

**Report by the National Physical Laboratory to the Department for Environment, Food and Rural Affairs, the Welsh Government, the Department of the Environment in Northern Ireland and the Scottish Government:**

**Annual Report for 2011 on the  
UK Heavy Metals Monitoring Network**

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**NOT RESTRICTED**

**JUNE 2012**

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Approved on behalf of NPLML by  
Mr Alan Brewin, Head of Analytical Science Division

## EXECUTIVE SUMMARY

This Report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Department for Environment, Food and Rural Affairs, the Welsh Government, the Department of the Environment Northern Ireland and the Scottish Government.

This is the Annual Report for 2011 and contains, in particular:

- Measured annual concentrations of all metals at all monitoring sites and performance against relevant data quality objectives and the requirements of the EC Air Quality Directives.
- Highlighting of exceedences, interpretation of data and discussion of trends across the Network.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events and changes to the Network during 2011.
- A summary of scientific research, publications, international representation and other activities related to the Network.

In summary, during 2011:

- There was **one** exceedence of a target or limit value across the Network.
- **Lead:** No annual average site concentrations above the Air Quality Directive's Lower Assessment Threshold were recorded.
- **Nickel:** One annual average site concentration above the Fourth Daughter Directive target value, one annual average site concentration above the Fourth Daughter Directive's upper assessment threshold and one annual average site concentration above the Fourth Daughter Directive's lower assessment were recorded.
- **Cadmium:** One annual average site concentration above the Fourth Daughter Directive's Lower Assessment Threshold was recorded.
- **Arsenic:** No annual average site concentrations above the Fourth Daughter Directive's Lower Assessment Threshold were recorded.
- **Total gaseous mercury:** Measured concentrations across the Network remain close to background concentration levels (with the exception of the site at Runcorn Weston Point).
- The annual average concentrations measured across the Network have not changed significantly.
- All data quality objectives specified in the New Air Quality Directive and Fourth Daughter Directive were met, including time coverage, data capture and measurement uncertainty requirements.
- Data capture across the Network was **96%** for the year.

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# 1 INTRODUCTION

This Report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Department for Environment, Food and Rural Affairs and the Devolved Administrations<sup>1</sup> (the Welsh Government, the Department of the Environment in Northern Ireland and the Scottish Government).

This is the Annual Summary Report for the UK Heavy Metals Monitoring Network (the 'Network') for 2011 and contains:

- Measured annual concentrations of all metals at all monitoring sites and performance against relevant data quality objectives and the requirements of the relevant EC Air Quality Directives – the New Air Quality Directive (2008/50/EC<sup>2</sup>) for lead, and the Fourth Air Quality Daughter Directive (DD) (2004/107/EC<sup>3</sup>) for nickel, arsenic, cadmium, and total gaseous mercury, and the Air Quality Strategy for England, Scotland, Wales and Northern Ireland<sup>4</sup> for lead.
- Highlighting of exceedences, interpretation of data and discussion of trends across the Network.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events and changes to the Network during 2011.
- A summary of scientific research, publications, international representation and other activities related to the Network.

## 1.1 BACKGROUND

Several requirements drive the need for air quality measurements, including: measuring the exposure of the general population to a variety of toxic compounds; assessing compliance with legislative limits or similar target values; informing policy development and assessing the effectiveness of abatement strategies. In addition there is a need to provide air quality information for the general public and to inform other scientific endeavours (for example, climate change research), and to provide an infrastructure that can readily respond to new and rapidly changing requirements, such as the specification of new pollutants requiring measurement, or assessment of episodes, such as local, regional or trans-boundary pollution events.

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1 The Devolved Administrations are in detail: the Welsh Government, the Northern Ireland Executive, represented by the Department of the Environment in Northern Ireland (DoENI), and the Scottish Government, represented by the Scottish Government Enterprise and Environment Directorate.

2 Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, *Official Journal L 152*, 11/06/2008 P. 0001-0044.

3 Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, *Official Journal L 023*, 26/01/2005 P. 0003-0016.

4 Air Quality Strategy for England, Scotland, Wales and Northern Ireland, 2007, Cmd paper No 7169 NIA 61/06-07.

The determination of the total concentrations<sup>5</sup> of metals in ambient air is of great importance within this framework. The general public and the environment can be exposed to several classes of hazardous compounds containing metallic elements, which occur naturally or are released by domestic or industrial processes. The total concentration levels of Pb, Ni, As and Cd, allowable in the PM<sub>10</sub> fraction of ambient air (particles with an equivalent aerodynamic diameter of 10 µm or less), are now limited by European legislation.

Human exposure to toxic air pollutants at sufficient concentrations and over long enough time periods may engender increased chances of serious health effects including cancer. Such health effects can include damage to the immune, reproductive and respiratory systems and developmental and neurological impairment. In addition to exposure from breathing in these pollutants, some pollutants such as mercury may also deposit from the air onto the earth or water, where they may enter the terrestrial and aquatic food chains, eventually resulting in human exposure through ingestion of contaminated food.

Emissions of metals in the UK arise from a variety of sources including in particular:

- Industrial combustion;
- Domestic combustion;
- Public power combustion;
- Metals processing industry;
- Road transport;
- Waste incineration;
- Chemical industry processes;
- Iron and steel industry.

The National Atmospheric Emissions Inventory has more details of anthropogenic sources and emissions of metallic pollutants in the UK<sup>6</sup>. These emissions have declined over many years and this has generally been mirrored by the decrease in measured ambient levels, although in recent years both trends have flattened out. The correlation between these two data sets is quite strong, and indeed measured ambient concentrations across the Network have recently been compared against emissions<sup>7</sup>. This has shown that an additional benefit of the Network is to contribute supplementary evidence to show that trends in emissions inventory data for metals are correct. The UK emissions since 1980 of metals relevant to those measured on the Network are displayed in Figure 1.

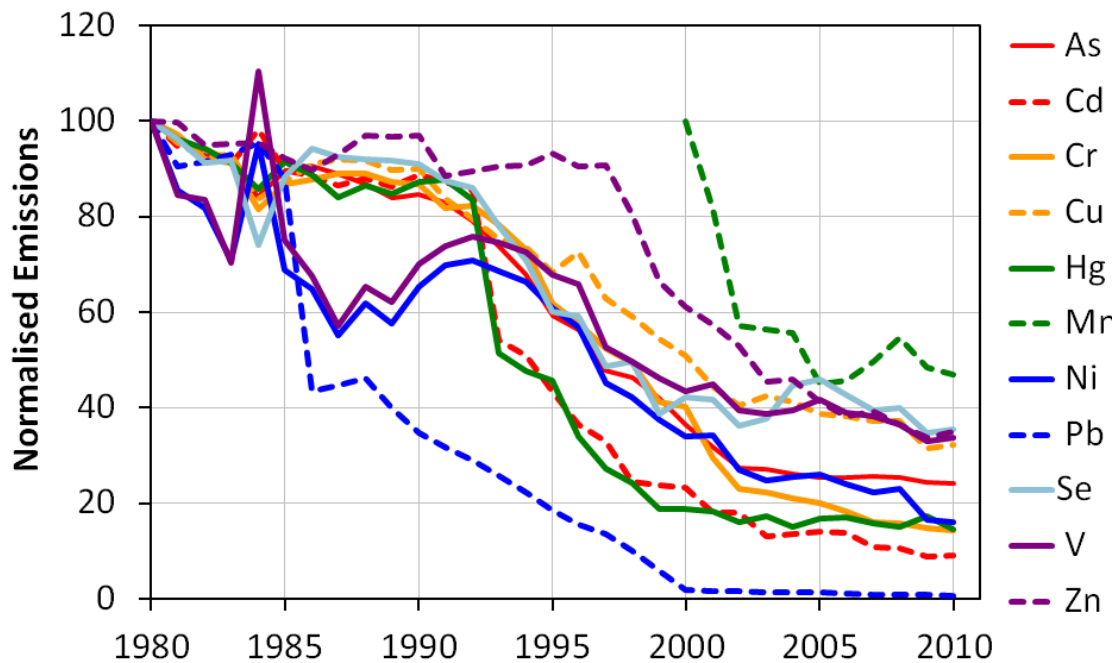
In order to demonstrate compliance with legislation that provides limit and target values relating to ambient air and to measure human and environmental exposure, the total concentration levels of ambient metals, at multiple sites on nationwide air quality monitoring networks, need to be measured. The UK Heavy Metals Monitoring Network is a regulatory air quality monitoring network that discharges the majority of the UK's obligation under the EC Air Quality Directives relating to the monitoring of the mass concentrations of Pb, Ni, As and Cd, in the PM<sub>10</sub> phase of ambient air, and total gaseous mercury [referred to as: Hg(v)].

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<sup>5</sup> The term 'concentration' is used in this report to refer to mass concentration.

<sup>6</sup> [www.naei.org.uk](http://www.naei.org.uk)

<sup>7</sup> Comparison of estimated annual emissions and measured annual ambient concentrations of metals in the UK 1980–2007, R J C, Brown, *J. Environ. Monit.*, 2010, **12**, 665-671.



**Figure 1.** Estimated UK annual emissions of the metals from 1980 to 2010, normalised to their values in 1980 such that 1980 = 100 (except for Mn where values are only available since 2000 and therefore have been normalised to this year). The absolute levels of emissions in 1980, in tonnes, were: Cd, 26; Cr, 183; Cu, 158; Ni, 491; Pb, 8300; Se 90; V, 1420; and Zn, 1013. The absolute level of Mn emissions in 2000 was 72 tonnes. Emissions data are not available for Co, Fe and Pt, although these are measured by the Network.

The Network has a number of objectives:

- To achieve compliance with monitoring requirements set out in European legislation;
- To provide data to the UK Government and European Commission on the UK's performance against the limit values, target values, and data quality objectives described in the relevant legislation;
- To assess impacts around 'hot spots' of metallic pollution to air, particularly in industrial areas;
- To produce accurate and reliable data for dissemination to the general public and for use by scientific and medical researchers and the air quality community.

Further information on the history of the UK Heavy Metals Monitoring Network can be found in an NPL publication that marked a quarter of a century of the nationwide monitoring of metals in ambient air<sup>8</sup>.

<sup>8</sup> Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends, Brown, R J C, *et al*, *Environmental Monitoring and Assessment*, 2008, **142**, 127-140.



## 2 NETWORK OPERATION

The UK Heavy Metals Monitoring Network in 2011 comprised 25 monitoring sites around the country (15 in England, 7 in Wales, 2 in Scotland, and 1 in Northern Ireland) sampling in the PM<sub>10</sub> phase of ambient air onto filters (see Annex 1). These filters are then returned to NPL where they are analysed to determine the content of various metals in the particulate matter, in order to produce concentration values for these metals in ambient air. Total gaseous mercury is additionally sampled onto adsorption tubes at 13 of these Network sites (7 in England, 3 in Wales, 2 in Scotland, and 1 in Northern Ireland). These absorption tubes are then analysed at NPL to produce concentration values for total gaseous mercury in ambient air. Relevant activity related to Network operation during 2011 is detailed below.

### 2.1 OVERVIEW

NPL's management of the UK Heavy Metals Monitoring Network in 2011 has included the following key activities:

- NPL staff visited and fully audited all sites on the Network. This included the calibration and basic maintenance of the Partisol and total gaseous mercury samplers and re-assessment of local site operators' (LSOs') procedures. A further visit to each site was made during the year to perform a flow calibration and leak check on the Partisol samplers.
- The Equipment Support Unit (ESU) made service visits to all Network sites twice during the year, and this has included the flow calibration of instruments.
- Data capture has remained at a very high level across the Network and is at its highest level since NPL began operating the Network (see Figure 3).
- The UK Heavy Metals Monitoring Network and the data it produces has received extensive exposure in learned journals during 2011.

### 2.2 SITE AUDITS

During 2011 NPL visited all the Network sites to perform annual site audits. At these visits the site infrastructure, performance and integrity were assessed. The LSOs were also audited and received extra training where required.

A list of sites comprising the Network as of the end of 2011, with locations, site codes, site names, site designations, identified point sources in the vicinity where applicable, is given in Annex 1.

During each Network site audit visit NPL:

- Audited the procedures of the LSO on-site, giving introductory training where necessary, and encouraged LSOs to feed-back into the running of the Network;
- Assessed the current condition of all on-site equipment, including the condition of the PM<sub>10</sub> sampling head and impactor plate;

- Calibrated the flows of both the particulate (for volumetric and standard flow), and gaseous phase (volumetric flow), monitoring equipment;
- Leak tested both the particulate, and gaseous phase, monitoring equipment;
- Calibrated the site rotameter (used by the LSOs for determining the flow rate through the total gaseous mercury sampling line).

This flow calibration data is used to correct the volumes recorded by the Partisol instruments and mercury vapour sampling equipment prior to the calculation of ambient concentrations. In summary:

- All of the sites have been audited fully and were found to be performing well.
- Site infrastructure was assessed and no major or minor problems were found.
- Audits of the flow-rate of the Partisol samplers and the mercury vapour sampling equipment were satisfactory and no remedial action was required.
- The LSOs were performing their duties to a high standard. Some small issues were identified and rectified during the audits in order to improve performance even further.

The auditing of the sampler flow rates also allowed a comparison of the ESU and NPL flow calibrators. (The ESU recorded the sampler flow rate during their service visits.) The flow measurements were in good agreement with an average difference of only 2.7 %, which is well within the uncertainty of the flow measurement itself. As expected, the best agreements were found when the periods between the NPL and ESU visits were very short. As the periods between visits became longer, the difference increased as a function of the flow rate of the samplers and the calibration of the flow measuring equipment drifting slowly over time.

