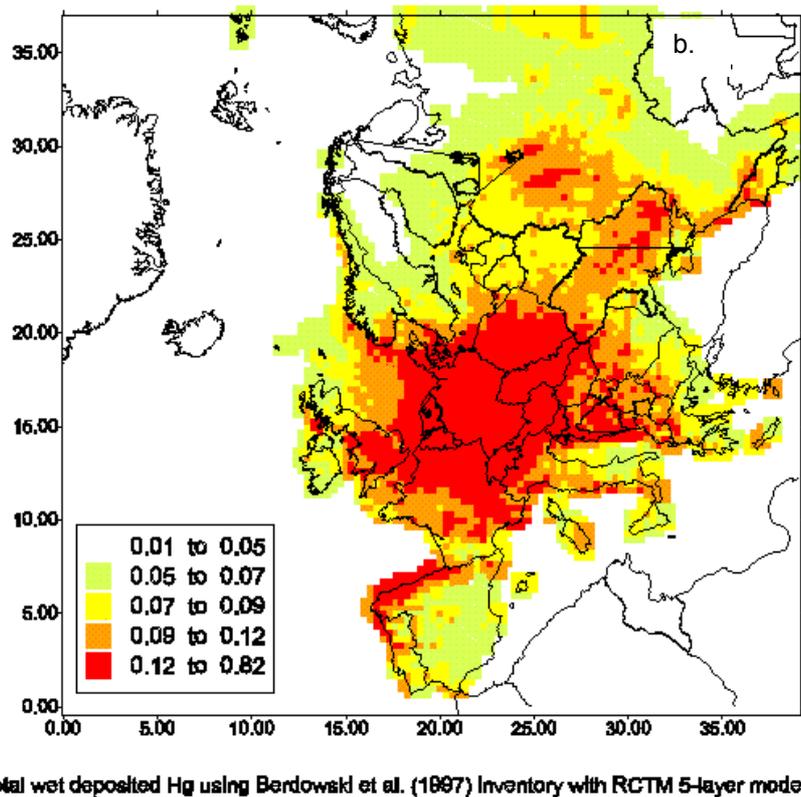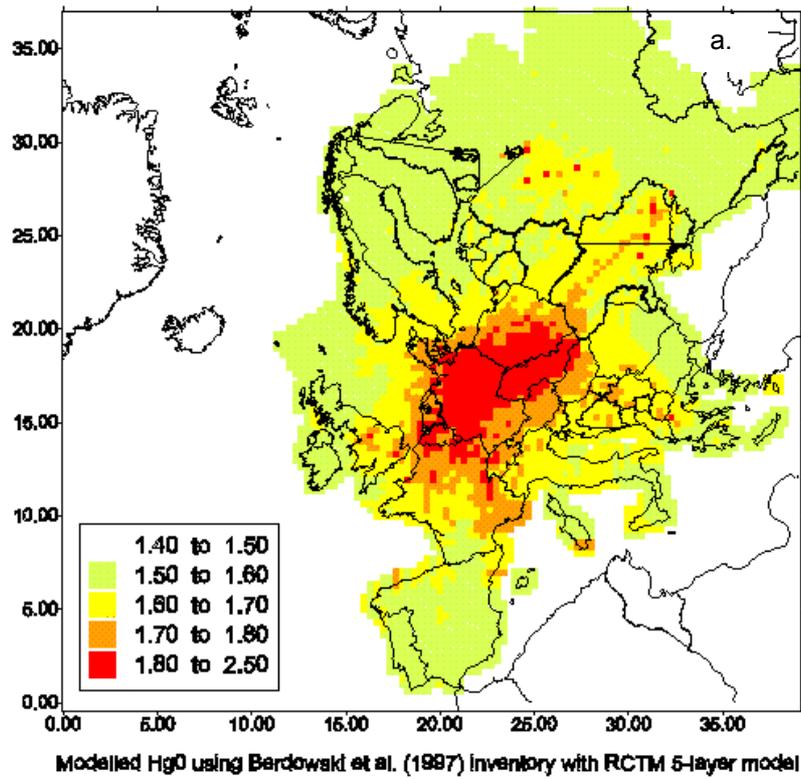
5.5.3 The modelled UK mercury budget using RCTM—Discussion

5.5.3.1 The UK-scale modelling results in a UK deposition of Hg of 9.9 tonnes yr^{-1} for an emission of 12.7 tonnes yr^{-1}. Of this 9.9 tonnes, 6.4 tonnes or 65% of the deposition is attributable to RGM in the base case. Of this 6.4 tonnes, 3.7 tonnes (58% of RGM) originates from UK sources. In the low Hg^0 scenario (Table 5.7), the overall deposition to the UK increases, largely because of increased deposition of RGM. In the high Hg^0 scenario, UK deposition decreases by 16%, largely because of decreased RGM deposition. Evidently, the budget is rather sensitive to the proportion of emissions that are assumed to be in the RGM form. The amount deposited according to RCTM is rather similar to that calculated by the EMEP MSC-E model (see Table 5.2) but the attribution and speciation are rather different. Approximately 39% of the deposition is RGM according to the EMEP MSC-E model but 65% according to RCTM. Curiously, the EMEP MSC-E emissions speciation for the UK assumes a higher proportion of RGM: Hg^0 52%; RGM 34%; Hg-p 10% (Ryaboshapko et al., 1998), cf. 24% used in this work. The treatment of wet and dry deposition processes is similar in both models in their assumptions of Hg-p behaving like sub-micron sulphate particles and RGM behaving like HNO_3. It is likely that the explanation for the differences lie in the differing horizontal and vertical scales. The EMEP MSC-E model operates on a 50 km × 50 km scale, which has been shown to be inadequate for representing detailed S and N deposition in the UK (Lee and Kingdon, 2000b). Moreover, the EMEP MSC-E model has only 4 layers in the vertical, the bottom 2 layers being 0–100 m and 100–400 m. The RCTM model has 5 model layers (of a total of 10) approximately equivalent to the EMEP MSC-E model's lowest 2. Given the completely different model structures, this explanation can at best be speculative. Previous investigations into different budgets for S between a UK regional model and the MSC-W Lagrangian acid deposition model have been similarly inconclusive (Lee and Kingdon, 2000b).

5.5.3.2 In terms of ground-level concentrations of Hg^0, the RCTM model results look reasonable, with enhancements in concentration over the assumed background in some of the main source regions. The comparison can only be subjective, given that there is only once data set with which the concentrations can be compared (Lee et al., 1998a). Nonetheless, the model is in good agreement with these measurements indicating concentrations between approximately 1.6 and 1.7 ng m^{-3}; the measurements of TGM giving a mean concentration of 1.68 ng m^{-3}.

5.5.3.3 The modelled RCTM wet deposition also gives a good representation of the UK precipitation pattern, in contrast to the EMEP MSC-E modelled wet deposition, this being a simple result of the better scale resolution of RCTM. A comparison of modelled wet deposition with measurements is difficult: the only measurements available are those of Alloway et al. (1998), which have problems because of the choice of sampling methodology, as outlined in Sections 3 and 5.4. The implied modified wet deposition budget is 17.1 tonnes yr^{-1} (see Section 5.4) approximately twice

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that modelled using RCTM, noting that the recalculated Alloway *et al.* (1998) budget is for England and Wales and the RCTM budget is the UK.

5.5.3.4   Of particular interest, given the budget differences in species attribution between the EMEP MSC-E model results and RCTM results, is the spatial distribution of the different fractions of RGM and Hg-p wet deposited, as shown in Figure 5.6. These distributions show what might be reasonably expected: RGM wet deposition dominates in much of lowland England, where it is easily removed close to sources, despite the lower precipitation rates. In Northern England, Scotland, Wales and the south-east extremity of England, wet deposition of Hg-p dominates total Hg deposition. The spatial patterns are interpreted as being the product of the UK precipitation distribution and the proximity of RGM wet deposition to sources.

5.5.3.5   The UK budget has been characterized with the RCTM model. From these results, it has been calculated that 25% of the deposition arises from the Northern Hemisphere background concentrations; 41% comes from UK sources; 34% from other European countries. The UK budget is summarized in Figure 5.8.
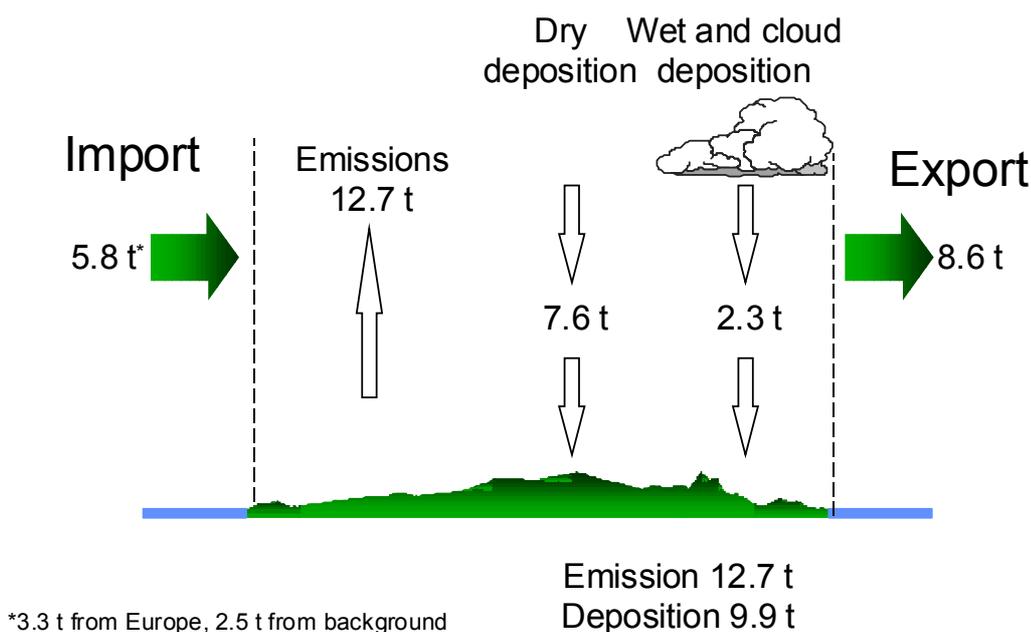
Figure 5-8 RCTM modelled Hg budget for the UK

5.5.3.6   In terms of budgets, RCTM model results show some interesting differences to those of the EMEP MSC-E model (Ryaboshapko *et al.*, 1998). A much larger proportion of deposition is attributable to Northern Hemisphere background from the RCTM results, at 25% (2.506 tonnes Hg yr^{-1}) cf. 12% as calculated by EMEP MSC-E (1.121 tonnes yr^{-1}). The RCTM-calculated import from other European countries is 34%, rather different to the 21% calculated by EMEP MSC-E. This discrepancy in import estimates is not altogether unexpected as previous experience has

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shown that EMEP MSC-W modelling of UK S and N budgets show a smaller import term to the UK than have other UK modelling efforts (e.g. Lee *et al.*, 2000a,b; RGAR, 1997; Lee and Kingdon, 2000b). The cause of these systematic differences has not yet been resolved, despite an investigation of this (Lee and Kingdon, 2000b). Despite the differences in the inventories used in the RCTM UK-scale modelling and EMEP-domain scale modelling, the coarser 50 km × 50 km resolution RCTM simulation shows some similarities to the EMEP MSC-E Hg modelling in terms of the inconsistencies of wet deposition patterns with the UK precipitation pattern, and the much coarser pattern of Hg^0 surface concentrations (see Figure 5.7).

