Quantifying missing annual emission sources of heavy metals in the United Kingdom with an atmospheric transport model

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HIGHLIGHTS

- Concentrations and deposition of 9 heavy metals in the UK were simulated.
- Modelled data were well correlated to measured concentrations and deposition.
- The model greatly underestimated metal deposition and air concentrations.
- Under-estimation was attributed to wind-driven re-suspension of surface dust.
- Estimates of heavy metal emissions by re-suspension are highly uncertain.

ARTICLE INFO

ABSTRACT

An atmospheric chemical transport model was adapted to simulate the concentration and deposition of heavy metals (arsenic, cadmium, chromium, copper, lead, nickel, selenium, vanadium, and zinc) in the United Kingdom. The model showed that wet deposition was the most important process for the transfer of metals from the atmosphere to the land surface. The model achieved a good correlation with annually averaged measurements of metal concentrations in air. The correlation with measurements of wet deposition was less strong due to the complexity of the atmospheric processes involved in the washout of particulate matter which were not fully captured by the model.

The measured wet deposition and air concentration of heavy metals were significantly underestimated by the model for all metals (except vanadium) by factors between 2 and 10. These results suggest major missing sources of annual heavy metal emissions which are currently not included in the official inventory. Primary emissions were able to account for only 9%, 21%, 29%, 21%, 36%, 7% and 23% of the measured concentrations for As, Cd, Cr, Cu, Ni, Pb and Zn. A likely additional contribution to atmospheric heavy metal concentrations is the wind driven re-suspension of surface dust still present in the environment from the legacy of much higher historic emissions. Inclusion of two independent estimates of emissions from re-suspension in the model was found to give an improved agreement with measurements. However, an accurate estimate of the magnitude of re-suspended emissions is restricted by the lack of measurements of metal concentrations in the re-suspended surface dust layer.

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1. Introduction

Trace metals of primary concern for human health and the natural environment include arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), vanadium (V), and zinc (Zn). These trace elements are present in various forms in the environment in water, soil, and air. The organic forms, in particular, are readily taken up and absorbed by biota, and accumulate in food chains, imposing a health risk to wildlife. The metals of concern for natural ecosystems include Cd, Cu, Cr, Ni, Pb, V and Zn (Spurgeon et al., 2007). These have been shown to be detrimental to soil microbes and vegetation when critical limits are exceeded (RoTAP, 2012). Estimates in the United Kingdom (UK) have indicated areas of both managed and unmanaged woodland where critical load exceedances occur for

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Cu, Pb and Zn. The metals which are the most detrimental to human health are Pb, Cd, and Hg (WHO/CLRTAP, 2007) Lead is toxic at very low exposure levels, and has acute and chronic effects on human health. It is a multi-organ system toxicant that can cause neurological, cardiovascular, renal, gastrointestinal, haematological, and reproductive effects. Cadmium is a toxic element for humans that can result in kidney and bone damage, and is carcinogenic by inhalation. Mercury can damage the liver, the kidneys, and the digestive and respiratory systems, as well as cause brain and neurological damage. In natural ecosystems it is toxic to aquatic life. Morrison et al. (2013) have correlated social deprivation in Glasgow, Scotland with high metal content in soils, illustrating that the legacy of environmental pollution can remain in post-industrial areas for many decades after heavy industry has declined.

Concern over the presence of heavy metals in the natural environment initiated monitoring studies in the UK. Soil samples from stratified random 1 km × 1 km squares were analysed as part of a countryside survey in 2000 and 2007 (RoTAP, 2012). Concentrations of many of the heavy metals were highly correlated, with two clusters of spatial patterns: Pb and Cd had similar distributions, which were different from another cluster containing V, Ni, Cu, and Zn. A survey of mosses at 170 sites revealed a decrease in heavy metal concentrations between 1995 and 2005 which was consistent with reductions in emissions (Harmens et al., 2009).

Assessment of the impact of atmospheric metal deposition on natural ecosystems is made using 'critical loads'. A critical load is defined as the rate of deposition which at the steady state leads to the metal concentrations in soils and water reaching a threshold for adverse effects. Critical loads in the UK have been mapped for Cd, Pb, Cu, Ni, and Zn for a number of different ecosystems by Hall et al. (2006). Critical loads were sensitive to soil type, with more than 95% of the critical load values for Cd calculated to be between 1 and 100 g/ha/year, with a mean value of 18 g/ha/year. The values for Pb were higher, with 95% lying between 5 and 500 g ha^{-1} year^{-1}, and a mean value of 85 g ha^{-1} year^{-1}. For the year 2005 it was estimated that over 50% of forests were subject to deposition exceeding the critical loads for Cu, Pb, and Zn (RoTAP, 2012). Exceedance of the critical load was not evident for Cd and Ni.

The United Nations Economic Commission for Europe (UNECE) protocol on heavy metals (www.unece.org/env/lrtap/) was signed in 1998, targeting the emissions of three key metals, Pb, Cd, and Hg. This committed the UK to reduce the emissions of these metals to below those of 1990 as well as phasing out leaded petrol and requiring the use of the best available technology (BAT) to reduce emissions from stationary sources. The sources of emissions of heavy metals to the atmosphere are quite diverse and in the UK have declined over time (Table 1 in the Supplementary material (SI)). Whilst the primary source of Pb was previously road transport, national emissions have fallen significantly since the introduction of lead-free fuel in the 1990s, and the iron and steel industry is now the main emission source. Vanadium is produced almost exclusively from oil combustion, with international shipping making a major contribution to emissions (Wang et al., 2013). Arsenic emissions are mostly generated by the disposal of treated wood by burning. A detailed breakdown of emission sources for heavy metals in the UK is presented in the National Atmospheric Emissions Inventory (NAEI: http://www.naei.org.uk/). During the period between 1990 and 2006, emissions of heavy metals from the UK have fallen significantly, with the greatest emission reduction (of 97%) for Pb (Fig. 1).

Atmospheric chemical transport models (ACTMs) are increasingly being used, with spatially distributed information on emissions, to calculate the concentration in air and deposition to land of pollutants. Whilst many applications of ACTMs have been reported to study acid deposition and nitrogen deposition, and surface ozone (RoTAP, 2012), fewer studies to simulate the concentration and deposition of heavy metals have been undertaken. Chen et al. (2013) used a combination of size-segregated measurement and modelling to demonstrate that the size of particulates containing heavy metals in southern Spain was dependent on the specific source of emissions. Heavy metal pollution in the region was dominated by the fine and ultra-fine size categories. Member states of the European Community are obliged to both report annual atmospheric emissions of heavy metals and to monitor metal concentrations in air. However, most countries support only a small number of monitoring sites and reporting is restricted to an annual emission inventory without the spatial mapping of emissions.