NPL visited each site a second time during the year to perform a flow calibration and leak check of the samplers. Together with the two flow calibrations and leak checks performed by the ESU during the year this meets the requirement for a three-monthly flow and leak check required by EN 14902.

### **2.3 EQUIPMENT SERVICING AND BREAKDOWNS**

During 2011 the ESU twice fully serviced, carried out preventative maintenance and calibrated the flow of the Partisol samplers at all Network sites.

During 2011, NPL called-out the ESU to deal with Partisol sampler faults at: Cardiff Rumney, Motherwell (twice), Manchester, Pontardawe Tawe Terrace, Scunthorpe Low Santon, Sheffield Brinsworth and Sheffield Centre (twice).

During 2011, failed or failing mercury vapour sampling pumps were replaced at: London Westminster and Walsall Centre (twice).

### **2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION**

Changes to the operation of the Network during the year are detailed below:

- The Network sites at Bristol Avonmouth and Bristol Hallen closed on 5<sup>th</sup> January 2011.
- The local authority site at Pontardawe Tawe Terrace was affiliated to the Network on 12<sup>th</sup> January 2011, becoming: "Site 113: Pontardawe Tawe Terrace".

- The downwind pair site to Pontardawe Tawe Terrace, a new site “Site 115: Pontardawe Brecon Road began monitoring on 10<sup>th</sup> August 2011.”
- From 1<sup>st</sup> April 2011 the Partisol sampler at London Marylebone Road taking samples for metals analysis, run previously by Kings College ERG, was affiliated to the Network, becoming “Site 114: London Marylebone Road”.
- The spare mercury vapour sampling equipment recovered from Bristol Avonmouth was relocated to Port Talbot Margam and began sampling on the 1<sup>st</sup> June 2011.
- The station at Redcar ceased sampling at the beginning of October 2011 owing to the demolition of the building on which it was sited. A new station, to be known as 116: Redcar Dormanstown, was installed in late January 2012.

The major issues to report with regard to site infrastructure during 2011 were:

- In October 2011, a replacement electric socket to supply the sampler at Runcorn Weston Point was fitted after inspection showed water ingress. This issue was logged with the central Health and Safety data base.
- In mid-December 2011, the Partisol sampler at Swansea Coedgwilym fell off the roof of the hut where it was sited. The sampler was re-installed on the roof in late January 2012 with appropriate additional fixings to prevent a repeat incident.
- New Partisol 2000B samplers were installed across the Network during the second quarter of 2011. A minor amount of data loss was initially caused at some sites by slight differences between the software and operation of the new and old Partisols. These issues have now been resolved with input from the ESU and extra training for LSOs.

## **2.5 NEW CONTRACT ARRANGEMENTS**

During 2011 NPL re-won the contract to operate the Network until 2014 (under contract number RMP 5506). As a result of this new contract the time periods over which Network results were ratified and reported changed.

In the new contract (starting from April 2011) results have been produced four-weekly for metals in the particulate phase at all sites except: Sheffield Brinsworth, Sheffield Centre, Swansea Coedgwilym, Swansea Morriston, Pontardawe Tawe Terrace and Pontardawe Brecon Road where results are produced weekly. From the start of 2012 weekly results will be produced at Walsall Willenhall instead of Sheffield Centre. In the new contract, mercury vapour results are now reported four-weekly at all sites except for Walsall Willenhall, Walsall Centre and Runcorn Weston Point where data is reported weekly.

In addition, under the new contract, Co and Se have been measured by the Network for the first time, from May 2011 onwards.

### 3 SAMPLING AND ANALYTICAL METHODOLOGY

An overview of the sampling and analytical procedures used to analyse samples from the Network is given below.

#### 3.1 SAMPLING METHODOLOGY: PARTICULATE-PHASE METALS

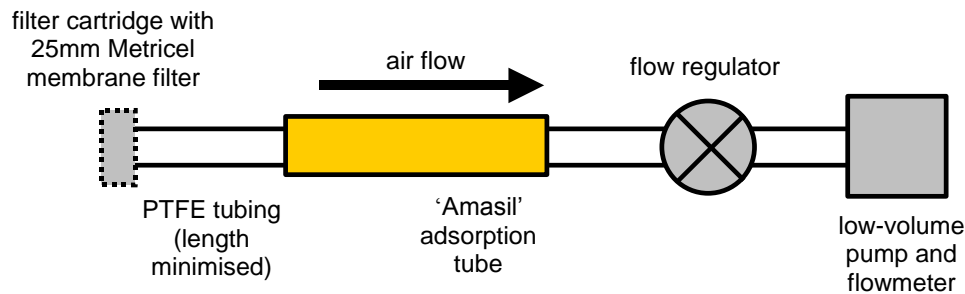
Particulate samples were taken at all sites in the Network using Partisol 2000 instruments (fitted with PM<sub>10</sub> heads) operating at a calibrated flow rate, nominally of 1 m<sup>3</sup> h<sup>-1</sup>, in accordance with EN 12341 (see Image 1). Samples were taken for a period of one week onto 47 mm diameter GN Metrical membrane filters.



**Image 1.** The Partisol 2000 sampler at the Network monitoring site at Eskdalemuir. The grey box attached to the side of the sampler contains the mercury vapour sampling equipment.

#### 3.2 SAMPLING METHODOLOGY: TOTAL GASEOUS MERCURY

Sampling for total gaseous mercury took place at 13 of the 24 Network sites using a low-volume pump (calibrated annually by NPL). Air was pumped through Amasil (gold-coated silica) tubes at a rate of 100 ml min<sup>-1</sup> for either one week or four weeks, depending on the specific site and the required resolution of data. The mercury vapour sampling equipment is housed in a specially designed box on the side of the Partisol 2000 samplers (see Image 1). A schematic diagram of the mercury vapour sampling equipment is given in Figure 2.



**Figure 2.** Schematic diagram of the total gaseous mercury sampling apparatus. The 25 mm diameter filter was used to remove any particulate material.

### 3.3 ANALYTICAL METHODOLOGY: PARTICULATE-PHASE METALS

Analysis for particulate-phase metals took place at NPL using PerkinElmer Elan DRC II and Elan 9000 ICP-MSs, following NPL's procedure, accredited by UKAS to ISO 17025, which is fully compliant with the requirements of EN 14902 (see Image 3).

Upon arrival at NPL, the filters were cut accurately in half (for sites where weekly results are produced) and into quarters (where four weekly results are produced). For the sites producing weekly data each portion is digested at temperatures up to 220°C using an Anton Parr Multiwave 3000 microwave. For the sites producing four-weekly data one quarter of each of the four filters comprising the four week period are digested. The digestion mixtures used were:

- Hg & Pt: 5 ml of nitric acid and 5 ml hydrochloric acid.
- All other metals: 8 ml of nitric acid and 2 ml hydrogen peroxide.

ICP-MS analysis of the digested solutions took place using at least four gravimetrically-prepared calibration solutions. A quality assurance (QA) standard was repeatedly analysed (after every two solutions), and the change in response of the QA standard was mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS was corrected for by use of an internal standards mixture (containing Y, In, Bi, Sc, Ga & Rh) continuously added to all the samples via a mixing block. Each sample was analysed in triplicate, each analysis consisting of five replicates.

The amount of each metal in solution (and its uncertainty) was then determined by a method of generalised least squares using XLGenline (an NPL-developed program) to construct a calibration curve.

### 3.4 ANALYTICAL METHODOLOGY: TOTAL GASEOUS MERCURY

Analysis of total gaseous mercury samples took place at NPL using a PS Analytical Sir Galahad II analyser with a fluorescence detector, using NPL's procedure, accredited by UKAS to ISO 17025, which is in accordance with the published reference method EN 15852 (see Image 3). (The manual variant of EN 15852 used on the Network has been recently shown to be equivalent to the automatic reference

method within the uncertainty of the analytical determination <sup>9)</sup> The instrument was calibrated by use of a gas-tight syringe, making multiple injections of known amounts of mercury vapour onto the permanent trap of the analyser.

Sampled adsorption tubes were placed in the remote port of the instrument and heated to 900°C, desorbing the mercury onto a permanent trap. Subsequent heating of this trap then desorbed the mercury onto the detector.

### 3.5 MEASUREMENT UNITS

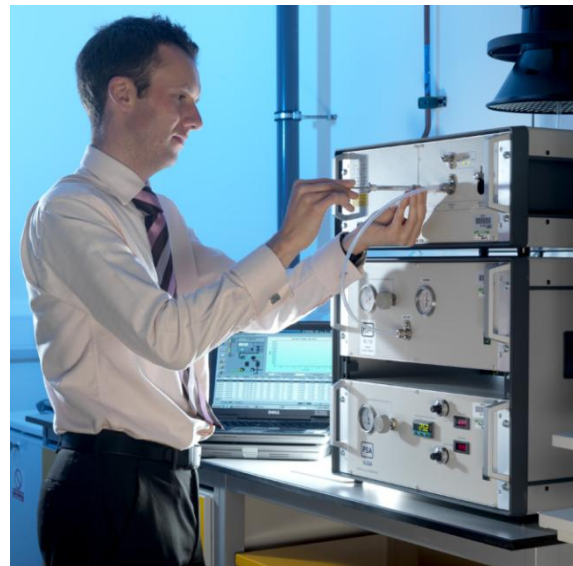
Results produced by the Network are expressed as required by the relevant air quality Directives as mass concentrations, in nanograms (of the relevant metal) per cubic metre of 'as sampled' ambient air for the particulate phase metals, and per cubic meter of air under the reference conditions given in EN 15852 for total gaseous mercury (a temperature of 293.15 K and pressure of 101.325 kPa). The units used in both cases are:  $\text{ng m}^{-3}$ .

### 3.6 MEASUREMENT UNCERTAINTY

For each result produced by the Network an estimate of the uncertainty in this value is also made according to an ISO GUM (Guide to the Expression of Uncertainty in Measurement) approach. These uncertainties are used to calculate the uncertainties in the annual average values for each element and ensure that the final results meet the data quality objectives for uncertainty specified in the relevant legislation.



**Image 2:** One of two dedicated ICP-MS instruments comprising the UK ambient metals analysis facility at NPL.



**Image 3:** One of two thermal desorption-atomic fluorescence analysers comprising the UK total gaseous mercury analysis facility at NPL

<sup>9</sup> Field comparison of manual and semi-automatic methods for the measurement of total gaseous mercury in ambient air and assessment of equivalence. R J C Brown, et al., *Journal of Environmental Monitoring*, 2012, **14** (2), 657-665.

## 4 METHOD PERFORMANCE CHARACTERISTICS AND QUALITY CONTROL

The application of the technical procedures used to analyse samples from the Network (metals in the particulate phase by ICP-MS, and mercury vapour by atomic fluorescence spectroscopy) was audited by UKAS in 2011, and both retained accreditation to ISO 17025 from UKAS with no mandatory corrective actions.

### 4.1 LIMITS OF DETECTION: PARTICULATE-PHASE METALS

Indicative detection limits achievable by NPL using a UKAS accredited ICP-MS method, fully compatible with EN 14902, are shown in Table 1. The solution limits of detection were calculated using the method outlined in EN 14902, repeatedly analysing a typical acid blank solution and taking into account the variability between individual instrumental readings. Values for the limits of detection have been calculated assuming a solution mass of 53 g and a volume of sampled air of 168 m<sup>3</sup> (equivalent to seven days sampling at 1.0 m<sup>3</sup> h<sup>-1</sup>).

Analyte	Limit of Detection		
	Solution (ng g <sup>-1</sup> )	Filter (ng)	Air (ng m <sup>-3</sup> )
As	0.08	4.2	0.03
Cd	0.003	0.16	0.001
Co	0.003	0.2	0.001
Cr	0.08	4.1	0.02
Cu	0.07	3.6	0.02
Fe	0.5	25	0.15
Mn	0.009	0.5	0.003
Ni	0.03	1.7	0.01
Pb	0.04	2.0	0.01
Pt	0.003	0.2	0.001
Se	0.003	0.2	0.001
V	0.007	0.4	0.002
Zn	0.2	11	0.06
Hg(p)	0.003	0.2	0.001

**Table 1.** Indicative limits of detection for particulate-phase metals.

## 4.2 LIMITS OF DETECTION: TOTAL GASEOUS MERCURY

The limit of detection routinely achievable for analysis of total gaseous mercury at NPL using its UKAS accredited procedure, which is consistent with the standard method EN 15852, is 0.02 ng per tube, equivalent to an air concentration of approximately 0.02 ng m<sup>-3</sup> (assuming a volume of sampled air of 1.01 m<sup>3</sup>, equivalent to one week's sampling at 100 ml min<sup>-1</sup>). This value was calculated using a minimum detectable peak height of three times the baseline noise (with the instrument detector being operated at its usual sensitivity setting).

## 4.3 QA/QC PROCEDURES

A sub-set of the quality assurance and quality control procedures employed during Network operation to ensure the quality of the data produced are listed below:

Sampling:

- Despatch and analysis of one field-blank filter and one field-blank adsorption tube per site per quarter.
- Thorough checks of the returned filters and adsorption tubes to check for damage during transport. Rejection of damaged filters or tubes.
- Logging of all samples on NPL's Network database. Rejection of any unidentifiable samples and full investigation of any discrepancies.
- Continued training of, and regular communication with, the LSOs. This includes assessment of performance during site audits.