5.5.3.7   Clearly, the background conditions make an important contribution to the UK deposition budget, as modelled by RCTM. In order to determine how much comes from background Hg-p and how much is derived from Hg^0 oxidation and dry deposition, a further simulation was run with no emissions across the model domain and initialising Hg^0 concentrations but not Hg-p. This resulted in a deposition to the UK of 2.47 tonnes yr^{-1} (cf. 2.51 from Hg^0 and Hg-p). Of this 2.47 tonnes, 1.79 tonnes was from dry deposited Hg^0 (73%) and 0.68 tonnes (27%) was Hg-p (from oxidized Hg^0). This emphasizes the importance and sensitivity of model results to the dry deposition rate for Hg^0, a very poorly characterized parameter. That very little Hg deposition arises from background Hg-p is unsurprising: with a washout rate equal to that of sulphate particles, it will make only a small contribution (~2.5%) to UK deposition. This result is similar to results obtained from initializing background sulphate particles in a simulation of UK acid deposition (Lee *et al.*, 2000a).

5.5.3.8   In terms of overall model performance, it is rather surprising that such a simple model gives what appears to be quite reasonable results. This, however, could be fortuitous. Moreover, the measurement basis is very weak with which model results can be compared. That the model works reasonably is nevertheless no defence of the simplistic treatment of some processes. It is only likely that more can be learnt if a more sophisticated modelling facility is available. For example, if some of the chemical conversion processes are dependent upon species that are changing, then the effects of these processes cannot be simulated nor investigated for future scenarios. One such example is that of ozone: chemical conversion processes of Hg^0 to Hg^{II} partially depend upon ozone. This highlights 3 particular problems with the approach taken here: firstly, there is no 'chemistry' so that factors affecting the process cannot be represented; secondly, there is evidence of differential changes in ozone in the European boundary layer and the Northern Hemisphere background troposphere, thus such changes and their impacts on Hg deposition cannot be represented; thirdly, given the limited evidence that Hg^0 is well-mixed in the Northern Hemisphere troposphere, a boundary layer model cannot adequately treat changes that may arise.

5.5.3.9   There are other reasons for emphasizing the importance of an improved modelling approach, for example the changing boundary conditions in future scenarios but the example of ozone given

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above summarizes some of the simplifications made. A possible modelling solution would be a number of parallel approaches, rather than one unified model. For example, a <u>global model</u> that simulates the processes clearly occurring on long time scales will determine the boundary conditions of a <u>regional-scale tropospheric model</u> operating on the EMEP domain but with full tropospheric chemistry. A <u>simplified regional scale model</u> such as that presented here may remain useful for investigating sensitivities present in other models that have more complete descriptions of the underlying physical and chemical processes.

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6 The relationship between emissions and ambient concentrations of mercury

Summary

- In the absence of an ongoing Hg monitoring network this chapter discusses the spatial relationship between emissions, concentrations and deposition using the EMEP model results. At a 50 km resolution reasonable correlations are found between the spatial patterns of emission and concentration only for the more reactive species Hg-p and RGM. For these forms of Hg, emission reductions will have a significant effect on their air concentrations. Because of the strong spatial correlation between the concentration and deposition of RGM, reductions of RGM concentrations will directly influence its deposition. Although the concentration of reactive Hg is small compared with Hg^0, together with methylmercury they represent the more toxic forms of Hg.
- The concentration of total Hg is dominated by Hg^0, which is at least as strongly influenced by the background concentration and non-UK sources as by UK sources.
- High temporal resolution measurements of TGM performed in Southern England and on the west coast of Ireland indicate lower air concentrations in summer than in winter, which is thought to be primarily the result of conversion of Hg^0 into more rapidly-depositing divalent Hg at high oxidant levels. The seasonal cycle in the emissions, with peaks in the winter, adds to this effect.
- The temporal and spatial distribution of ozone is likely to affect the spatial patterns in concentrations and deposition. Where ozone concentrations are large, the concentration of TGM will decrease while the concentration of RGM will increase.
- Measurements indicate that natural sources have an important influence on total Hg concentrations, especially in remote areas. However, natural emissions should be largest in summer, and therefore their seasonal cycle is more than offset by the cycles in chemistry and man-made sources.
- The current measurement database for the UK is inadequate to fully investigate the relationships between emissions and ambient levels or to validate model predictions.

6.1 Model results

6.1.1 The concentrations of total Hg are dominated by Hg^0, owing to its lack of reactivity and long atmospheric lifetime (1-2 years). The reactive forms (RGM) and especially organic forms of Hg are of greater toxicological importance and should also be considered. In this short chapter we discuss the relationship between ambient concentrations of the dominant forms of Hg and the emissions, from model runs by EMEP (Ilyin *et al*., 2000). Ideally, concentrations measured throughout the UK would be compared with the emissions and modelled concentrations. However, the analytical techniques, that have been used to obtain the few Hg wet deposition measurements that are available for the UK, have been declared inadequate for model evaluation by EMEP and the CCC. This is because the majority of the measurements reported were below the detection limit (see Section 3.3.5). In addition, measurements stopped in 1992 and they are therefore of limited use for comparison with current emission scenarios, whilst no high-resolution spatially disaggre-

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gated emission estimates exist prior to 1997. The data from the dust gauge network are currently only available as two to three-year averages and can therefore not be used to compare temporal patterns in emissions and deposition. Furthermore, the collection efficiency of these collectors for the different species of Hg is inadequately characterized.

6.1.2   The emissions used by the EMEP atmospheric transport model are presented in Figure 2.2, while the predicted fields of concentration and deposition are shown in Figures 5.1a and b, respectively. The output of the RCTM model, based on the same emissions, is shown in Figure 5.5. These model results allow some conclusions on the relationship between emissions, concentrations and deposition to be drawn.

6.1.3   Table 6.1 summarizes the correlation coefficients between the spatial distributions of emissions, depositions and air concentrations. It is clear that emissions of total Hg and Hg^0 are not spatially correlated with the concentration or deposition of any species. This is because of the high background concentration of Hg^0 as well as to its slow deposition rate and long atmospheric lifetime, so that a high correlation would not be expected. If RGM and Hg-p are considered individually, a moderate spatial correlation between concentrations, emission from UK sources and RGM deposition emerges.

6.1.4   The high correlation (R = 1.00) between the deposition and concentration of RGM further demonstrates the fast deposition rate of this species. Hg-p deposition is closely linked to Hg^0 concentration, indicating that the role of Hg^0 as a precursor for Hg-p is very important.

6.1.5   Divergence of the correlation coefficients from 1 may be taken as an indicator for spatial non-linearity between emissions, concentrations and deposition, although the complexity in spatial patterns of emissions and deposition and their interaction with meteorology prevent simple interpretation of these correlation coefficients.

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Table 6-1 Spatial correlation coefficients between emissions, depositions and surface air concentrations of the 50 km values predicted by the EMEP model. Note: Since the speciated emissions used for the EMEP modelling were not available the speciation derived in Section 2.4 was used. Only correlation coefficients > 0.40 are shown, while coefficients > 0.80 are printed in bold

	species	Emissions				Depositions								Air concentrations				
		all	Hg⁰	Hg-p	RGM	total all	dry all	wet all	Non-UK all	UK only all	Hg-p	Hg⁰	RGM	all	Hg-p	Hg⁰	RGM	DMM
Emission	all	**1.00**																
	Hg⁰	**1.00**	**1.00**															
	Hg-p	**0.92**	**0.89**	**1.00**														
	RGM	**0.94**	**0.91**	**0.93**	**1.00**													
Tot dep.	all	0.33	0.28	0.53	0.47	**1.00**												
Dry dep.	all	0.29	0.25	0.45	0.39	**0.94**	**1.00**											
Wet dep.	all	0.34	0.28	0.55	0.49	**0.97**	**0.83**	**1.00**										
Non-UK dep.	all	0.18	0.16	0.28	0.24	0.77	**0.89**	0.64	**1.00**									
UK only dep.	all	0.35	0.29	0.57	0.50	**0.90**	0.73	**0.95**	0.42	**1.00**								
Tot dep.	Hg-p	0.22	0.18	0.35	0.38	**0.85**	**0.83**	**0.80**	0.77	0.69	**1.00**							
	Hg⁰	0.24	0.21	0.36	0.48	0.76	**0.89**	0.63	**0.88**	0.49	0.56	**1.00**						
	RGM	0.35	0.29	0.56	0.50	**0.92**	0.74	**0.97**	0.48	**0.98**	0.70	0.50	**1.00**					
Concentrations	all	0.28	0.24	0.44	0.38	**0.89**	**0.89**	**0.83**	0.75	0.76	**0.85**	0.68	0.78	**1.00**				
	Hg-p	0.35	0.30	0.55	0.48	**0.94**	**0.83**	**0.95**	0.62	**0.92**	0.69	0.66	**0.95**	**0.87**	**1.00**			
	Hg⁰	0.26	0.22	0.40	0.35	**0.86**	**0.88**	0.79	0.76	0.70	**0.85**	0.68	0.72	**0.99**	**0.82**	**1.00**		
	RGM	0.35	0.29	0.56	0.49	**0.91**	0.74	**0.96**	0.46	**0.98**	0.69	0.48	**1.00**	0.79	**0.96**	0.73	**1.00**	
	DMM	0.34	0.29	0.50	0.45	**0.80**	0.71	**0.80**	0.54	0.77	0.58	0.56	**0.81**	0.77	**0.89**	0.73	**0.83**	**1.00**

6.2 Factors leading to non-linearities in the relationship between emissions, ambient concentrations and deposition

6.2.1 There are many reasons why the relationship between emissions, concentrations and deposition is strongly non-linear, including the concentrations of other pollutants, background concentrations and the influence of meteorological parameters.

