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

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H I G H L I G H T S

- 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.

A R T I C L E I N F O

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A B S T R A C T

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.

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).

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Estimates in the United Kingdom (UK) have indicated areas of both managed and unmanaged woodland where critical load exceedances occur for 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 $year^{-1}$. 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

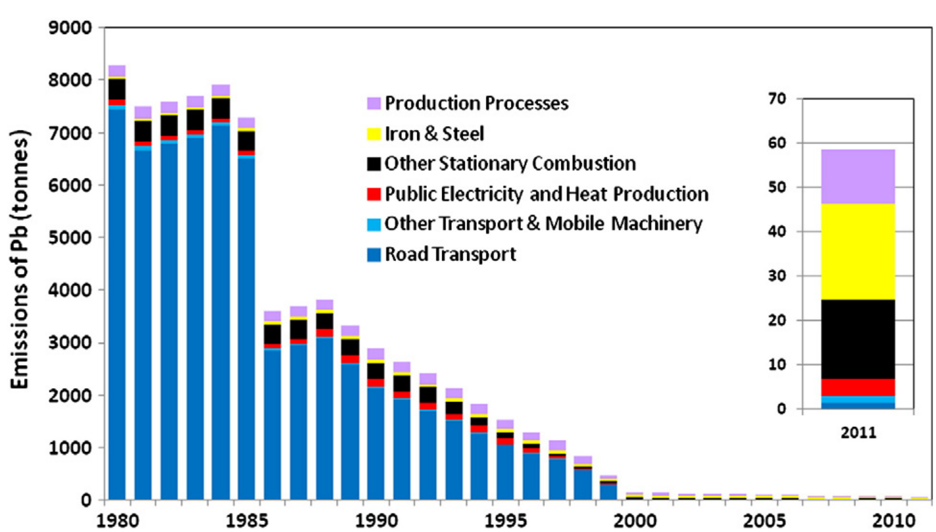

Fig. 1. Trend in emissions of Pb from the UK.