Particulate phase metals (ICP-MS analysis):

- Optimisation of the ICP-MS prior to each set of analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular extraction of an appropriate certified reference material (e.g. NIST SRM 1648a or NIES No.8) to check the recovery of the digestion method. Recoveries must be within the limits specified by EN 14902.
- Regular measurement of filter blanks to ensure appropriate blank subtractions are made from measured values.
- Maximum levels for the standard deviation of the five internal standard-corrected measured intensities of each analysis of each sample.
- The XLGenline maximum absolute weighted residual for all calibration curves must be less than 1.
- Ratification of all data by an NPL Quality Circle of recognised senior NPL scientific experts independent of the analytical team.

Total gaseous mercury (atomic fluorescence analysis):

- Regular recovery tests carried out by analysing tubes spiked with a known quantity of mercury. Recoveries of between 95% and 105% must be achieved.
- Control limits on changes in instrument sensitivity between analyses.
- Analysis of clean tubes to ensure that blank levels are sufficiently low.
- Novel bracketing calibration procedure for each tube analysed in order to minimise the effect of instrumental drift.
- Ratification of all data by an NPL Quality Circle of recognised senior NPL scientific experts independent of the analytical team.



#### 4.4 MEASUREMENT UNCERTAINTY

The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2011 are shown in Table 2. All figures are a combination of the analytical and sampling uncertainties and have been derived using full, ISO GUM compliant, uncertainty budgets. All values are stated to a coverage factor of  $k = 2$ , providing a level of confidence of approximately 95%.

Analyte	Expanded relative uncertainty	
	Single measurement range	EC Directive maximum
As	16 - 26 %	40 %
Cd	13 - 20 %	40 %
Co	18 - 38 %	-
Cr	14 - 32 %	-
Cu	11 - 15 %	-
Fe	12 - 17 %	-
Mn	11 - 15 %	-
Ni	10 - 14 %	40 %
Pb	8 - 13 %	25 %
Pt	40 - 50 % <sup>‡</sup>	-
Se	20 - 35 %	-
V	11 - 16 %	-
Zn	10 - 14 %	-
Hg(p)	20 - 40 %	-
Hg(v)	13 - 20 %	50 %

**Table 2.** The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2011. The 'EC Directive maximum' column shows the maximum permissible uncertainty at the target value allowed by the relevant EU Air Quality Directive. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. <sup>‡</sup> Many Pt measurements are below the limit of detection, the uncertainty quoted refers to those measurements that are above the detection limit.

The measurement uncertainties displayed in Table 2 are representative of the range of uncertainties covering the majority of individual measurements over a typical sampling period (here, one week), as required by the EU Air Quality Directives. The vast majority of the measurements used to compile the data in Table 2 were of ambient concentrations well below the appropriate target values. It is calculated that in the region of the appropriate target value – where the EU Air Quality Directive's uncertainty data quality objectives apply (except for Hg(v) where there is no target value) – these relative uncertainties will be significantly lower.

## 5 DATA QUALITY

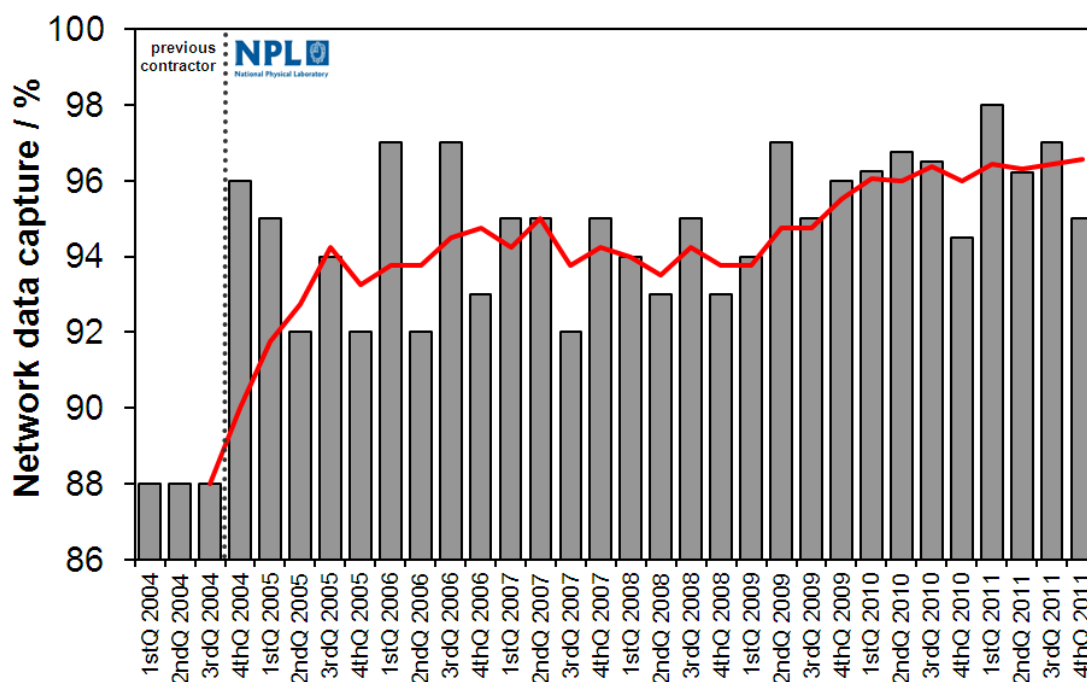
### 5.1 DATA CAPTURE

All data capture figures are based on a target time coverage of 100 %. (The Fourth DD requires a time coverage of only 50 % for fixed measurements of As, Ni and Cd.) Therefore any lost time coverage has a direct and equal effect on the data capture achieved. This is the most stringent way by which to calculate data capture percentages and represents the absolute percentage of all available time during the year for which valid data has been produced.

Data capture across the entire Network during 2010 was **96%**. Of the data lost:

- Approximately 50 % was excluded because the minimum number of valid sampling hours was not achieved during the sampling period;
- Approximately 50 % was lost owing to equipment failure or site operation problems, and;
- Less than 1 % was excluded at the analytical stage (owing to contamination of samples, instrument failure, exclusion during data ratification, etc).

The breakdown of the overall data capture between the particulate and gaseous phase, and at each site, is displayed in Table 3. The quarterly data capture, and the rolling annual average data capture, achieved by the Network over the last seven years are displayed in Figure 3. The yearly average data capture is currently at its highest level since NPL began operating the Network.



**Figure 3.** Network data capture from 2004-2011 (inclusive). Quarterly data capture is indicated by the grey bars, whilst the rolling annual average data capture is given by the red line. Data to the right of the dotted vertical line is associated with NPL's current operation of the Network; data to the left of the dotted line is associated with the previous contractor's operation of the Network.

Site Number: Site Location	Data Capture / %	
	Particulate phase	Gaseous phase
<b>Whole Network</b>	<b>96.4</b>	<b>97.2</b>
46: Walsall Centre	93.4	90.7
58: Sheffield Brinsworth	98.1	N/A
59: Runcorn Weston Point	87.4	97.4
61: London Cromwell Road	98.1	100
62: London Horseferry Road	100	99.1
65: Eskdalemuir	92.9	100
66: Motherwell Centre	90.1	92.3
67: Manchester Wythenshawe	96.2	100
68: Cardiff Llandaff	98.9	100
69: Walsall Willenhall	99.7	94.8
100: Swansea Coedgwilym	92.7	N/A
101: Swansea Morriston	94.5	92.6
103: Belfast Centre	100	96.7
104: Port Talbot Margam	97.1	100
105: Sheffield Centre	91.1	100
106: Scunthorpe Town	100	N/A
107: Scunthorpe Low Santon	98.8	N/A
108: Redcar	100	N/A
109: Cardiff Rumney	94.3	N/A
110: Chadwell St Mary	100	N/A
111: Redcar Normanby	100	N/A
112: Dartford Bean	98.1	N/A
113: Pontardawe Tawe Terrace	93.3	N/A
114: London Marylebone Road*	100	N/A
115: Pontardawe Brecon Road*	94.4	N/A

**Table 3.** Data capture across the UK Heavy Metals Monitoring Network during 2011.

\* Data capture refers to the period of time after which the station entered into operation or was affiliated to the Network.

## 5.2 DATA PROCESSING AND RATIFICATION

Analysis of the Network samples produces individual concentration values for four-weekly or weekly periods. These individual measurement results each have a stated measurement uncertainty, quoted at the 95% confidence level, associated with them. Annual means at each site are produced by calculating the means of these values, weighted according to the data capture during each period. Network-wide annual means are then produced by averaging annual means from the individual sites, again using appropriate weighing if a site has been monitoring for less than the full year.

An NPL QA/QC circle (the 'quality circle') ratifies ambient concentration data produced by the UK Heavy Metals Monitoring Network. NPL personnel performing the ratification procedure are independent of the Network analysis and management process. It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place in accordance with several guidelines, outlined below:

- 1) Only data where the valid sampling hours are greater or equal to 75% of the total sampling hours will be eligible to produce valid concentration data, and count towards the total data capture percentage.
- 2) Data not meeting the data quality objectives for uncertainty or time coverage for the relevant air quality directive are not eligible to produce concentration data and is counted as lost data capture.
- 3) Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.
- 4) Upon production, weekly data for each element at each site is plotted in a time series, or displayed as a continuous list of values which may be easily compared.
- 5) In the first instance these data are assessed visually for any obvious discrepancies with due regard to long terms trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data, including the use of powerful chemometric techniques<sup>10</sup>.
- 6) If valid reasons for obviously discrepant values are found (e.g. incorrect calculation, low exposure time, non-valid exposure volume, analytical error) these values may be either excluded or corrected (depending on the nature of the error).
- 7) As part of the internal quality and technical auditing procedures, a selection of ambient air concentrations calculated each month are thoroughly audited by a party independent of the analysis procedure. For these samples, the sample number, target analyte, auditor, audit date and status of the data is recorded in the designated Excel spreadsheet after auditing. These audits concentrate most heavily on Ni, As, Cd, Pb and Hg vapour analyses, as these are directly relevant to EC Air Quality Directives.

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<sup>10</sup> Using principal component analysis to detect outliers in ambient air monitoring studies, Brown, R J C, Goddard, S L, Brown, A S, *International Journal of Environmental Analytical Chemistry*, 2010, **90**, 761–772.

### 5.3 MEASUREMENT UNCERTAINTY OF ANNUAL AVERAGE

ISO 11222 “Air quality - Determination of the uncertainty of the time average of air quality measurements” is used to determine the uncertainty in the annual mean for each element at each sampling location. This is easily done since NPL produce a statement of uncertainty with each measurement result.

Data capture across the Network remains high (and any gaps in coverage have generally occurred evenly throughout the year) the uncertainty in the annual mean values will be dominated by the analytical and sampling uncertainty, with only small uncertainty contributions due to less than 100% time coverage. (The effect of these contributions is calculated using the method described in ISO 11222 “Air quality - Determination of the uncertainty of the time average of air quality measurements”.)

In all cases annual mean uncertainties are compliant with the data quality objectives for uncertainty in the EC Air Quality Directives. Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant EC Air Quality Directives metals are given in the table below:

Analyte	Relative Expanded Uncertainty	
	Annual Mean	EC Directive maximum
As	25 %	40 %
Cd	14 %	40 %
Ni	16 %	40 %
Pb	14 %	25 %
Hg(v)	20 %	50 %

**Table 4.** Relative expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Daughter Directive metals, averaged across the Network. Hg(v) refers to total gaseous mercury. For Hg(v) there is no limit or target value stated in the Fourth DD at which this maximum allowable uncertainty applies.

## 6 NETWORK DATA

### 6.1 MEASURED CONCENTRATIONS

The annual mean measured metals concentrations, averaged over all sites (Table 5), and at individual sites (Table 6), are given below. Table 5 also displays the maximum annual mean concentration measured at any monitoring site across the Network and the median annual concentration across all sites. In addition all data is available from Defra's UK-AIR website: <http://uk-air.defra.gov.uk/data/>

Analyte	2011 UK Mean Annual Concentration / ng m <sup>-3</sup>	2011 UK Median Annual Concentration / ng m <sup>-3</sup>	2011 Maximum Annual Mean Concentration / ng m <sup>-3</sup>	EC limit or target value (UK objective) / ng m <sup>-3</sup>
As	0.66	0.71	1.16	6
Cd	0.35	0.20	2.92	5
Co	0.21	0.16	0.93	-
Cr	6.06	4.34	40.2	-
Cu	18.2	7.28	88.0	-
Fe	616	334	3575	-
Mn	14.5	7.36	89.2	-
Ni	3.98	1.58	27.7	20
Pb	14.9	9.97	85.2	500 (250)
Pt	0.003	0.002	0.015	-
Se	0.58	0.51	2.20	-
V	1.62	1.32	5.45	-
Zn	56.0	26.6	689	-
Hg(p)	0.040	0.018	0.512	-
Hg(v)	4.04	2.01	21.1	-

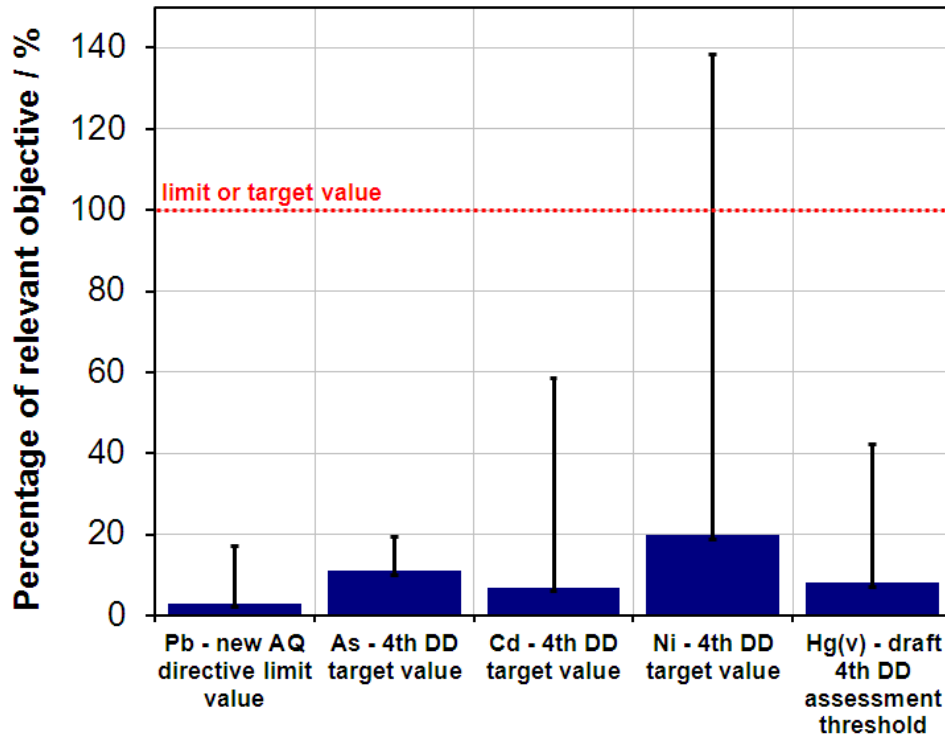
**Table 5.** The 2011 annual mean concentrations averaged over all sites on the UK Heavy Metals Monitoring Network, the annual median concentrations across all sites, and the maximum annual mean concentration measured at any monitoring site. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. The EC limit or target value (and/or UK objective, in brackets) is also listed, where applicable.

