Report

Monitoring of Lead, Arsenic, Cadmium, Nickel and Mercury around Industrial Sites

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Summary

This report on 'Monitoring of Lead, Arsenic, Nickel, Mercury and Cadmium Around Industrial Sites' has been compiled by Stanger Science and Environment on behalf of DEFRA (formerly DETR), the National Assembly for Wales, the Scottish Executive, and the Department of the Environment in Northern Ireland under contract EPG 1/3/140. The purpose of the monitoring was to assess:

- provide baseline information on the ambient levels of Pb, As, Cd, Ni and Hg around industrial sites
- determine the likelihood of problems in complying with the EU Limit Value and current AQS objective(s) for Pb
- determine the current UK position on ambient metals monitoring for Cd, Ni and As in anticipation of any proposed Limit Values to be set by the EU
- assign significance to the occurrence of vapour-phase Hg and particulate-phase Hg emissions
- determine the relationship between short-term (24-hour measurements) and long-term (7-day) sampling regimes for metals
- identify industrial sectors at risk of exceeding current and proposed Limit Values and to provide recommendations for future monitoring requirements and/or further research needs

Legislative Background

The European Air Quality Framework Directive (96/62/EC) sets out the strategic framework for ambient air quality assessment and management for twelve pollutants. The aims of the Directive are to establish Limit Values and (where appropriate) alert thresholds for concentrations of pollutants in ambient air (through Daughter Directives) intended to avoid, prevent or reduce harmful effects on human health and the environment as a whole. The Directive also aims to assess concentrations of pollutants based on a common method and criteria and obtain adequate information on concentrations in order to make information available to the public.

The Directive places a legal obligation on the EU Member States to achieve the Limit Values. In its review of the 1997 National Air Quality Strategy Government recommended that the EU Limit Value for Pb be adopted in the UK with the consequence that the achievement date was brought forward from 31 December 2005 to 31 December 2004. The objective value adopted was 0.5 $\mu g/m^3$ measured as an annual average concentration. In the 2000 Strategy the Government tightened this objective, based upon a recommendation from its Expert Panel on Air Quality Standards to 0.25 $\mu g/m^3$ to be met by 2008.

A common position is currently being sought with regards to the setting of Limit Values for other metals (Cd, Ni and As) across Member States. The EC Working Group on Arsenic, Cadmium and Nickel Compounds has completed its final draft of the position paper and the European Commission will formally bring forward proposals in the Autumn. It is anticipated these initial proposals will include Limit Values for:

Arsenic	6 ng/m^3
Cadmium	5 ng/m^3
Nickel	20 ng/m^3
Mercury	50 ng/m^3

For the purposes of analysis and interpretation of the results of the 12-month monitoring programme, the above values have been used.

Monitoring Results

Monitoring was undertaken in the vicinity of 30 sites throughout the UK covering a wide variety of industrial sectors. As far as possible the location of monitoring equipment was at the anticipated point of maximum concentration but where members of the public must reasonably be expected to be exposed but no modelling or screening was undertaken in order to determine the exact location of equipment.

Weekly measurements of particulate concentrations of Pb, As, Cd, Ni and Hg were undertaken at all 30 sites on the PM_{10} fraction. In addition, at 5 of the 30 sites, fixed 24-hour monitoring of PM_{10} was undertaken. Daily samples were bulked for analysis of Pb, As, Cd, Ni and Hg to cover the same 7-day period in order to compare sampling regimes. Vapour-phase Hg measurements were undertaken at 5 of the 30 sites using gold-adsorption traps.

Results[1] of the 12-month monitoring programme undertaken during December 1999 - November 2000 indicate no exceedences of the Limit Value for Pb (0.5 $\mu g/m^3$). There were also no exceedences of the UK annual mean objective value of 0.25 $\mu g/m^3$ (to be achieved by 31 December 2008). One site (IMI Refiners Ltd in Walsall) approached the 2008 objective value with an annual mean of 0.237 $\mu g/m^3$. However, trend analysis has shown that values have decreased significantly over previous years as a result of reduced capacity in production due to the phased closure of various plant at the site. In general, sites showed annual mean Pb concentrations in the range 0.010 - 0.050 $\mu g/m^3$.

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[1] Overall uncertainty (analytical and sampling) has been estimated at between ± 25% and ± 30%.

For As, Cd and Ni, exceedences of the proposed EU Limit Values as proposed by the EC Air Quality Steering Group and the Upper and Lower Assessment Thresholds were recorded:

For Cd, the proposed Limit Value of 5 ng/m^3 was exceeded at two sites. Annual mean concentrations of 7.37 ng/m^3 and 7.73 ng/m^3 were recorded at IMI Refiners Ltd in Walsall, and Britannia Zinc Ltd in Avonmouth, respectively. In addition, the Upper Assessment Threshold was exceeded at Sidney Smith iron foundry, which recorded an annual mean value of 3.50 ng/m^3. No other site recorded an annual mean concentration above the Lower Assessment Threshold.

Annual mean Ni concentrations indicate only one marginal exceedence of the proposed Limit Value of 20 ng/m^3. This was found at the INCO nickel refinery (20.6 ng/m^3). Additionally, the proposed Lower Assessment Threshold (10ng/m^3) for Ni was breached at the Bruhl UK Ltd works in Sandwell (13.4 ng/m^3).

For As, one site showed an annual mean concentration greater than the proposed Limit Value of 6 ng/m^3. An annual mean of 8.36 ng/m^3 was measured at IMI Refiners Ltd, Walsall. Additionally, the proposed Upper Assessment Threshold (3.6 ng/m^3) value for As was breached at the site at Walkers Galvanizing (annual mean As of 4.22 ng/m^3). However, data capture at this site was very low (28%) due to recurrent problems in equipment malfunction leading to considerable uncertainty surrounding the estimate of the annual mean concentration. The proposed Lower Assessment Threshold was breached at a number of sites including; White Rose Environmental (3.31 ng/m^3); Wolverhampton MWI (3.11 ng/m^3); Corus Engineering Steels Ltd (3.01 ng/m^3); Paramount Batteries (2.91 ng/m^3) and Bruhl UK Ltd (2.67 ng/m^3).

For Hg, results of the particulate phase measurements indicate that concentrations were generally low at all monitoring locations, with levels around the limit of detection (0.06 ng/m^3). The highest annual mean particulate phase Hg concentration (0.64 ng/m^3) was found at ICI Chemicals and Polymers plc in Runcorn. Elevated concentrations, 0.48 ng/m^3 and 0.41 ng/m^3 were also found at Walkers Galvanizing and IMI Refiners Ltd plants in Walsall, respectively. Concentrations at other sites were similar at around 0.25 ng/m^3 (Britannia Zinc Ltd., Avonmouth; British Steel, Llanwern; and Bruhl UK Ltd in Sandwell).

Vapour-phase Hg concentrations ($Hg_{[vap]}$) were also monitored at 5 sites. Results covering March 2000 - November 2000 highlight differences between sites and variation in the week-to-week concentrations. Typically, weekly values of $Hg_{[vap]}$ were in the range 1 - 8 ng/m^3 with period mean (March - November) values around 2 -3 ng/m^3. However, the weekly mean $Hg_{[vap]}$ concentrations at ICI Chemical and Polymers plc plant in

Runcorn showed much elevated concentrations when compared to other sites. Here, weekly measurements ranged from 3 - 69 ng/m^3 with a period mean of 24.1 ng/m^3 for the period March 2000 - November 2000.

A comparison of results at five sites between weekly (7-day) measurements and 7 day bulked (24-hour) samples show very good agreement (linear regression coefficients (r^2) > 0.95) for Pb, As and Cd. For nickel, $r^2 = 0.82$ was found, whilst for Hg, a weak relationship between the two sampling regimes was found ($r^2 < 0.1$) when compared to other elements. Increased uncertainty with respect to measurements made at, or below, the limit of detection of Hg is likely to be responsible for the difference in r^2 when compared to other elements. In general, results show the sampling approach of 7-day continuous sampling is a cost-effective response to the sampling regime of the First Daughter Directive for Pb. Moreover, the results indicate that the regime may prove to be equally as cost-effective in responding to the 4th Daughter Directive on As, Cd and Ni. For Hg, an increased level of uncertainty at low concentrations around the limits of detection invalidates this approach.

Conclusions and Recommendations

The current monitoring programme highlights that the EU Limit Value and UK air quality objective(s) for Pb (0.5 $\mu g/m^3$ to be achieved by 31 December 2004) was not exceeded at any of the monitoring locations in the vicinity of industrial processes. The more stringent objective of lead (0.25 $\mu g/m^3$ to be achieved by 31 December 2008) is currently not exceeded at any of the monitoring locations. However, in the case of the latter, the value of 0.25 $\mu g/m^3$ is approached at the IMI Refiners Ltd site in Walsall. Additional monitoring undertaken in the UK in accordance with Directive 82/884/EEC indicates that the Limit Value is currently (1999) exceeded in the vicinity of the Brookside Metal Co Ltd site in Willenhall, West Midlands. In addition, results of a detailed sector analysis for Pb indicates that current problems in complying with the AQS objective of 0.25 μgm^{-3} may exist at the Britannia Recycling (secondary lead) in Wakefield, and the Dens Metals plant in Dundee. Proposed changes to emissions abatement controls are likely to mean that such levels will not be a problem in the year 2008, however, work may be required in order to clarify the current baseline conditions.