6.2.2 The conversion rate of Hg⁰ into RGM (either gaseous or particle-bound) is strongly influenced by the presence of oxidants, primarily ozone. Therefore, the effect of the presence of oxidants is fourfold: (i) concentrations of Hg⁰ are lowered, (ii) concentrations of Hg-p and RGM are increased, (iii) the deposition of total Hg is increased and (iv) as an effect the concentration of TGM is also decreased (Sommar *et al*., 1999). The importance of this effect for the UK is indicated by TGM concentration measurements in England and on the west coast of Ireland, both of which show smaller values in summer than in winter (Lee *et al*., 1998a; Ebinghaus *et al*., 1999a).
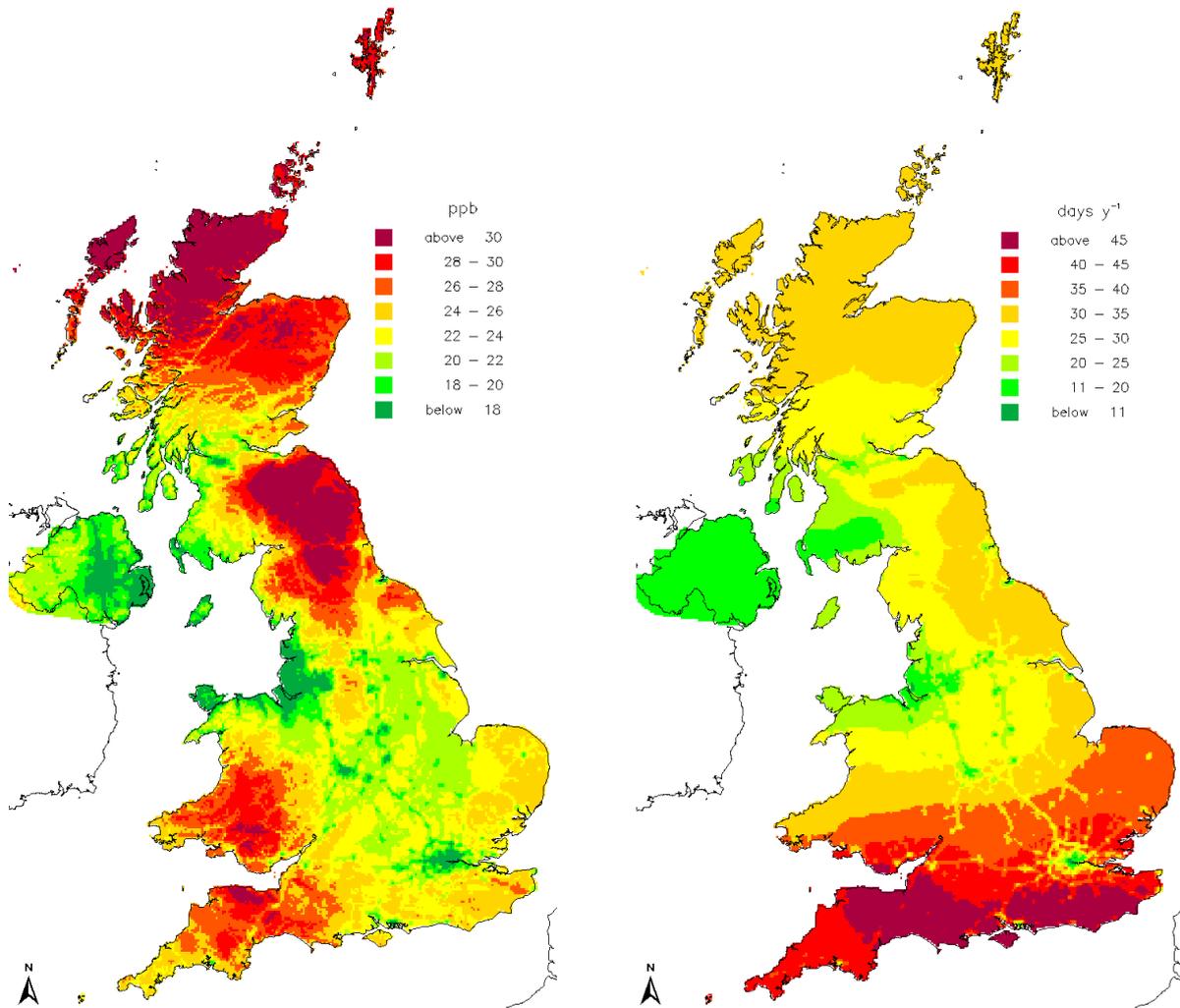
Figure 6-1 (a) Annual mean ozone concentrations derived from measured concentration data for 1996, corrected for the effects of O₃ destruction by NO in urban areas. (b) The number of days in 1996 on which the 8-hour running mean exceeded 50 ppb (Coyle et al., 2000)

6.2.3   Ozone concentrations commonly show a seasonal cycle with a spring (April/May) maximum and an autumn minimum (November/December). The O_3 concentration field is influenced by the increase of O_3 with height and depletion of O_3 in urban areas through reaction with NO, resulting in particularly high mean concentrations in Northern and Southeast Scotland, Northern England as well as the Southwest of England and Wales (Figure 6.1a). Unlike the mean values, the frequency of high O_3 episodes is also influenced by advection of polluted air masses from continental Europe and therefore largest in the South of England (Figure 6.1b).

6.2.4   Wet deposition of Hg^0 appears to be promoted by its adsorption to carbonaceous particles (e.g. Petersen *et al*., 1995), and therefore the concentration of soot particles will determine removal rates and thus influence Hg air concentrations.

6.2.5   The only measurements of TGM in the UK indicated background concentrations of approximately 1.5 ng m^{-3} for 1995/96 (cf. Section 3.3.5), with peaks of up to 4 ng m^{-3}, while at 1.68 ng m^{-3} the

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average concentration was only slightly higher (Lee *et al*., 1998a). Schmolke *et al*. (1999) presented a comparison of TGM time-series, simultaneously measured at two Swedish and two East German sites. During more recent measurements at Mace Head on the West Coast of Galway, Ireland, Ebinghaus *et al*. (1999a) observed average TGM concentrations at 1.77 ng m^{-3}, with a background concentration of 1.71 ng m^{-3} for 'clean' wind directions originating from the sea. The measurements indicate low standard deviations of around 0.1 ng m^{-3} for 30 min. averages at the Irish and Norwegian background sites and standard deviations of 0.3 and 0.5 ng m^{-3} at the central and northern German sites, respectively. By comparison, the UK data show a large standard deviation of 1.2 ng m^{-3}, indicating that the UK site was even more heavily influenced by local and regional point sources than the site north of Berlin. It may be concluded that the variation in the background concentration makes an important contribution to the overall variability of Hg air concentrations, especially in remote regions.

6.2.6   Meteorological parameters control not only the emissions from natural sources (see below), but they also strongly influence the conversion rate of Hg^{0} to reactive Hg as well as the deposition rates of all Hg species. Dry deposition rates are partially controlled by atmospheric turbulence and are larger in windy and in unstable conditions, which dominate in summer. Wet deposition depends on precipitation and may be enhanced in the presence of orographic clouds or through fog deposition. An increased deposition naturally lowers the air concentration.

6.3   Other factors determining concentrations of atmospheric mercury

6.3.1   Health concerns are focused upon those places where concentrations and/or deposition are largest. High concentrations are found downwind of major point sources such as power plants, chloralkali works and any incinerators (see Figures 3.12 and 3.13). Spatial peaks in concentrations from such sources will not be resolved by the resolutions of current long-range transport models (e.g. 50 km in the EMEP model, 20–5 km in the RCTM model, 5 km in the CEH model and much coarser for concentration maps derived from measurement networks).

6.3.2   From Table 6.1 it is clear that the variability of concentrations will, to some degree, be determined by the variability in the emissions, at least for Hg-p and RGM. As mentioned before, man-made emissions of Hg are believed to be approximately 10–30% larger in winter than in summer. It has been suggested that the variation in emissions is secondary compared with the summer depletion of Hg by oxidant reaction described above (Slemr and Scheel, 1998). In contrast, natural emissions (and/or re-emissions) are mediated by solar radiation and temperature (e.g. Carpi and Lindberg, 1997), and therefore show a peak in summer and during daytime. Although in the UK this effect appears to be more than offset by the depletion of Hg through oxidants and the seasonality in industrial emissions, Lindberg *et al.* (1991) observed maximum Hg concentrations in summer at a remote site with high natural emissions.

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6.3.3   There are no gas-phase Hg measurements in UK urban background environments and therefore it is currently uncertain whether Hg concentrations are significantly larger than in rural environments (Lee *et al*., 1998a). The limited data from Stanger (see Chapter 3) would, however, imply this, but the measurements were made in close proximity to known sources, not urban background sites. Evidence from measurements made in other countries suggests that this may be the case but this is not verified for the UK. Urban measurements of Hg-p in the UK have shown significant variability on a 3-month time-scale (cf. Figure 3.2) of more than one order of magnitude. Some features in the time-series, such as a high concentration in 1983-1984, are generic to all city sites and this suggests controlling parameters that are common to all sites. Possible causes include lower than average wind speeds during this period as well as high ozone concentrations that may have promoted the conversion from Hg^0 to Hg-p.

6.3.4   In cities, concentrations do not depend only on the emission strength but also critically on the ventilation rate, which is strongly related to wind speed. For example, ethane is assumed to be emitted at a relatively constant rate from leaks in the gas supply network. Nevertheless, ethane concentrations at street level can vary markedly with time, whilst the averaged diurnal cycle shows a clear night-time maximum during night, arising from a reduction in the PBL height.

6.3.5   Lee *et al*. (1998a) could not detect elevated TGM concentrations in the plume of the Didcot A coal-fired power plant during a 10-month monitoring study at a downwind distance of 6 km (cf. Section 3.3.4). It was speculated, however, that elevated concentrations under westerly wind directions may have been the result of emissions from a lead/zinc smelter, some 70 km distant which is the largest point source in the UK (3.2 tonnes yr^{-1}).

6.3.6   In an early study, Turner *et al*. (1979) observed Hg concentrations as high as 1000 ng m^{-3} near chloroalkali plants, although subsequent abatement measures will have reduced the emission from such plants. In the same study, the contribution of industrial combustion to local Hg concentrations was estimated by analogy to the ratio of SO_2 emissions to SO_2 concentration to be below 0.8 ng m^{-3}, an order of magnitude smaller than measured concentrations. Similar to Lee *et al*. (1998a), Turner *et al*. (1979) concluded that high level industrial combustion sources were unlikely to give rise to elevated Hg concentrations at ground level, but that "*even in relatively industrial and densely populated southern Britain, away from known industrial users of mercury, concentrations may be very largely controlled by natural sources*". However, the discrepancy may equally be because of the use of underestimated Hg emission factors and/or the lack of information on small sources. Nevertheless, it appears that more insight into the variability in industrial emissions is needed.

7 Current mercury concentrations in relation to adverse human health and other environmental effects

Summary

- Of the Hg compounds present in the environment, methylated Hg is the most toxic, causing neurotoxicological disorders. No measurements of methylated Hg have been made in air in the UK but according to current understanding, the levels, if above current detection limits in air, are likely to be very low and have an insignificant effect upon human health.

- Methylmercury has been found in precipitation, from unknown sources, but the major sites of methylation of Hg is within ecosystems, and within fish themselves.

- Deposition of atmospheric Hg is likely to be the most important contributor to Hg available for methylation in the environment.

- The three major routes of Hg uptake by humans are: direct inhalation; consumption of foodstuffs from land; consumption of fish and their predators. Of these, the most significant is consumption of fish and their predators. Direct inhalation at ambient levels is an insignificant pathway. However, inhalation of Hg from dental amalgam is possibly a significant, but contentious, pathway.