Site	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Pt	Se	V	Zn	Hg (p)	Hg (v)
46: Walsall Centre	0.97	0.71	0.16	4.66	17.8	368	10.7	1.55	19.4	0.002	0.49	1.37	66.2	0.022	5.07
58: Sheffield Brinsworth	0.93	0.42	0.64	40.2	22.0	542	39.0	15.4	25.1	0.015	0.95	1.57	117	0.065	N/A
59: Runcorn Weston Point	0.71	0.15	0.16	2.49	7.24	205	4.37	1.29	9.25	0.002	2.20	1.55	15.8	0.512	21.1
61: London Cromwell Road 2	0.74	0.39	0.20	7.31	44.9	1023	10.9	2.23	12.3	0.004	0.59	2.42	28.7	0.029	2.01
62: London Westminster	0.65	0.18	0.11	3.44	16.3	419	5.75	1.55	9.36	0.004	0.39	1.97	19.7	0.018	2.95
65: Eskdalemuir	0.11	0.03	0.04	2.20	0.86	36	0.98	0.40	1.23	0.001	0.14	0.38	2.69	0.008	1.47
66: Motherwell South	0.22	0.05	0.05	2.45	2.54	59	1.37	0.38	2.19	0.001	0.20	0.47	4.35	0.008	1.52
67: Manchester Wythenshawe	0.75	0.14	0.18	7.09	44.9	1055	10.9	1.49	7.26	0.006	0.64	1.15	30.8	0.017	2.14
68: Cardiff Llandaff	0.70	0.21	0.12	4.76	23.7	686	9.35	1.58	11.7	0.003	0.23	1.32	35.3	0.014	1.72
69: Walsall Bilston Lane	1.16	2.92	0.44	7.13	68.3	455	14.1	2.46	85.2	0.002	0.51	1.19	689	0.053	6.94
100: Swansea Coedgwilym	0.50	0.17	0.31	3.23	4.16	157	3.78	10.9	7.88	0.001	0.56	1.04	14.3	0.014	N/A
101: Swansea Morriston	0.66	0.27	0.18	4.47	33.5	555	8.60	8.24	18.1	0.002	0.73	1.32	32.1	0.022	1.94
103: Belfast Centre	0.29	0.10	0.10	2.30	6.43	204	3.16	0.66	4.04	0.005	0.12	1.02	11.7	0.008	2.29
104: Port Talbot Margam	0.71	0.49	0.18	4.34	8.64	3575	60.4	1.70	15.6	0.001	0.40	2.71	87.3	0.023	1.83
105: Sheffield Centre	0.59	0.19	0.11	6.93	11.3	334	12.2	2.16	11.9	0.001	1.02	1.27	27.9	0.028	1.53
106: Scunthorpe Town	0.77	0.19	0.13	5.23	6.06	684	26.1	1.41	20.5	0.001	0.98	1.70	26.1	0.021	N/A
107: Scunthorpe Low Santon	0.86	0.20	0.22	5.48	5.61	1757	89.2	1.58	39.4	0.001	1.19	5.45	33.0	0.022	N/A
108: Redcar	0.53	0.10	0.10	2.70	3.52	249	7.36	1.70	6.05	0.006	0.25	1.18	11.6	0.012	N/A
109: Cardiff Rumney	0.72	0.20	0.07	2.50	6.14	222	6.40	0.94	9.42	0.001	0.51	1.25	28.3	0.012	N/A
110: Chadwell St Mary	0.77	0.53	0.16	3.18	10.1	293	5.72	2.35	15.1	0.001	0.77	3.31	26.6	0.012	N/A
111: Redcar Normanby	0.33	0.08	0.04	2.11	2.63	97	2.95	0.69	4.22	0.003	0.12	0.60	8.15	0.009	N/A
112: Dartford Bean	0.62	0.34	0.09	2.22	7.28	184	3.91	1.49	9.97	0.001	0.10	2.10	16.0	0.012	N/A
113: Pontardawe Tawe Terrace	0.52	0.21	0.93	8.44	6.63	218	5.14	27.7	11.4	0.001	0.56	1.04	16.9	0.034	N/A
114: London Marylebone Road	0.74	0.31	0.24	12.8	88.0	1846	17.1	2.96	9.40	0.004	0.24	2.05	37.9	0.020	N/A
115: Pontadawe Brecon Road	0.85	0.15	0.23	3.90	5.81	182	3.28	6.52	5.77	0.001	0.49	0.94	12.3	0.004	N/A

**Table 6.** The 2011 annual mean concentrations (in ng/m<sup>3</sup>) measured at individual sites on the UK Heavy Metals Monitoring Network. The monthly measured metals concentrations from all Network sites are summarised in the tables in Annex 3. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. Colour coding for concentrations: above target value, above upper assessment threshold, above lower assessment threshold, below lower assessment threshold.

## 6.2 MEASURED CONCENTRATIONS WITH RESPECT TO THE REQUIREMENTS OF THE EU AIR QUALITY DIRECTIVES

The annual mean concentrations are compared against the relevant limit and target values, contained within the EU Air Quality Directives, in the figure below:



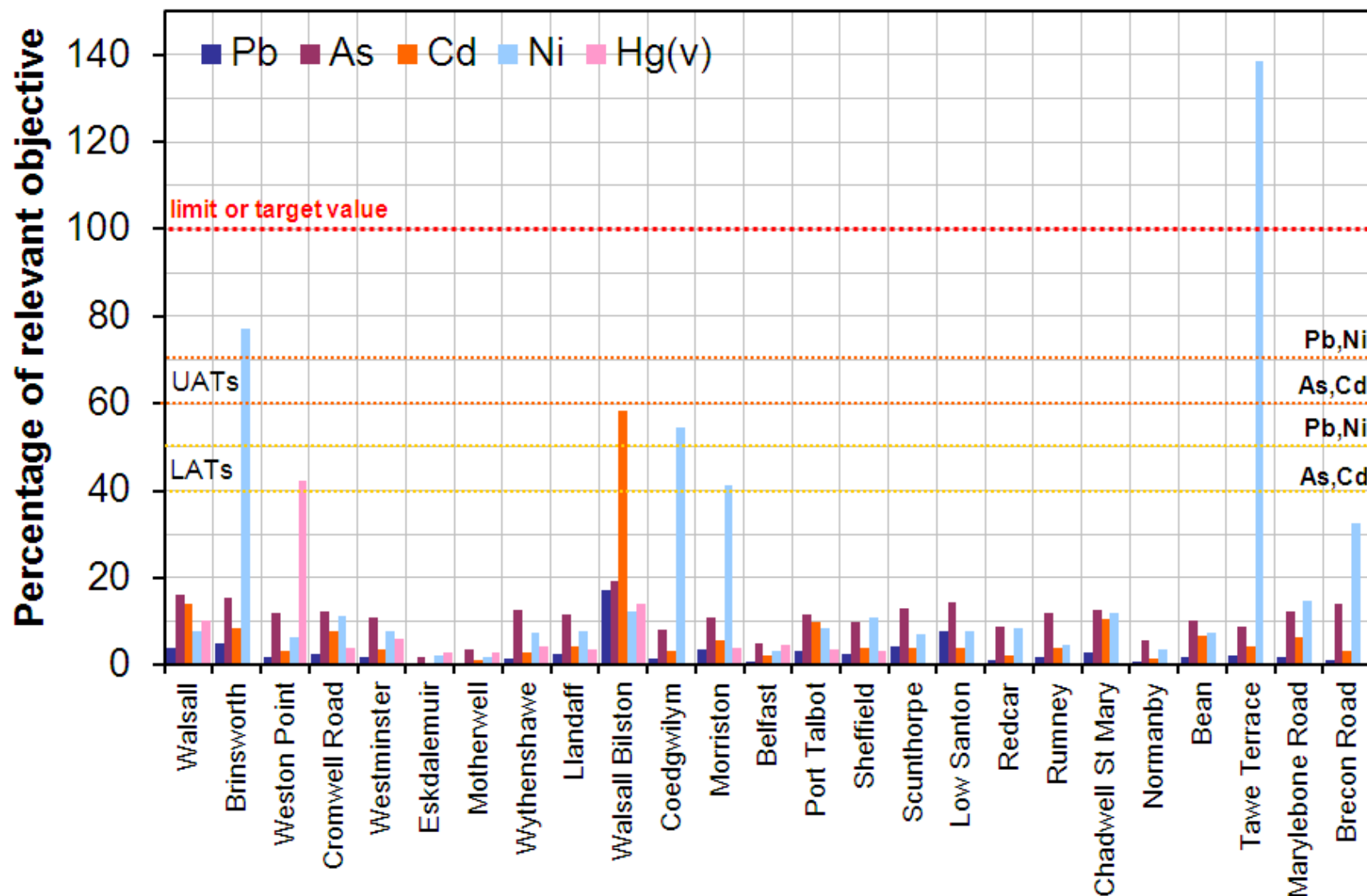
**Figure 4.** A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth Daughter Directives on the UK Heavy Metals Monitoring Network in 2011 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the annual means at the site with the highest concentrations. Hg(v) refers to the total gaseous mercury concentrations. The mercury objective is taken from a threshold value quoted in a draft of the Fourth DD.

In all cases the annual mean values are well below the limit and target values. Additionally the highest annual average at an individual site does not exceed any target or limit values.

Annual mean concentration values for the relevant EC Air Quality Directives metals at all Network sites are displayed in Figure 5.

The highest annual mean value for nickel has been found at Site 113: Pontardawe Tawe Terrace. The highest annual mean values for cadmium, arsenic and lead are found at Site 69: Walsall Bilston Lane. The highest annual mean value for total gaseous mercury has been found at Site 59: Runcorn Weston Point.





**Figure 5.** A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2011 as a percentage of the relevant target values, lower assessment thresholds (LATs) and upper assessment thresholds (UATs). The mercury objective originates from a threshold value quoted in a draft of the Fourth DD. Hg(v) represents total gaseous mercury.

In only four instances do the measured annual mean values exceed the relevant lower assessment thresholds:

**Annual Mean Concentrations above Target or Limit Values:**

- Nickel at Site 113: Pontardawe Tawe Terrace: 138 % of the target value.

**Annual Mean Concentrations above the Upper Assessment Threshold:**

- Nickel at Site 58: Sheffield Brinsworth: 77 % of the target value.

**Annual Mean Concentrations above the Lower Assessment Thresholds:**

- Nickel at Site 100: Swansea Coedgwilym: 55 % of the target value.
- Cadmium at Site 69: Walsall Willenhall: 58 % of the target value.

All other annual mean values at all sites for Ni, As, Cd and Pb are below the relevant Lower Assessment Thresholds.

**Notable Concentrations:**

- Total gaseous mercury at Site 59: Runcorn Weston Point. The measured concentration represents 42 % of the target value of 50 ng m<sup>-3</sup> quoted in a draft version of the Fourth DD.

The site at Pontardawe Tawe Terrace is situated close to the Wall Colmonoy nickel alloy production facility in Pontardawe. Whilst the Tawe Terrace site is nominally upwind of the facility it is very close to the source of nickel emissions and is located on the valley floor and hence measures higher concentrations than the downwind site at Pontardawe Brecon Road which is at several metres elevation up the valley.

The site at Swansea Coedgwilym is situated near to the Vale nickel refinery in Clydach, producing speciality nickel products and nickel-coated materials. The site at Swansea Morrision is the upwind pair of the Swansea Coedgwilym site but may also be exposed to relatively high concentrations when the wind is not in the prevailing direction.

The site at Sheffield Brinsworth is located next to the Outokumpu steel rolling mill and processing plant producing specialist steel strip, and coil, products.