In this paper we consider 9 heavy metals (As, Cd, Cr, Cu, Pb, Ni, Se, V, and Zn) which are known to pose threats to both human health and natural ecosystems. We hypothesised that the official estimates of annual primary emissions to the atmosphere are insufficient to account for measured concentrations of metals in air and their deposition by precipitation. An ACTM was used with spatially disaggregated emission data to calculate the deposition and concentration of the metals in the UK. Comparison with data from an extensive monitoring network allowed quantification of the level of the missing emission sources. Two independent estimates of the wind-driven re-suspension of heavy metals in surface dust have been included in the model simulations to ascertain
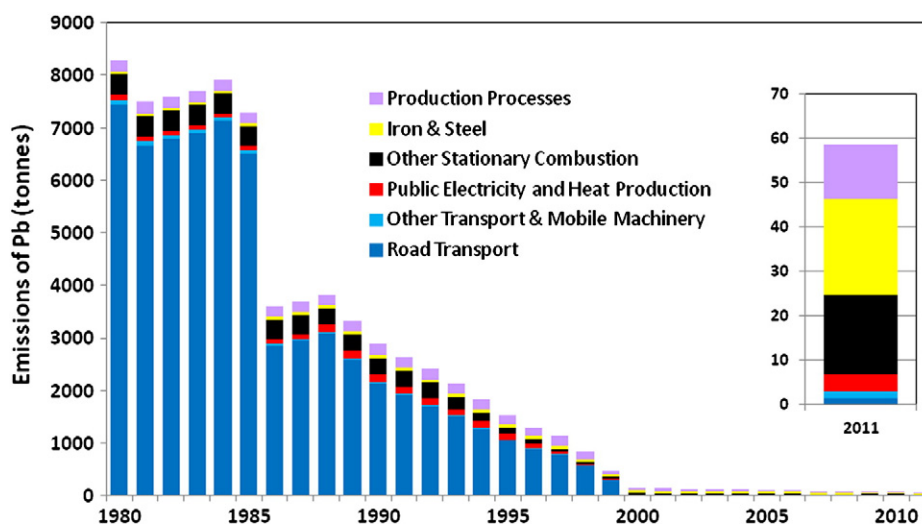

Fig. 1. Trend in emissions of Pb from the UK.

whether these additional sources are able to close the gap between the official primary emissions and the measurements.

2. Methods

2.1. Overview of emission inventories

The Parties to the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) are required to report national emissions of Cd, Pb, and Hg under the Heavy Metals Protocol. For the UK, emissions of these metals, as well as As, Cr, Cu, Hg, Ni, Se, V, and Zn are compiled within the National Atmospheric Emissions Inventory (NAEI) (http://www.naei.org.uk/). The UK emissions used in this study are summarised in Table 1. Dore et al. (2008) describe estimates of the uncertainties in metal emission inventories, shown in Table 1, which are based on the methodology proposed by the UNECE Taskforce on Emission Inventories and Projections. The lowest uncertainty is for V and Se, with principal sources from fuel combustion and chemical manufacture, and the highest uncertainty is for As which originates mostly from the burning of impregnated wood.

Small particle-borne metals deposit relatively slowly and may be transported over long distances of several hundreds or a thousand km (RoTAP, 2012). The atmospheric transport model developed for this work, FRAME-HM (the Fine Resolution Atmospheric Multi-pollutant Atmospheric Exchange for Heavy Metals), was operated on the 50 km × 50 km EMEP (European Monitoring and Evaluation Programme) grid (http://www.emep.int/grid/EMEP_domain.pdf) to represent the contribution of imported emissions from Europe to concentration and deposition over the UK. Emissions from European sources were taken from the ESPREME (integrated assessment of heavy metal releases in Europe) data base (ESPREME, 2007). The ESPREME data used included European emissions of As, Cd, Cr, Ni, and Pb, whilst for the UK gridded emissions data for all 9 metals were available from the National Atmospheric Emissions Inventory. European emissions of Cu, Se, V, and Zn were estimated by cross-correlating these metals against those with similar emission source profiles for which European data was available. The magnitude of European emissions for these missing metals was calculated using the surrogate data by assuming the same relative scaling factors as those found for UK emissions. For example, the dominant sources for emissions of Cu are automobile tyre and brake wear, industrial combustion, and public electricity production. These emission sources are similar to those for Ni. The surrogate emission map of Cu for Europe was therefore generated by using the existing Ni map and assuming that the magnitude of European Cu emission scales are relative to Ni with the same ratio as in the UK. For this study, however, it should be noted that the detailed spatial distribution of emissions in Europe is less important than that for the UK as the European scale simulation is used only to generate boundary conditions of concentrations in air for the regional UK simulation.

Table 1
Summary of UK national emissions for the year 2006 used in this study [Mg yr^{-1}] including primary emissions from the National Atmospheric Emissions Inventory, estimates of re-suspension from Abbott (2008) and estimates of re-suspension dynamically generated with the MSC-E approach.

Metal	Emissions from the NAEI	Uncertainty in primary emissions (%)	Re-suspension (Abbott)	Re-suspension (EMEP)
As	13.8	−60 to +200	4.8	–
Cd	3.6	−20 to +50	0.52	3.1
Cr	33.5	−30 to +70	–	–
Cu	60.3	−40 to +80	–	–
Ni	118	−30 to +50	26.2	–
Pb	87.9	−30 to +50	40.8	469
Se	38.3	−20 to +30	–	–
V	555	−20 to +30	–	–
Zn	388	−30 to +60	–	–

Studies on the uncertainty associated with heavy metal emissions in the UK were undertaken by Dore et al. (2008). Although a Monte-Carlo uncertainty analysis of Pb emissions in the UK gave a confidence interval of −20% to +30%, the possibility of significant emission sources which are unknown or not included in the emission inventory was considered. For example, there may be significant fugitive emissions from plant activities which are not captured by stack monitoring. Also recent work from Denmark suggests that emissions of metals from road transport (due to combustion of lubricant oils and additives) may be a significant source that is currently not included in national inventories (Winther and Slento, 2010). The content of heavy metals in coal imported from different regions of the world is known to vary greatly, by up to several orders of magnitude, even within the same region. Emissions from power stations and other large point sources are taken from a direct emission measurement. This part of the national emission data is associated with relatively low uncertainty. For smaller point sources in the NAEI, metal emissions are calculated from the metal content of the fuel and the amount of fuel used. The metal content of the fuel can be particularly high in uncertainty because historically the fuel analysis result is at or near the limit of detection. Furthermore, the metal content can be variable, depending on the origins of the fuel. Emissions based on such calculations may therefore be highly uncertain.

