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# Using metal ratios to detect emissions from municipal waste incinerators in ambient air pollution data

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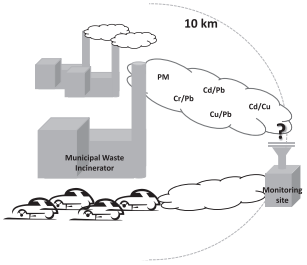
## HIGHLIGHTS

- Metal ratios used to fingerprint emissions from UK municipal waste incinerators.
- Weekly ambient metals data and high-resolved met data were used.
- No evidence of incinerator emissions within 10 km around four installations.
- Ambient metal ratios agreeing with emissions in sites within 10 km of two plants.
- Plume grounding detected for less than 0.2% of the time, contributing little to PM.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This study aimed to fingerprint emissions from six municipal waste incinerators (MWIs) and then test if these fingerprint ratios could be found in ambient air samples. Stack emissions tests from MWIs comprised As, Cd, Cr, Cu, Pb, Mn, Ni, V and Hg. Those pairs of metals showing good correlation ($R > 0.75$) were taken as tracers of MWI emissions and ratios calculated: Cu/Pb; Cd/Pb; Cd/Cu and Cr/Pb. Emissions ratios from MWIs differed significantly from those in ambient rural locations and those close to traffic. In order to identify MWI emissions in ambient air two analysis tests were carried out. The first, aimed to explore if MWI emissions dominate the ambient concentrations. The mean ambient ratio of each of the four metal ratios were calculated for six ambient sampling sites within 10 km from a MWI under stable meteorological conditions when the wind blew from the direction of the incinerator. Under these meteorological conditions ambient Cd/Pb was within the range of MWI emissions at one location, two monitoring sites measured mean Cr/Pb ratios representative of the MWI emissions and the four sites measured values of Cu/Pb within the range of MWI emissions. No ambient measurements had mean Cd/Cu ratios within the MWI values. Even though MWI was not the main source determining the ambient metal ratios, possible occasional plume grounding might have occurred. The second test then examined possible plume grounding by identifying the periods when all metal ratios differed from rural and traffic

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values at the same time and were consistent with MWI emissions. Metal ratios consistent with MWI emissions were found in ambient air within 10 km of one MWI for about 0.2% of study period. Emissions consistent with a second MWI were similarly detected at two ambient measurement sites about 0.1% and 0.02% of the time. Where plume grounding was detected, the maximum annual mean particulate matter (PM) from the MWI was estimated to be 0.03 μg $m^{-3}$ to 0.12 μg $m^{-3}$; 2–3 orders of magnitude smaller than background ambient $PM_{10}$ concentrations. Ambient concentrations of Cr increased by 1.6–3.0 times when MWI emissions were detected. From our analysis we found no evidence of incinerator emissions in ambient metal concentrations around four UK MWIs. The six UK MWIs studied contributed little to ambient $PM_{10}$ concentrations.



## 1. Introduction

Municipal waste consists of a mix of combustible and non-combustible materials such as paper, plastic, food waste, glass, defunct household appliances and other non-hazardous materials (EMEP- EEA, 2013) that might vary by time and by city, town or village. The use of Municipal Solid Waste Incinerators (MWIs) has been increasing in the United Kingdom (UK) as a means to treat municipal waste due to European Union (EU) restrictions on the use of landfills. Modern European MWIs have operated under the EU Waste Incineration Directive (EU-WID) 2000/76/EC which set limits on emissions for heavy metals, dioxins and furans, carbon monoxide, dust, total organic carbon, hydrogen chloride, hydrogen fluoride, sulphur dioxide and nitrogen oxides. The EU-WID came into operation in 2002 for new MWIs and applied to all existent ones from 2005. The later Directive on Industrial Emissions (IED) (2010/75/EU) merged seven directives, including the EU-WID, into one piece of legislation, in order to harmonise the various strands of industrial regulation. The implementation of the IED in the UK was set to 2013 for new installations and 2014 for the existing ones.

Despite the strict limits on emissions, there is still considerable public concern about possible health effects associated with incineration. Some epidemiological studies have reported significant positive relationships with broad groups of congenital anomalies in populations living near MWIs. However, the results from these studies remain inconclusive due to limitations on exposure assessment, possible confounding risk factors and lack of statistical power (Ashworth et al., 2014).

Previous studies found no evidence that incinerators had a major or modest impact on particulate concentrations either in the United States (Shy et al., 1995) or in the UK (Ashworth et al., 2013). Despite this, older MWI have been found to be a source of heavy metals to the atmosphere (Sakata et al., 2000; Hu et al., 2003; Moffet et al., 2008) and high concentrations could be found in soil and vegetation samples in the vicinities of MWIs (Morselli et al., 2002).

In this study we aimed to fingerprint emissions from UK MWIs by identifying characteristic metal emission ratios and then test if these fingerprint ratios can be found in ambient air samples around MWI. Our analysis was part of a UK Public Health England (PHE) project investigating birth outcomes in the population living around (10 km distance) MWIs in England, Wales and Scotland.

## 2. Methods

### 2.1. Metals emissions from MWI and ambient concentrations

Quarterly stack emissions tests from MWIs were made available by the UK Environment Agency (EA). Particulate matter was sampled isokinetically from each MWI stack onto quartz filters. Following acid digestion with a mixture of nitric and hydrofluoric acid, stack samples were analysed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) according to EN 14385:2004. This method is validated against matrix reference material BCR-037. Samples were analysed for Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Manganese (Mn), Nickel (Ni), Vanadium (V) and Mercury (Hg). Emissions data were available from 2003 until 2010. For most of the samples the metals concentrations were aggregated for reporting purposes (EU-WID compliance) and the concentration for each metal was not available. Only 52 tests among all the UK MWI had detailed concentration values for each metal and these were used for fingerprinting. This detailed metals emissions data came from 10 (of a total of 22) UK MWIs: Crymlyn Burrows, Chineham, Coventry, SELCHP, Dudley, Bolton, Stockton-on-Tees, Stroke-on-Trent, Tyseley and Wolverhampton.

Ambient concentrations of As, Cd, Cr, Cu, Iron (Fe), Hg, Mn, Ni, Pb, Platinum (Pt), V and Zinc (Zn) in $PM_{10}$ (particulate matter with aerodynamic diameter <10 μm) were measured by sampling onto a filter (cellulose ester) for weekly periods using a Partisol 2000 sampler according to EN12341:2014. The ambient air filters were digested in a mixture of nitric acid and hydrogen peroxide in a microwave oven, according to EN 14902:2005, and followed by analysis by ICP-MS. This procedure was validated by the digestion and measurement of suitable matrix reference materials, such as NIST SRM 1648a – urban particulate matter. The recoveries of all relevant metals were consistent with the certified values within the uncertainty of the measurements. The analysis was undertaken by the National Physical Laboratory (NPL) for sites belonging to the urban and industrial metals network; and by the Centre for Ecology and Hydrology (CEH) for the rural metals network. These data are available as monthly means at http://uk-air.defra.gov.uk/.