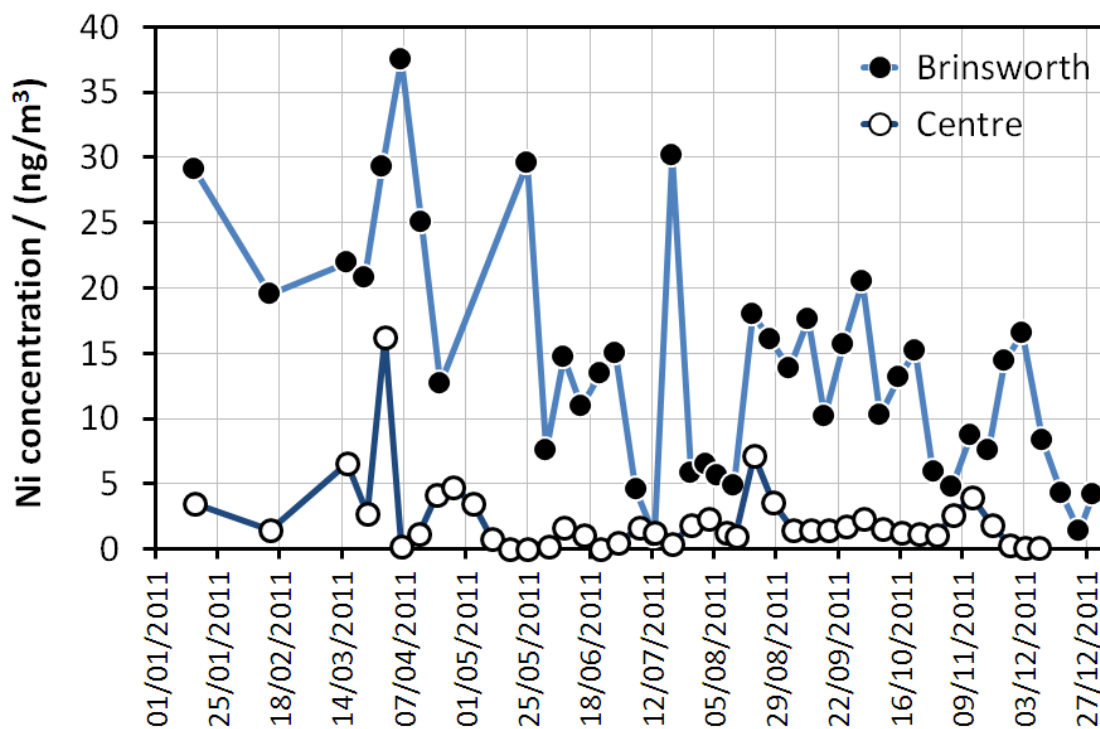
The site at Walsall Bilston Lane, is close to Brookside Metal Company, a producer of gunmetal, brass, bronze and other copper alloy ingots.

The site at Runcorn Weston Point is in the vicinity of a chlor-alkali facility using some mercury-based technology.

### 6.3 WITHIN YEAR CONCENTRATION TRENDS

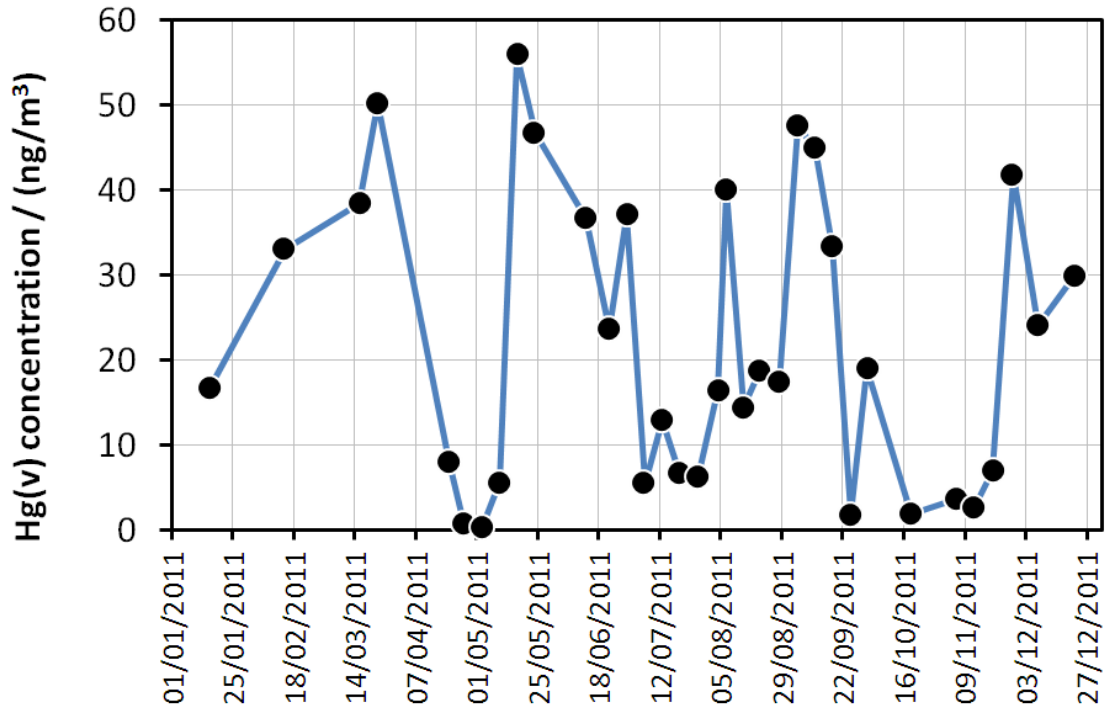
Seasonal trends are rarely observed for metals concentrations on the Network. This is not because there is no seasonality in the emissions of metals but more that the seasonality is small compared to the random effects of variability in the local meteorological conditions and uncertainty of the analysis of the samples. However distinct seasonality has been observed from arsenic<sup>11</sup>, which is generally emitted from diffuse combustion sources, not point sources, and therefore is affect much less by meteorological conditions.

The weekly measurements made under the new contract (from April onwards) allow an opportunity to examine the within year variability and trends of measured concentrations. This has been done for metals where values are in excess of, or close to, the lower assessment threshold and their paired sites, where appropriate, in the Figures below. (Cadmium at Walsall Willenhall did not make weekly measurements in 2011, but will do so in 2012, and so this data is displayed as monthly, and then four-weekly, averages).

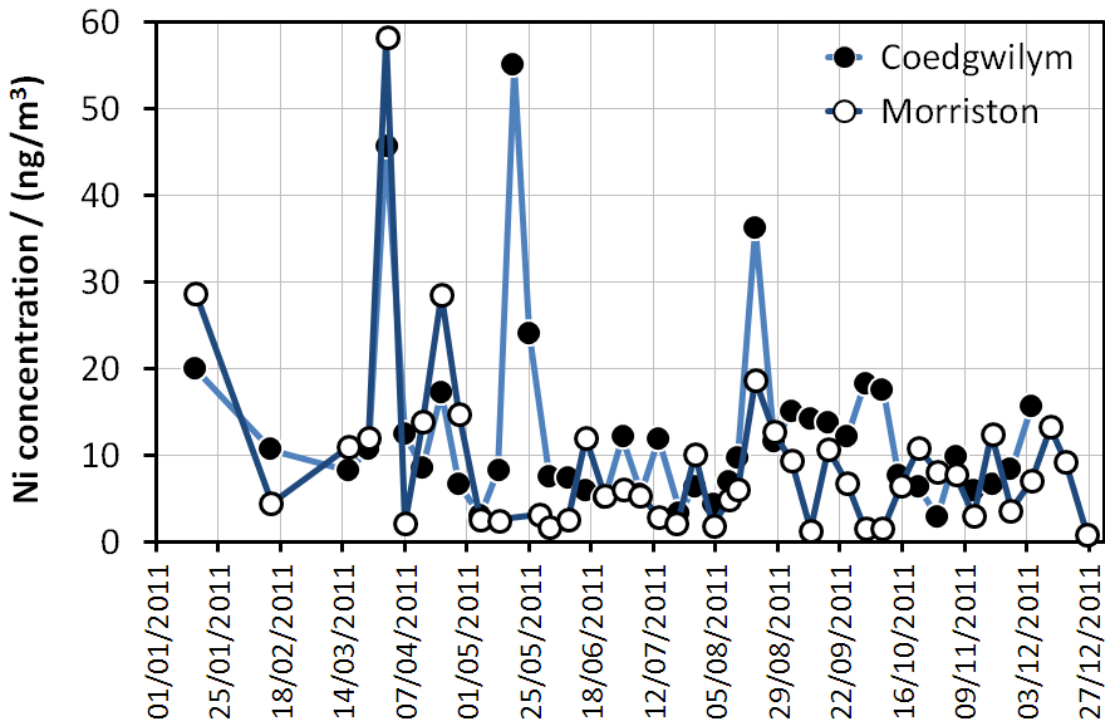


**Figure 6.** Measured Ni concentrations at Site 58: Sheffield Brinsworth and Site 105: Sheffield Centre, in 2011. The values are displayed at the centre of the sampling period to which they refer. Weekly analysis was performed from April onwards.

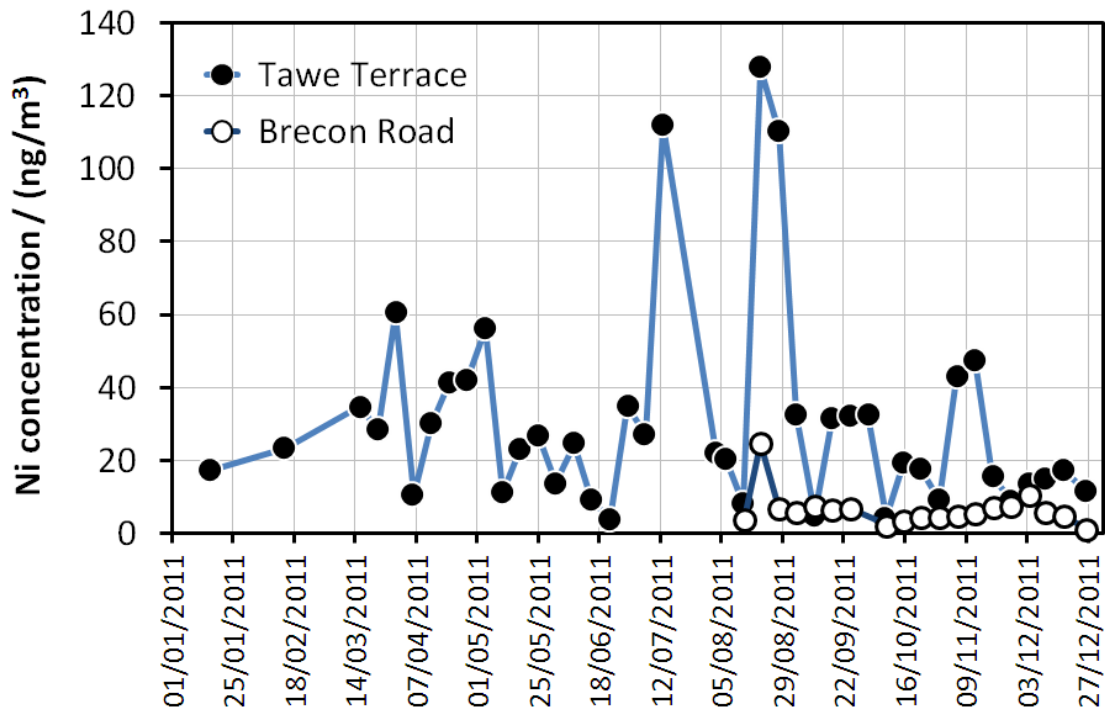
<sup>11</sup> Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends, Brown, R J C, et al, *Environmental Monitoring and Assessment*, 2008, **142**, 127-140.



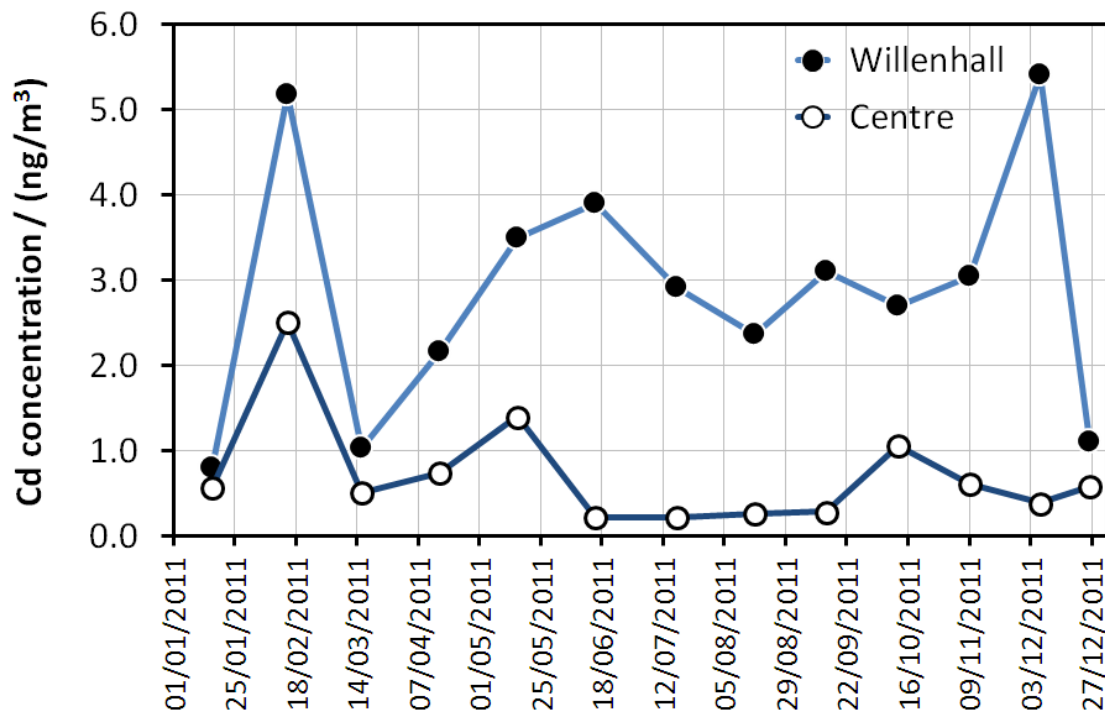
**Figure 7.** Measured Hg(v) concentrations at Site 59: Runcorn Weston Point in 2011. The values are displayed at the centre of the sampling period to which they refer. Weekly analysis was performed from April onwards.