Results of the current work have highlighted possible exceedences of proposed Limit Values for As, Cd and Ni may occur and further monitoring and assessment is therefore advisable at these sites and in some sectors.

The recommendations for future monitoring work in the UK are:

1. That monitoring be continued at the IMI Refiners Ltd site in order to more accurately determine compliance with the UK AQS objective of 0.25 $\mu g/m^3$ for 2008.
2. Current monitoring in the vicinity of Brookside Metal Co Ltd undertaken in accordance with Directive 82/884/EEC be reviewed in the light of the proposed Fourth Daughter Directive with a view to changing from sampling using an M-Type sampler to sampling using a Partisol 2000 on the PM_{10} fraction.
3. Monitor in the vicinity of Britannia Zinc Ltd, Avonmouth at a second site located downwind of the main stack(s) associated with the process.
4. Monitoring for Pb be undertaken at Britannia Recycling in Wakefield and Dens Metals in Dundee in order to clarify the current position with respect to ambient Pb concentrations and to determine the effectiveness of proposed abatement strategies for future years.
5. To continue monitoring for As at the following sites: IMI Refiners Ltd (Site 2); Bruhl UK Ltd (Site 26); White Rose Environmental (Site 22); Wolverhampton MWI (Site 30); Corus Engineering Steels Ltd (Site 7); Paramount Batteries (Site 10); and Walkers Galvanizing (Site 15);
6. To continue monitoring for Cd at the following sites: IMI Refiners Ltd (Site 2); Britannia Zinc Ltd (Site 3); Sidney Smith (Site 27); Bruhl UK Ltd ((Site 26); and Walkers Galvanizing (Site 15);
7. To continue monitoring for Ni at the following sites: INCO Europe (Site 13) and Bruhl UK Ltd (Site 26).
8. In addition, it is recommended that further desktop studies be undertaken on the Iron Foundry and Galvanizing sectors authorised under LAPC in order to acquire detailed emissions data from local authorities throughout the UK which have plants authorised under the relevant Process Guidance Notes 2/5 and 2/2, respectively.
9. For mercury no exceedances of the proposed limit value are likely but monitoring at ICI Runcorn is advisable as a result of the elevated concentrations that have been recorded relative to other locations.

1 Introduction

1.1 Background to the study

The European Union has been legislating to control emissions of air pollutants and to establish air quality objectives across Member States with the view to consolidating air quality legislation. Directive 96/62/EC, the Air Quality Framework Directive, sets down the strategic framework for tackling air quality by setting European-wide Limit Values for 12 pollutants in a series of daughter directives.

The first Daughter Directive (1999/30/EC) reached a common position in April 1999 with respect to the setting of Limit Values for sulphur dioxide, nitrogen dioxide, particles and lead. The Commission's proposals for the second Daughter Directive on benzene and carbon monoxide was subsequently published in 1999 followed by proposals for a third Daughter Directive covering benzene and carbon monoxide. Currently, the European Union is proposing to develop the fourth Daughter Directive covering arsenic, cadmium and nickel. The EC Working Group on Arsenic, Cadmium and Nickel Compounds has completed its final draft of the position paper in October 2000. The EC is bringing forward proposals for a fourth Air Quality Daughter Directive and is expected to propose Limit Values for four metals:

- Arsenic
- Cadmium
- Nickel
- Mercury

At present, in the UK, there is limited monitoring information to give a clear picture of the extent to which emissions from industrial sites may lead to localised elevated levels of lead (Pb) cadmium (Cd), nickel (Ni), arsenic (As) or mercury (Hg).

To improve the available information on ambient metal concentrations in the UK a 12 month monitoring programme was commissioned by the Department of the Environment, Food and Rural Affairs (formerly the Department of the Environment, Transport and the Regions), the Scottish Executive, The National Assembly for Wales and the Department of the Environment in Northern Ireland. The aim of this programme was to monitor ambient levels of Pb, As, Cd, Ni and Hg at 30 sites in the vicinity of industrial processes throughout the UK. In addition, vapour-phase Hg is monitored at 5 of these sites. The following objectives for the monitoring were identified:

- provide baseline information on the ambient levels of these air pollutants around industrial sites
- determine the likelihood of problems in complying with the EU Limit Value and current AQS objective(s) for Pb

- determine the current UK position on ambient metals monitoring for Cd, Ni and As in anticipation of any proposed Limit Values to be set by the EU
- assign significance to the occurrence of vapour-phase Hg and particulate-phase Hg emissions
- determine the relationship between short-term (24-hour measurements) and long-term (7-day) monitoring methods for metals
- identify industrial sectors at risk of exceeding current and likely Limit Values and to provide recommendations for future monitoring requirements and/or further research needs

1.2 Legislative background

1.2.1 First Daughter Directive

The first Daughter Directive (1999/30/EC) reached a common position across European Member States for sulphur dioxide (SO_2), nitrogen dioxide (NO_2), particulate (PM_{10}) and lead (Pb). The aims of the Directive were to establish Limit Values and alert thresholds for concentrations of pollutants in ambient air intended to avoid, prevent or reduce harmful effects on human health and the environment as a whole. For lead, the Directive establishes a limit value of $0.25\mu g/m^3$ to be achieved by 2005. In the immediate vicinity (within 1000 m) of specific industrial processes on sites contaminated by decades of industrial activity there is a derogation to achieve the limit value by 2010. The Directive also includes requirements to assess concentrations of pollutants based on a common method and criteria and obtain adequate information on concentrations in order to make information available to the public.

The European Union is currently developing proposals for the fourth Daughter Directive, which will aim to reach a common position across Member States with respect to the setting of Limit Values for cadmium (Cd), arsenic (As) and nickel (Ni). The EC Air Quality Working Group has completed its final draft of the position paper in October 2000. The EC Ambient Air Steering Group has since discussed the draft in May 2001 and proposed Limit Values for the three metals as shown in Table 1.1.

1.2.2 UK Air Quality Strategy

The Air Quality Strategy for England, Scotland, Wales and Northern Ireland (AQS) was published in January 2000 and provides a revised framework for reducing air pollution at national and local levels from a wide range of emission sources.

Central to the Strategy are health-based standards for the eight air pollutants of current greatest concern. These standards are based on recommendations made by the Government's Expert Panel on Air Quality Standards (EPAQS). From these standards, air quality objectives have been derived, which take account of the costs and benefits, as well as of the feasibility and practicality, of moving towards the standards.

In 1997, the Government incorporated the Limit Value for Pb (0.5 $\mu g/m^3$) within the National Air Quality Strategy to be achieved by 31 December 2004. In 2000, taking account of advice from EPAQS to reduce lead levels to as low as practically achievable, a second objective of 0.25 $\mu g/m^3$ to be achieved by 2008 was introduced into the Strategy.

1.2.3 Fourth Air Quality Daughter Directive

The European Commission is currently considering whether to bring forward proposals within a Fourth Air Quality Daughter Directive to manage levels of As, Cd, Ni and Hg. The Commissions proposals are expected to be published in Autumn 2001. In order to compare measured concentrations of these metals presented within this report with appropriate criteria guidance was sought from DEFRA. Table 1.1 presents possible limit values and other assessment criteria that are anticipated to be included in the Commissions proposals. In addition, proposed criteria for data quality objectives are given in Table 1.2.

Table 1.1: Assumed Limit Values and Assessment Thresholds

Determinant	**Limit Value**	**Averaging Period**	**Long term objective**	**Margin of tolerance**	**Date by which Limit Value is to be met**	**Upper Assessment Threshold**	**Lower Assessment Threshold**
Arsenic	6 ng/m^3	Calendar year	0.6 ng/m^3	3 ng/m^3 (50%) reducing on 1 January 2005 and every 12 months thereafter by 0.5 ng/m3 to reach 0% by January 2010	1 January 2010	60% of Limit Value (3.6 ng/m^3)	40% of Limit Value (2.4 ng/m^3)
Cadmium	5 ng/m^3	Calendar year		2.5 ng/m^3 (50%) reducing on 1 January 2005 and every 12 months thereafter by 0.5 ng/m3 to reach 0% by January 2010	1 January 2010	60% of Limit Value (3 ng/m^3)	40% of Limit Value (2 ng/m^3)
Nickel	20 ng/m^3	Calendar year		10 ng/m^3 (50%) reducing on 1 January 2005 and every 12 months thereafter by 2 ng/m3 to reach 0% by January 2010	1 January 2010	70% of Limit Value (14 ng/m^3)	50% of Limit Value (10 ng/m^3)
Mercury	50 ng/m^3	Calendar year					

Table 1.2 Proposed data quality objectives

	Arsenic, cadmium and nickel	**Total gaseous mercury**
Measurements:		
Uncertainty	40%	50%
Minimum data capture	90%	90%
Minimum time coverage:		
Fixed Measurements	50%	33%
Indicative measurements	14%	14%
Modelling		
Uncertainty	50%	50%
Objective estimation		
Uncertainty	100%	100%

Upper and Lower Assessment Thresholds (UAT and LAT) are important parameters for defining three assessment regimes as determined through breaches of the appropriate threshold values. That is, where pollutant concentrations exceed the UAT, measurements are mandatory. Where pollutant concentrations fall between the UAT and LAT, assessments can combine both measurement and modelling approaches. Pollutant concentrations below the LAT require only model calculations and or objective estimates in order to satisfy an assessment.