- According to current understanding there is unlikely to be a direct relationship between atmospheric Hg at ambient levels and human health.

- Air quality standards for Hg are not widely formulated. Those identified were from the Former Soviet Union States and Poland. The specified levels are generally at least one order of magnitude greater than those found in the UK.

- As direct inhalation of Hg in ambient air is an insignificant pathway for humans, an air quality standard is not relevant nor appropriate.

- Accumulation of Hg in the environment is highly relevant and is best tackled by a 'critical loads' approach as deposition is the major pathway for biologically available Hg.

- The data on Hg in UK biota has been reviewed. Whilst the data are difficult to interpret in terms of any trends, Hg has been found in fish at levels greater than those set by an EU Directive (93/351/EEC).

- There is evidence that UK fish-eating birds have higher levels of Hg in their body tissues than non fish-eaters. High levels of Hg have been found in otters in Scotland: it is possible that this is a significant factor affecting their survival.

- It is possible that bioaccumulation of Hg is an ecological threat to UK fish, birds and mammals. From the data reviewed, it appears that a small proportion of these UK biota may have, or have had concentrations of Hg present in body tissues at concentrations that are close to toxicity. Whilst there is some evidence for declines in tissue concentrations, this should be considered in the light of potentially increasing levels of atmospheric Hg that may more than compensate for recent declines.

7.1 Effects of mercury on humans

7.1.1 Exposure pathways

7.1.1.1 There are five basic pathways by which man may be exposed to Hg (all forms): direct inhalation of ambient air; inhalation of Hg vapour from dental amalgam fillings; dermal absorption; ingestion of foodstuffs grown on land; and ingestion of fish products.

7.1.1.2 Looking at these in turn, **direct inhalation** of Hg will most likely be in the form Hg^0 as, has been shown in previous chapters, this makes up 95% of the atmospheric burden of all forms of Hg. As previously outlined in Chapter 2, the atmospheric components of Hg are Hg^0, Hg-p, RGM and MHg. RGM generally includes MHg. Measurements of the directly toxic form, MHg, are scarce and were reviewed in Chapter 3, where it was pointed out that there are no UK measurements, to our knowledge

7.1.1.3 Despite the lack of a measurement database for MHg, other studies have discounted inhalation of ambient air as a significant pathway to man. The extensive US study of Hg—*Mercury Study Report to Congress*—in volumes IV (Mahaffey *et al*., 1997a) and VII (Mahaffey *et al*., 1997b) concluded that inhalation was a minor route of uptake in comparison to ingestion, citing the earlier WHO Assessment (WHO, 1990). This is despite the fact that 80% of Hg vapour (of which a large proportion is Hg^0) inhaled is retained (WHO, 1991)

7.1.1.4 Dermal absorption is unlikely to be of any significance at environmental concentrations: it is only a significant risk in accidental or occupational exposures that will give rise to acute toxic dermatitis from alkyl Hg compounds (WHO, 1996).

7.1.1.5 Mercury emissions from dental amalgam fillings have been studied by a number of authors. From mass balance considerations, Skare (1995) estimated that the Hg balance of an individual with a moderate load of amalgam (e.g. 30 restored surfaces) involves around 60 μg Hg day^{-1}. A fifth of these emissions (12 μg day^{-1}) are systemically taken up. This figure is four times higher than the average Hg uptake from food, derived from UK dietary studies (see below). The Hg exposure to dental amalgam predicted in other studies ranged from 0.90 – 1.10 μg day^{-1} (Mackert, 1987) up to 7.0 - 8.4 μg day^{-1} (Vimy *et al*., 1986). Richardson *et al*. (1995) estimated that 80% of the inhaled Hg was absorbed and contributed about 42% to the total Hg uptake. The other main source was estimated to be fish consumption (40%). Other studies have discounted emissions from dental amalgam as a major source of human mercury exposure (e.g. Hassett Sipple *et al*., 1997).

7.1.1.6 In the same Canadian study (Richardson *et al*., 1995) exposure to indoor air has been proposed as a further source of mercury inhalation accounting for 14% of the overall inhalation dose. Mercury concentrations in rooms painted with Hg-containing interior latex paints (Beusterien *et al*., 1991) may remain elevated for up to 33 months. Although Hg-containing paints have been phased out it is likely that elevated concentrations persist, whilst a contribution of 14% appears to be a large overestimate. No data exist on Hg concentrations in UK houses.

7.1.1.7   **Ingestion of foodstuffs from land** is one of the more significant potential exposure pathways for man. Two potential sub-pathways are available here: atmospheric Hg→green plants→human consumption, or soil Hg→green plants→human consumption. Of the two, Mahaffey *et al*. (1997a) considered the soil Hg etc. route the less important. Inorganic divalent Hg in soil forms complexes with fulvic and humic acids because of Hg's affinity for sulphur-containing functional groups. Once complexed, this limits the mobility of Hg in soil. Thus, such Hg complexes only find their way to water bodies from suspended soil or humus. Some divalent Hg, however, is absorbed onto soluble organic ligands and other forms of dissolved organic carbon (DOC) and then subject to run-off. Thus, deposition of Hg to soil represents a large reservoir (Meili *et al*., 1991) that would be subject to leaching many years after any significant reduction in deposition. Some of this Hg in the soil is reduced to elemental Hg and may be volatilized (Carpi and Lindberg, 1997). Atmospheric uptake of Hg is difficult to quantify as elemental Hg has not been detected in plant tissues (Cappon, 1987). Plants, however, do have an ability to methylate mercury (Fortmann *et al*., 1978).

7.1.1.8   From the above brief description of soil processes, it is clear that soil Hg represents a significant reservoir that is, in theory, available to plants. However, plant uptake of soil Hg appears to be rather insignificant (Lindqvist *et al*., 1991; Zillioux *et al*., 1993). Thus, Hg uptake from ingestion of plants by livestock and subsequent tissue accumulation is low.

7.1.1.9   The input of Hg to soils can also occur via application of sewage sludge. The removal of Hg by waste-water treatment plants is very effective, averaging 96% across one particular plant (Balough and Liang, 1995). The fate of the Hg is the secondary sludge, which can be incinerated or applied to land. However, the application of the sewage sludge to land does not seem to result in higher concentrations of Hg in plants. Granato *et al*. (1995) describe a study in which large application rates of sewage sludge were made over nearly two decades. It was found that 80% or more of the Hg applied was retained in the topsoil but that this did not result in increased concentrations of Hg in tissue from plants grown on the treated soil.

7.1.1.10   Estimates of the total Hg intake through food, based on UK total dietary studies, range from 1 to 2 μg Hg day^{-1} based on the food consumption data of the National Food Survey (NFS) and 3 μg Hg day^{-1}, using the data provided by the Dietary and Nutritional Survey of British Adults (NADS) (MAFF, 1998; see Table 7.1 for breakdown). In this study the 97.5 percentile intake was estimated as 6 μg day^{-1}, mainly due to a higher consumption of fish. In addition, for the UK, a daily Hg intake of up to 5 μg day^{-1} was derived by Galal-Gorchev (1993).

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Table 7-1 Estimated total dietary intake of mercury (μg/person/day) for adults in the UK in 1991 (from MAFF, 1998)

Food group	Residual concentration (μg/kg)		Intake (μg/person / day)		
	Range	Mean	Average (upper bound) intake using NFS consumption data	Mean consumer intake using NADS consumption data	'High level' intake using NADS consumption data
Bread	< 1 - 2	< 1	0.1	0.1	0.3
Miscellaneous cereals	< 1 - 2	< 1	0.1	0.1	0.3
Carcass meat	< 1 - 13	< 3	0.1	0.2	0.6
Offals	< 1 - 180	< 18	< 0.1	0.3	1
Meat products	< 1 - 3	< 2	0.1	0.1	0.4
Poultry	< 1 - 4	< 2	< 0.1	0.1	0.3
Fish	< 1 - 210	45	0.6	20	50
Oils and fats	< 1 - 6	< 1	0.1	0.0	0.0
Eggs	< 1 - 5	< 2	< 0.1	0.1	0.2
Sugar and preserves	< 1 - 2	< 1	< 0.1	0.0	0.1
Green vegetables	< 1 - 5	< 1	< 0.1	0.1	0.1
Potatoes	< 1 - 4	< 1	0.1	0.1	0.3
Other vegetables	< 1 - 2	< 1	< 0.1	0.1	0.2
Canned vegetables	< 1 - 3	< 1	< 0.1	0.0	0.2
Fresh fruit	< 1 - 12	< 1	< 0.1	0.1	0.3
Fruit products	< 1 - 2	< 1	< 0.1	0.1	0.3
Beverages	< 0.5 - 1	< 0.5	< 0.4	0.3	0.8
Milk	< 0.5 – 0.5	< 0.5	< 0.2	0.1	0.3
Dairy products	< 1 - 4	< 1	< 0.1	0.1	0.2
Nuts	< 1 - 3	< 1	< 0.1	0.0	0.0
Total			2	3	6

7.1.1.11   Of by far the most significance is the **ingestion of fish products** for Hg exposure to man. This will be considered in detail here as the Hg compound of significance in this pathway is the MHg form, for which the environmental pathways will be explained.

7.1.1.12   Mercury in surface waters can be converted to the toxic methylated form by methylating bacteria or chemical methylation by dissolved humic substances. Methylmercury is then taken up by fish, either through direct absorption through the gills or, of more significance, through ingestion of sediment materials, insects or other fish. Thus it is the higher predatory fish that tend to accumulate the most MHg. The MHg is not toxic to the fish when they are exposed to continuous low doses but they accumulate it in muscle and bone tissues. Of the Hg species present in surface waters, only the MHg bioaccumulates. The recommended limit in many countries for Hg in fish is between 0.5–1.0 μg g^{-1} (Driscoll *et al.*, 1994).

7.1.1.13   Thus, it is through the ingestion of fish products (and possibly fish-predators) that humans are at most risk. This has certainly been considered a real risk in North America, where fish consumption is limited or banned from certain lakes. Driscoll *et al.* (1994) report that 11,000 lakes in Michigan had an 'advisory' imposed upon them for fish caught.

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7.1.2 Toxicological effects of mercury on humans

7.1.2.1 In this section, the toxicological effects of Hg are only considered rather briefly. A review of all the effects and relevant data is beyond the scope of this study and would require the input from the relevant disciplines. Rather, a very brief review of where other work may be found is provided.

7.1.2.2 The US Mercury Study (Volume V) provided an assessment of human health effects of Hg and mercury compounds (Hassett Sipple *et al.*, 1997). In addition, Ratcliffe *et al.* (1996) have published a review of evidence for adverse health effects on humans. Hassett Sipple et al. (1997) considered potential effects of elemental Hg, inorganic Hg and MHg. All three forms considered were capable of presenting a human health hazard. There was only limited evidence for Hg and Hg compounds being carcinogenic: the most widespread observed effect was neurotoxicity of which, MHg was of the most significance. The developing foetus was thought to be at particular risk from MHg exposure. The review of Ratcliffe *et al.* (1996) focused upon the use of data from the various published studies. The studies that showed the clearest neurotoxicological effects were those based upon accidental releases of large amounts of MHg; specifically, the Minamata and Iraq disasters. Many of the other studies reviewed were based on observational evidence from specific instances of individual exposures. Only two long-terms systematic studies have been made on exposure and effects: one investigating dose-response relationships of the human population in the Seychelles Islands and another assessing Hg exposure to the human population of the Faroe Islands from consumption of marine fish and mammals.