2.2. The atmospheric transport model FRAME-HM

The atmospheric transport model FRAME-HM, is based on the FRAME model (Singles et al., 1998; Fournier et al., 2004). This model is a multi-layer Lagrangian trajectory model, which may be run with the average meteorology for individual years and has been applied mostly for estimating acid deposition and nitrogen deposition, and the exceedance of critical loads (Matejko et al., 2009; Dore et al., 2012).

The model simulates an air column moving along straight line trajectories over the UK. Separate horizontal trajectories of the air column are run at a 1° resolution for all grid edge points. The model has a horizontal resolution of 5 km and 33 vertical layers of varying thicknesses from 1 m at the surface, increasing to 100 m in thickness at heights above 100 m. This allows a detailed vertical resolution of modelled air concentrations near the surface where many pollutants are emitted, and measurements of air concentrations are made. Area emissions are injected into the atmosphere at different heights depending on the classification of the emission sources whilst point sources are treated individually with a plume rise model to calculate an 'effective stack height' (Vieno et al., 2010). The deposition from sources outside the UK was estimated using FRAME at a 50 km × 50 km resolution covering Europe to create boundary concentration files for the UK domain. The advantage of this approach is the applicability of the same diffusion and deposition routines used in both the European and UK scale simulations.

The diffusion between the layers was calculated using the k-theory and solved with a finite volume method. Wind frequency and wind speed roses were used to give the appropriate weighting to directional deposition and concentration for the calculation of total deposition and concentration (Dore et al., 2006). The data on wind speed and direction was taken from 12-hourly radio-sonde ascents from 7 stations in the UK for the year 2006. The wind direction (Fig. 1, Supplementary material) was most frequently from the south-west. Wind direction measurements recorded in the 500–1000 m altitude range above the friction layer, were used to define the direction of large-scale flow. The transport scheme in FRAME is much simpler than the dynamic approach adopted in complex Eulerian models. However, the model has been demonstrated to obtain a good agreement with measurements of wet deposition (Dore et al., 2007) and air concentrations (Chemel et al., 2011) of sulphur and nitrogen species, and to perform well when compared to Eulerian models (Carslaw, 2011). The FRAME-HM model is simpler than the version used for acid deposition as no chemical reactions are included. Werner et al. (2011) applied the model to

simulate the concentration of base cation particulates in air, obtaining a reasonable agreement with measurements in the UK. The model is therefore considered suitable for the simulation of the concentration and deposition of heavy metals. Technical details on the calculation of dry and wet deposition are included in the Supplementary material.

2.3. Wind-driven re-suspension

In addition to the model simulation using the official emissions from the NAEI as input, scenarios have also been undertaken with the FRAME model that include wind-driven sources of heavy metal re-suspension which are not part of the official inventory. The historical legacy of significantly higher metal emissions during the previous few decades means that these pollutants are still present in the environment and can be re-suspended for instance from agricultural areas and bare soils by wind erosion, and from roads by vehicle turbulence. Wind erosion occurs when the friction velocity (which is directly related to the shear stress) exceeds a threshold value. The friction velocity is a function of surface wind speed and roughness. The threshold wind friction velocity depends on the soil particle size, wetness, clay content, and protection of the erodible soil by drag partitioning, and typically has values in the range 0.2–0.5 ms^{-1}. At wind speeds for which the friction velocity exceeds the threshold value, surface particles begin to creep with the wind, a process known as 'saltation'. This leads to the 'sand-blasting' of large agglomerated particles causing the release of smaller particles which contribute to the vertical flux of wind-driven re-suspension of particulate matter.

Estimates of the magnitude and spatial distribution of annual re-suspended emissions of lead and cadmium across Europe have been undertaken by the EMEP Meteorological Synthesizing Centre — East (MSC-E) following methods developed by Mansell et al. (2006) in the United States. In the EMEP model, a dynamic meteorological simulation was used to simulate the hourly evolution of wind speed and precipitation. The re-suspension process was halted after precipitation and re-initialised after a period of days which was dependent on the season, soil type and precipitation intensity. This varied from 0.7 days for lower precipitation amounts (less than 50 mm) to sandy soils during the warmer summer months to 10 days for higher precipitation amounts (greater than 50 mm) to clay soils during the colder winter months. A sand-blasting was model was applied which included three distinct particle size modes with diameters of 1.5, 6.7 and 14.2 μm. A spatially resolved dataset of soil size distribution was generated from the International Satellite Land-Surface Climatology Project, and the heavy metal content in topsoil was taken from the Geochemical Atlas of Europe (FOREGS, 2005). There is evidence of higher metal contents in the surface soil layer, which occurs due to the presence of cadmium in fertilisers applied to agricultural soil as well as the high concentrations of lead in road dust in urban areas caused by the historic use of leaded petrol (Akbar et al., 2006). Therefore, enrichment factors of 5–50 for Pb and 5–10 for Cd were applied for the metal content of re-suspended particulate matter, with the highest factor corresponding to urban soils. The mass of re-suspended heavy metals was calculated from the product of the respective metal contents in surface soil and the total mass of re-suspended particulate matter.

The contributions of wind re-suspension to total deposition were generally found to be comparable to anthropogenic sources (for Pb and Cd) in the majority of countries modelled by MSC-E with the EMEP model (Table 1; Travnikov et al., 2012). For countries with very large reductions in Pb emissions during the 1990–2010 simulated period (i.e. the UK) it was notable that the contribution from legacy (re-suspended) emissions became larger than that from primary emissions during the middle of this time period (around the year 2000). Furthermore, a large inter-annual variation in the contribution to metal concentrations from re-suspension was apparent due to the natural variation of meteorology. During the years with a greater frequency of high wind speed events, re-suspended emissions were significantly higher.

Estimates of the magnitude and spatial distribution of annual re-suspended emissions of lead, cadmium, nickel and arsenic in the UK were also undertaken by Abbott (2008). The calculations were made with measured meteorological data and a high resolution land cover map. The national soil inventory was used to define the metal content in soils in England and Wales and the Geochemical Atlas of Europe was used for other regions. The parameterisations of the threshold surface friction velocity, saltation, and sand-blasting were based on those used by EMEP. By summing the hourly contributions, the total re-suspended mass of heavy metals was calculated. Abbott (2008) estimated this to be approximately one third of the primary emissions included in the NAEI for As, Ni, and Pb, and 14% for Cd. The contribution from soils was found to be more than an order of magnitude higher than that from vehicles.