The results of the current programme are discussed in the context of the above data quality objectives in the relevant following sections of this report.

Currently, the European Centre for Standardization (CEN) Working Group 14 is developing the European Reference Method for ambient monitoring of Pb, As, Cd, and Ni. Further details of the programme are outlined in Appendix J of this report.

For Hg, the EU Working Group are currently considering the position of Member States with respect to this pollutant (and its species) which will be given further consideration by a separate CEN Working Group.

2 Site Selection

2.1 Consultation

Thirty key industrial locations (shown in Table 2.1) were identified for inclusion in the current work programme. Potential sites were nominated by DEFRA, the devolved administrations and the Department of Trade and Industry (DTI) for inclusion. Sites were selected following an extensive consultation process (a list of consultees is provided in Appendix A) that initially identified relevant industrial sectors that should be included within the monitoring programme and secondly which specific processes. Once identified, sites were assessed to determine which industrial sectors were covered, geographic location, and their proximity to residential areas.

2.2 Basis of site selection

Macro- and micro-scale criteria are given in Council Directive 1999/30/EC for the general requirements for the siting of monitoring equipment. For the protection of human health, the Directive states that:

> *'. . . . sampling points should (i) provide data on the areas within zones where the highest concentrations are likely to occur to which the population is likely to be directly or indirectly exposed for a period which is significant in relation to the averaging period of the Limit Value(s) . . . . . . (ii) which are representative of the exposure of the general population.'*

The above have also been transposed into the UK AQS objective for Local Air Quality Management[2] which stipulate that for the longer-term objectives, focus should be

> *'. . upon the following non-occupational, near ground level outdoor locations; background locations; roadside locations; and other areas of elevated pollutant concentrations where a person might be reasonably be expected to be exposed (e.g. in the vicinity of housing, schools or hospitals etc) over the relevant averaging time of the objective'*.

Where possible, monitoring locations have been chosen as being downwind of the main stack(s) and/or fugitive dust emissions at each site, where it is anticipated that maximal annual average concentrations would occur. For fugitive dust emissions, site locations have been determined as being close to the site boundaries. In the case of stack emissions, site locations have been determined using nominal stack-height plume-grounding distances. Consequently, where stacks

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[2] LAQM.TG1(00). Monitoring for Reviews and Assessments. DETR, the Scottish Executive, The National Assembly for Wales and the Department of the Environment (NI). May 2000.

have been identified as being the main emission point monitoring locations may be some distance (200 - 500 metres) from the site boundary.

At the local level, site selection was also restricted by a number of operational issues. These included: the availability of power for the monitoring equipment; the ability to ensure that the site was secure; and the appropriateness of the site location as a potential receptor point (i.e. representative of the general exposure of the population). For a few sites, appropriate locations were therefore sited upwind of the main emission source as a consequence of proximity of residential areas and/or consideration to security. Moreover, where an industrial process is located at a coastal site, the maximum concentration has been determined as likely to occur some distance from the coast, at sea. Consequently, for a few sites, maximum annual mean concentrations may not be represented.

Particular problems occurred with Site 3 (Britannia Zinc Ltd). BZL consider that Hallen village (2km north-west of the site) is the location of highest concentrations of Pb resulting from its operations. However, the current work undertook monitoring in the vicinity of residential properties adjacent to the Port Health Centre, in which a contribution to the local air quality may derive from general activities of the Port and the Avonmouth area including a large proportion of fugitive emissions. It is therefore debatable whether pollutant concentrations measured cannot be directly related to the operations of BZL.

No modelling work or screening of emissions has been carried out to determine the exact monitoring location in the vicinity of the industrial sites. However, where possible, requests were made to the individual companies for the supply of information relating to the original Integrated Pollution Control (IPC) applications (and any subsequent environmental assessments for variations thereof). Figure 2.1 shows the spatial distribution of sites (along with side codes as shown in Table 2.1) for the 30 sites throughout the UK.

Figure 2.1. Spatial distribution of monitoring sites (and site specific codes) across the UK

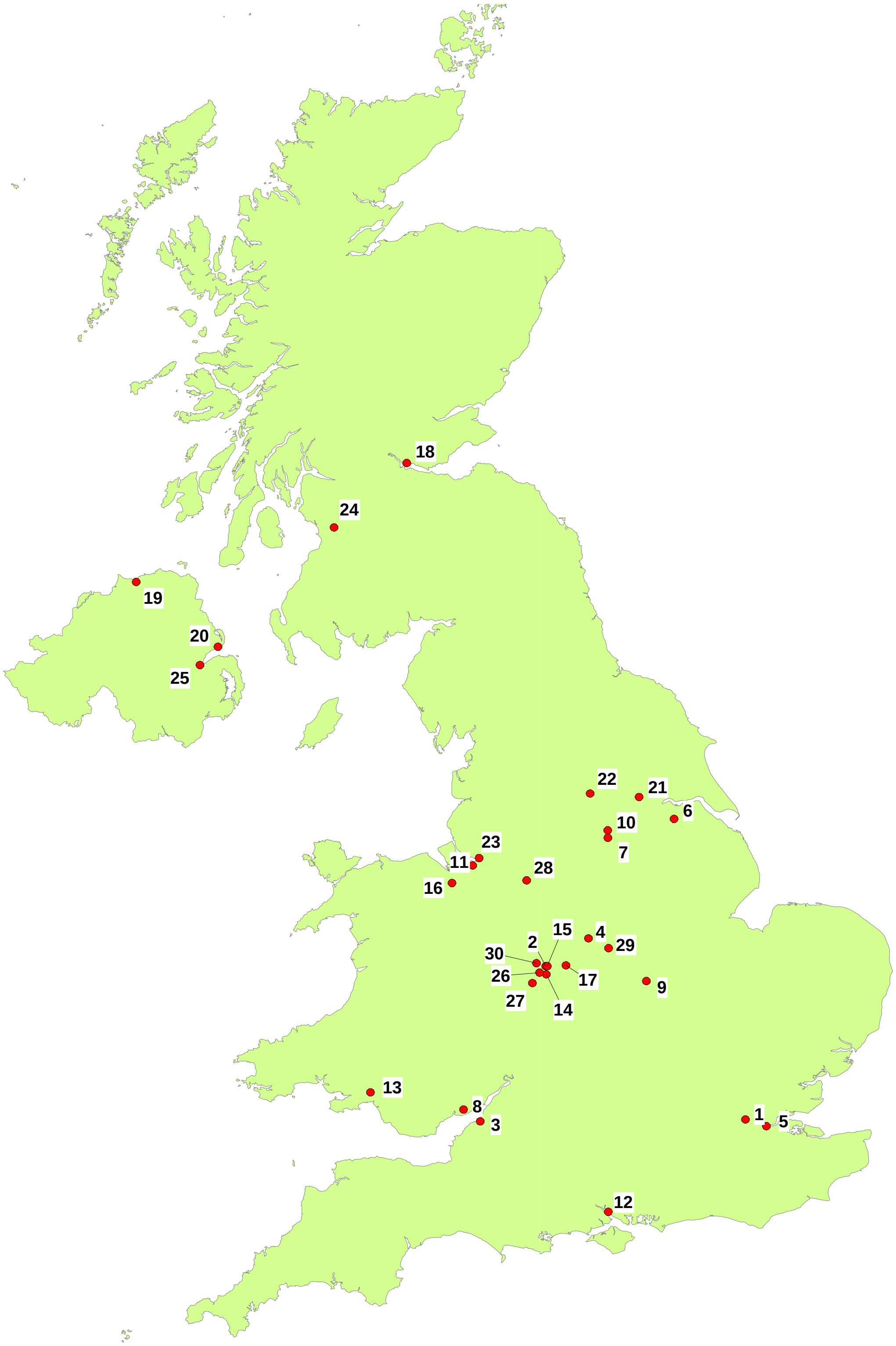

Table 2.1: Industrial Process Types, Company Names, Site Reference Codes and Annual Emissions (Kg/annum).