7.2 Ambient air quality standards for mercury

7.2.1 Legislative framework relevant to the UK

7.2.1.1 At present, there is no ambient air quality standard for Hg, in any form, for the UK. The legislative framework that might encompass atmospheric Hg includes the UNECE-CLRTAP Heavy Metals Protocol (1998), the Air Quality Framework Directive (Directive 96/62/EC) and the UK's Air Quality Strategy. Of these, only the UNECE Heavy Metals Protocol considers Hg, in terms of emissions. The Air Quality Framework Directive is made up of a number of 'Daughter Directives' that consider particular pollutants, one of which is Hg. A Daughter Directive for Hg has not yet been formulated but when it is, it is also likely to be considered in subsequent revisions of the UK's Air Quality Strategy.

7.2.2 Identified air quality standards for mercury

7.2.2.1 At the moment, there are very few ambient air quality standards for Hg. A survey of national air quality standards was made by informal contact with national and international agencies and by

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searching the world-wide-web. The sole source of information identified was the UNECE Major Review of Strategies and Policies, which gives air quality standards for 6 UNECE countries. These are detailed in Table 7.2 below.

Table 7-2 Ambient air quality standards for mercury

Country	Standard
Russia	0.3 µg m^{-3}, 24 hour and 1 year averages
Armenia	0.3 µg m^{-3}, 24 hour and 1 year averages
Lithuania	0.3 µg m^{-3}, 24 hour and 1 year averages
Belarus	0.3 µg m^{-3}, 24 hour and 1 year averages
Croatia	0.01 µg m^{-3}, 24 hour averages
Poland	0.7 µg m^{-3}, annual 99.8 percentile of 30 min
	0.04 µg m^{-3}, 1 year averages

7.2.2.2   The WHO 'Air Quality Guidelines for Europe' (WHO, 1987) discusses Hg, briefly reviewing air concentration data, routes of exposure, health effects and potential human health risks. In general, the ambient air concentration data reviewed were rather old. The report concluded that an ambient air quality guideline value could not be proposed because post-deposition effects could not be adequately quantified, these being proposed to be a more important route of exposure.

7.3   The relationship between ambient concentrations and human health

7.3.1   It is perhaps of just as much relevance to highlight the fact that air quality standards were not identified for countries where there has been some historical concern, e.g. the United States, Japan, the Nordic Countries and Canada. Air quality standards were not even discussed nor mentioned in the comprehensive 8 volume US '*Mercury Study—Report to Congress*'. This is simply because the main route of exposure to Hg is considered to be by food consumption, and that particularly of fish.

7.3.2   The WHO 'Air Quality Guidelines for Europe' (WHO, 1987) provided a useful estimation of daily intake and retention, which is reproduced in entirety in Table 7.3 below.

Table 7-3 Estimated average daily intake (retention) of mercury and its compounds, reproduced from WHO (1987)

Media	Estimated average daily intake (retention) in ng of mercury per day		
	Mercury vapour	Inorganic mercury compounds	Methylmercury
Atmosphere	200[a] (160)[b]	0[c]	0[c]
Food:			
fish	0	80d (8)[b]	3200[d] (2880)[b]
other	0	?[e]	?
Drinking water	0	50 (5)[b]	0

[a] Assumes an air concentration of 10 ng m^{-3} and a daily respiratory volume of 20 m^3 (note that WHO, 1987 assumes this average concentration for urban areas, and an average of 2 ng m^{-3} is assumed for rural areas)

[b] Figures in parentheses are the amount retained that was estimated based upon a retention of 80% of inhaled vapour, 90% of ingested methylmercury and 10% of inorganic mercury.

[c] It was assumed that concentrations of species other than Hg^0 were negligible.

[d] It was assumed that 80% of the total mercury in edible fish tissues is in the form of methylmercury and 20% in the form of inorganic mercury compounds. It was also assumed that 90% of the methylmercury and 10% of the inorganic mercury was absorbed.

[e] Concentrations of inorganic mercury in many food items are below the detection limit.

7.3.3   From Table 7.2, it can be seen that the direct inhalation route of atmospheric Hg is insignificant as a route of uptake, a conclusion consistent with other WHO work (WHO, 1990) and the conclusions of the US Mercury Study. This, of course, assumes some average conditions and not those close to sources. As outlined in Section 3, there is some evidence of 'hot-spots' of ambient concentrations, particularly so from the data collected in the vicinity of a chlor-alkali plant where concentrations of TGM reached approximately 70 ng m^{-3} and averaged 30 ng m^{-3}. Nonetheless, using the simple exposure methodology of WMO (1987), this implies a daily average intake of 600 ng Hg per day (480 ng retained), compared with 3,200 ng (2,880 ng retained) from fish.

7.3.4   The data and assessments reviewed above would imply that there is very unlikely to be a direct relationship between human health and ambient concentrations of atmospheric Hg. Taking this a step further, it therefore seems nonsensical to formulate an air quality standard that relates directly to human health as ambient concentrations make only a small contribution to human exposure. This is not to imply that ambient concentrations or emissions do not matter but rather that deposition levels are of far more relevance to protection of human health. By protection of ecosystems the risks of human exposure from the consumption of Hg-contaminated biota are minimized. It would seem obvious that formulating a 'critical load' for ecosystems would be a more sensible initial proposal than an ambient air quality standard.

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7.4 Mercury in the biosphere

7.4.1 Effects of mercury on biota

7.4.1.1 Most forms of Hg are known to be harmful to life but it is MHg, an organometallic compound, which is most toxic. As an organometallic compound, MHg is more easily passed across cell membranes and efficiently absorbed in the alimentary canal. Once it has entered the food chain it has a long biological half-life which means MHg is rapidly bioaccumulated (Dixon and Jones, 1994). The importance of monitoring Hg in the environment is emphasized by this bioaccumulation potential which can result in organisms with Hg concentrations many orders of magnitude greater than ambient levels. Where this occurs in edible organisms there is a threat to human health through ingestion.

7.4.2 There is evidence that atmospheric deposition is a major pathway for mercury entering the food chain (Lindqvist and Rodhe, 1985). Thus, Hg contamination could be higher in areas with greater annual average rainfall amounts (Kruuk *et al.*, 1997). A continuous low level input of Hg from the atmosphere can have a great impact on ecosystems as the Hg concentrations become enriched (Downs *et al.*, 1999b). Mercury deposited from the atmosphere may rapidly become bound to organic matter and subsequent mobilization, associated with dissolved organic matter, has been found to contribute to Hg concentrations within organisms (Mierle and Ingram, 1991).

7.4.3 Increases in industrial Hg emissions led to the belief that Hg from the atmosphere constituted a major source of Hg to aquatic organisms, particularly in the absence of point source discharges. This was corroborated by a rise in background concentrations in fish, suggesting a man-made origin of the Hg (Downs *et al.*, 1997). Metals are also introduced into the aquatic environment by a variety of processes such as geological weathering, industrial dumping, leaching of fertilizers and discharge of sewage as well as atmospheric deposition (Wright and Mason, 1999).

7.4.4 Much of the recent work on Hg concentrations in organisms in the UK has concentrated on aquatic biota, particularly fish. Heavy metals, such as Hg, are of particular concern in water because of their toxicity and ability to accumulate in food chains; this has lead to the placement of Hg on list 1 of the EEC Dangerous Substances Directive, making routine monitoring of water concentrations mandatory.

7.4.5 After Hg has entered the water system, environmental parameters determine its availability to aquatic life: these parameters include water quality, methylation and speciation of Hg, the role of bacteria and organism condition and physiology (Downs *et al.*, 1997). The relative importance of each pathway is dependent on trophic concentration, duration and intensity of exposure as well as factors such as pH, dissolved organic carbon, temperature and redox potential. The combination of these factors controls methylation rates in aquatic systems (Zilloux *et al.*, 1993)

7.4.6   Methylmercury accumulates in aquatic organisms to concentrations much greater than the concentrations found in the water column or precipitation. Mercury is directly accumulated from the surrounding waters by pelagic organisms low in the food chain and then biomagnified as it passes up the chain. Different forms of Hg accumulate in different places; in phytoplankton MHg tends to accumulate within the cell cytoplasm (Konovolov, 1994) whilst inorganic Hg is stored in cell membranes. Zooplankton tend to digest the cytoplasm but excrete the cell membranes of phytoplankon they feed on, substantially bioconcentrating MHg (Mason *et al*, 1995). A similar biomagnification effect occurs when zooplankton is consumed by fish.

7.4.7   Mercury in UK Plant Life

7.4.7.1   Relatively little work has been done on Hg concentrations in British plant life although the Joint Food Safety and Standards Group studied wild edible fungi and blackberries collected from urban and rural areas between 1998 and 1999, determining metal concentrations. The Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment concluded that the metal concentrations present, including that of Hg, were at low enough levels not to be of concern (MAFF, 2000).

7.4.7.2   Mercury concentrations in the macroalgae *Pelvetia canaliculata* and *Enteromorpha* spp. were determined during a recent estuarine survey. The concentrations determined were low, between 0.05 and 0.08 mg kg^{-1} dry weight for *Pelvetia canaliculata* and between 0.02 and 0.05 mg kg^{-1} dry weight for *Enteromorpha* (Wright and Mason, 1999).

7.4.8   Mercury in UK Invertebrates

7.4.8.1   It can be important to monitor all concentrations in the food chain, as changes in Hg concentration will show up first at lower trophic levels before passing upwards to the higher levels. Some invertebrates, particularly shellfish, are consumed directly by humans and require monitoring for toxic contaminants.

7.4.8.2   Invertebrate species differ in their ability to accumulate heavy metals such as Hg, surveys of invertebrates taken from estuaries and unpolluted rivers in eastern England appears to confirm this (Tables 7.4 and 7.5).