Due to high sampling temperatures the stack filters are quartz and a hydrofluoric (HF) acid matrix is required to digest them to ensure that any deeply trapped PM is recovered, and to perform an appropriate blank correction. By contrast only nitric acid digestion is needed to fully digest cellulose ester filters used for ambient measurements and HF digestion is not required. Kulkarni et al. (2007) underlined the importance of HF digest for ambient PM samples with high silica mineral content. This was unlikely to be an issue in our study since large mineral particle emissions from the MWI would have been preferentially trapped in the bag filtration system that have higher efficiency for larger particles (Buonanno et al., 2009; Ashworth et al., 2013) and mineral dust episodes such as those from the Sahara are rare in the UK (Ryall et al., 2002).

In order to fingerprint emissions from MWIs, the correlation coefficient between metals was calculated from the stack measurements. Those pairs of metals showing good correlation ($R > 0.75$) across all MWI sites were taken as potential tracers for MWI emissions. Ratios were then calculated by means of Reduced Major Axis (RMA) regression (Ayres, 2001; Warton et al., 2006). Due to insufficient samples it was not possible to create fingerprint

profiles for individual MWI.

Ratios for the same metals were calculated from ambient samples from the rural network (n = 579 samples from 11 sites in 2010) and from Cromwell Road site in London as representative of metal ratios from traffic sources (data from 2004 to 2011, n = 311).

### 2.2. Detecting MWI emissions in ambient air

Six metals sampling sites were located within 10 km of a MWI in the UK (Fig. 1; Table 1) with weekly samples of ambient metals concentrations. Most of the ambient metals sampling sites were located close to heavily industrialized areas. The sampling sites Walsall Bilston Lane (Background metals site) and Walsall Centre (Industrial metals site), near the Wolverhampton and Dudley MWIs respectively, had multiple industries related to metals refining and finishing located nearby. Although the Redcar Normanby site was an urban background site, the same wind direction towards the Stockton-on-Tees MWI included industrial premises such as chemical, plastics and acrylics manufacturers and an oil refinery. London Westminster and Sheffield Centre were urban background sites located near traffic. London Westminster site had no industrial sources nearby. NE of the Sheffield Centre metals site (in the same direction as the MWI) there were several industries producing industrial alloys, cast products and steel. The Swansea Morriston sampling site was located just off a main road running SW – NE. The Crymlyn Burrows MWI was located SE of the metals site with the UK's largest steel production plant (Port Talbot) located ~3 km to the east of the MWI.

The analysis period for each MWI was determined by the operational times for each MWI and the coincidental availability of ambient metal measurements (Table 1).

To assess if emissions from MWIs were detected at the metals sites, two sets of analysis were undertaken: the first aimed to explore if MWI emissions dominate the ambient concentrations; the second tested if all four ratios differed from rural or traffic values at the same time and were consistent with MWI emissions. For the first analysis, bivariate polar plots (BPP) of those metal ratios that were identified as good tracers of MWI emissions were calculated using the Openair R-package (Carslaw and Ropkins, 2012). BPP determine the mean value of an ambient metals ratio against wind direction and wind speed. BPP have been used previously in receptor analysis to identify the location of potential sources of air pollution (Carslaw, 2005). For the second analysis, the Polar Annulus (PA) function of the Openair R-package was calculated. PA plots show the time series of the measured ambient ratio by wind direction.

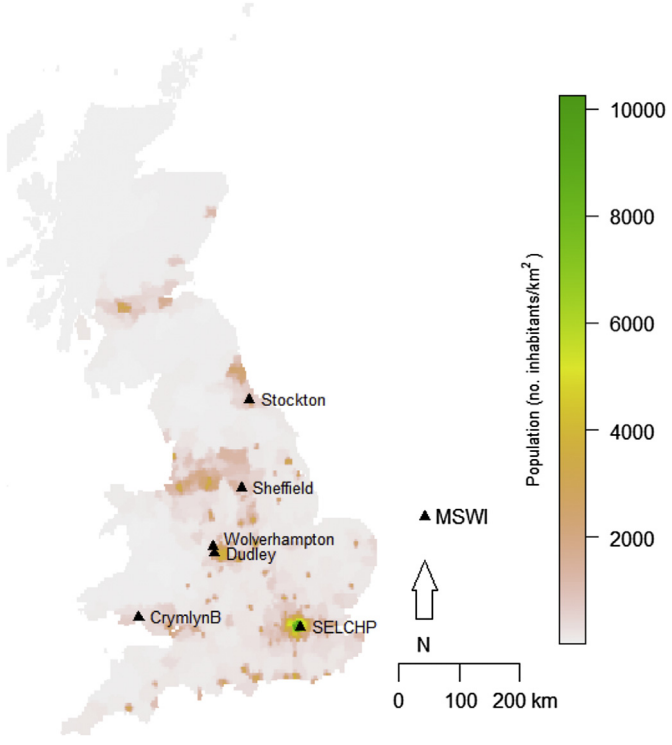


**Fig. 1.** Map of the UK MWI included in this study. Base map: population density in 2000 (CIESIN, 2011).

Previous studies have successfully determined the sources and their contribution to pollutant concentrations measured at low-frequency (e.g. daily, weekly). Different techniques have been proposed in the literature based on the frequency of the wind for a given wind sector (e.g. Cosemans et al., 2008; Godri et al., 2010). Here, high resolution (hourly) meteorological measurements were used to compute BPP and PA. The same weekly metals concentration was assigned to each hourly measurement of wind speed and direction.

Meteorological data were obtained from weather stations within 30 km of a MWI and processed using the Atmospheric Dispersion Modelling System Urban (ADMS-Urban). ADMS-Urban uses meteorological variables including wind speed, wind direction, temperature and cloud cover to calculate parameters that are used in the dispersion algorithms such as boundary layer height, Monin-Obukhov length, etc. The meteorological input data was extracted from the closest weather station following the MetOffice quality standards. Missing cloud cover records were completed using data from the nearest met station with 90% completeness where necessary.