			Emissions per (Kg/annum[3])				
Site Code[4]	**Process type**	**Company name**	**Pb**	**As**	**Cd**	**Ni**	**Hg**
1	Copper & Copper Alloy Production / Fabrication	A. Cohen & Co., Greenwich	< 10	-	-	-	-
2		IMI Refiners, Walsall	4,738	180	76	345	-
3	Lead Production / Recycling	Britannia Zinc Ltd, Bristol	10,867	610	1,252	24	294
4		Midland Lead Refiners, S. Derbyshire	< 10	< 1	< 0.1	-	< 0.1
5		Britannia Refined Metals, Gravesham	2,190	-	135	-	-
6	Steel Industry	Corus UK Ltd, N. Lincolnshire	715	-	-	-	-
7		Corus Engineering Steels Ltd, Rotherham	14,540	128	-	360	1,125
8		Corus UK Ltd, Llanwern	7,178	27	83	207	51
9	Lead Acid Battery Production	Tungsten Batteries Ltd, Harborough	142	-	-	-	-
10		Paramount Batteries, Barnsley	< 10	-	-	-	-
11	Lead Anti-Knock	Associated Octel Co. Ltd, Ellesmere Port	25,610	-	-	-	-
12	Oil Refinery	Esso Petroleum Co. Ltd, New Forest	52	46	14	3,097	4
13	Nickel Refinery	INCO Europe, Swansea	13	-	-	1,374	-
14	Galvanisers	Cerro Extruded Metals, Sandwell	12	-	-	-	-
15		Walkers Galvanizing, Walsall	N/a	N/a	N/a	N/a	N/a
16	Cement Manufacture	Castle Cement, Flintshire	1,000	< 2	6	-	6
17	Crematoria	Sutton Coldfield Crematorium, Birmingham	N/a	N/a	N/a	N/a	N/a
18	Power generation	Longannet Power Station, Fife[5]	2,140	470	50	1,170	190
19		Coolkeeragh Power Station, Derry[6]	36	4	36	1,100	4

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[3] 1999 Pollution Inventory - Environment Agency and Department of the Environment (Northern Ireland) for sites 19 and 20. '-' denotes no emissions identified with process. 'N/a indicates emissions not available (Part B process regulated through LAPC)

[4] Project-Specific Designation

			Emissions per (Kg/annum[3])				
Site Code[4]	**Process type**	**Company name**	**Pb**	**As**	**Cd**	**Ni**	**Hg**
20		Kilroot Power Station, Carrickfergus[6]	130	15	13	64	73
21		Drax Power Station, Selby	2,100	120	66	180	120
22	Waste Incineration	White Rose Environmental, Leeds	N/a	N/a	N/a	N/a	N/a
30		Wolverhampton Municipal Waste Incinerator	35	< 1	< 2	< 10	26
23	Chloralkali	ICI Chemicals & Polymers Plc, Halton	79	-	-	66	-
24	Non-Ferrous Alloy metals	Glacier Vandervell Ltd, E. Ayrshire	N/a	N/a	N/a	N/a	N/a
25	Mixed	Belfast Harbour Estate	N/a	N/a	N/a	N/a	N/a
	Iron Foundry						
26	- hot-blast cupola	Bruhl UK Ltd, Sandwell	N/a	N/a	N/a	N/a	N/a
27	- cold-blast cupola	Sidney Smith, Dudley	N/a	N/a	N/a	N/a	N/a
28	Non-Ferrous Part B	FE Mottram, Congleton	< 10	-	-	-	-
29	Roadstone Coating Plant	Cliffe Hill Quarry, Leicestershire	N/a	N/a	N/a	N/a	N/a

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[5] Scottish Power's 1999-2000 Environment Report '24hour Scottish Power' (http://www.scottishpower.plc.uk)

[6] Estimate provided by DoE Northern Ireland from the Industrial Source Release Register of Part A Processes. Personal communication David Bell.

2.3 Micro-scale considerations

Further consideration was given during site selection to the most appropriate locations for monitoring equipment. Installation guidance notes were compiled according to the characteristics of the individual sites. Broadly, these fell into two categories: rooftop and ground level installations. These guidance notes are summarised in Appendix B and were used to obtain consistency in approach across sites.

Installation of equipment was carried out on behalf of Stanger Science and Environment by the ETI Group Ltd using the guidance notes summarised in Appendix B.

2.4 Site descriptions

The final 30 chosen sites are summarised by sector in Table 2.1 and are described in detail in Appendix L, alongside maps showing the location of the monitoring site in relation to the process site location.

3 Sampling and Analysis Methodology and Operation

3.1 Particulate-phase Pb, As, Cd, Ni, Hg (and V)

The Daughter Directive (1999/30/EC) specifies a 365-day 24-hour measurement to assess ambient levels of Pb against the Limit Value. To undertake such a programme at 30 sites would prove to be prohibitively expensive and logistically difficult. Consequently, a 7-day sampling regime was proposed using Rupprecht & Patashnick (R&P) Partisol 2000 units.

In parallel with 7-day measurements, sampling was undertaken at five sites using R&P Partisol Plus (Model 2025) units. These units are a sequential version of the Partisol 2000 units incorporating automatic filter exchange, which enables less labour-intensive 24-hour monitoring. The purpose of inclusion of daily sampling at five sites was to provide a basis of proving equivalence to the 265-day 24-hour sampling regime stipulated by the Directive. This would be determined through a comparison of weekly samples against bulked analysis of the parallel 7-day 24-hour sampling. The sites selected for duel monitoring were:

- Site Code 2: IMI Walsall
- Site Code 3: Britannia Zinc Ltd
- Site Code 5: Britannia Refined Metals
- Site Code 8: Corus UK Ltd, Llanwern
- Site Code 18: Longannet Power Station

Both samplers used size-selective inlets measuring PM_{10} size fraction[7].

Further specific details of the two sampling units and common elements of the two sampling regimes are shown in Appendix F.

For all monitoring locations, PM_{10} collected on cellulose nitrate filters were analysed for Pb, As, Cd, Ni, and Hg. In addition, vanadium (V) measurements were made for material collected at Site Code 20. This was undertaken at the request of the Department of the Environment in Northern Ireland in anticipation of a proposal by NIGEN Ltd. to move from burning coal to burning Orimulsion®, a recently developed fuel consisting of an emulsion of natural bitumen.

For all metals, no speciation was undertaken as part of the current contract which reports only total metal concentrations (except in the case Hg where measurements were undertaken to determine the partitioning between vapour and particulate-phase concentrations). For health

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[7] PM_{10} - particulate matter capable of passing an inlet of defined characteristics with a 50% sampling efficiency at 10 µm aerodynamic diameter.

effects, it is understood that certain metal species are responsible for adverse effects. Appendix K sets out proposals surrounding the determination of the major species of As, Ni and Hg known to be of importance with regards to adverse health effects by way of recommendations for further work.

Particulate phase concentrations of Pb, As, Cd, Ni, Hg (and V) were measured using inductively-coupled plasma atomic emissions spectrometry (ICP-AES). Subsequent problems were experienced for As and Hg analysis using ICP-AES which resulted in using another UKAS accredited laboratory for analysis of these two metals by ICP- mass spectrometry (ICP-MS)[8]. Throughout the project, UKAS accreditation was maintained as shown in Appendix H which summarises the analytical techniques and the relevant dates to which they apply. Further details regarding the nature and scale of the problems encountered with ICP-AES are provided in Appendix H.

Currently, the European Centre for Standardization (CEN) is developing the proposed reference method for sampling and analysis of Pb, Cd, As and Ni through Working Group 14 (WG14). Further details of the proposed reference method and the overall programme for WG14, and the UK participation thereof, are given in Appendix J.

3.2 Vapour-phase Hg

Mercury and its compounds are of sufficient volatility at ambient temperatures to necessitate vapour-phase monitoring. That is, elemental mercury can be present in vapour or as an aerosol of liquid droplets; organically bound mercury compounds are present predominantly in the vapour-phase; inorganic mercury compounds are relatively non-volatile and subsequently exist as particulate. However, some inorganic compounds (such as mercuric chloride) are present substantially as vapour.

Monitoring of vapour-phase mercury was undertaken at the following 5 sites:

- Site Code 7: Corus Engineering Steels Ltd
- Site Code 16: Castle Cement, Wrexham
- Site Code 17: Sutton Coldfield Crematorium
- Site Code 18: Longannet Power Station - Scottish Power
- Site Code 23: ICI Chemicals and Polymers Ltd

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[8] CRE Group Ltd., Stoke Orchard, Cheltenham, Gloucestershire GL52 7RZ and Harwell Scientifics Ltd., 551 Harwell, Didcot, Oxfordshire OX11 0RA

Adsorption traps[9] were used to capture all vapour-phase forms of mercury from air. Particulate-phase mercury compounds were removed prior to the inlet of the gold adsorption traps using an in-line filter.

Exposed gold adsorption traps were returned to be PS Analytical Ltd. for analysis. Analysis was undertaken using the Sir Galahad analyser calibrated using vapour injections of known volumes of air containing elemental mercury. The analytical method has a detection limit of 10 picogrammes (pg).

Further details of the analytical method are given in Appendix F.

3.3 Local Site Operation

Operation of sampling units was undertaken through local site operators (LSOs) appointed by Stanger Science and Environment. A full list of appointed LSOs and the sites under their responsibility is shown in Appendix C.

LSOs were provided with training in the use of equipment at the time of installation and supplied with a procedure manual in order to maintain consistency in operation across sites.

LSOs were requested to complete a weekly record sheet notifying Stanger Science and Environment of the status of the equipment at the time of weekly site attendance. Additionally, LSOs were requested to inform Stanger Science and Environment of whether filter exchange had been successfully completed and the equipment operational when leaving site. Where necessary, ETI Group Ltd were requested to attend site where LSOs reported equipment malfunctions.