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Table 7-4 Mean mercury found in riverine invertebrates (from Barak and Mason, 1989)

Invertebrate species	Mercury concentration in mg kg^{-1}
Asellus spp.	0.028 – 0.046
Gammarus spp.	0.027
Haemopsis spp.	0.030
Limnaea spp.	0.024 – 0.036
Sigara spp.	0.030 – 0.039
Trichoptera	0.035 – 0.060
Ephemeroptera	0.023 – 0.026
Dytiscus spp.	0.033 – 0.069
Sialis spp.	0.020 – 0.070
Agriidae	0.025 – 0.033

Table 7-5 Mean mercury found in estuarine invertebrates (from Wright and Mason, 1999)

Invertebrate species	Hg concentration in mg kg^{-1} dry weight – Orwell estuary	Hg concentration in mg kg^{-1} dry weight – Stour estuary
Littorina littorea	0.11 – 0.99	0.05 – 0.21
Mytilus edulis	0.29 – 0.65	0.24 – 0.45
Nereis diversicolor	0.03 – 1.59	0.21 – 0.46
Cerastoderma edule	0.34 – 0.94	0.23 – 0.43
Mya arenaria	0.28 – 0.37	Not recorded
Arenicola marina	0.87 – 1.63	0.18 – 0.29

7.4.8.3   The concentrations of Hg found in *Mytilus edulis* from the east of England varied between 0.24 and 0.65 mg kg^{-1} (Wright and Mason, 1999) which is similar to the concentrations of 0.28 to 1.53 mg kg^{-1} recorded in *Mytilus edulis* taken from Cork Harbour (Berrow, 1991).

7.4.9   Mercury in UK Reptiles

7.4.9.1   Mercury concentrations were measured in a leatherback turtle (*Dermochelys coriacea*) stranded dead in 1988 (Davenport and Wrench, 1990) and from three more turtles during a survey from 1992 to 1996 (Godley *et al.*, 1998). The Hg concentrations found in all four individuals were similar, between 0.29 and 1.2 mg kg^{-1} in the livers and between 0.04 and 0.12 mg kg^{-1} in muscle. These concentrations are very low suggesting that Hg is unlikely to have adversely affected the health of these animals (Godley *et al.*, 1998).

7.4.10   Mercury in UK Fish

7.4.10.1   Concerns over risks to human health have meant that common edible organisms such as fish have been studied for Hg contamination in detail than many other organisms.

7.4.10.2   It has been suggested that Hg in flesh, present in organic forms, represents long-term pollution while Hg in the liver, usually in inorganic forms, is present for a short time only, so that high Hg concentrations in the liver suggest an ongoing source of Hg pollution (Mason and Barak, 1990). Although the majority of Hg in fish is present as MHg, inorganic Hg may also enter fish through skin, gills or the gastrointestinal tract where it may subsequently be methylated by mucus (Downs *et al.*, 1999b).

7.4.10.3   There is little evidence to suggest that Hg concentrations in open seas or oceanic fish has increased due to human activities. This assertion is contrast to the global biogeochemical model studies of Mason *et al.* (1994). However, it is simply the case that long-term monitoring is not in place, so that the quantitative evidence is lacking. Where 'hotspots' occur they are usually due to a localized discharge of inorganic Hg (Bryan and Langston, 1992). A survey of Hg in the stomach contents of dab (*Limanda limanda*) carried out between 1986 and 1988 showed declining concentrations of Hg. This survey was carried out in the north-east Irish sea and Mersey estuary areas that receive significant Hg contamination through sewage dumping and industrial waste as well as from atmospheric inputs. Mercury concentrations seemed to fall over the survey period with a mean Hg stomach content of approximately 0.1 mg kg^{-1} in 1989 and a maximum value of 0.35 mg kg^{-1}, in 1986 the values had been higher with some values over 0.75 mg kg^{-1} although the majority were less than 0.2 mg kg^{-1} (Leah *et al,* 1991b).

7.4.10.4   A study of Hg concentrations in the muscle tissue of flounder (*Platichthys flesus*) caught in the north-east Irish Sea showed variations in Hg concentrations. Fish caught in waters close to Ireland, Wales or the Isle of Man had lower Hg concentrations, 0.008 – 0.331 mg kg^{-1} wet weight, while fish caught closer to Liverpool bay had significantly higher concentrations, up to 1.96 mg kg^{-1} (Leah *et al.*, 1992).

7.4.10.5   Concentrations of Hg in the Irish Sea have been reported as less than 0.5 mg kg^{-1} wet weight in plaice, *Pleuronectes platessa*, less than 1.1 mg kg^{-1} wet weight in dab, *Limanda limanda* and less than 2.5 mg kg^{-1} wet weight in lesser spotted dogfish, *Scyliorhinus caniculus* (Leah *et al.*, 1991a).

7.4.10.6   The Hg concentration in stomach contents of fish caught close to the mouth of the river Tyne in 1992 were significantly lower. Mean Hg concentration in stomach contents was 0.105 mg kg^{-1} in dab (*Limanda limanda*), 0.076 mg kg^{-1} in herring (*Clupea harengus*), 0.028 mg kg^{-1} in plaice (*Pleuronectes platessa*), 0.097 mg kg^{-1} in roker (*Raja clavata*) and 0.141 mg kg^{-1} in whiting (*Merlangius merlangus*) (Dixon and Jones, 1994).

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7.4.10.7   The behaviour of fish can have an impact on the concentration to which Hg is accumulated (Downs *et al.*, 1997). The eel, *Anguilla anguilla,* has been extensively studied for Hg contamination. The carnivorous diet, efficient Hg-adsorbing intestines, high lipid content and widespread distribution of eels make them ideal for biomonitoring studies of Hg. In addition, that they are consumed by humans is also an important factor (Downs *et al.*, 1999a).

7.4.10.8   Several studies have been undertaken on Hg concentrations in eels and roach in East Anglian rivers. Recent results have shown that total Hg concentrations are below the limit set by EU directive (93/351/EEC) of 1.0 mg kg^{-1} wet weight for edible, high fat content fish, such as eel and pike, and 0.5 mg kg^{-1} for all other fish, including roach (Downs *et al.*, 1999a).

7.4.10.9   A survey of Hg concentrations in eels collected from 57 sites across eastern England between 1986 and 1987 found concentrations of between 0.09 and 1.30 mg kg^{-1} in flesh and between 0.01 and 3.36 mg kg^{-1} in liver tissue (Mason and Barak, 1990). Some of the eels contained concentrations higher than the maximum limit set by EU Directive (93/351/EEC).

7.4.10.10   The lower, more current figures may be the result of emission controls to air and water that have been imposed on industry in recent years. However, Hg is still entering the environment and is available for accumulation in fish tissue (Downs *et al.*, 1999a)

Table 7-6 Mercury found in East Anglian eels (Anguilla anguilla)

Mean Hg in µg kg^{-1}	Hg Range in µg kg^{-1}	Study Site	Reference
20	1 - 82	Ant, East Anglia	Downs *et al*., 1999a
170	14 - 788	Yare, East Anglia	Downs *et al*., 1999a
82	22 - 168	Waveney, East Anglia	Downs *et al*., 1999a
159	52 - 287	Colne, East Anglia	Downs *et al*., 1999a
151	55 - 467	Pant, East Anglia	Downs *et al*., 1999a
255	57 - 501	Yare, East Anglia	Edwards *et al*., 1999
230	100 - 760	Colne, East Anglia	Mason and Barak, 1990
240	90 - 910	Blackwater, East Anglia	Mason and Barak, 1990
309	94 - 664	East Anglia	Mason, 1987

7.4.11   Mercury in UK Birds

7.4.11.1   A long-term survey of pollutants in the livers of five species of predatory birds was conducted between 1963 and 1990. The species studied were the sparrowhawk (*Accipiter nisus*), the kestrel (*Falco tinnunculus*), the grey heron (*Ardea cinerea*), the kingfisher (*Alcedo atthis*) and the great-crested grebe (*Podiceps cristatus*). All the species except the great-crested grebe showed a general downward trend in Hg concentrations over the length of the study (Newton *et al.,* 1993).

Table 7-7 Total mercury found in the livers of predatory birds (from Newton et al., 1993)

Bird Species	Mercury concentration in 1963-1970 in mg kg^{-1}	Mercury concentration in 1986-1990 in mg kg^{-1}
Sparrowhawk	4.60 (2.55 – 8.28)	0.98 (0.15 – 6.28)
Kestrel	5.77 (2.98 – 11.17)	0.22 (0.02 – 2.21)
Heron	44.14 (20.31 – 95.94)	11.98 (4.24 – 33.82)
Great-crested grebe	Not recorded	11.87 (5.19 – 27.15)
Kingfisher	Not recorded	1.05 (0.21 – 5.15)

7.4.11.2   A general link between Hg content and diet was established during this study, with the three fish eating species (heron, grebe and kingfisher) tending to have higher Hg concentrations. Particularly high Hg concentrations were noted in the heron which is thought to be because of their consumption of large, fatty fish such as eels that carry a higher burden of Hg (Newton *et al.,* 1993).

7.4.11.3   In a more recent survey concentrations of Hg were measured in cormorant (*Phalacrocorax carbo*) eggs that had failed to hatch, the mean concentration was 2.63 mg kg^{-1}, with a range of 1.38 – 7.68 mg kg^{-1} (Mason *et al.*, 1997). The cormorant colony studied was situated in eastern England where the adult birds fed on fish caught in the coastal waters of the outer Thames estuary, an area with a history of pollution. The relatively low concentration of Hg observed in the cormorant eggs had no apparent impact on the colony size, which was still expanding and supports the trend of falling Hg concentrations noted in British grey herons previously (Newton *et al.*, 1993).

7.4.11.4   Some birds, including migratory waders, possess a mechanism for protecting against Hg, and other contaminants, pollutants are eliminated into the feathers which are then lost during the annual moult (Evans *et al.*, 1987).

7.4.12   Mercury in UK Mammals

7.4.12.1   Surveys of the otter (*Lutra lutra*) are valuable as, being at the top of the food chain, they are prone to bioaccumulation of toxins. Otters feed mainly on fish, including eels which may be particularly rich in Hg due to their high lipid content. The Hg concentrations found in the livers of the 112 Scottish otters ranged from 0.11 to 13.43 mg kg^{-1} wet weight (mean 4.04 mg kg^{-1}) and 0.33 to 44.71 mg kg^{-1} dry weight (mean 13.28 mg kg^{-1}). These results indicate that a very few individual otters may have accumulated enough Hg to affect their survival during times of stress but that it is unlikely that the otter population in Scotland is suppressed by such contamination. However, as Hg concentrations in both the otters and their prey are relatively high, it is possible that any future increase in environmental Hg would have a significant impact on survival (Kruuk *et al.*, 1997).

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7.4.12.2 Marine mammals tend to have significantly higher Hg concentrations than other marine organisms, with particularly high concentrations found in the liver (Law *et al.*, 1991). The high concentrations are a result of a variety of factors, probably of most significance is that the Hg content of prey is usually in the methylated form. Juvenile mammals have also been identified with very high Hg concentrations, studies on dolphins have shown that MHg can cross the placenta, accumulating in the fetus so that the young begin life with elevated Hg concentrations (André *et al*, 1990).

7.4.12.3 Several studies have been undertaken on Hg concentrations in British marine mammals in recent years. In a study of marine mammals between 1988 and 1989 a Hg concentration of 430 mg kg^{-1} (wet weight) was found in the liver of a grey seal from the Wirral, although results from most other animals were less than 100 mg kg^{-1} wet weight (Law *et al.*, 1991). A follow-up study (1989–1991) of marine mammals from the Welsh coast and Irish Sea found Hg concentrations of between 0.5 and 280 mg kg^{-1} wet weight in livers (Law *et al.*, 1992).