During unstable meteorological conditions buoyant motions are enhanced causing rapid dispersion of emissions. Under poor mixing (stable) conditions MWI plume will mix less with the surrounding air keeping its chemical composition. Highest concentrations attributable to the MWI at the ambient metal sites are therefore expected under stable atmospheric conditions. For this reason, analysis of ambient data was focused on the times when stable atmospheric conditions were met.

Atmospheric stability conditions were defined as:

$$z^{*}\mathrm{L} = z^{*}1/\mathrm{L_{MO}}$$

where $z$ is the boundary layer height and $\mathrm{L_{MO}}$ is the Monin-Obukhov length. Stability conditions were classified as unstable for $-1000 < z^{*}\mathrm{L_{MO}} \leq -0.2$; neutral for $-0.2 < z^{*}\mathrm{L_{MO}} \leq -0.2$; and stable for $0.2 < z^{*}\mathrm{L_{MO}} \leq 50$.

During stable conditions an elevated point source (such as the MWI chimney) may be above the boundary layer height ($z$). At these times emissions can be released above the temperature inversion and hence not influence ground-level concentrations. With the exception of SELCHP MWI, $z$ was lower than the MWI chimneys at all times. At SELCHP, the stack was above the boundary layer for 22% of the hours when stable conditions were met.

$\mathrm{NO_X}$, $\mathrm{SO_2}$ and PM emissions reported by the MWI operators were used to assess the days when the plants were operating for inclusion in the BPP and PA calculations. The total analysis period covered 11,437 days.

In order to test our assumptions about higher attributable MWI emissions under stable conditions and whether emissions from stacks could be identified using weekly samples instead of highly-resolved data (i.e. hourly concentrations), two sensitivity tests were undertaken. These used air quality data from the Harwell monitoring site (1.3265°W, 51.5711°N). Harwell is a rural monitoring site

**Table 1**
List of MWI and ambient metals sites (AMS) within 10 km.

| MWI | Stack height (m) | Start year | Median PM emissions (kg day$^{-1}$) | Ambient metals site (AMS) | Type of AMS | Distance MWI to AMS (km) | Analysis period (no. days) |
|---|---|---|---|---|---|---|---|
| Crymlyn Burrows | 40 | 2003 | 0.7 | Swansea Morriston | Traffic | 5.2 | 847 |
| Dudley | 47 | 1998 | 1.8 | Walsall Bilston Lane | Background | 9.7 | 1578 |
| Dudley | 47 | 1998 | 1.8 | Walsall Centre | Industrial | 10.3 | 1515 |
| Stockton-on-Tees | 70 | 1998 | 4.5 | Redcar Normanby | Background | 9.1 | 745 |
| Sheffield | 76 | 1990 | 0.7 | Sheffield Centre | Background | 1.9 | 910 |
| SELCHP | 100 | 1994 | 14.8 | London Westminster | Background | 6.0 | 1889 |
| Wolverhampton | 76 | 1998 | 3.0 | Walsall Bilston Lane | Background | 5.8 | 1996 |
| Wolverhampton | 76 | 1998 | 3.0 | Walsall Centre | Industrial | 8.1 | 1957 |

belonging to the UK Automatic Urban and Rural Network (AURN) located 7.3 km from the coal-fired Didcot Power Station, a well known source of atmospheric $SO_2$ (McGonigle et al., 2004; Charron et al., 2005). The first test was based on BPP for $SO_2$ concentrations under unstable, neutral and stable conditions. BPP for $SO_2$ concentrations under stable conditions showed higher concentrations in the direction of the Power Station compared to those measured under unstable conditions (Supplementary Figure A1). Moreover, under unstable conditions, the source of $SO_2$ in the direction of the Power Station was spread over a wider range of wind sectors and wind speeds due to enhanced atmospheric mixing conditions. In the second test, BPP and PA for weekly $SO_2$ concentrations were compared to those using hourly data. Under stable conditions, using weekly mean $SO_2$ with hourly resolved meteorological data, BBP analysis located the same source of $SO_2$ as using hourly data (Supplementary Figure A2). The PA time series of the trends of the $SO_2$ source computed from the hourly and weekly datasets were also similar (Supplementary Figure A3). The use of weekly means combined with high-resolved meteorological data can therefore be confidently used to detect point sources of atmospheric pollution and to assess the temporal changes in their intensity.

### 2.3. Quantification of ambient MWI PM using a single metals tracer

Analysis of ambient metal ratios can be used to detect MWI emissions but not quantify their impacts on ambient PM concentrations. To quantify Particulate Matter (PM) at receptor locations the ratio of PM/metal emitted by the MWIs was calculated from stack emissions tests by RMA regression.

ADMS-Urban was also used to model daily mean PM concentrations at post-code resolution for each MWI following the methods detailed in Ashworth et al. (2013). Metals concentrations were then estimated at the receptor (ambient metal site) based on modelled PM and calculated stack emission ratios.

## 3. Results

### 3.1. Metals emissions from MWI

The MWI listed in Table 1 were installations that were adapted to the EU-WID except Crymlyn Burrows which was commissioned following EU-WID. Results from MWI stack tests are summarized in Table 2. The ambient concentrations measured at rural metals sites are also given for comparison. Sorted from largest to smallest emissions concentrations (median values), MWI were emitters of Pb > Cr > Ni > Mn > Cu > Cd > As > V. When compared to the median rural background concentrations, MWI emissions contained greater quantities of Cr ($41 \times 10^3$ times larger than rural concentrations), Cd ($22 \times 10^3$ times larger), Ni ($13 \times 10^3$), Pb ($5 \times 10^3$) and Cu ($3 \times 10^3$).

Emissions of Cu–Pb showed a good correlation ($R = 0.91$, $N = 18$, $p < 0.001$) followed by Cd/Pb ($R = 0.86$, $N = 19$, $p < 0.001$), Cd/Cu ($R = 0.77$, $N = 50$, $p < 0.001$) and Cr/Pb ($R = 0.68$, $N = 19$, $p < 0.05$) (Table 3). We therefore selected the emissions ratios of these four pairs of metals as potential tracers for MWI emissions. Additionally their values also differed from those found in rural and traffic locations (Table 4). However, these four ratios represented only three pieces of independent information since (Cd/Pb)/(Cd/Cu) = (Cu/Pb).

Since Cr and Cd were the two metals with the greatest enrichment factors (Table 2), ratios of PM/Cd and PM/Cr were calculated from emissions samples. Emissions rates of PM/Cd showed a good correlation coefficient ($R = 0.94$, $p < 0.01$, $n = 34$) while PM/Cr was weaker ($R = 0.41$, $p < 0.05$, $n = 33$). Cd therefore was therefore additionally selected as tracer for PM emitted by MWI using a ratio of 6724 [5999–7647, 2σ] mgPM (mgCd)$^{-1}$ (Table 5).