**Figure 8.** Measured Ni concentrations at Site 100: Swansea Coedgwilym and Site 101: Swansea Morriston, in 2011. The values are displayed at the centre of the sampling period to which they refer. Weekly analysis was performed from April onwards.



**Figure 9.** Measured Ni concentrations at Site 113: Pontardawe Tawe Terrace and Site 114: Pontardawe Brecon Road, in 2011. The values are displayed at the centre of the sampling period to which they refer. Weekly analysis was performed from April onwards.



**Figure 10.** Measured Cd concentration at Site 69: Walsall Willenhall and Site 46: Walsall Centre, in 2011. The values are displayed at the centre of the sampling period to which they refer. Four-weekly analysis was performed from April onwards.

It is clear from these Figures 6 to 10 that the variability in measured concentrations from week to week is often large – much more so than when these values are averaged over a monthly period.

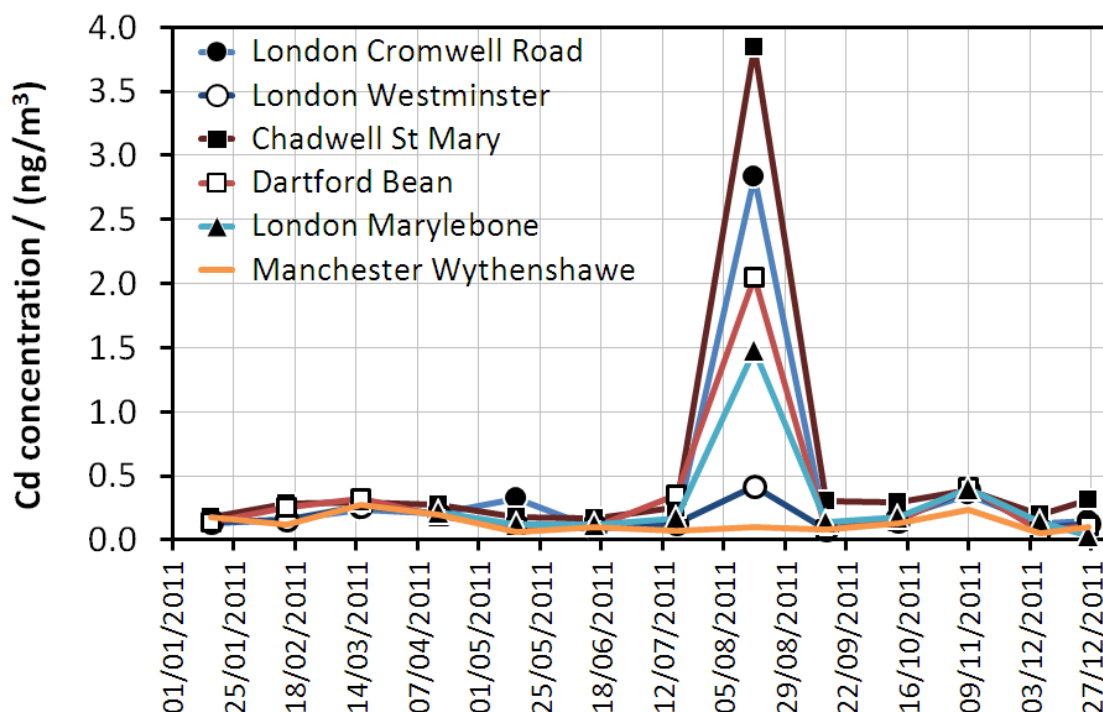
High concentration spikes often make a significant contribution to the annual average – for instance the Ni spike in South Wales in mid-August which seems to have originated close to the Tawe Terrace site, but travelled down the valley and influenced concentrations at Swansea Coedgwilym and Swansea Morrision. Determining the origin of these high concentration events will be crucial to reducing average concentrations in future.

At Sheffield Brinsworth Ni concentrations seem to have begun the year at quite high levels and then fallen steadily until mid-year, after which they have shown less change, although this trend is obscured somewhat by the increase resolution of the data from August onwards.

Cd concentrations at Walsall Willenhall have been consistently higher throughout the year than at Walsall Centre. The weekly data that will be provided for Walsall Willenhall in 2012 will give a clearer indication of the variability of these concentrations.

#### 6.4 HIGH CONCENTRATION EPISODE

There was one notable high concentration episode in 2011 associated with cadmium in the South East of England, shown below in Figure 11.



**Figure 11.** Measured Cd concentrations at the sites indicated on the graph. The values are displayed at the centre of the sampling period to which they refer. The values for Manchester Wythenshawe are included for comparison as a representative urban background site not in the south-east of England.

The high Cd concentrations observed in August are significantly in excess of what is expected at a UK urban sites (c.f. the Manchester Wythenshawe site). The metals refining facility that the Dartford Bean and Chadwell St Mary sites were established to monitor could have been the cause of such a release which, coupled with winds from the east, also resulted in high concentrations of Cd in London during this period. The Environment Agency was informed of this high concentration event. Apart from these high concentrations measured in August the other concentrations measured at these five stations in the south-east of England throughout the rest of the year were low.

## 6.5 MEASURED CONCENTRATIONS OF NON-DIRECTIVE METALS

Figure 12 shows the concentrations of the other non-directive metals normalised to the annual average for each metal.

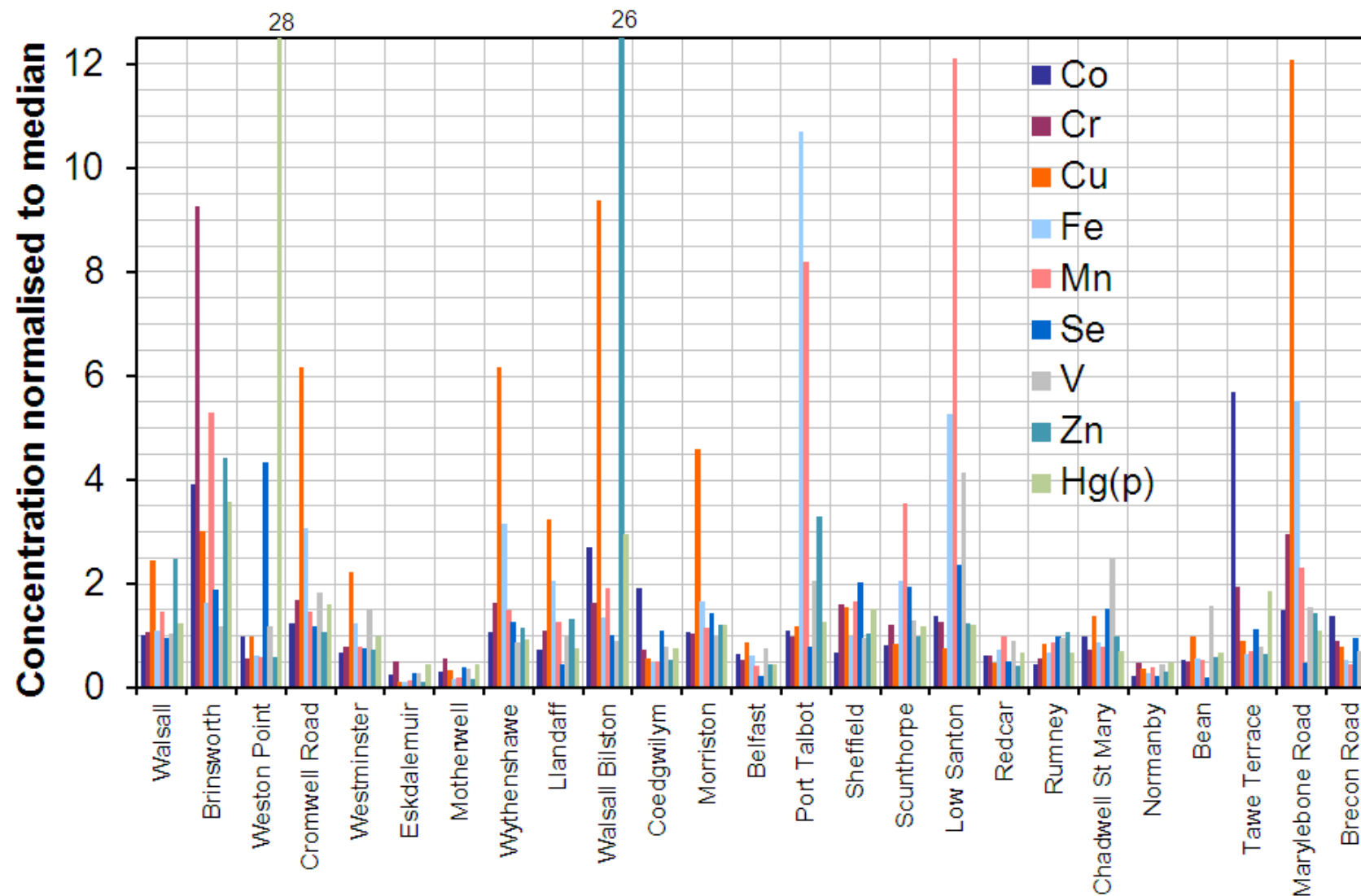
As expected, downwind sites all exhibit higher measured concentrations than their respective upwind site pairs. This continues to provide extra confidence that the direction of the prevailing weather conditions has been correctly assessed at each location and that the monitoring site pairs have been properly located. However, the concentrations recorded to date at these new sites are well below those predicted in the report<sup>12</sup> that recommended the locations of these sites based on modelled exceedences of lower assessment thresholds in the vicinity of point sources. This may be because the model over-estimated fugitive emissions around these point sources.

High concentration values for non-Directive metals are usually owing to specific processes close to the monitoring sites concerned. For instance:

- Copper and iron at roadside sites such as London Cromwell Road, London Marylebone Road, Swansea Morrision and Manchester Wythenshawe from non-exhaust emissions and resuspension;
- Iron and Manganese at Port Talbot Margam and Scunthorpe Low Santon, near to steel works;
- Chromium, manganese and zinc at Sheffield Brinsworth near to a steel rolling mill;
- Particulate phase mercury at Runcorn Weston Point close to a chlor-alkali plant and probable contributions from resuspension from contaminated land;
- Copper and zinc at Walsall Bilston Lane close to a metal refining works;
- Cobalt at Pontardawe Tawe Terrace close to a nickel-cobalt alloy production process;
- Elevated vanadium at Scunthorpe Low Santon and Chadwell St Mary, possible owing to the steel works and nearby metals refining processes, respectively;
- Elevated selenium at Runcorn Weston Point, possibly coming from nearby processes. More data is required to determine whether this is a real effect.

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<sup>12</sup> AEAT Report AEAT/ENV/2243 "Preliminary Assessment of PAH and heavy metal levels in the UK", Bush, T, AEAT, February 2007.



**Figure 12.** A summary of the annual mean measured concentrations of the non-directive metals at all sites on the UK Heavy Metals Monitoring Network in 2011, normalised to the UK annual median concentration for the relevant element. Bars that are off-scale have their values indicated at the top of the chart. Hg(p) refers to particulate phase mercury.