Table 7-8 Total mercury found in the livers of marine mammals

Mammal	Mercury concentration in mg kg^{-1} wet weight	Location	Reference
Grey seal (*Halichoerus grypus*)	12–430	Liverpool Bay	Law *et al.*, 1991
Grey seal (*Halichoerus grypus*)	1.5–280	Liverpool Bay	Law *et al.*, 1992
Grey seal (*Halichoerus grypus*)	3.5–95	Northern Ireland	Law *et al.*, 1991
Grey seal (*Halichoerus grypus*)	3.5–11	Northern Ireland	Law *et al.*, 1992
Common seal (*Phoca vitulina*)	0.98–170	Northern Ireland	Law *et al.*, 1991
Common seal (*Phoca vitulina*)	5–170	Northern Ireland	Law *et al.*, 1992
Common porpoise (*Phocoena phocoena*)	1.4–30	Northern Ireland	Law *et al.*, 1991
Common porpoise (*Phocoena phocoena*)	0.6–2.8	Cardigan Bay	Law *et al.*, 1991
Common porpoise (*Phocoena phocoena*)	0.8–190	Cardigan Bay	Law *et al.*, 1992

7.4.12.4 *Post mortem* analyses were carried out on two whales that were stranded on British beaches. Mercury concentrations in liver tissue were determined as 248 mg kg^{-1} wet weight in the Blainville's Beaked Whale, *Mesoplodon densirostris*, and 88 mg kg^{-1} wet weight in the killer whale, *Orcinus orca* (Law *et al.*, 1997).

8 Gaps in knowledge for selection of an air quality standard for mercury and emissions targets for the protection of human health and the environment

Summary

- Ambient concentrations of Hg in the UK are several orders of magnitude lower than concentrations at which direct toxicological effects occur.
- More data are required on concentrations of methylmercury in selected biota to assess the risk posed to humans and the biota themselves.
- The contribution of dental amalgam emissions to human exposure in UK conditions needs to be quantified.
- The major routes of Hg uptake for the UK population are from food (mainly fish) and most likely from emissions of dental amalgam. Therefore an air quality standard for mercury is inappropriate for the protection for human health.
- A 'critical loads' approach provides a methodology to protect human health and the environment.
- Therefore **the major gap in knowledge** is the information necessary to quantitatively link critical loads of mercury and human health effects with the major sources of mercury in the UK environment.
- Measurements are inadequate to derive concentration and deposition fields of Hg for the UK.
- Emission inventories are estimated to be accurate to approximately ±50% and are currently inadequate to define the UK source strength
- Uncertainties in the underlying processes of deposition and chemical behaviour currently make the modelling of Hg transport and fate a somewhat speculative exercise. Specifically, dry deposition rates, the major route of wet scavenging and oxidation rates of Hg need to be refined.
- These conclusions should be considered in the light and context of evidence for increasing background concentrations of elemental gaseous Hg from sources outside of Europe, that will have significant impacts on Europe and the UK.

8.1 Key issues in protection of human health and the environment

8.1.1 There is evidence that some UK biota contain concentrations of MHg that are potentially harmful to human health, if consumed, and to the biota themselves (see Chapter 7). The data on MHg concentrations are not systematic, nor complete. Long-term monitoring may be necessary to improve and build upon existing data sets.

8.2 Key issues for air quality standards

8.2.1 An air quality standard is inappropriate for Hg. As propounded in Chapter 7, inhalation of ambient Hg is unlikely to constitute a significant human health hazard, unless high concentrations of MHg are found close to sources. In the UK, there have been no measurements of MHg but other data suggest that concentrations are likely to be low.

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8.2.2   Although an air quality standard is normally required for a Daughter Directive pollutant, an EU Working Group has recognized that this is not the appropriate regulatory instrument to protect human health (Munthe, 2000, pers. comm.).

8.2.3   The major gaps in knowledge are the concentrations themselves, their speciation, deposition rates and transboundary fluxes.

8.3   A critical loads approach for atmospheric mercury

8.3.1   In Chapter 7 it was concluded that (i) the primary uptake route of Hg is through ingestion and (ii) the main entry pathway of Hg into the food chain is by atmospheric deposition.

8.3.2   It is clear that the principal route of human uptake is by consumption of fish and possibly their predators. These biota bioaccumulate MHg, the toxic form of Hg. Excepting areas that have been either contaminated or subject to direct discharges, the bioaccumulation of MHg arises primarily from atmospheric inputs of Hg. Thus, deposition of Hg species needs to be limited.

8.3.3   One obvious way of achieving this would be the regulation of ambient concentrations. However, as has been shown in Chapter 6, the relationship between concentrations and deposition is strongly non-linear and differs greatly for the different forms of Hg. Hence concentrations of the different forms of Hg (Hg^0, RGM and Hg-p) would have to be regulated individually as it is done for example for gaseous sulphur dioxide and sulphate aerosol. Furthermore, the regulation of ambient concentrations is a highly inefficient way to control deposition levels of a pollutant that has an atmospheric lifetime for its predominant form, Hg^0, of ~1 year.

8.3.4   A critical loads approach is therefore proposed instead of an air quality standard to protect human health. There are several ways to quantify deposition fluxes, including:

(i)   the use of concentrations in food;
(ii)   the use of concentrations in accumulating biota, such as mosses, as a proxy for the deposition;
(iii)   direct measurement of the (wet-)deposition field;
(iv)   modelling of the deposition.

8.4   Key issues for emissions targets

8.4.1   The essential issue for emissions targets is the knowledge of a critical deposition load for Hg. In order to define critical loads and exceedance/protection, the deposition loading must be known. In order to define emissions targets, modelling must be undertaken to relate the deposition to UK emissions. The shortcomings of current models, modelling approaches and measurement data, both as model input and for model validation, have been discussed in detail in Chapters 4 and 5 and may be summarized as follows:

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8.4.2   Current model results (and therefore budget estimates) vary greatly between studies. This is partly because of differences in the parameterizations of the deposition rates. Total deposition to the UK is particularly sensitive to the dry deposition rate of Hg^0, which needs to better characterized. Local and regional deposition is most sensitive to the fraction of Hg emitted as RGM. A first national UK estimate of the speciation of Hg emission was carried out in Chapter 2 and needs to be refined, preferably based upon process-specific measurements of emission factors. The fraction of deposition to the UK of Hg that originates from outside the country and can therefore not be controlled by national emission targets, depends critically on the reaction rate of Hg^0 into reactive forms. Here, current chemical modules in atmospheric transport models are insufficiently parameterized, as discussed in detail in Chapter 5.

8.4.3   The logic underpinning current budget estimates of Hg in the atmosphere over the UK are inconsistent. Current budgets include *deposition* from the global Hg^0 pool, which is partly derived from natural emission and re-emission, but natural emissions and re-emissions originating from the UK and Europe are not included. This leads to an underestimation of the export of Hg from the UK. The quantification of natural emission and re-emissions and their controls is vital in assessing potential effects of UK emissions.

8.4.4   There are no UK deposition measurements, which have been deemed fit for model validation by the EMEP-CCC of the CLRTAP. The only deposition measurements with spatial coverage for England and Wales (MAFF dust deposit collector network) were made using a collector type for which the collection efficiencies are poorly characterized. Concentration measurements are only available at 3 rural sites for Hg-p and 1 site for TGM.

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9   Conclusions

1. Mercury is a global or at least hemispherical problem; its sources are both man-made and natural, with approximately 75% of the global total arising from man's activities.

Emissions:

2. Mercury concentrations in the Northern Hemisphere increased until 1990. Measurements in Europe suggest a decrease of about 45% between 1990 and 1996, but concentrations have now started to increase again. The decrease was stronger than the decrease in coal combustion, indicating that (i) the contribution from man-made sources has been underestimated or (ii) non-coal sources have been underestimated.

3. Emission estimates for the UK are highly uncertain and differ by a factor of 2.5, with the NAEI reporting emission values at the lower end of the range.

4. According to the NAEI, 40% of the man-made Hg sources in the UK originate from the 10 major point sources. It should be assessed whether targeting the top industrial Hg emitters would be a cost-effective way to significantly reduce the UK Hg emissions to air. According to the NAEI, 25% of the UK Hg emissions can be attributed to a single plant.

5. There is no inventory for natural/re-emission sources of mercury in the UK, which could be as large as 10 – 50% of the man-made sources. In this report we have estimated this contribution to be about 11%.

6. Man-made emissions are probably 10 – 30 % larger in the winter than in summer, with a maximum of the natural sources in summer.

7. The overall speciation of the UK industrial sources is estimated as: 67% Hg^0, 9% Hg-p and 24% RGM. However, this estimate is based on few measurements, none of which originate from the UK. Too little information is available on methylmercury to be able to estimate its contribution to total Hg.

8. High chlorine coal is an important source for RGM.

9. The NAEI is highly dependent upon emissions reported by operators of Part A processes to the ISR. These emission figures have not been independently validated.

10. Mercury emissions from coal combustion, especially in power generation, are estimated to be a large fraction of the UK total and require more accurate reporting, and validation.

11. Mobile measurements of Hg^0 and RGM could provide a means of identifying local sources of Hg, which may be underestimated in the ISR database.

12. The NAEI should provide information on speciation and stack parameters to provide a robust basis for modelling activities and budget estimates.

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13. Considerable efforts should be made to improve the quantification and geographical allocation of the emissions from waste combustion (MSW, crematoria, clinical waste, and industrial waste). These are particularly important sources of RGM, which is deposited close to the source.

Concentrations and deposition:

14. Very few measurements of air concentrations of Hg or its speciation are available for the UK.

15. The only bulk deposition measurements carried out in the UK (1989 – 1992 at Banchory, East Ruston and Staxton Wold) were analysed with inappropriate analytical techniques and show mostly values below the detection limit. For reasons of poor quality the data have been rejected by the Chemical Coordination Centre of the CLRTAP.

16. The only deposition measurements providing spatial distribution (the dust gauge network for England & Wales) were made with a collector type for which the dry deposition collection efficiency for particles and RGM is unknown. Nevertheless, these measurements imply deposition between 17 and 45 tonnes yr^{-1} for England and Wales, a factor of 2 to 5 larger than predicted by models using current industrial emission inventories. Thus, the actual deposition to the UK landscape is highly uncertain.

17. There are no Hg dry deposition flux measurements for the UK and very few for Europe, in general.

18. Local and regional deposition is dominated by RGM. Waste, coal, and oil combustion sources emit a large fraction of RGM, which is deposited relatively close to the source. It is likely that deposition hotspots occur throughout the country that have not yet been defined.

Mercury budget for the UK:

19. Mercury budgets for the UK can only be constructed from modelling. These results are highly uncertain as there are insufficient data for satisfactory model validation.

20. Both EMEP MSC-East atmospheric transport modelling and the modelling undertaken here suggests that the UK is a net exporter of atmospheric mercury.