### 3.2. Detecting MWI emissions in ambient air

Fig. 2a shows an example of BPP for the Cr/Pb ratio calculated using weekly samples from the Redcar Normanby site, 9.1 km from the Stockton-on-Tees incinerator. Values of Cr/Pb fell within the range of MWI emissions for wind speeds higher than 10 m s$^{-1}$ when the wind blew from the direction of the incinerator (Fig. 2b). For wind speeds lower than 10 m s$^{-1}$, values of Cr/Pb ranged between that found in rural areas and the ratio expected from traffic sources.

Ambient ratios measured at the metal sites from the wind direction of each MWI were compared with the values from MWI stacks (Table 6). With the sole exception of the Walsall Centre sampling site in the direction of Wolverhampton incinerator, mean Cd/Pb, mean Cd/Cu and mean Cd/Pb were not within the range of MWI emissions for any of the ambient measurements near a MWI. However, near the Dudley, Stockton-on-Tees and Wolverhampton MWI ambient ratios were above the rural background values for Cd/Cu; and above the traffic values for Cd/Pb near Stockton-on-Tees and Wolverhampton. The metals sites near Stockton-on-Tees and Sheffield measured Cr/Pb ratios representative of the MWI emissions. The values of the Cu/Pb ratio near Dudley, Stockton-on-Tees, Sheffield and Wolverhampton fell within the range of values representative of the MWI emissions.

From analysis of the mean ambient metal ratios when the wind blew from the direction of an incinerator it was clear that the MWIs were not the main source of the tracer metals. Only Redcar Normanby measured mean ratios within the MWI emissions range (Cr/Pb and Cu/Pb) and different from the rural (Cd/Cu) and traffic values (Cd/Pb). However, emissions from MWI might influence the burden of metals in the area and grounding of MWI plume might have occasionally occurred. This would lead to a mixture of sources on a weekly filter producing a ratio that was between rural conditions and the incinerator emissions. Fig. 3 shows the time series of the Cr/

**Table 2**
Minimum, mean and maximum metal concentrations from MWI stack tests from 2003 to 2010. Ambient concentrations measured at rural metals sites in 2010 are also shown.

| | MWI stack emissions (2003–2010) | | | | Ambient rural concentration (2010) | | | |
|---|---|---|---|---|---|---|---|---|
| Metal | Min (μg m$^{-3}$) | Median (μg m$^{-3}$) | Max (μg m$^{-3}$) | *N* | Min (ng m$^{-3}$) | Median (ng m$^{-3}$) | Max (ng m$^{-3}$) | *N* |
| As | 0.00 | 0.85 | 97.00 | 50 | 0.05 | 0.40 | 13.6 | 579 |
| Cd | 0.00 | 1.30 | 26.50 | 52 | 0.01 | 0.06 | 2.05 | 579 |
| Cr | 0.00 | 10.60 | 94.00 | 51 | 0.24 | 0.26 | 7.06 | 579 |
| Cu | 1.00 | 6.10 | 160.00 | 50 | 0.12 | 1.98 | 60.3 | 579 |
| Pb | 0.00 | 16.00 | 200.00 | 19 | 0.36 | 3.38 | 184 | 579 |
| Mn | 0.40 | 6.30 | 92.30 | 52 | 0.04 | 1.55 | 52.1 | 579 |
| Ni | 0.00 | 6.80 | 177.50 | 49 | 0.06 | 0.52 | 9.74 | 579 |
| V | 0.00 | 0.75 | 12.20 | 49 | 0.12 | 0.74 | 11.2 | 579 |

**Table 3**
Correlation coefficients between the metals emitted by the MWI in the UK from 2003 to 2010.

| | As | Cd | Cr | Cu | Pb | Mn | Ni | V |
|---|---|---|---|---|---|---|---|---|
| As | 1 | | | | | | | |
| Cd | −0.05 | 1 | | | | | | |
| Cr | 0.08 | 0.36 | 1 | | | | | |
| Cu | 0.00 | **0.77** | 0.57 | 1 | | | | |
| Pb | 0.03 | **0.86** | **0.68** | **0.91** | 1 | | | |
| Mn | 0.02 | 0.42 | 0.13 | 0.39 | 0.42 | 1 | | |
| Ni | −0.06 | 0.06 | 0.03 | 0.06 | −0.04 | 0.24 | 1 | |
| V | 0.11 | 0.40 | 0.02 | 0.20 | −0.05 | 0.42 | 0.05 | 1 |

Pb ratios measured at the Swansea Morriston metals site when the wind blew from Crymlyn Burrows MWI. Despite the Cr/Pb mean ratio being between the rural and traffic values (Table 6), some of the measured ratios measured fell within the MWI emissions range (Fig. 3).

Most of the MWI are located in areas of diverse industrial sources which could confound the analysis. Even though an ambient metal ratio was within the range of MWI emissions (Fig. 3), we could not with certainty attribute ambient metals concentrations to direct emissions from MWIs. It was clearly not possible to fingerprint all of the potential emissions sources. We therefore considered the time series of the four ratios measured at each site to determine whether all the metal ratios were consistent with MWI emissions or were different from rural or traffic values at the same time. Fig. 4 shows the time series of the four metal ratios measured at Redcar Normanby from the direction of the Stockton-on-Tees incinerator. Measurements of Cr/Pb were within the range of MWI emissions on three occasions and these were coincidental

**Table 4**
Mean and 95% confidence interval of the metals ratio values representative of MWI emissions, ambient rural and ambient traffic locations.

| Metals ratio | MWI (mean ± 2σ) | Rural (mean ± 2σ) | Traffic (mean ± 2σ) |
|---|---|---|---|
| Cd/Cu | 0.14 [0.12–0.17] | (0.26 [0.24–0.28])·10$^{-1}$ | (0.07 [0.06–0.08])·10$^{-1}$ |
| Cd/Pb | 0.08 [0.06–0.10] | (1.31 [1.27–1.35])·10$^{-2}$ | (0.17 [0.16–0.18])·10$^{-1}$ |
| Cr/Pb | 0.56 [0.38–0.75] | 0.13 [0.12–0.14] | 0.28 [0.25–0.31] |
| Cu/Pb | 0.83 [0.67–0.99] | 0.51 [0.47–0.54] | 2.38 [2.14–2.63] |

**Table 5**
Mean and 95% confidence interval of the $PM_{10}$/Cd and $PM_{10}$/Cr ratios representative of MWI emissions.