## 7 TRENDS IN MEASURED CONCENTRATIONS

### 7.1 UK TRENDS

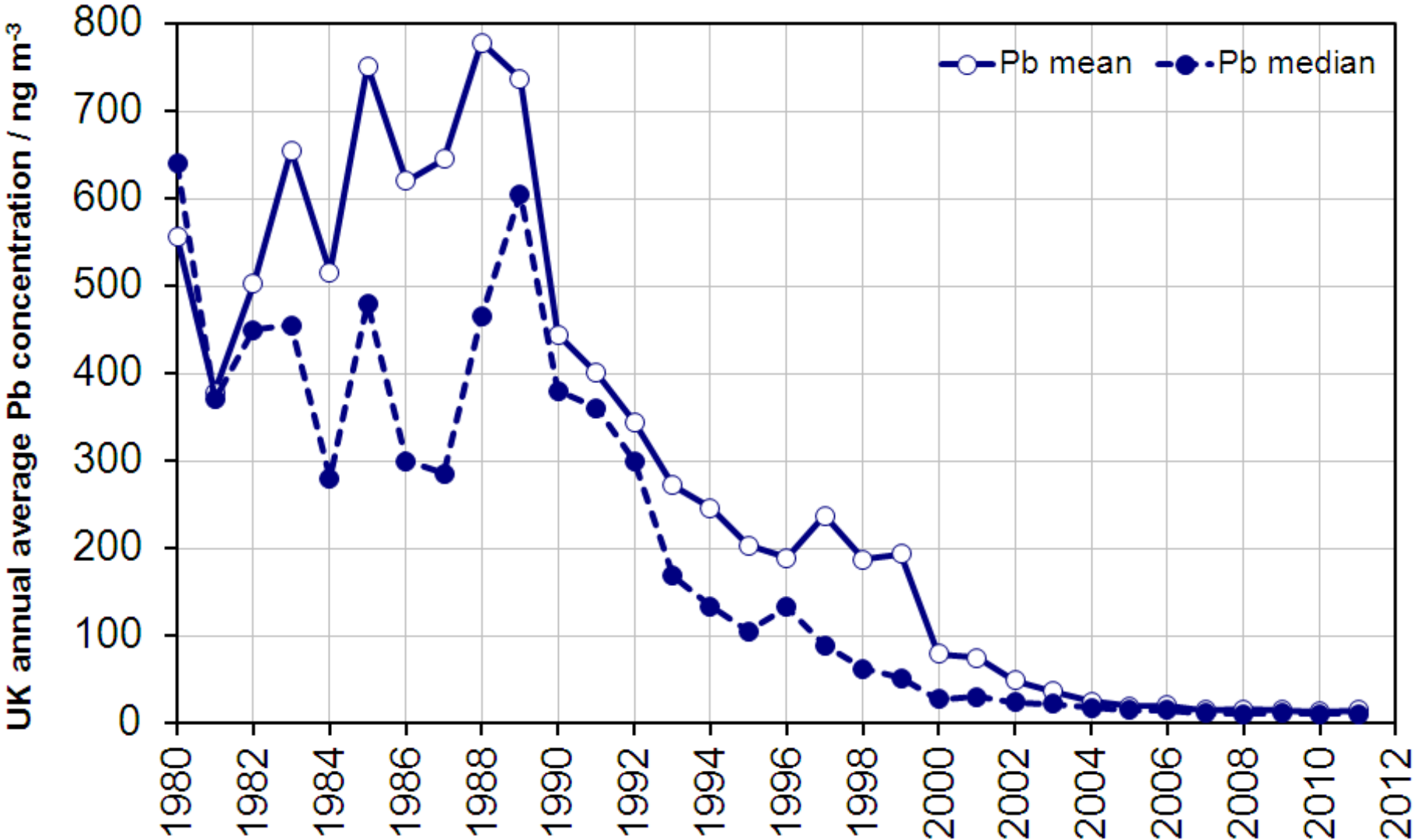
Trends in concentrations measured over the last 30 years for the metals relevant to the EU Air Quality Directives are summarised in Figures 13 and 14, where both the UK mean and UK median concentrations are displayed. The median has been used in addition to the mean since it is less sensitive to the effect of significant changes in sites measuring high concentrations, and to changes in the number and location of monitoring stations making up the Network.

The trends in both the UK annual mean and median observed for the other metals measured by the Network are shown in Figures 15 and 16. (Co and Se are not included since they have only been measured for one year. Pt is excluded since many values are below the detection limit).

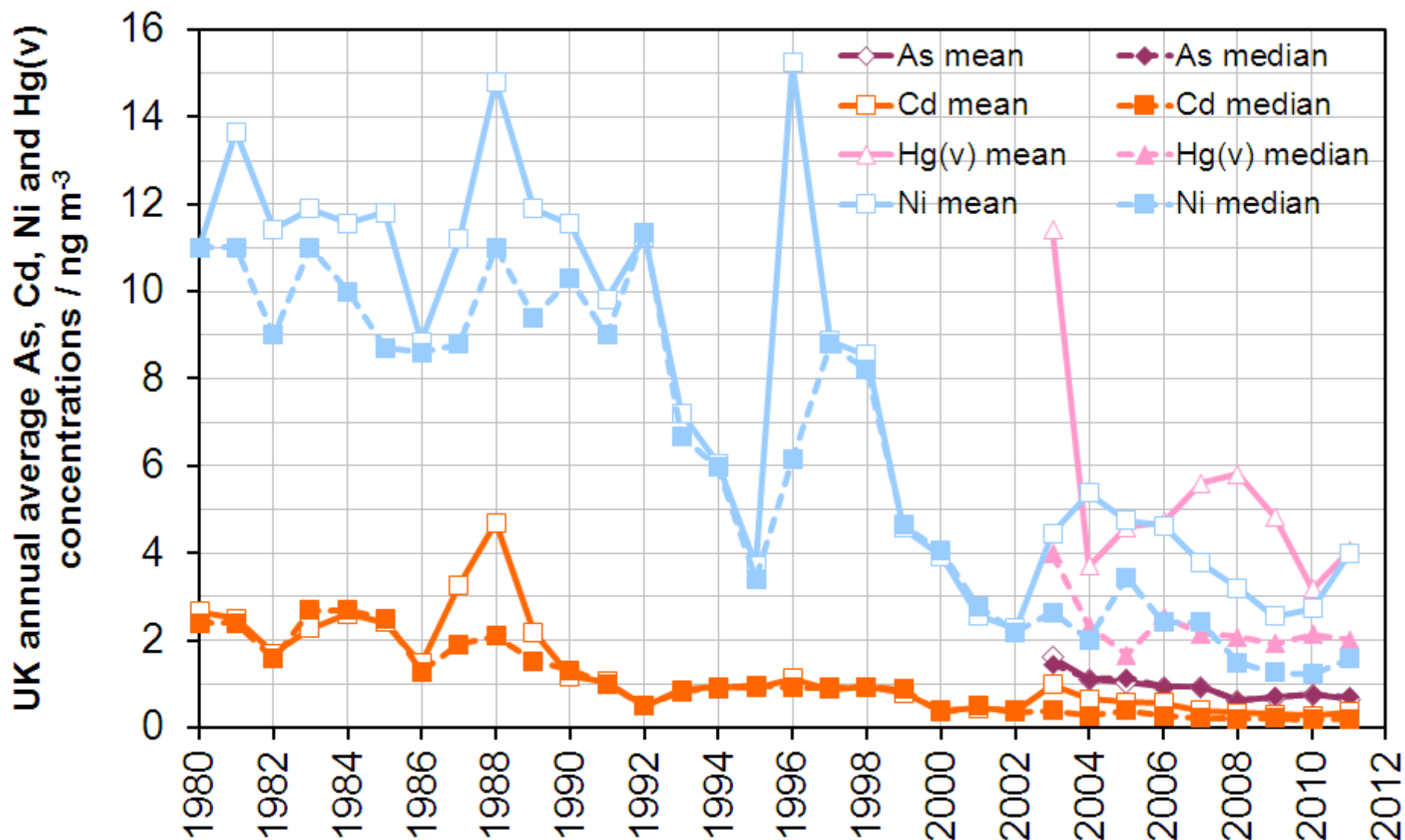
Where mean values are significantly higher than median values, this indicates that there are a small number of sites with very high concentrations levels whose measured values and variability have a disproportionate effect on the overall mean. Under these circumstances the median value may give a more representative reflection of the long-term concentration trends.

Annual mean concentrations for all elements have generally fallen over the period for which data is available – this generally mirrors the decrease in emissions over this period.

In recent years this trend has levelled off to yield more stable concentrations. Indeed the largest influences from year to year have tended to come from either meteorological variability or from changes in the composition of the Network – as was the case for many elements between 2010 and 2011.



**Figure 13.** The mean and median of station annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 31 years. The EC limit value for lead is 500 ng m<sup>-3</sup> and the UK Air Quality Objective for lead is 250 ng m<sup>-3</sup>.



**Figure 14.** The mean and median of station annual average concentrations of Ni, As, Cd and total gaseous mercury [Hg(v)] measured on the UK Heavy Metals Monitoring Network over the last 31 years. The EC targets values for Ni, As and Cd are 20 ng m<sup>-3</sup>, 6 ng m<sup>-3</sup> and 5 ng m<sup>-3</sup> respectively.

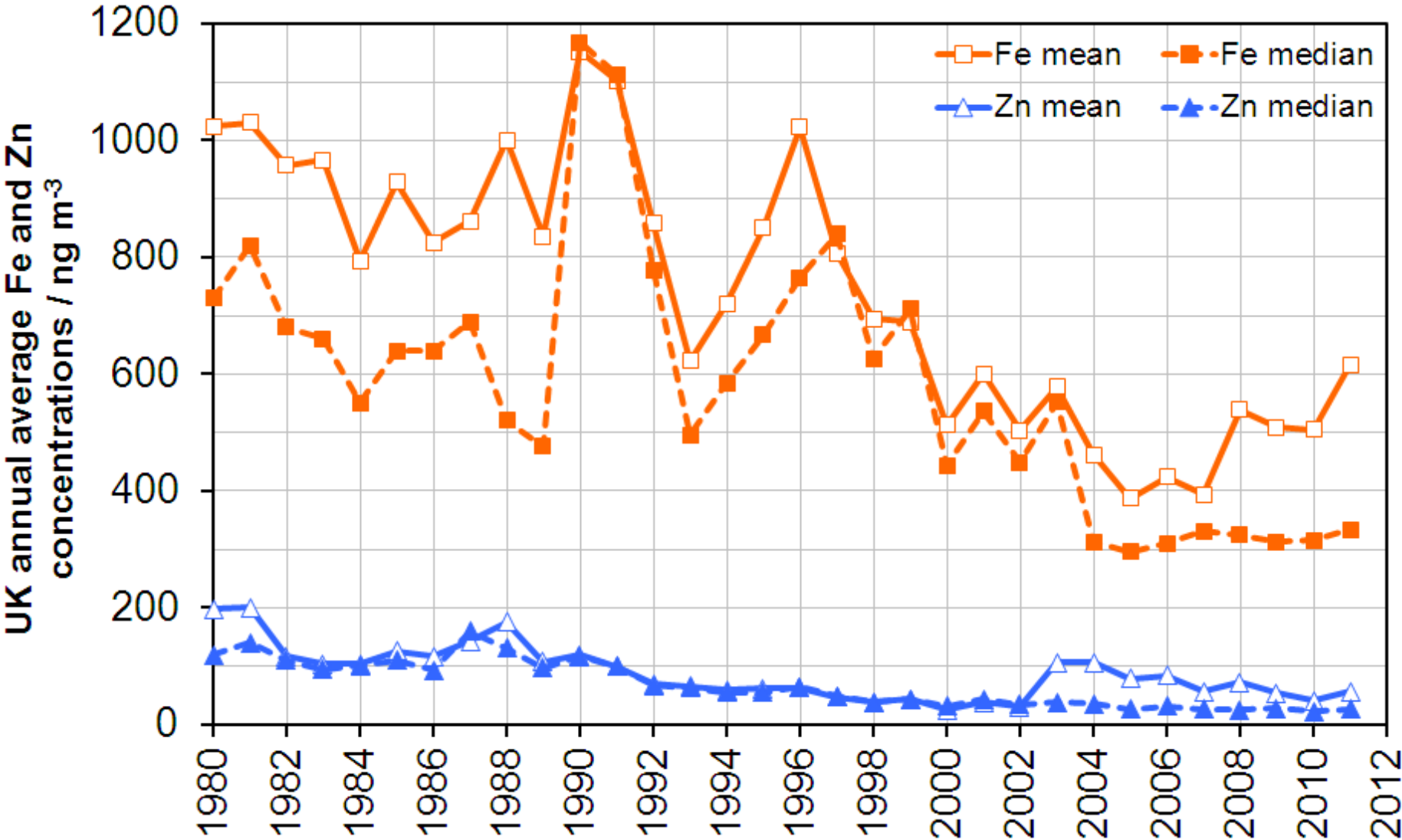
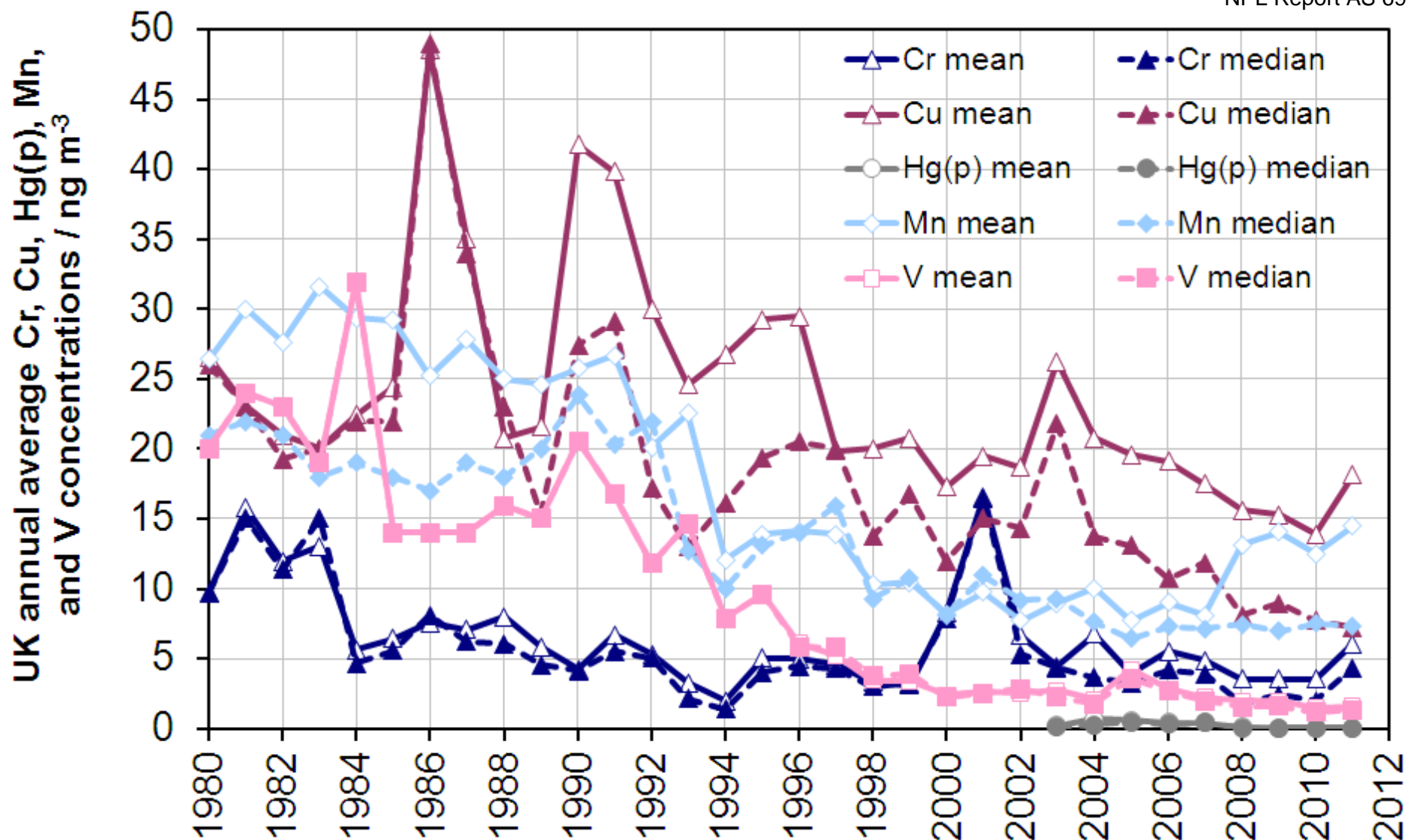