21. An atmospheric Hg budget has been constructed for the UK for 1998 based on modelling undertaken for this report and compared with two sets of results from EMEP MSC-East modelling. The results differ significantly. However, the EMEP MSC-East results and attribution for 1995 and 1998 differ markedly.

22. According to the EMEP MSC-East (2000) report, in 1998, 26% of the Hg emitted in the UK from manmade sources (12.4 tonnes Hg yr^{-1}) was deposited to the country, while the remainder (74%) was exported. Of the total UK deposition of 9 tonnes Hg yr^{-1} estimated for 1998, 36% originated from the UK, 4% from other European countries and 60% from sources of indeterminate origin. For 1995 conditions, EMEP MSC-East estimated that for the same UK deposition of ~9 tonnes Hg yr^{-1}, 55% originated from the UK, 8% from other European countries and 36% from sources of indeterminate origin. These discrepancies are not explained.

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23. The modelling undertaken here indicated a similar UK deposition of 9.9 tonnes Hg yr^{-1} for 1998 conditions but a very different attribution budget to that of EMEP MSC-East. It was calculated that 25% of UK deposition arises from the Northern Hemisphere background concentrations; 41% from UK sources; and 34% from other European countries. Based upon other experience, such differences between coarser-scale and finer-scale modelling are not entirely unexpected. Nevertheless, the differences between the 3 sets of model results are too large to be satisfactory, other constraints (e.g. model validation) aside.

24. Thus, despite the large uncertainties, it appears that between a quarter and two thirds of the deposition to the UK originates from the global background. At the upper end of this range, this severely limits the potential effects of UK and even European abatement strategies on deposition reduction.

25. Comparing the deposition estimated by EMEP and the speciation of the emission derived as part of this study, the amount of RGM deposited to the UK is roughly balanced by the amount of RGM emitted from the UK. In contrast, more than twice as much Hg-p is deposited as emitted, and the emission of Hg^0 is three times as large as its deposition (Table 5-2).

26. Owing to the importance of the hemispheric background concentration, modelling of the transport and deposition of Hg needs to be carried out on a global or at least hemispheric scale.

Mercury and human health:

27. The limited data on ambient air concentrations of Hg are orders of magnitude lower than the concentrations at which direct toxicological effects occur. Direct exposure and inhalation are not therefore an issue at the ambient air concentrations found in the UK.

28. The primary effects of Hg on human health are via the bio-accumulation in the food-chain, mainly through the consumption of fish and offal.

29. Whilst the total Hg content of UK fish and other foods is reasonably well known, not much information is available on the concentrations of the toxic methylmercury form.

30. The exposure to Hg emitted by dental amalgam fillings is highly uncertain but could equal the dose experienced through ingestion but not necessarily that in the toxic methylmercury form.

31. Indoor air concentrations of mercury have been found to be elevated owing to the use of Hg containing latex paint in other countries. No information is available on indoor air concentrations of Hg in the UK.

32. The links between emissions, concentrations, deposition and bio-accumulation of Hg all remain largely unknown, so that establishing threshold air concentrations to protect human health has no quantitative basis. An air quality standard for Hg concentrations is not therefore appropriate to protect human health in the UK.

33. We conclude that a 'critical loads' approach for protection of human health from effects of Hg offers the most effective assessment and control strategy.

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10 Recommendations

The following recommendations are structured as potential 'Work Packages', <u>all of which we consider equally important</u>.

The priority of the individual tasks *within* these Work Packages has been given in parentheses with three stars (✷✷✷) indicating the highest priority. The priorities have been assigned according to the current weaknesses in scientific understanding of the subject in relation to overall policy requirements.

Whilst all Work Packages are of equal importance, we nevertheless point out that the establishment of a measurement network of the deposition and concentration of Hg to be of highest priority of all, since without it a critical loads methodology cannot be developed, model performance cannot be evaluated and emission estimates cannot be validated. In essence, this requirement is the starting point. However, as noted in Work Package 2, a careful measurement strategy needs first of all to be formulated based upon initial measurements.

Thus, where possible, we have noted that some initiatives, whilst equally important, need to be implemented sequentially: this is noted by, e.g, 'STAGE 1'.

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Work Package 1: Development of a critical loads methodology for mercury

According to the WHO (1972), an intake of total Hg and methylmercury of 45 and 30 µg Hg day^{-1}, respectively, is considered '*tolerable*'. In contrast, in the same report the '*acceptable*' intake is clearly stated as '*none*'. The main routes of Hg uptake are through food (mainly fish) and from dental amalgam fillings and not from the ambient air, although Hg concentrations in UK houses should be investigated. The development of a mercury air quality standard for the UK is not therefore the most effective means of providing protection to the human population. This is consistent with the legislation in those countries that have been most concerned about the adverse effects of Hg, including the US, Canada and the Scandinavia. We therefore recommend the development of a 'critical loads' approach for mercury, in which the maximum allowable yearly deposition of Hg is defined for various surfaces, including water bodies, catchment areas, pastures and cropland. This approach needs to be based on the maximum allowable intake through food and consider the bio-accumulation of Hg. The development of a critical loads approach requires the quantification of:

- STAGE 1–allowable limits of Hg uptake for the UK population (✷✷✷);
- STAGE 2–linkages between deposition, bio-accumulation and dose to at-risk groups (✷✷✷);
- pathways of Hg in soils, catchments and water bodies (✷✷);
- chemical conversion processes in biota, soils and water (✷).

This recommendation is based purely on logical argument; the feasibility of defining these linkages has not been sufficiently explored. It is recommended that if this Work Package is pursued, the feasibility and process by which this Work Package is undertaken requires further scoping (✷✷✷).

In addition, the Hg dose experienced by the UK population from dental amalgam emissions and their contribution to methylmercury in the human body should be quantified (✷).

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Work Package 2: Assessment of the UK pollution climatology of mercury based upon concentrations, deposition and process measurements

We recommend that the air concentration and deposition climatology for Hg in the UK be defined. A rural measurement network with an adequate coverage should therefore be initiated. Such a measurement network would provide the following:

- concentration and deposition maps of Hg for the UK;
- total deposition to the UK derived from measurements to close the UK Hg budget;
- data for model validation for UK modelling activities (see Work Package 3);
- measurement data for the validation and improvement of the EMEP modelling activities as a UK contribution to the CLRTAP activities;
- a means to assess the effects of emissions control on atmospheric deposition and concentrations of Hg.

STAGE 1(✷✷✷)—With the current understanding of the behaviour of atmospheric Hg and land/atmosphere exchange of Hg at such a rudimentary level, a research site to investigate wet/dry fluxes and measure ambient concentrations of speciated Hg is required. This will enable a strategy for a measurement network to be established because, as we note below, insufficient data are available to design and initiate a cost-effective measurement/monitoring strategy. Moreover, such a research site would provide a vital and cost-effective means to support model development. Such a site would focus upon the processes controlling chemical behaviour of Hg and its surface/atmosphere exchange.

STAGE 2 (✷✷✷)—A measurement network for wet fluxes and ambient concentrations would then be established. Ideally, such a network would measure the wet-only deposition of Hg together with the air concentrations of TGM, RGM and Hg-p, using procedures that are consistent with those of the CLRTAP and WMO. In the first instance, we consider that a small number of sites (up to 10) may be sufficient to measure Hg^0, whereas a larger number of sites (>10) may be required to establish the more variable concentration fields of RGM and Hg-p. Wet deposition measurements would be required at more than 10 sites (similar to the acid deposition network) using wet-only or bulk collectors. The necessity for wet-only cf. bulk measurements should be investigated during STAGE 1. As noted above, a strategy for a cost-effective measurement network can only be formulated from initial measurements made in STAGE 1.

The suitability of proxies for deposition, such as biomonitors could be investigated as a potentially cost-effective way of increasing the spatial coverage of other measurements (✷).

Short-term measurements of the surface/atmosphere exchange fluxes of Hg should be made over a range of UK soils (including contaminated land), waters and vegetation to provide a measurement database for the development of a UK inventory of natural emissions and re-emissions of Hg (✷✷).

Given the large uncertainty in the emissions, a methodology to identify emission and deposition hotspots throughout the country needs to be developed and implemented (✷✷).

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Work Package 3: Modelling of source–receptor relationships for mercury

It has been shown in this report that deposition and bioaccumulation of Hg represent the principle threat to human health and ecosystems. Atmospheric transport and deposition modelling is the only way by which future emission targets can be defined for 'acceptable' (critical) deposition loadings. In addition, models provide the only means of establishing source-receptor relationships.

An improved modelling approach is required for Hg. As we have shown in this report, whilst some modelling has been undertaken, improvements to the current approaches are readily identified.

What makes Hg unique is its disparate time-scales in terms of the atmospheric lifetimes of its component species. This necessitates a careful consideration of background (hemispherical and global) concentrations. Moreover, the recent evidence of increasing European concentrations of Hg^0, speculated to be a result of rising emissions in the Far East underlines the importance of the so-called 'background'.

The three modelling approaches contrasted in this study (EMEP, 1998; EMEP, 2000 and the modelling carried out here) result in similar Hg deposition estimates for the UK but very different attribution. Moreover, the only available measurements of the Hg deposition field in the UK, although poorly characterized, indicate a much larger deposition than predicted by the numerical models.

We therefore recommend the initiation of a UK modelling activity of Hg to define source-receptor relationships that includes:

- a model that can adequately represent the known processes (chemistry/deposition) and readily incorporate the rapid advances being made (✳✳✳);

- improvement of the representation of background concentrations (✳✳✳);

- an improved simple model for sensitivity studies (✳✳);

- an improved approach for modelling the biogeochemical cycling of Hg over long time-scales (✳).

This modelling activity should utilize the data generated within Work Package 2 and be undertaken in conjunction with Work Package 2 to aid develop a measurement strategy.

Work Package 4: Improvement of the UK emissions inventory for mercury

The emissions database for industrial/man-made sources should be improved and we recommend the following:

- − the independent validation of the emissions data provided to the ISR (✴ ✴ ✴);

- − the introduction of chemical speciation into the NAEI (✴ ✴ ✴);

- − improved estimates and geographical allocation of the emissions from incineration and landfill (✴ ✴);

- − improvement of the database and spatial disaggregation procedures for residential/small industrial boiler combustion sources (✴).

We note that current problems arising from confidentiality of site-specific activity statistics need to be overcome to use site-specific activity figures in the emissions inventory.

In addition, whilst the UK industrial/man-made emissions estimates are unsatisfactorily uncertain, we note and emphasize that natural/re-emissions are, according to our initial estimations, 11% (range 2–75%) of total UK emissions. Therefore, we recommend the compilation of a spatially disaggregated inventory of re-emissions and natural emissions, which should be based upon both literature data and UK measurements performed under Work Package 2 (✴ ✴ ✴).

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Acknowledgements

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This document reviews the sources, sinks and ambient concentrations of atmospheric mercury in the United Kingdom in the context of UK and European air quality policy and legislation. The report identifies the gaps in knowledge and makes research recommendations for the closing of these gaps.

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