| | Cd | Cr |
|---|---|---|
| $PM_{10}$/metal (mean ± 2σ) | 6724 [5999–7647] | 1708 [1166–2249] |
| R | 0.94 | 0.41 |
| *N* | 34 | 33 |

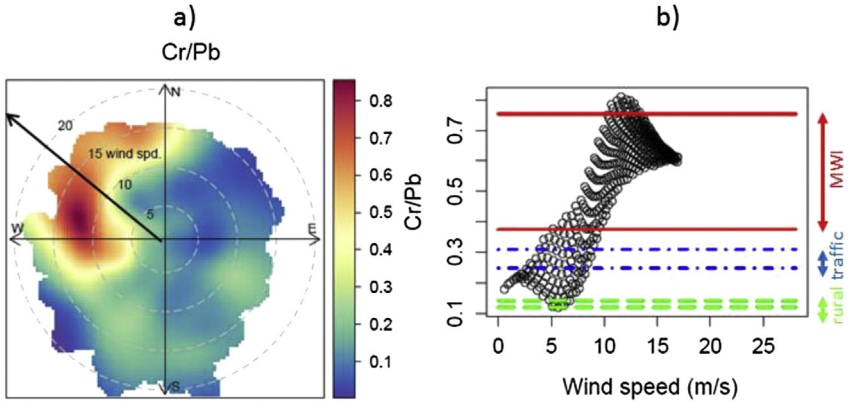


**Fig. 2.** (a) BPP for the Cr/Pb ratio measured at Redcar Normanby metals site under stable atmospheric conditions. Radially wind direction is plotted from north (N). The concentric lines indicate increasing intensity of the wind speed and the shading shows the mean ratio value. The arrow indicates the direction where the Stockton-on-Tees MWI is located. (b) Distribution of the ratio values against wind speed for the direction where the Stockton-on-Tees MWI is located. Solid red horizontal lines indicate the range of MWI emissions for the Cr/Pb ratio; green and blue dashed lines indicate the range for the rural and traffic, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 6**
Minimum and maximum ambient values for the four metal ratios measured in the ambient metals sites near a MWI when the wind blew from the incinerator (30° sectors). Numbers in italics indicate ratios that are different from rural or traffic ratios. * indicates ratios were within the MWI emissions representative values.

| Metals site | MWI | Cd/Cu | Cd/Pb | Cr/Pb | Cu/Pb |
|---|---|---|---|---|---|
| Swansea Morriston | Crymlyn Burrows | 0.01–0.02 | 0.01–0.02 | 0.03–0.27 | 1.21–1.79 |
| Walsall Bilston Lane | Dudley | *0.04–0.06* | *0.03–0.06* | 0.03–0.10 | 0.73–1.47* |
| Walsall Centre | Dudley | *0.02–0.05* | *0.02–0.04* | 0.08–0.17 | 0.70–0.93* |
| Redcar Normanby | Stockton-on-Tees | *0.03–0.05* | *0.02–0.02* | *0.12–0.81** | 0.49–0.82* |
| Sheffield Centre | Sheffield | 0.01–0.02 | 0.01–0.02 | *0.02–0.51** | 0.89–1.93* |
| London Westminster | SELCHP | 0.01–0.02 | 0.01–0.03 | 0.14–0.34 | 1.32–1.80 |
| Walsall Bilston Lane | Wolverhampton | *0.03–0.06* | *0.04–0.06* | 0.06–0.19 | 0.78–1.91* |
| Walsall Centre | Wolverhampton | *0.02–0.10* | *0.02–0.08** | 0.08–0.20 | 0.65–0.99* |

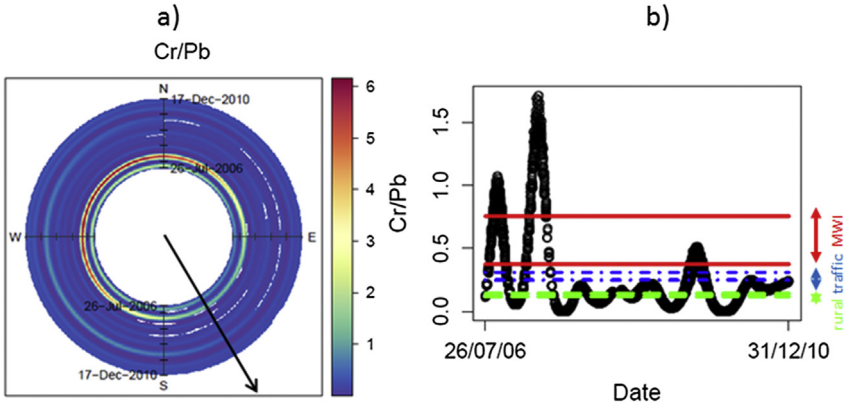


**Fig. 3.** (a) PA for the Cr/Pb ratio measured at Swansea Morriston metals site under stable atmospheric conditions. The arrow indicates the direction where the Crymlyn Burrows MWI is located. (b) Time series of the Cr/Pb ratio at the direction where the Crymlyn Burrows MWI is located. Solid horizontal red lines indicate the range of MWI emissions for the Cr/Pb ratio; green and blue dashed lines indicate the range for the rural and traffic representative values, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