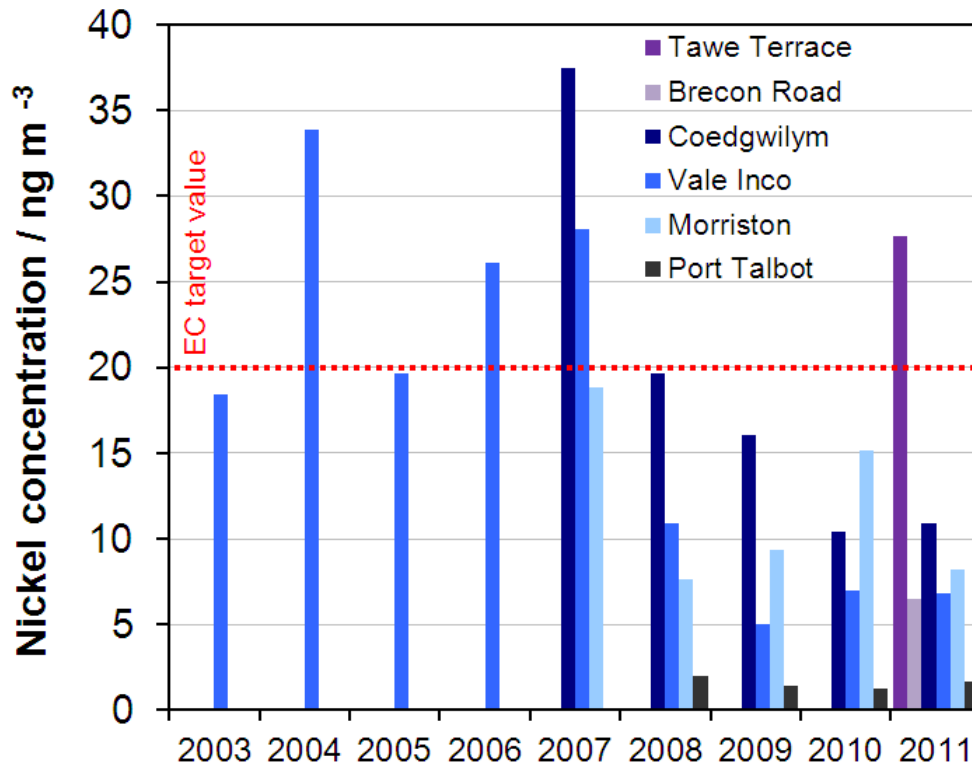
Figure 15. The mean and median of station annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 31 years.



**Figure 16.** The mean and median of station annual average concentrations of Cr, Cu, Hg(p), Mn and V measured on the UK Heavy Metals Monitoring Network over the last 31 years.

## 7.2 TRENDS IN NICKEL IN THE SWANSEA VALLEY

The annual average concentration of Nickel at Swansea measured over the last 9 years is shown in Figure 17.



**Figure 17.** The annual average nickel concentrations measured at monitoring sites in the Swansea area (indicated by the key) over the last 9 years. Nickel concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level. The red dotted line indicates the Fourth DD target value for nickel. (The data for Vale Inco in 2008 – 2011, and Coedgwilym and Morrision in 2007 are courtesy of Tom Price and the City and County of Swansea).

Swansea Vale Inco (located at: Glais Primary School, School Road, Glais, Swansea, SA7 9EY) was the UK Heavy Metals Monitoring site in the Swansea area from 2003 to 2007 inclusive: it is now operated as a City and County of Swansea local authority site with site auditing and analysis services provided by NPL. At the end of 2007 the local authority sites at Swansea Coedgwilym and Swansea Morrision were assimilated onto the Network.

All sites (excluding the new Pontardawe sites) have shown a decrease in measured concentrations from 2007 onwards. This correlates with abatement technologies being installed in late 2007 in order to reduce particle emissions from the point source in question. Another City and County of Swansea local authority site for which NPL provide the auditing and analytical service, YGG Gellionnen (location: YGG Gellionnen School, Gellionnen Road, Clydach, Pontardawe, SA6 5LB), has shown similar concentration trends over this period. Moreover, the relative

concentrations between these sites are broadly as predicted by NPL's recent modelling study of the area<sup>13</sup>.

It will be interesting to observe trends at the two new sites in the Pontardawe area over the coming years. The concentrations at Pontardawe Tawe Terrace in 2011 are similar to those observed at Swansea Coedgwilym prior to abatement measures being installed at the nearby industrial facility. Similar abatement processes at the industrial facility impacting on the Pontardawe Tawe Terrace site during 2011 and early 2012 should have a positive effect in reducing local Ni concentrations in the future.

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13 NPL Report AS 30, "Atmospheric Dispersion Modelling of Nickel in the Swansea Area", Hayman, G, February 2009

## 8 SCIENTIFIC RESEARCH, PUBLICATIONS AND RELATED ACTIVITIES

### 8.1 PUBLICATIONS

NPL has produced a number of articles in learned journals during 2011 that feature the data, analytical procedures and operation of the Network and research relevant to Network objectives. These articles are listed below.

a) Memory effects on adsorption tubes for mercury vapour measurement in ambient air: elucidation, quantification and strategies for mitigation of analytical bias

Brown, R J C; Kumar, Y; Brown, A S; Kim, K-H

*Environmental Science & Technology*, 2011, **45**, 7812–7818.

b) Measurement techniques for Hg species in ambient air

Pandey, S K; Kim, K-H; Brown, R J C

*Trends in Analytical Chemistry*, 2011, **30**, 899-917.

c) Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in PM<sub>10</sub> in Europe

Gerboles, M; Buzica, D; Brown, R J C, *et al.*

*Atmospheric Environment*, 2011, **45**, 3488-3499.

d) Uncertainty-weighted time-averaging of mercury vapour concentrations in ambient air: application to measurements in the United Kingdom

Brown, RJC; Muhunthan, D

*TheScientificWorldJOURNAL*, 2011, **11**, 242-252.

### 8.2 INTERNATIONAL AND STANDARDISATION ACTIVITY

NPL has continued to host and provide the secretariat for BSI committee EH/002/03 “Ambient Atmospheres” which is the UK mirror group shadowing the development of ambient and indoor air standards within CEN and ISO, in particular, CEN TC264 ‘Air Quality’ and ISO TC146 ‘Air Quality’.

BSI EH/2/3 voted in 2010 not to revise the current EN 14902 standard for particulate phase metals analysis, a decision supported by a large majority of the CEN Member Bodies in Europe. Hence there will be no changes to the fundamental analysis procedures used by the Network in the foreseeable future.

In addition, NPL has recently provided input to the consultation process to the revision of the current EC Air Quality Directives, especially in the areas of metals in the PM<sub>10</sub> phase and total gaseous mercury. NPL's input is a consequence of the work it does delivering air quality networks for Defra and its role in representing the UK on the EU network of Air Quality Reference Laboratories (AQUILA).



# ANNEX 1 LOCATION AND DETAILS OF SITES COMPRISING THE UK HEAVY METALS NETWORK



**Figure A1.** Location of monitoring sites comprising the UK Heavy Metals Monitoring Network during 2011 (indicated by the orange circles) – details of which are given in Table A1 below.

<b>NEW Site Code: Site Name (Abbreviated Site Name)</b>	<b>Site Address</b>	<b>Site Area and Classification (with identified point source, where applicable)</b>	<b>Pollutants measured</b>
46: Walsall Centre (Walsall)	74 Primley Avenue, Walsall, WS2 9UW	Industrial Urban (IMI Refiners Ltd, Walsall)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
58: Sheffield Brinsworth (Brinsworth)	BOC Gases, Bawtry Road, Brinsworth, Sheffield, S60 5NT	Urban Industrial (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
59: Runcorn Weston Point (Weston Point)	Weston Point County Primary School, Caster Avenue, Weston Point, Runcorn, WA7 4EQ	Urban Industrial (INEOS Enterprises Ltd, Weston Point)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
61: London Cromwell Road 2 (Cromwell Road)	Natural History Museum, Cromwell Road, London, SW7 5BD	Urban Traffic	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
62: London Westminster (Westminster)	Mortuary Car Park, Horseferry Road, London, SW1P 2EB	Urban Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
65: Eskdalemuir (Eskdalemuir)	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	Rural Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
66: Motherwell South (Motherwell)	Our Lady's High School, Dalzell Drive, Motherwell, North Lanarkshire, ML1 2DG	Urban Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
67: Manchester Wythenshawe (Wythenshawe)	Junction 4, M56, Newhall Green, Wythenshawe, Manchester, M22 8	Urban Traffic	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
68: Cardiff Llandaff (Llandaff)	Cleansing Depot, Waungron, Fairwater, Cardiff, CF5 2JJ	Urban Traffic (Celsa UK Ltd, Tremorfa)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
69: Walsall Bilston Lane (Walsall Bilston)	Adult Training Centre, Bilston Lane, Shepwell Green, Willenhall, Walsall, WV13 2QJ	Urban Background (Brookside Metals Ltd, Willenhall)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
100: Swansea Coedgwilym (Coedgwilym)	Coedgwilym Cemetery, Pontardawe Road, Clydach, Swansea, SA6 5PB	Urban Background (Vale Ltd, Swansea)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
101: Swansea Morrision (Morrision)	Morrision Groundhog, Wychtree Street, Morrision, Swansea, SA6 8EX	Urban Traffic (Vale Ltd, Swansea)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
103: Belfast Centre (Belfast)	Lombard Street, Belfast, BT1 1RB	Urban Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
104: Port Talbot Margam (Port Talbot)	Port Talbot Fire Station, Commercial Road, Port Talbot, West Glamorgan, SA13 1LG	Urban Industrial (Corus Group Ltd, Port Talbot)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
105: Sheffield Centre (Sheffield)	Charter Square, Sheffield, S1 4JD	Urban Background (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
106: Scunthorpe Town (Scunthorpe)	Rowlands Road, Scunthorpe, North Lincolnshire, DN16 1TJ	Urban Industrial (Corus Group Ltd, Scunthorpe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn

NEW Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Classification (with identified point source, where applicable)	Pollutants measured
107: Scunthorpe Low Santon (Low Santon)	Dawes Lane, Santon, Scunthorpe, North Lincolnshire, DN16 1XH	Urban Industrial (Corus Group Ltd, Scunthorpe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
108: Redcar (Redcar)	Further Education Centre, Corporation Road, Redcar, TS10 1HA	Suburban Background (Corus Group Ltd, Redcar)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
109: Cardiff Rumney (Rumney)	Greenway Primary School, Llanstephen Road, Rumney, Cardiff, CF3 3JG	Urban Background (Celsa UK Ltd, Tremorfa)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
110: Chadwell St Mary (Chadwell St Mary)	Council Area Housing Office, Linford Road, Chadwell St Mary, Essex, RM16 4JY	Urban Background (Britannia Refined Metals, Gravesend)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
111: Redcar Normanby (Normanby)	Tees, Esk and Wear Valleys NHS Trust, Flatts Lane, Normanby, Middlesbrough, TS6 0SZ	Urban Background (Corus Group Ltd, Redcar)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
112: Dartford Bean (Bean)	Bean Primary School, Bean, Dartford, Kent, DA2 8AW	Urban Background (Britannia Refined Metals, Gravesend)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
113: Pontardawe Tawe Terrace (Tawe Terrace)	Tawe Terrace, Pontardawe, Swansea, West Glamorgan, SA8 4HA	Industrial Urban (Wall Colmonoy, Pontardawe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
114: London Marylebone Road (Marylebone Road)	Marylebone Road (opposite Madame Tussauds), London, NW1 5LR	Traffic Urban	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
115: Pontardawe Brecon Road (Brecon Road)	Dany Bryn Residential Care, 84 Brecon Road, Pontardawe, Swansea, SA8 4PD	Industrial Urban (Wall Colmonoy, Pontardawe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn

**Table A1.** Details of the sites comprising the UK Heavy Metals Monitoring Network, including: site names, abbreviated site names, site locations, site are and classification, point source monitored (where applicable) and pollutants measured.

Next page:

**Image 4.** The Network monitoring site at Motherwell South.