3.4 Measurement uncertainty and limits of detection

Reproducibility studies have been undertaken prior to analysis in order to determine the uncertainty estimates associated with laboratory analysis. Within these studies, consideration has been given to both the precision of the analysis and to the bias[10].

Bias estimates were obtained through digestion and analysis of in-house reference filters (n = 10) loaded with known concentrations of each metal to determine percentage recovery. Precision data were determined through repeated analysis (n = 10) of quality control solutions of known concentration. Standard deviations were expressed as percentages (%RSD) and

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[9] Dumarey, R., Dams, R., and Hoste, J. (1985). Analytical Chemistry Vol. 57, pp. 2638 - 2643

[10] Precision is defined as the degree of agreement between successive measurements of a given concentration, whilst bias is determined through the accuracy of a measurement by comparison with a ‘true’ value of the concentration.

carried forward to the uncertainty estimation. The measurement of uncertainty was determined by combining the %RSD values for precision, bias and recovery using root squares to determine the expanded uncertainty of analysis. Table 3.1 shows the uncertainty values from reproducibility studies carried out for ICP-MS.

Table 3.1 ICP-MS Measurement Uncertainty (Reproducibility Studies)

	Pb	**As**	**Cd**	**Ni**	**Hg**	**V**
Long term precision (RSD)	2.24	1.96	4.14	2.87	5.26	2.46
Observed mean bias (%)	4	7	0	1	3	0
Recovery (RSD)	4.78	3.93	5.04	5.20	4.25	4.35
Combined uncertainty (RSD)	6.62	8.26	6.53	6.02	7.40	5.00
Expanded uncertainty (95% coverage factor)	14	17	13	12	15	10

In addition to the reproducibility studies, estimates of uncertainty have been made retrospectively based upon precision and recovery data gathered during the analysis of filters throughout the duration of the programme. That is, during the programme, analytical procedures have included analysis of blank (unexposed) filters and in-house 'spiked' reference filters. Sample filters were analysed in batches of seven. One filter blank and one spiked reference filter were included in each batch. In addition, duplicate measurements of a sample aliquot were included in each sample run. Consequently, a further estimate of uncertainty can be undertaken which includes all the variances of the influencing factors during the course of the programme. The results of this further analysis are shown in Tables 3.2 and 3.3 for ICP-MS and ICP-AES, respectively.

Table 3.2 ICP-MS Measurement Uncertainty (Retrospective Analysis)

	Pb	**As**	**Cd**	**Ni**	**Hg**	**V**
Long term precision (RSD)	2.39	2.00	2.52	2.05	5.91	1.50
Observed mean bias (%)	5	2	3	3	2	3
Recovery (RSD)	3.59	9.25	2.81	5.00	2.50	4.48
Combined uncertainty (RSD)	6.60	9.67	4.82	7.95	6.72	5.60
Expanded uncertainty (95% coverage factor)	13	20	10	16	14	11

Table 3.3 ICP-AES Measurement Uncertainty (Retrospective Analysis)[11]

	Pb	Cd	Ni	V
Long term precision (RSD)	2.25	2.34	2.58	4.80
Observed mean bias (%)	5	2	4	0
Recovery (RSD)	7.18	4.88	4.58	10.44
Combined uncertainty (RSD)	9.03	5.77	6.6	11.49
Expanded uncertainty (95% coverage factor)	18	12	13	23

Results of the reproducibility studies and the retrospective analysis of precision and bias estimate the analytical uncertainty for all samples should be taken at ± 20% for Pb, As, Cd, Ni, and Hg. For V an estimate of ± 25% is calculated. Uncertainty estimates are taken as a conservative measure for some elements in order to satisfy routine analysis and accreditation procedures.

In addition to uncertainty surrounding the laboratory analysis, further uncertainty exists with respect to the sampling methods employed. That is, with respect to collection efficiency and volume. Within the current study, standard R&P PM_{10} inlets have been used which have undergone detailed equivalence exercises with the EU Reference Method for PM_{10} measurements in accordance with EN12341[12]. Consequently, 100% collection efficiency for PM_{10} is assumed. For volume, a deviation from the set point of ± 5% is estimated from the required flow of 16.7 l/min. When the sampling flow falls outside ± 5% criteria the units register a critical error and ceases sampling. Consequently, a best estimate of uncertainty surrounding the volume and pneumatics of the units would be ± 5%.

The additive uncertainty surrounding the measurements made for ambient particulate phase metal concentrations in the current work is therefore in the region of ± 25% for Pb, As, Cd, Ni and Hg and ± 30% for V, and comprises both analytical and sampling uncertainties.

Table 3.4 sets out the limits of detection for the particulate phase laboratory analysis for which the analytical uncertainties have been determined.

Table 3.4 summarises the limits of detection were required for the analysis.

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[11] ICP-AES results for As and Hg not reported due to problems in analysis (refer to Appendix H)

[12] prEN12341 European Standard. Determination of the PM10 fraction of suspended particulate matter – reference method and field test procedure to demonstrate reference equivalence of measurement methods. European Committee for Standardization. 1998.

Table 3.4 Limits of detection of analysis

Determinant	**Limit of detection (ng/filter)**	**Limit of detection (ng/m^3)[13]**
Pb	> 175	> 1.04 (≈ 0.001µg/m^3)
As	> 10	> 0.06
Cd	> 25	> 0.15
Ni	> 50	> 0.30
Hg	> 10	> 0.06
V	> 75	> 0.45

For the purpose of calculating annual mean concentrations, where analysis indicates that the measured value is below the limit of detection (< LOD), the value has been taken as being one half of the limit of detection.

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[13] Based on a nominal sampling rate of 24m^3 per day for 7 days = 168m^3 total

4 Results

The following section outlines the results of the particulate-phase analysis for weekly measurements of metal concentrations. In addition, results are shown for the comparisons between weekly and bulked-daily measurements, and vapour-phase mercury analysis. Data capture statistics for the network are discussed in terms of the network as a whole and for individual sites.

4.1 Data Capture and Data Quality Objectives

Data capture statistics are quoted for each site in the individual site summary sheets shown in Appendix L.

For the network as a whole, the percentage data capture was 86.6% across all sites, although for individual sites data capture varied from 28.8% (at Site 15) to 100% (Sites 10, 24, 29 and 30). Of the 30 sites in all, 19 sites provided data capture statistics of >90%. A further 6 sites (25 sites total) showed data capture of >80%. Data capture at five sites was below 80%. These included: Site 4 (Midland Lead Refiners Ltd); Site 8 (Corus UK Ltd, Llanwern); Site 13 (INCO Europe); Site 15 (Walkers Galvanizing) and Site 18 (Longannet power station).

Problems in the performance of the equipment were repeatedly experienced at Site 13 and at Site 15 throughout the year whilst for Sites 4 and 8, problems in the performance of equipment were encountered during only the early stages of the programme. Problems encountered at Site 18 were experienced over the duration of the 12-month monitoring period and arose as a consequence of combination of adverse weather conditions and problems in monitor performance. Further specific details are provided in Appendix G.

The consequence of data loss is added uncertainty with respect to annual mean concentrations reported. In order to determine the impact of data loss on the annual mean concentration, analysis of data obtained from sites with 100% data capture has been undertaken. In general, the following scenarios occurred over the duration of twelve months:

- Loss of 4 consecutive weeks' data (code 48(C))
- Loss of 10 consecutive weeks' data (code 42)
- Loss of intermittent weeks' data throughout the year (code 48(NC))
- Delayed start-up leading to only 6-months data (code 26)

Analysis of data obtained from sites 20 and 24 (sites with 100% data capture) has been undertaken by removing periods of data commensurate with the above scenarios. This provides an initial understanding of the impacts of data loss on annual mean concentration. It is acknowledged that the approach is limited and that the impact of removal of data on annual mean concentration is dependent upon the week-to-week variation and concentrations measured. That is, where consistently low concentrations of metals are found, the removal of data is likely to have less of an impact on the annual mean when compared to removal of data from a site where week-to-week variation is much stronger and more ‘spikes’ are observed in the data set. Thus, site to site variation will exist.

The results are shown in Figure 4.1.

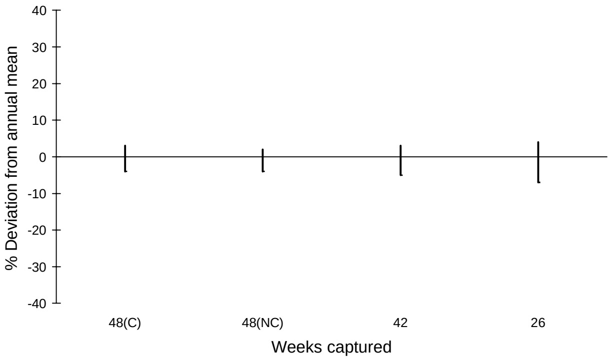
In general, the impact of data loss on the annual mean concentration becomes greater with increasing data loss, although this impact is shown to vary according to the element of concern. For example, for Pb (Figure 4.1 (a)), an mean based on 26-weeks measurements shows a deviation from the annual mean of between +4% and –7%, whilst the loss of 4 weeks continuous data (48(C)) shows a deviation from the annual mean of between +3% and –4%. In contrast, for Cd (Figure 4.1 (c)) results indicate that a mean based on 26 weeks measurements shows a deviation from the annual mean of between +10% and –35%. In contrast, the loss of 4 weeks consecutive data provides a deviation from the annual mean of between +4% and –14%.