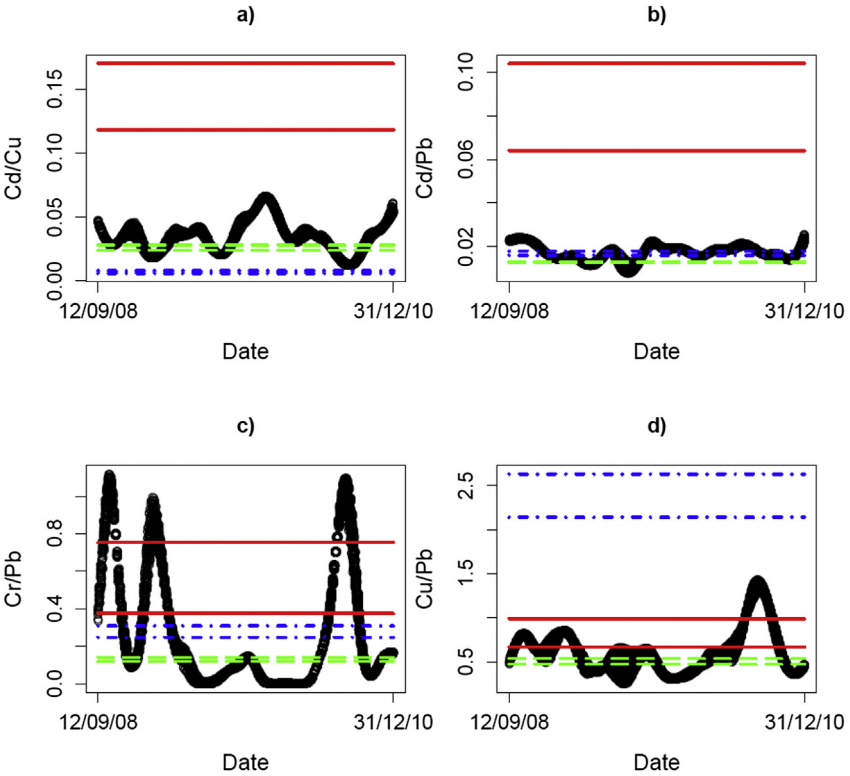


**Fig. 4.** Time series of Cd/Cu (a), Cd/Pb (b), Cr/Pb (c) and Cu/Pb (d) measured at Redcar Normanby when the wind blew from the direction where the Stockton-on-Tees MWI is located. Solid horizontal red lines indicate the range of MWI emissions; green and blue dashed lines indicate the range for the rural and traffic representative values, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with Cu/Pb values expected from MWI emissions. Measured Cd/Cu ratios were similar to the rural concentrations but some peaks were different from rural values indicating the presence of a source changing the metals ratio that might have been the incinerator. Similarly, Cd/Pb ratios ranged between the rural and traffic values with some peaks moving towards the MWI values.

A further example of this approach is shown in Fig. 5 which depicts the time series of the metal ratios measured at London Westminster for the wind sector where SELCHP MWI is located. Some peaks of the Cr/Pb ratio fell within the MWI ratio (Fig. 5c) but those peaks were identified as traffic sources by the other tracers, which was consistent with this being a highly trafficked location in central London, leading to the conclusion that these peaks were not due to the MWI plume grounding.

For the majority of the metals sampling sites located near an incinerator it was rare to measure simultaneously the four ratios within MWI values or different from the rural and traffic values (Table 7). Only the Redcar Normanby, Walsall Centre and Walsall Bilston Lane metals sites measured all four ratios coincidently; for 5.4%, 2.6% and 0.5% of the time, respectively, that the wind blew from the incinerator Stockton-on-Tees (Redcar Normanby) and Wolverhampton (Walsall Centre and Walsall Bilston Lane) in stable conditions.

For the metals sampling sites near Stockton and Wolverhampton MWIs, PM emitted by the MWI was estimated using the Cd concentration measured when grounding of the MWI plume was detected by all four tracer ratios; and assuming zero PM concentration from MWI when plume grounding was not detected. It is therefore an estimated maximum PM from MWI at the ambient metals site. The maximum PM concentration in ambient air from MWI emissions ranged from 0.029 μg $m^{-3}$ (Stockton-on-Tees MWI) to 0.123 μg $m^{-3}$ (Wolverhampton MWI). This differed from the mean PM concentrations predicted from the ADMS-Urban model that were 1–2 orders of magnitude smaller (Table 8).

The ambient concentration of heavy metals during plume grounding was compared with the mean concentration measured from other wind sectors (Table 9). The concentrations of Cr was higher at all measurement sites when MWI emissions were detected: 3.0 (at Redcar Normanby), 1.6 (Walsall Bilston Lane) and 2.4 (Walsall Centre) times larger compared with the mean concentration measured from the other wind sectors. Ni concentrations were higher at Walsall Bilston Lane when MWI emissions from Wolverhampton were detected (14.3 ± 2.3 ng $m^{-3}$) compared to the mean concentration measured from the other wind sectors (4.6 ± 5.8 ng $m^{-3}$). The other metals sites (Redcar Normanby and Walsall Centre) also measured higher mean concentrations but differences were not statistically significant.

The emission ratio in Table 5 can be combined with the ADMS-Urban PM estimates to calculate a metal concentration at each ambient metals site, as shown in Supplementary Material (Part B). This shows that the contribution of MWI emissions to the ambient levels of Cd and Cr were very small (ranging from 0.001% to 0.08%).

## 4. Discussion and conclusions

In our study we aimed to pin-point emissions from MWI using measurements of ambient heavy metal particle concentrations. Several studies have used receptor models to apportion particulate matter sources or to apportion bulk deposition near a MWI (Venturini et al., 2013). Receptor models are useful when the aim of the study is to identify the sources of pollution affecting an ambient measurement site. However, in our study we aimed to pin-point only one source of pollution (incinerator) instead of explaining all sources influencing the measured metals concentrations.

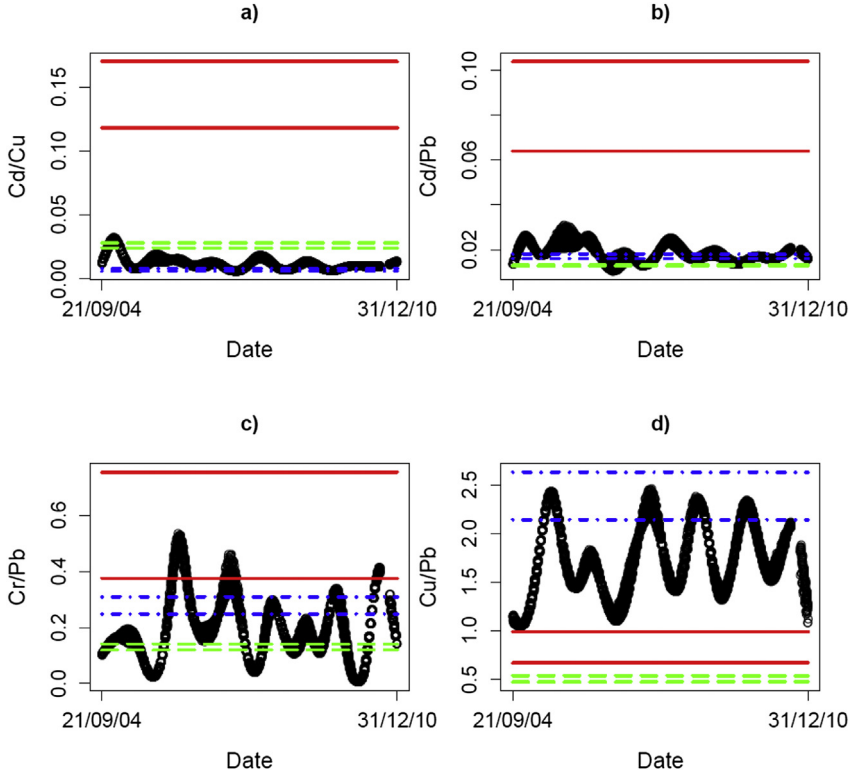


**Fig. 5.** Time series Cd/Cu (a), Cd/Pb (b), Cr/Pb (c) and Cu/Pb (d) ratios measured at London Westminster at the direction where the SELCHP MWI is located. Solid horizontal red lines indicate the range of MWI emissions; green and blue dashed lines indicate the range for the rural and traffic representative values, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 7**
Percentage of time that the four tracers were simultaneously within the range of MWI emissions or different from rural and traffic ambient sources.