The re-suspended emission estimates for the year 2006 are listed in Table 1. The EMEP estimates of heavy metal re-suspension are significantly higher than those calculated by Abbott (2008), by a factor of 6 for Cd and 11 for Pb due to the use of enrichment factors in the EMEP calculations in setting the metal concentrations in the surface soil layer.

Two scenarios were included in the model simulations with the representation of re-suspension of heavy metals by wind from agricultural areas and bare soils as well as from vehicle induced turbulence: scenario (1): magnitude and spatial distribution of annual emissions of Pb, Cd, Ni, and As from Abbott (2008); and scenario (2): magnitude of emissions from MSC-E (Travnikov et al., 2012) for Cd and Pb only with spatial distribution from Abbott (2008).

2.4. The National Heavy Metals Monitoring Network

A rural network for monitoring the concentrations of heavy metals in air and precipitation has been in operation in the UK since the year 2004 (Malcolm et al., 2010; http://uk-air.defra.gov.uk/networks/). For the year 2006 the network consisted of 13 sites (Fig. 2). Samples of precipitation were collected for analysis of concentrations of heavy metals and measurements of the concentration of heavy metals in air were made using a Partisol PM$_{10}$ sampler. The operational performance of the Partisol 2025 particulate samplers has been verified by the detailed Defra and Devolved Administrations study test for equivalence in 2004–2006. At three of the sites (Inverpolly, Lough Navaar and Penalt) measurements were made of air concentrations only whilst at the remainder of the sites measurements included both precipitation collections and air concentrations. All samples of air concentrations were collected on a weekly basis and precipitation samples were collected on a weekly basis at five of the sites (Auchencorth, Banchory, Cockley Beck, Monks Wood and Yarner Wood) with monthly sampling at the remaining five sites. The concentrations of the 9 trace metals included in this study were measured by ICP-MS analysis in a laboratory accredited by the United Kingdom Accreditation Service (UKAS). All data concentrations were analysed using strict quality assurance and quality control protocols. Air concentration measurements have been checked against an independent urban monitoring network (Brown et al., 2009). This network includes one site in northern England that is classified as 'rural'. A comparison of measurements from this site with the two nearest sites in the rural monitoring network showed agreement in long term average concentrations of heavy metals in air to approximately 30%. Wet deposition of heavy metals at the sites was calculated by combining the measured concentrations in precipitation with site-based measurements of precipitation from a tipping bucket rain gauge.

2.5. Data analysis

The modelled annual average air concentration and wet deposition for all metals were compared with the values obtained by averaging the weekly air concentration measurements and summing the wet deposition measurements at the monitoring sites.
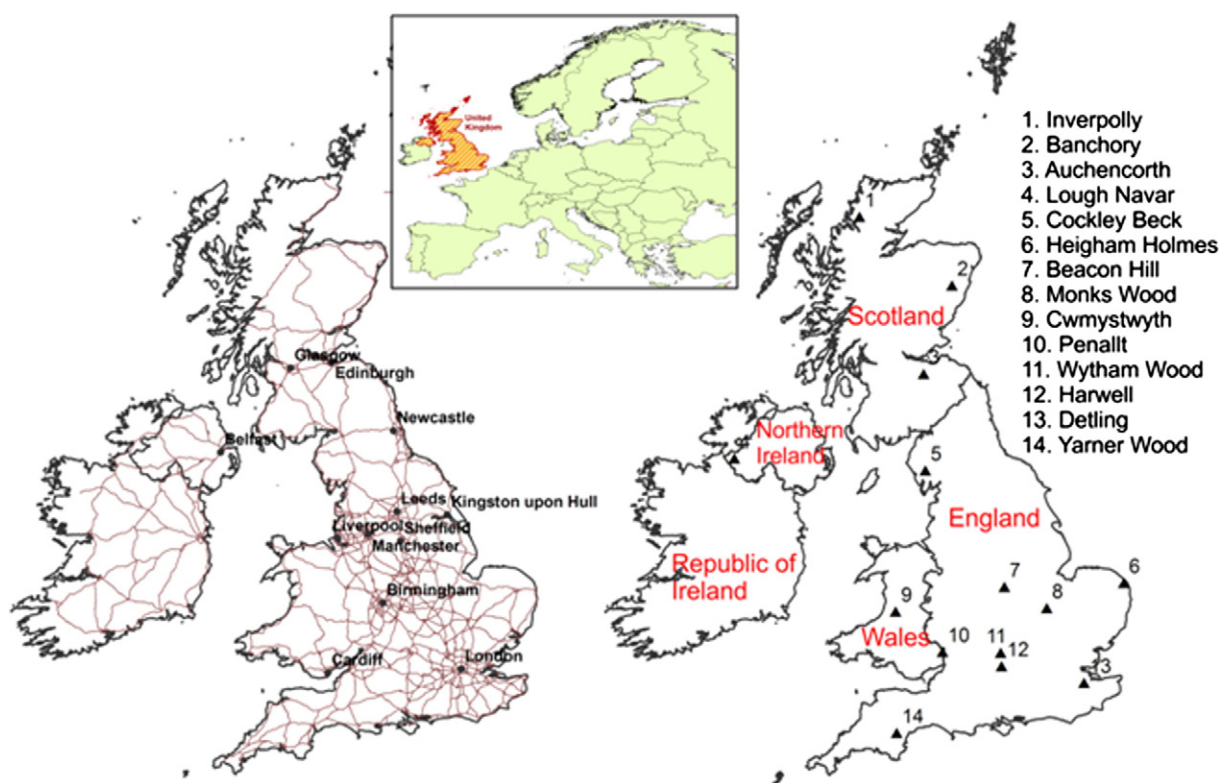
1. Inverpolly
2. Banchory
3. Auchencorth
4. Lough Navar
5. Cockley Beck
6. Heigham Holmes
7. Beacon Hill
8. Monks Wood
9. Cwmystwyth
10. Penallt
11. Wytham Wood
12. Harwell
13. Detling
14. Yarner Wood

Fig. 2. Maps of the UK illustrating: major cities and roads; regions of the UK and monitoring sites for the concentrations of heavy metals in air and precipitation; and location of the UK relative to the European continent.

The (Pearson) correlation coefficient (r) is a measure of the strength of the linear relationship between two variables and has been used to assess the correlation between modelled and measured metal air concentrations and wet deposition. The normalised mean bias (NMB) is defined as:

$$NMB = \sum_{i=1}^{n} M_i - O_i \bigg/ \sum_{i=1}^{n} M_i$$

where O_i represents the ith observed value and M_i represents the ith modelled value for a total of n observations. The NMB illustrates the model over- or overestimate relative to measurements and is useful for comparing pollutants that cover different concentration scales as the mean bias is normalised by dividing by the observed concentration. p-Tests were undertaken to illustrate the significance of the correlation of modelled air concentrations and wet deposition with measurements.