Where data loss has occurred intermittently throughout the year, (i.e. non-consecutive weeks (48(NC)) the impact on the annual mean is marginally less when compared to the loss of consecutive weeks’ data. Moreover, results of data removal indicate that the influence of data loss is one that leads to a general underestimation of the annual mean as opposed to an overestimation.

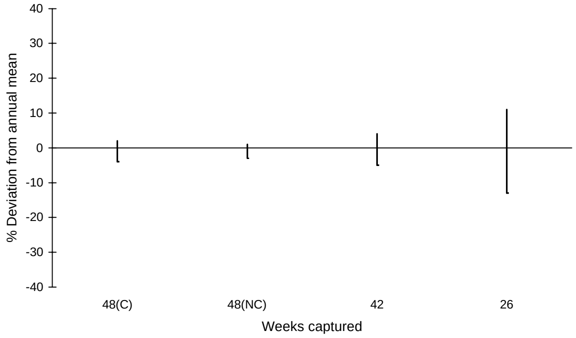
The analysis of data removal from sites reporting 100% data capture indicates that, for a typical scenario of intermittent data loss, the deviation from the annual mean concentration would be in the region of +4% and -10%. It is recommended that such deviations be considered where less than a full data set is reported. For a few sites, where data capture is considerably low (e.g. Site 15 and Site 30) due to either delayed start or recurrent equipment failure, it is recommended that deviations from the annual mean in the range of +10% and -25% be considered. Results for Hg (Figure 4.1(e)) indicate that higher levels of deviation from the annual mean concentrations are observed than those given for other metals. The results highlight the increased uncertainty regarding the analysis of filters for this metal where reported concentrations are around the limit of detection.

Figure 4.1: Influence of data loss on annual mean concentration

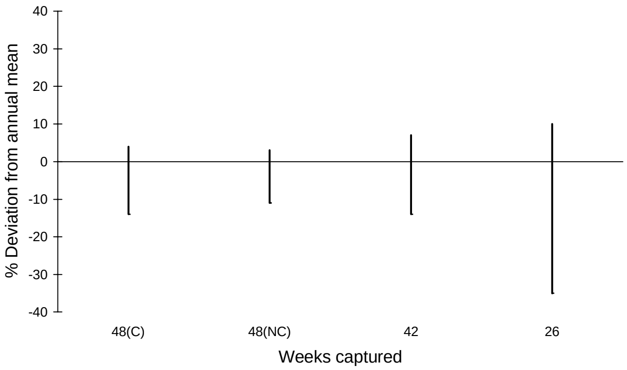
(a) Lead



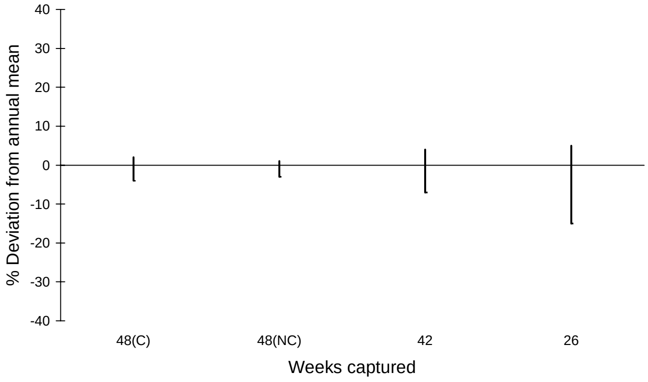
(b) Arsenic



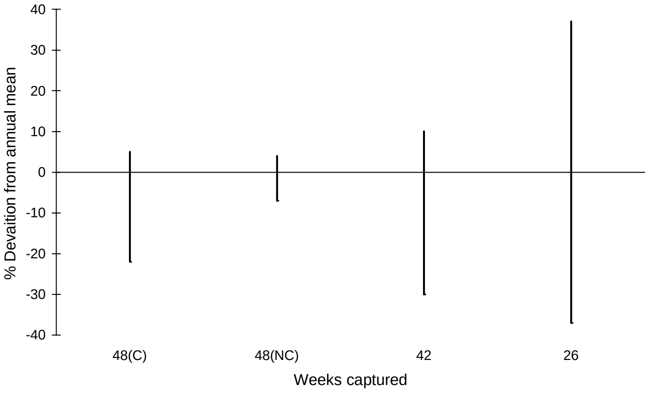
(c) Cadmium



(d) Nickel



(e) Mercury



4.2 Particulate Phase Weekly Measurements

Weekly particulate-phase concentrations of Pb, As, Cd, Ni, Hg (and V) are shown in Appendix L. Results are shown as tabular summaries providing mean, maximum and minimum weekly values alongside information surrounding each site (description, address, process name and industrial sector). In addition, the temporal distribution of Pb, As, Cd, Ni, Hg [and V] concentrations are shown.

Results show variation from site-to-site, both with respect to the concentration of each metals, and with respect to the temporal distribution of metals. The following provides a summary of the particulate-phase results of the weekly monitoring programme.

Table 4.1 summarises the concentrations of Pb, As, Cd, Ni, Hg [and V] for the duration of the programme. These are considered for the individual metals in the following sections:

4.2.1 Lead (Pb)

Annual mean Pb concentrations in the vicinity of the sites are generally below 0.05 μg/m^3. However, a number of locations recorded annual mean values higher than this value. These include: Site 1 (0.056 μg/m^3); Site 2 (0.237 μg/m^3); Site 3 (0.104 μg/m^3); Site 4 (0.072 μg/m^3); Site 6 (0.115 μg/m^3); Site 7 (0.146 μg/m^3); Site 14 (0.087 μg/m^3); Site 15 (0.091 μg/m^3); Site 26 (0.063 μg/m^3); and, Site 30 (0.055 μg/m^3).

The highest annual mean Pb concentrations were recorded at IMI Refiners Ltd (Site 2; 0.237μg/m^3) and Corus Engineering Steels Ltd (Site 7; 0.146 μg/m^3).

4.2.2 Arsenic (As)

Annual mean As concentrations were typically in the region of 1 - 2 ng/m^3. Higher annual mean concentrations were observed at a number of sites, which showed values in the range of 2.3 - 8.4 ng/m^3. The highest annual mean concentration was found at IMI Refiners Ltd (Site 2; 0.8 ng/m^3) whilst the second-highest annual mean concentrations was found at Walkers Galvanizing (Site 15; 4.22 ng/m^3).

4.2.3 Cadmium (Cd)

For the majority of locations annual mean Cd concentrations were below 1 ng/m^3. Typical annual mean concentrations were within the range of 0.1 - 0.8 ng/m^3. However, at a number of sites, annual mean concentrations of > 1 ng/m^3 and up to approaching 8 ng/m^3. These included monitoring sites in the vicinity of IMI Refiners Ltd (Site 2); Britannia Zinc Ltd (Site 3), Corus UK Ltd, Llanwern (Site 8), Walkers Galvanizing (Site 15), Bruhl UK Ltd (Site 26) and Sidney Smith (Site 27).

Of these, IMI Refiners Ltd and Britannia Zinc Ltd showed the highest annual mean Cd concentrations of 7.37 ng/m^3 and 7.73 ng/m^3, respectively.

4.2.4 Nickel (Ni)

Annual mean Ni concentrations show typical values in the vicinity of the industrial sites of the order 0.5 - 3.5 ng/m^3. A number of sites show values above this range: IMI Refiners Ltd (Site 2) with a value of 7.44 ng/m^3; and, Corus Engineering Steels Ltd (Site 7) with a value of 8.25 ng/m^3. The highest annual mean concentrations of Ni were recorded at INCO Europe (Site 13) and Bruhl UK Ltd (Site 26). Annual mean Ni concentrations at these sites were 20.6 ng/m^3 and 13.4 ng/m^3, respectively.

4.2.5 Mercury (Hg)

Annual mean Hg concentrations were generally low at all monitoring locations. For a number of sites, measurements were around the limit of detection of the analytical methods (circa. 0.05 ng/m^3). However, slightly elevated annual mean concentrations were found at a number of monitoring locations with values in the range 0.08 - 0.27 ng/m^3.

The highest annual mean Hg concentrations were found at Site 23 (ICI Chemicals and Polymers plc; 0.64 ng/m^3); Site 2 (IMI Refiners Ltd; 0.41 ng/m^3) and Site 15 (Walkers Galvanizing; 0.48 ng/m^3).

4.2.6 Vanadium (V)

In addition to Pb, As, Cd, Ni and Hg, vanadium (V) was also measured at Site Code 20 at the request of the Department of the Environment in Northern Ireland. The annual mean concentration of V at Kilroot Power Station was 2.56 ng/m^3 (data not shown).