| MWI | Ambient metals site | % time with wind from MWI under stable conditions | % of the study period |
|---|---|---|---|
| Crymlyn Burrows | Swansea Morriston | 0.0 | 0.0 |
| Dudley | Walsall Bilston Lane | 0.0 | 0.0 |
| Dudley | Walsall Centre | 0.0 | 0.0 |
| Stockton-on-Tees | Redcar Normanby | 5.4 | 0.2 |
| Sheffield | Sheffield Centre | 0.0 | 0.0 |
| SELCHP | London Westminster | 0.0 | 0.0 |
| Wolverhampton | Walsall Bilston Lane | 0.5 | 0.0 |
| Wolverhampton | Walsall Centre | 2.6 | 0.1 |

**Table 8**
Estimated PM from MWIs at ambient metals sites.

| MWI | Ambient metals site | Maximum PM from MWI ambient data (mean ± σ) (μg $m^{-3}$) | PM from MWI ADMS-Urban (mean ± σ) (μg $m^{-3}$) |
|---|---|---|---|
| Stockton-on-Tees | Redcar Normanby | 0.029 ± 0.002 | $0.008 \cdot 10^{-1}$ ± 0.002 |
| Wolverhampton | Walsall Bilston Lane | 0.038 ± 0.002 | 0.002 ± 0.003 |
| Wolverhampton | Walsall Centre | 0.123 ± 0.007 | 0.001 ± 0.002 |

First, we successfully fingerprinted emissions from modern MWI in the UK using stack emissions samples of heavy metals. The ratios used to fingerprint MWI emissions in UK were consistent with emissions from burning electronic waste (that emits Cu and Pb) (Gullett et al., 2007), mixed paper and plastics (which emit Pb and Cd), and batteries (which emit Cd; Hasselriis and Licata, 1996; WHO, 2010), materials all expected to be found in municipal waste. Cr is emitted when burning coloured newsprint and mixed paper, plastic film, lawn waste, wood, textiles, footware and fines (Hasselriis and Licata, 1996). It has not been previously used as a tracer of MWI emissions despite being emitted in high abundance relative to rural concentrations (Table 2).

Unfortunately the number of stack samples available to calculate emission ratios was not enough to calculate individual source profiles for each MWI or to assess their changes over time. However, emission ratios of heavy metals were expected to be consistent between MWI for two reasons. First, the metals with best correlation coefficients share common origins within waste material. In a previous study from a MWI in British Columbia found that many waste types contributing to Pb emissions also exhibited high levels of Cr. Garden waste and certain type of paper fractions (commonly found in municipal waste) contain the highest concentrations of Pb, Cr and Cd. Emissions of Cr and Cd versus Pb also showed a linear relationship (Hasselriis and Licata, 1996). This is in agreement with our results. Second, all MWI in England and Wales used the same abatement techniques for heavy metals. These include injection of activated carbon (to capture mercury) and bag filters (to remove particulates). Furthermore the Cd/Pb ratio in our study was almost identical to that reported for modern European MWI in Nielsen et al. (2010) (Table 10). Other ratios were more similar to Nielsen et al. (2010) values than the older studies of Morselli et al. (2002) and Hu et al. (2003). Although it did not affect our study, the revised Restriction of the use of certain Hazardous Substances (RoHS) directive (2011/65/EU), that became effective on January 2013, limits the use of hazardous substances (such as Pb, Hg, Cd, and Cr (VI), among other substances) in electrical and electronic equipment. Emissions of heavy metals from incinerators are therefore expected to decrease and this will impact on future emission ratios.

In order to properly detect sources of atmospheric pollution in ambient data three requirements are needed: i) the dataset collected must include daily, seasonal and yearly variations of the source (Cohen et al., 2014); ii) the emissions tracers are not transformed in the atmosphere between emission and detection; and iii) the ambient measurements should include the chemical species emitted by the source (Cohen et al., 2014) at a measurable concentration.

The stack emissions used to fingerprint MWI emissions

**Table 9**
Mean ± standard deviation of heavy metals concentration (ng $m^{-3}$) measured at the ambient metals site when MWI emissions were detected and for the other wind directions. Bold numbers indicate those heavy metals that concentrations (within 95% confidence) were higher when MWI plume was detected.

| | Redcar Normanby (Stockton-on-Tees) | Walsall Bilston Lane (Wolverhampton) | Walsall Centre (Wolverhampton) |
|---|---|---|---|
| As MWI plume | 0.20 ± 0.03 | 0.88 ± 0.06 | 1.17 ± 0.08 |
| As other sectors | 0.40 ± 0.21 | 1.17 ± 0.38 | 1.05 ± 0.34 |
| Cd MWI plume | 0.08 ± 0.01 | 1.17 ± 0.06 | 0.71 ± 0.03 |
| Cd other sectors | 0.09 ± 0.04 | 2.58 ± 1.30 | 0.61 ± 0.40 |
| Cr MWI plume | **2.32 ± 0.80** | **5.84 ± 0.21** | **6.08 ± 0.78** |
| Cr other sectors | **0.78 ± 0.90** | **3.66 ± 1.78** | **2.50 ± 1.77** |
| Cu MWI plume | 2.58 ± 0.20 | 27.22 ± 1.06 | 17.94 ± 1.23 |
| Cu other sectors | 2.71 ± 1.06 | 50.3 6 ± 17.57 | 16.74 ± 6.63 |
| Pb MWI plume | 3.50 ± 0.39 | 48.09 ± 1.57 | 22.57 ± 1.25 |
| Pb other sectors | 5.70 ± 2.85 | 70.1 4 ± 31.76 | 19.90 ± 6.46 |
| Mn MWI plume | 4.20 ± 1.19 | 9.72 ± 0.26 | 8.56 ± 0.72 |
| Mn other sectors | 5.19 ± 3.89 | 11.25 ± 2.75 | 9.67 ± 1.97 |
| Ni MWI plume | 0.60 ± 0.42 | **14.26 ± 2.33** | 8.34 ± 2.81 |
| Ni other sectors | 0.45 ± 0.42 | **4.59 ± 5.83** | 3.84 ± 6.33 |
| V MWI plume | 0.86 ± 1.13 | 2.44 ± 0.10 | 5.27 ± 1.13 |
| V other sectors | 0.91 ± 1.25 | 1.87 ± 1.22 | 2.45 ± 3.15 |