3. Results and discussion

3.1. Air concentration and deposition

The modelled concentration in air and dry and wet deposition over the UK are illustrated in Fig. 3 for Cd and Pb for scenario 0 (with no re-suspension). In general a strong gradient was evident, with higher concentrations found in central and northern England, due to a long range transport of pollutants from European sources, as well as the greater intensity of industrial and urban emissions in the region of the major cities of Birmingham, Manchester, Liverpool, Kingston upon Hull and Sheffield. The pattern of dry deposition can be seen to be similar to that for air concentrations. The influence of emissions from major urban areas and the road network is most pronounced for air

concentrations and dry deposition of Cd. Furthermore high values for wet deposition occur in more remote areas with lower air concentrations but high annual precipitation, such as the Highlands of Scotland.

In general, air concentrations and wet deposition of Cd and Pb were under-estimated by the model (Fig. 4a and b). The low modelled air concentrations suggest that dry deposition of metals is also under-estimated by the model. For both metals there is evidence of a much stronger correlation with measured air concentrations (r of 0.92 for Cd and 0.94 for Pb) than with wet deposition (r of 0.65 for Cd and 0.82 for Pb). This may reflect the complexity of the wet deposition process which is not fully captured by the model. Secondly, there could be greater uncertainty in measured metal wet deposition than in measured air concentrations due to contamination by dry deposition of metals to the surface of the collectors. The low slope of the Pb correlation plots (0.08 for air concentration; 0.17 for wet deposition) illustrates that overall Pb concentrations in both air and precipitation are greatly under-estimated by the model. This is a clear indication of missing or under-estimated emission sources.

The correlation with measurements of concentrations in air and wet deposition respectively for all the metals considered in the study for the scenario with only primary emissions included (scenario 0) is illustrated in Tables 2a and 2b respectively. As with Cd and Pb the p-values illustrate that modelled metal concentrations generally have a high level of correlation with the measured air concentrations (with r of 0.87 averaged for all metals except Se; Table 2a). There is a less close correlation with wet deposition (with an average r of 0.69 for all metals except Se; Table 2b). p-Tests performed on the correlation coefficient for wet deposition show that the correlation is most significant for Ni, Pb, and V. For V there are over-estimated emissions in the NAEI as both air concentrations and wet deposition are significantly overestimated by the model (normalised mean biases, NMBs, of 4.2 and 8.5 respectively). The poorest correlation was for Se wet deposition where the model
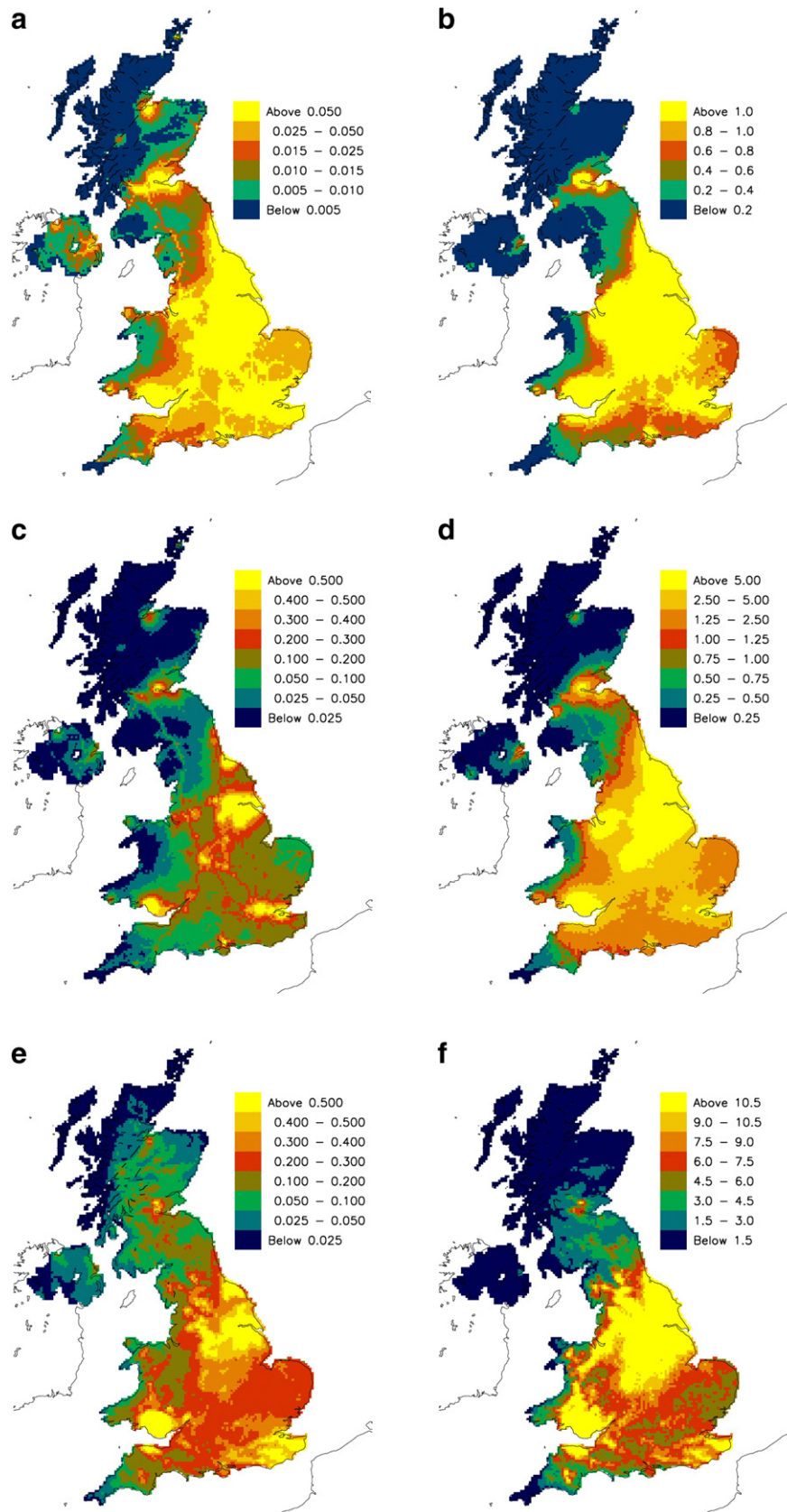
Fig. 3. (a) Modelled concentration of Cd in air (ng m^{-3}). (b) Modelled concentration of Pb in air (ng m^{-3}). (c) Modelled dry deposition of Cd (g Ha^{-1}). (d) Modelled dry deposition of Pb (g Ha^{-1}). (e) Modelled wet deposition of Cd (g Ha^{-1}). (f) Modelled wet deposition of Pb (g Ha^{-1}).
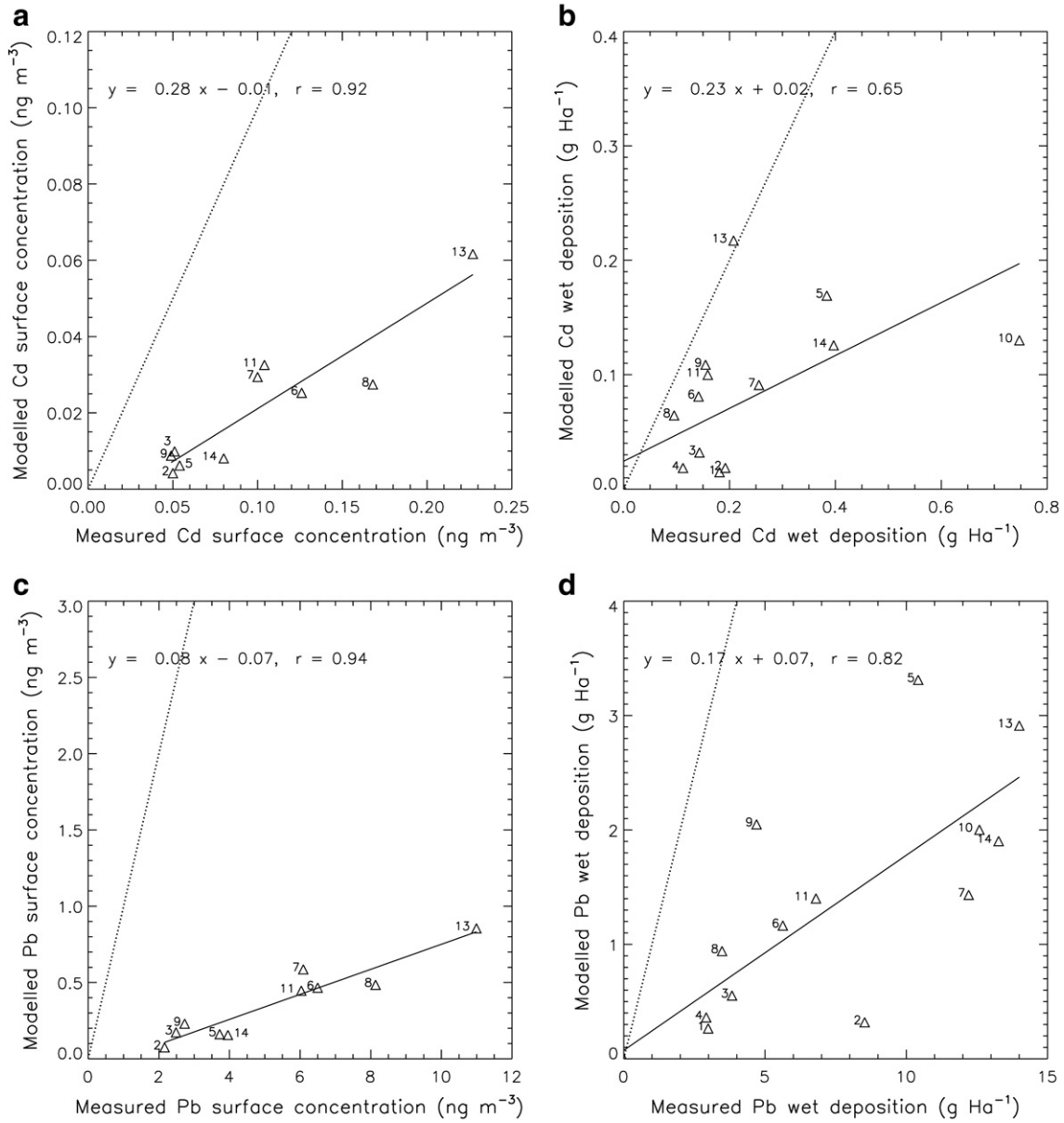
Fig. 4. (a): Correlation of modelled concentrations of Cd in air with measurements. (b): Correlation of modelled wet deposition of Cd with measurements. (c): Correlation of modelled concentrations of Pb in air with measurements. (d): Correlation of modelled wet deposition of Pb with measurements.