Table 4.1: Annual mean concentrations (ng/m^3 and µg/m^3) for Pb, As, Cd, Ni, Hg, in the vicinity of industrial processes throughout the UK

Site Code	Process Name	Industrial Sector	Pb (µg/m^3)	As (ng/m^3)	Cd (ng/m^3)	Ni (ng/m^3)	Hg (ng/m^3)
1	A Cohen & Co Ltd.	Copper and Copper Alloy	0.056	1.59	0.55	2.61	0.07
2	IMI Refiners Ltd.	Copper and Copper Alloy	0.237	8.36	7.37	7.44	0.41
3	Britannia Zinc Ltd.	Lead Producer/Recycle	0.104	1.89	7.73	2.67	0.22
4	Midland Lead Refiners	Lead Producer/Recycle	0.072	1.78	0.52	1.72	0.12
5	Britannia Refined Metals	Lead Producer/Recycle	0.035	1.31	0.47	2.92	0.07
6	Corus UK Ltd.	Steel Industry	0.115	1.70	0.62	2.28	0.07
7	Corus Engineering Steels Ltd	Steel Industry	0.146	3.01	0.81	8.25	0.13
8	Corus UK Ltd, Llanwern	Integrated Steel	0.040	1.70	1.40	3.43	0.27
9	Tungsten Batteries Ltd.	Lead Acid Battery	0.031	1.08	0.24	1.03	0.10
10	Paramount Batteries	Lead Acid Battery	0.050	2.91	0.59	3.69	0.09
11	Associated Octel Company Ltd.	Lead Anti-Knock Ingredients	0.013	0.95	0.17	1.41	0.04
12	Esso Petroleum Company Ltd.	Oil Refinery	0.012	0.90	0.20	2.40	0.04
13	INCO Europe	Nickel Refinery	0.018	1.18	0.27	20.6	0.14
14	Cerro Extruded Metals	Copper and Copper Alloy - Non Ferrous Part B	0.087	1.84	0.76	1.93	0.12
15	Walkers Galvanizing	Galvanising	0.091	4.22	1.94	2.61	0.48
16	Castle Cement	Cement Manufacture	0.018	1.03	0.22	0.71	0.10
17	Sutton Coldfield Crematorium	Crematoria	0.017	1.15	0.38	1.15	0.05
18	Scottish Power - Longannet Power Station	Coal-Fired Power Station (no FGD)	0.008	0.70	0.12	1.21	0.04
19	Coolkeeragh Power Station	Oil-Fired Power Station	0.003	0.72	0.13	2.05	0.06
20	NIGEN Ltd. – Kilroot Power Station	Coal-Fired Power Station (proposal to burn Orimulsion)	0.004	0.47	0.13	1.25	0.05
21	National Power Plc. - Drax Power Station	Coal-Fired Power Station (with FGD)	0.014	1.16	0.25	1.88	0.06
22	White Rose Environmental	Clinical Waste Incinerator	0.031	3.31	0.57	2.48	0.09

Site Code	Process Name	Industrial Sector	Pb ($\mu g/m^3$)	As (ng/m^3)	Cd (ng/m^3)	Ni (ng/m^3)	Hg (ng/m^3)
23	ICI Chemicals and Polymers Plc.	Chloroalkali	0.017	1.00	0.23	1.78	0.64
24	Glacier Vandervell Ltd.	Non-Ferrous Alloy	0.030	0.54	0.53	0.85	0.15
25	Belfast Harbour Estate - Mixed Industrial Area	Mixed	0.012	1.01	0.14	3.59	0.08
26	Bruhl UK Ltd.	Iron Foundry (Hot-Blast Cupola)	0.063	2.67	1.18	13.4	0.24
27	Sidney Smith	Iron Foundry (Cold-Blast Cupola)	0.037	2.30	3.50	1.71	0.09
28	FE Mottram Ltd, Congleton	Non-Ferrous Part B	0.014	1.19	0.34	1.34	0.08
29	Cliffe Hill Quarry	Roadstone Coating	0.013	1.28	0.26	1.33	0.06
30	Wolverhampton MWI	Municipal Waste Incinerator	0.055	3.11	0.82	1.78	0.10

4.3 Comparative Measurements

Linear regression analysis has been undertaken in order to compare results of the 7-day (weekly) sampling with those of the bulked daily samples. The line of best fit (of the form y = ax + b) has been calculated for each metal across all sites using paired values only above the limits of detection (as outlined in Section 3.4). Results for individual elements are shown in Appendix I for the two sampling regimes for Pb, As, Cd, Ni, and Hg, respectively. Table 4.2 summarises the regression coefficients and regression equations for each of the metals, alongside the number of paired values (n) upon which the analysis is based.

Results of the comparative data show good agreement ($r^2 > 0.95$) between the two monitoring regimes for Pb, As and Cd. A weaker relationship ($r^2 = 0.82$) is shown for Ni concentrations, whilst the relationship between weekly and bulked-daily sampling for Hg is weaker still ($r^2 < 0.1$).

Table 4.2 Summary of regression statistics for comparisons of results between weekly sampling and bulked 24-hour sampling equivalents.

Determinant	**n**	**r^2**	**Equation (y = ax+b)**	**Weekly ($\mu g/m^3$)**	**Bulked Daily ($\mu g/m^3$)**	**% Difference (over bulked-daily)**
Pb	134	0.9629	Y = 0.9957x – 0.0017	0.0682	0.0662	+2.9%
As	133	0.9660	Y = 1.0072x + 0.2285	2.53	2.77	-9.5%
Cd	118	0.9875	Y = 1.0923x – 0.121	5.15	5.50	-6.8%
Ni	115	0.8238	Y = 0.8678x – 0.0482	3.67	3.14	+14.4%
Hg	39	0.0892	Y = 0.3762 + 0.433	0.60	0.66	-10.0%

The extent of agreement between the two sampling regimes is reflected in the period mean concentrations for each element as shown in Table 4.2 across all sites. Further comparisons for individual sites are shown in Appendix I for period mean concentrations. In general, for Pb, As and Cd, the two mean values agree to within ± 20% which is in agreement with the uncertainty budget provided in Section 3.4.

For Ni, the percentage difference between the two sampling regimes is generally higher when compared to those results for Pb, As and Cd. For example, a difference between the Ni means across all sites is -14.4% compared to differences for Pb, As and Cd in the range of -9.5% to +2.9%. For Site 8, the difference between the two sampling regimes for Ni is as high as 52%.

The comparison of means for Hg is more variable than other elements. Although across all sites a difference of -10% was observed, for individual sites, differences in results between the two sampling regimes varied from +69% for Site 8 and -84% for Site 3.

4.4 Vapour-phase Hg

Results of the vapour-phase Hg ($Hg_{[Vap]}$) analysis are shown in Figure 4.2 for each of the five monitoring locations in the vicinity of the following industrial processes;

- Site 7 (Corus UK Ltd);
- Site 16 (Castle Cement);
- Site 17 (Sutton Coldfield);
- Site 18 (Longannet Power Station), and;
- Site 23 (ICI Polymers and Chemicals plc).

In addition, maximum, minimum and mean weekly values are shown in Table 4.3

Table 4.3 Maximum, minimum and average weekly vapour-phase Hg concentrations (ng/m^3)

Site	**Weekly Hg[vap] Concentration (ng/m^3)**		
	Max	**Min**	**Mean**
Site 7	6.3	0.4	2.92
Site 16	12.0	0.9	2.84
Site 17	8.5	0.7	2.99
Site 18	6.0	0.4	2.09
Site 23	69.2	2.8	24.11

Typically, mean $Hg_{[Vap]}$ concentrations for the period March - November were in the range of 2 - 3 ng/m^3 (Table 4.3). However, considerably higher concentrations of $Hg_{[Vap]}$ were found at ICI Polymers and Chemicals plant (Site 23) when compared to other sites. The mean weekly value for $Hg_{[Vap]}$ at this site was 24.11 ng/m^3 compared to the typical values of 2 - 3 ng/m^3 observed at other sites.

Figure 4.3 shows temporal variations in weekly mean $Hg_{[Vap]}$ concentrations at each of the sites. Results show considerably higher weekly variation in the $Hg_{[Vap]}$ at Site 23 when compared to other sites. The range in weekly mean values at Site 23 were 2.8 - 69.2 ng/m^3 compared to other sites which typically showed weekly mean values in the range 0.4 - 8.5 ng/m^3 (for Site 16, the highest weekly mean value observed was 12.0 ng/m^3).

Figure 4.2 Weekly vapour-phase mercury ($Hg_{[vap]}$) concentrations (ng/m^3) at Sites 7,16, 17, 18 and 23.