**Table 10**
Value for the ratios representative of MWI emissions reported in this study and in the literature.

| | This study | Nielsen et al. (2010) | EMEP-CORINAIR (2006) Morselli et al. (2002) | Hu et al. (2003) | Mamuro et al. (1980) |
|---|---|---|---|---|---|
| Cu/Pb | 0.83 [0.67–0.99] | 0.24 [0.17–0.32] | (0.89 [0.39–0.84])·$10^{-3}$ | – | – |
| Cd/Pb | 0.08 [0.06–0.10] | 0.08 [0.07–0.09] | 0.03[0.03–0.03] | 0.05 | 0.03 |
| Cd/Cu | 0.14 [0.12–0.170] | 0.34 [0.28–0.41] | 36.56 [83.61–17.66] | 0.21 | – |
| Cr/Pb | 0.564 [0.38–0.75] | 0.28 [0.25–0.32] | (0.02 [0.01–0.04])·$10^{-1}$ | – | – |

comprised only a short snapshot of the MWI output throughout the study period (daily emissions on quarterly basis). Metals emissions from the MWI might change weekly, seasonally and/or on yearly basis. However the standard deviation in the four metal ratios was small meaning that these could be used with confidence as MWI tracers.

The ambient dataset available for this study ranged from 2 to 5.5 years depending on the MWI (Table 1). It comprised weekly samples of heavy metals and hourly meteorological information. Wind direction dependent emission ratios have been used successfully elsewhere in receptor analysis; for instance Johnson et al. (2014) recently used V, Ni, sulphur and black carbon ratios to examine the influence of shipping emissions on ambient air pollution in Brisbane, Australia. Although daily variations of the source cannot be observed in the weekly samples, analysis on a test dataset from the Harwell – Didcot Power Station showed that weekly mean concentrations combined with hourly meteorological data can accurately detect a point source and track temporal changes under stable meteorological conditions. Following results from the Harwell – Didcot Power Station test, the analysis of UK MWIs focused on stable meteorological conditions. These were met between 51–68% of the time when the wind blew from the direction of the MWIs.

The fingerprint metal ratios from MWI stack emissions were found to be very different to those in ambient rural environments and those close to traffic. Particulate metals are a primary emission from MWI (Table 2) and bag-filtered stack emissions from MWIs do not contain a significant amount of particulates greater than 10 μm diameter (Buonanno et al., 2009; Ashworth et al., 2013). Over the maximum 10 km distance considered in the study the different particulate metals should therefore be subject to the same rates of dispersion and deposition. Although concentrations of particulate metals would be expected to decrease with distance from the stack, the emissions ratios will be conserved in the MWI plume.

Detecting stack emissions using ratios in ambient data is most likely to be successful if the stack is the only source of the tracer species. The presence of other sources emitting the same species at different rates might change the ratios in ambient data making difficult to isolate sources. Some studies have used the ratio of heavy metals (e.g. Cd) related to Pb to detect the influence of MWI emissions in urban ambient air (e.g. Sakata et al., 2000). However, Pb emissions in Europe mainly come from area sources such as traffic (Pacyna et al., 2007, 2009; Noble et al., 2008) while Cd is emitted primarily from point sources (e.g. waste incinerators). The dissimilar distribution of emissions of Cd and Pb would represent a challenge for the detection of MWI emissions in ambient air as the emissions from other sources would modify the ratio measured at the measurement site. Ambient ratios different from the rural and traffic values might indicate the presence of other sources emitting metals to the atmosphere (e.g. MWIs). Most of the MWI in the UK are located in heavily industrialized areas and these might also modify the ambient metal ratios. In order to overcome this type of confounding behaviour, we used four tracer ratios to identify emissions from MWIs. Our technique identified that traffic was the main source of metals in central London demonstrating its specificity. Despite three of the four ratios used to fingerprint MWI emissions being related (Cd/Pb, Cd/Cu and Cu/Pb) the combination provided specific source information. For example, at the end of the time series shown in Fig. 4 ambient values of Cu/Pb were within the MWI emissions value although Cd/Cu and Cd/Pb values clearly indicated the dominance of traffic emissions.

In summary we did not detect incinerator source profiles in ambient particulate matter metal concentrations around four UK MWIs. However, MWI emissions might still influence ground-level concentrations but the location of the sampling sites did not detect them. Despite the ambient sampling locations were not ideally placed to detect the influence of the MWIs (e.g. not downwind in the prevalent wind direction, near other metals emitting industrial sources, etc.) and the time resolution of measurements were only weekly samples, we successfully identified emissions from MWI for two installations in UK. Metal ratios consistent with MWI emissions were found in ambient measurements within 10 km of the Stockton MWI for about 5.4% of the time when the wind blew from the incinerator under stable conditions. The Wolverhampton MWI was similarly detected at two ambient metals sites, about 2.6% and 0.5% of the time when the wind blew from the incinerator under stable conditions. This was 0.2% of the total study period at Stockton and a maximum of 0.1% of the study period at Wolverhampton. Stockton-on-Tees and Wolverhampton are the second and third largest UK MWI in terms of daily PM emissions (Table 1), which might explain their detection in the study. Using metal tracers we estimated a maximum ambient PM from these two MWIs between 0.03 and 0.12 μg $m^{-3}$ at our receptor sites. These concentration estimates were one to two orders of magnitude larger than the dispersion-modelled mean PM concentrations which were between $10^{-4}$ and $2 \cdot 10^{-3}$ μg $m^{-3}$ at the metals sites. It must be remembered that our tracer method assumed that all Cd during plume grounding arose from the MWI which would lead to an overestimate of the ambient contribution. Importantly, however, both the emission ratio and dispersion modelled estimates were very low compared to background levels. Annual $PM_{10}$ ambient levels ranged from 20 to 31 μg $m^{-3}$ at urban background and roadside sites between 2003 and 2010 (DEFRA, 2014); 2–3 (compared to emission ratio estimates) and 3–4 (ADMS) orders of magnitude larger. It is not feasible to measure increments of this order of magnitude above background PM values using state-of-the-art instruments. For all the metals sites where MWI emissions were detected, higher of Cr concentrations were detected during the grounding periods compared with other wind sectors; Ni concentrations were also higher at 95% confidence interval for one metals site. This is consistent with the relative abundance of these metals in MWI emissions.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.05.002.

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