Table 2a
Correlation of model with measurements of concentrations in air (ng m^{-3}) according to the line of best fit y = mx + c where y represents the modelled values and x represents the measured values; r is the correlation coefficient; p-value is calculated from a p-test performed on the correlation coefficient; and NMB is the normalised mean bias. Scenario 0: no re-suspension; 1: Abbott re-suspension; and 2: EMEP re-suspension.

Metal	Slope (m)	Intercept (c)	r	p-Value	NMB	NMB	NMB
scenario	0	0	0	0	0	1	2
As	0.10	0.0	0.72	0.0055	−0.91	−0.87	–
Cd	0.28	0.01	0.92	8.5×10^{-6}	−0.79	−0.75	−0.58
Cr	0.61	−0.16	0.90	2.8×10^{-5}	−0.71	–	–
Cu	0.19	0.02	0.93	4.1×10^{-6}	−0.79	–	–
Ni	0.23	0.14	0.74	0.0038	−0.64	−0.48	–
Pb	0.08	−0.07	0.94	1.8×10^{-6}	−0.93	−0.89	−0.45
Se	1.00	−0.30	0.74	0.0038	−0.64	–	–
V	5.13	−0.30	0.87	1.1×10^{-4}	4.22	–	–
Zn	0.34	−1.07	0.96	2.0×10^{-7}	−0.77	–	–

showed no correlation with measurements. With the exception of V, all the modelled data show significant negative NMBs for both concentration and wet deposition. These results suggest that the official NAEI emission estimates are insufficient to account for observed concentrations of heavy metals by factors ranging from 2 to 10. The primary emissions can explain only 9%, 21%, 29%, 21%, 36%, 7% and 23% of measurements of air concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn, respectively, corresponding to missing emission sources of 13, 3, 24, 48, 76, 82 and 300 Mg yr^{-1}.

Sites 2, 14, 5 and 8 (Banchory, Yarner Wood, Cockley Beck and Monks Wood) show the greatest under-estimate of concentrations of Cd and Pb in air (Fig. 4a and b). Sites 1, 2, 4 and 3 (Inverpolly, Banchory, Lough Navaar and Auchencorth) show the greatest under-estimate of wet deposition (note that air Cd and Pb concentrations were not measured at sites 1 and 4). A similar pattern was observed from the analysis of correlation plots for the other heavy metals (Figs. 3.1 to 3.4, Supplementary material). Three of these sites (Banchory in Scotland, Lough

Table 2b

Correlation of model with measurements of wet deposition (g m^{-2}) for scenario 0 (no re-suspension) according to the line of best fit y = mx + c where y represents the modelled values and x represents the measured values; r is the correlation coefficient; p-value is calculated from a p-test performed on the correlation coefficient; and NMB is the normalised mean bias.

Metal	Slope	Intercept	r	p-Value	NMB
As	0.11	0.03	0.65	0.042	−0.87
Cd	0.23	0.02	0.65	0.042	−0.63
Cr	0.44	0.08	0.62	0.056	−0.48
Cu	0.20	0.13	0.65	0.042	−0.78
Ni	0.43	0.10	0.79	0.0065	−0.52
Pb	0.17	0.07	0.82	0.0037	−0.82
Se	0.04	0.74	0.07	0.85	−0.52
V	7.21	8.5	0.79	0.0065	8.49
Zn	0.32	1.6	0.54	0.11	−0.64

Navar in Northern Ireland and Cockley Beck in northern England) are remotely located in cooler, high rainfall areas of the UK where the soil is expected to be wet for much of the year and therefore re-suspension may be less significant. This spatial structure in the difference between modelled and measured air concentration and wet deposition may therefore be caused by the model under-estimating the long-range transport of heavy metals. Site 13 (Detling) is located in the drier south-eastern region of the country and, although classified as a rural site, is several km away from a major road and motorway. Whilst it may be expected that this site would be exposed to re-suspended emissions from vehicles, in practise the site shows a lower degree of under-estimation of air concentrations and wet deposition than other sites (Fig. 4a and b). Xia and Gao (2011) made measurements of heavy metal concentrations in particulate matter at three sites within 150 m of a road with heavy traffic in New Jersey, USA. The concentrations of Al, Cd, Cr, Cu, Fe and Pb along the three sites were found to decrease significantly with distance from the highway.

On average, for all the metals, wet deposition accounted for 64% of total deposition and dry deposition for 36% (Table 3). This result is in agreement with results from monitoring studies of heavy metal fluxes at a rural wetland in northwest France (Connan et al., 2013) which found that wet deposition was the dominant mechanism for transferring heavy metals (Cd, Pb, Ni, Zn) from the atmosphere to the surface. The percentage of dry deposition varied between 23% and 46% depending on the metal. A number of factors determine the balance between dry deposition and wet deposition. These include: the size distribution of particles used in the model for each metal (deposition model, Supplementary material; Allen et al., 2001), the washout coefficient for the metal (Seinfeld and Pandis, 1998), and the height of metal emissions. Metals which are emitted close to the surface, and have a size distribution weighted to the larger particles are more efficiently dry deposited, whilst higher washout coefficients by precipitation lead to greater wet deposition.

Table 3

Dry and wet modelled deposition budgets for the UK (Mg).

Metal	Dry	Wet	Total
As	2.6	5.0	7.6
Cd	1.2	1.8	3.0
Cr	8.4	14.0	22.4
Cu	22	35	57
Ni	26	33	59
Pb	24	31	55
Se	8.7	23.4	32.1
V	540	930	1470
Zn	110	360	470

3.2. Emission scenarios

Use of the official UK national atmospheric emissions in the FRAME atmospheric transport model leads to a major under-estimate when compared to measurements of air concentrations and wet deposition of all heavy metals (except vanadium). A number of possibilities should be considered which could explain this gap: underestimated primary emissions; role of re-suspension; inaccuracy in the atmospheric transport model; systematic error in measurement techniques; and underestimation of long range transport from European sources. Whilst the use of the EMEP emissions has been shown to generate good model agreement with measurements (Travnikov et al., 2012), it should be emphasised that few measurements of enrichment factors have been undertaken, and therefore, their spatial distribution remains highly uncertain.

Two scenarios with increased emissions were considered that included the representation of re-suspension of heavy metals by wind (discussed above). The inclusion of the re-suspension estimates in simulation 1 does lead to an improvement in the comparison with measurements. The NMB for correlation with measurements of concentration of metals in air was found to change from −0.91, −0.79, −0.64 and −0.93 for the baseline scenario to −0.87, −0.75, −0.48 and −0.89 for scenario 1 for As, Cd, Ni, and Pb respectively. Whilst this marks a minor improvement in the comparison with measurements, these estimates of metal emissions from re-suspension are clearly insufficient to close the gap between the modelled concentrations and the measurements. The concentrations of metals in soil, used for these emission estimates, were taken from an integrated soil core concentration from the top 15 cm. This is likely to have led to an underestimate of the true re-suspension which is determined by metal concentrations in the soil surface. However, few measurements are available of such concentrations. The correlation with measurements of metal concentrations in air was found to improve for As and Cd and deteriorate for Ni and Pb when re-suspension was included. Abbott (2008) noted a good correlation with measurements when only re-suspended concentrations were used with an atmospheric dispersion model.

Scenario 2 considered estimates of total re-suspended emissions for Cd and Pb from the UK based on EMEP values. These are significantly higher than those of Abbott (2008) by factors of 6 and 10 for Cd and Pb respectively. Although these estimates of re-suspension adopt a similar parameterisation to that of Abbott (2008), a significant difference is that the estimates of surface soil concentrations included the use of enrichment factors in the EMEP calculations in setting the metal concentrations in the surface soil layer. This scenario assumes that total re-suspension of Cd (3.1 Mg) is similar to the mass of primary emissions (3.6 Mg; Tables 2a and 2b). With this scenario, the NMB for correlation with measurements of Cd concentration in air is significantly improved (from −0.79 to −0.58) but concentrations, as well as wet deposition remain under-estimated. For Pb, the large value of estimated re-suspended mass (469 Mg) compared to primary emissions (88 Mg), leads to a major improvement in NMB for air concentration from −0.93 to −0.45 (Tables 2a and 2b) but a deterioration in the correlation coefficient (from r = 0.94 to r = 0.59). Whilst the use of the EMEP emissions has been shown in independent studies to generate good model agreement with measurements (Travnikov et al., 2012), it should be emphasised that few measurements of enrichment factors have been undertaken and therefore their spatial distribution remains highly uncertain.

The possibility of missing or under-estimated primary emission sources must also be considered as a factor contributing to the underestimate in modelled heavy metal concentrations. The sources contributing to anthropogenic emissions of heavy metals vary significantly depending on the metal. For some metals the most important sources are the combustion of coal in the power generating industry and the metallurgy industry. In the model emission input data these large point sources from tall stacks are treated individually with a plume

rise model to determine an effective stack height for emissions. The metals which have emissions dominated by point source emissions are: Pb, Se, Cd, and Cr with the point source emissions comprising 74%, 65%, 57% and 52% of the total UK emissions, respectively. The large uncertainty of metal content in coal used in small point sources as well as the possibility of missing fugitive emissions from these sources could partially account for the model under-estimates. Road transport makes a significant contribution to primary emissions for certain metals. These include V, Zn, and Se, with emissions from road transport comprising 59%, 21%, and 21% of total emissions from the UK for the year 2006. The high level of uncertainty in emissions from this source may also be a factor contributing to the model over-estimates of V concentration in air and precipitation. In contrast, however, Zn concentrations are under-estimated, whilst there is a notable lack of correlation of Se with measurements of wet deposition (Tables 2a and 2b).

A source of over-estimation of wet deposition of heavy metals can occur in the national monitoring network due to the use of bulk collectors which may be contaminated by dry deposition of particulates to the collector surface. This may account for an over-estimate of approximately 30% in wet deposition (RoTAP, 2012).

Estimates of emissions of heavy metals from sea in the vicinity of the UK have been calculated using the information on metal concentrations in sea water (Floor Anthoni, 2006) and sea salt emission data (Werner et al., 2011). Generally metal concentrations in sea water are relatively low, that is why emissions from marine sources were found to be small relative to anthropogenic sources and (in agreement with the results of Travnikov et al., 2012 for other European stations) would make only a small contribution to air concentrations.

The model calculates a budget of the sources (import and emissions) and sinks (deposition and export) along each trajectory over the UK. A summary calculation for all trajectories demonstrated that, whilst the UK deposition budget is dominated by UK sources (65–75%), more than half of UK emissions are exported for all metals. Therefore, the UK is shown to be a net exporter of atmospheric trace metal pollutants, strengthening the case for the investigation of the mass difference between known (reported) emissions and measured deposition. An under-estimate of imported material in the European model simulation could also contribute to the under-estimated air concentrations and deposition in the UK. In general, similar issues regarding uncertainty in re-suspended material and in primary emissions in the UK are also relevant to the contribution from European import.

3.3. Annual variation of metal concentrations in air

Analysis of data from weekly particulate sampling during 2006 was made for both a remote site in northern Scotland (Banchory) and a site in south-east England located near to both European sources and locally to major roads (Detling). The analysis revealed no clear evidence of a seasonal cycle in measured metal concentrations in air (Supplementary material, Figs. 2.1–2.6). However episodic peaks of high concentrations were evident at both stations during the period 12 May–19 June 2006. Back trajectories were calculated with the HYSPLIT trajectory model (Draxler and Rolph, 2013). Analysis of trajectories at the beginning of this period from Detling shows that the air mass originated from northern central Europe, a region of high population density with significant emissions from both industry and vehicles. The flow of air to the UK is most frequently from the south-west (Fig. 1, Supplementary material) under conditions of much cleaner air with a maritime origin.

An alternative possibility is that short term peaks in heavy metal concentrations in air could be caused by incidents of re-suspension of surface soil. Analysis of boundary layer wind speeds measured by radio-sonde ascents in the vicinity of Detling (Dore et al., 2006) shows that the average wind speed during the period of high measured metal concentrations in air was 11.0 m s^{-1}, only marginally higher than the annual average for the year 2006 of 9.9 ms^{-1}. The precipitation measured at Detling for the four weeks from 12 May to 9 June 2006 was 83 mm, somewhat higher than the monthly average for 2006 of 61 mm. The meteorological data therefore does not suggest the presence of dry windy conditions which would be required to generate a high level of re-suspension of particulates from surface soil. A strong correlation in the signals for Cd and Pb concentrations at both stations can be seen (with correlation coefficient r = 0.92 for Detling). Pb concentration measurements at Detling were also well correlated with As (r = 0.97) and Zn (r = 0.96).

4. Conclusion

The detailed UK heavy metal monitoring network (including measurements of air concentrations at ten sites and wet deposition at 13 sites) provided a good opportunity to validate an atmospheric chemical transport model using wet deposition and air concentration observations using the official national emission estimates for 9 different heavy metals. The comparison of the measured wet deposition and air concentrations with the model showed that whilst good correlation was obtained (r of 0.92 and 0.94 for Cd and Pb concentrations in air respectively) all metal concentrations except for V were significantly underestimated by the model, by factors varying from approximately 2 to 10.

Inclusion of the estimates of the emissions of heavy metals caused by wind-driven re-suspension led to an improved agreement of the model with measurements of metal concentrations in air. The NMB changed from −0.93 to −0.45 for Pb and from −0.79 to −0.58 for Cd for re-suspension scenario 2. However, the magnitude of this contribution to the concentrations of heavy metal concentrations in air remains uncertain due to an absence of measurements of metal concentrations in the re-suspended surface dust layer. Estimates of metal re-suspension in the UK based on either measurements of concentrations in soil cores or inferred using enhancement factors gave very different results. It is likely that a combination of missing or under-estimated sources of primary metal emissions combined with the re-suspension of deposited material from historic emissions is responsible for the underestimated model concentrations in air and precipitation. Comparison with measurements also suggests that there is some under-estimate of the long range transport of particulates containing heavy metals by the model. Analysis of the chemical composition of road-side dust and surface agricultural soil would be useful in establishing the contribution to metal emissions from traffic-induced re-suspension in urban areas and wind-induced re-suspension in rural areas.

It is notable that the greatest under-estimate in modelled concentrations in air and precipitation was for Pb, the metal for which the reduction in primary emissions has been the greatest during the last two decades. This is further evidence that the historical legacy of higher heavy metal emissions can explain the under-estimate in modelled concentrations.

A relatively simple atmospheric transport model using annually averaged meteorology was used in this study. Whilst the model was able to achieve a reasonable correlation with annually averaged metal concentrations in air, it is unable to represent the episodic nature of meteorological events leading to high deposition events. Application of more complex Eulerian models, which include dynamic meteorology, may be useful since they can simulate episodic re-suspension of heavy metals during high winds.

Conflict of interest

The authors declare that there are no conflicts of interest.

(ARL) for the provision of the HYSPLIT transport and dispersion model and website.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.scitotenv.2014.02.001.

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