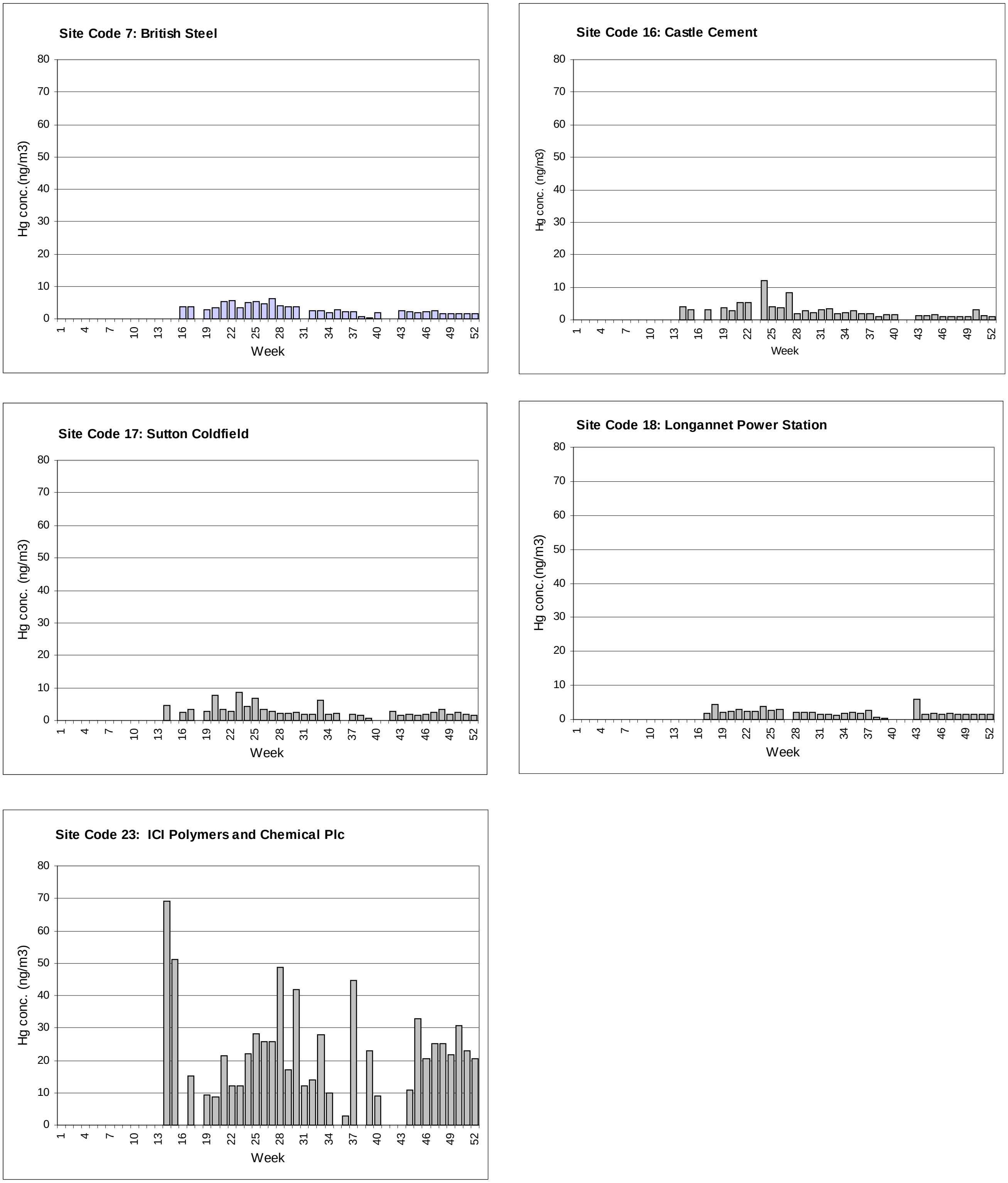
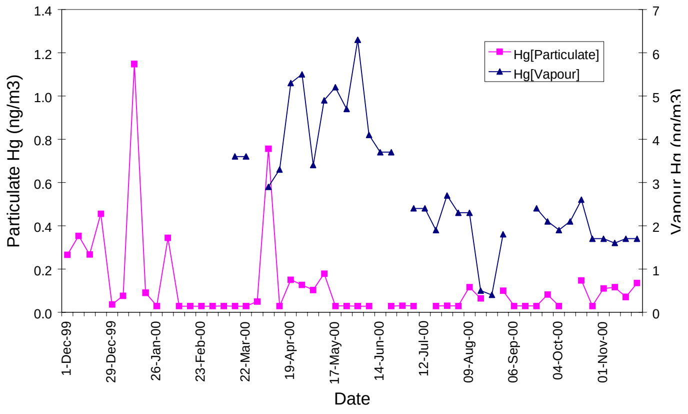
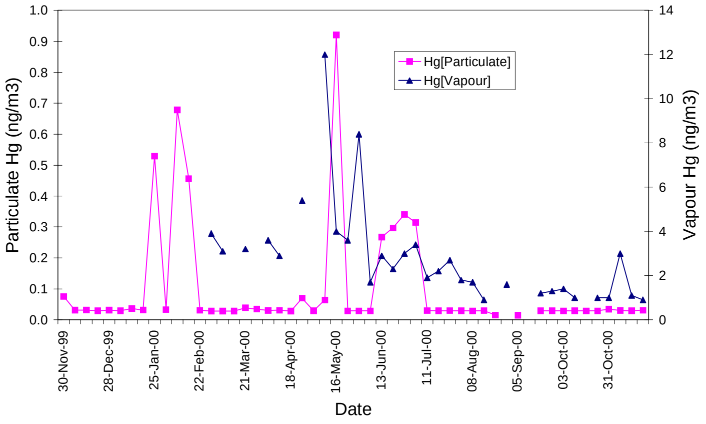


Figure 4.3 Temporal trends in Particulate and Vapour-phase mercury (Hg) concentrations (ng/m^3)

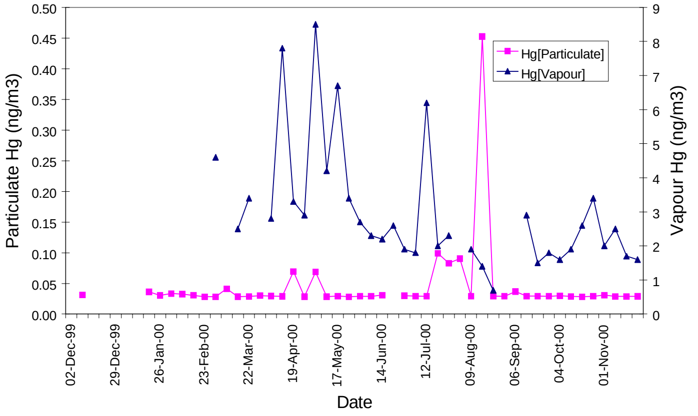
Site Code 7: British Steel



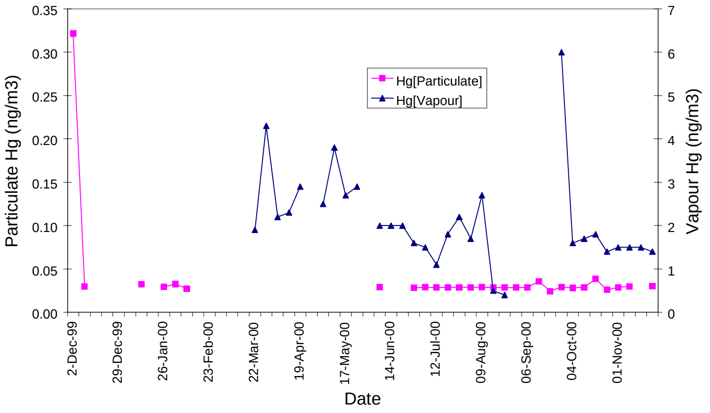
Site Code 16: Castle Cement



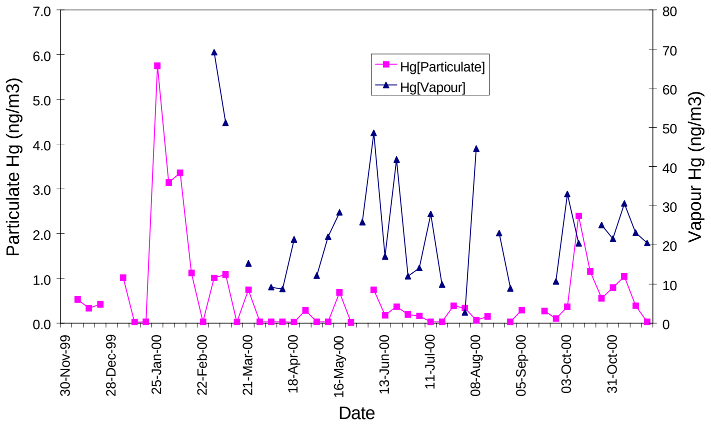
Site Code 17: Sutton Coldfield



Site Code 18: Longannet Power Station



Site Code 23: ICI Polymers and Chemicals Plc



5 Conclusions and recommendations

5.1 Conclusions

Results of the current work show ambient annual mean Pb concentrations to be below the current EU Limit Value (transposed into UK legislation through the revised UK Air Quality Strategy) objective of 0.5 μg/m^3 (to be achieved by 31 December 2004). Moreover, measured annual mean concentrations show only one site to be of concern with respect to the proposed UK objective of 0.25 μg/m^3 to be achieved by 31 December 2008. The highest annual mean concentration of Pb measured in the current programme was 0.237 μg/m^3 registered at the site adjacent to the IMI Refiners Ltd works in Walsall. The second highest annual mean Pb concentration was measured at Britannia Zinc Ltd in Avonmouth (0.104 μg/m^3), well below current objective values. Typical, Pb concentrations in the vicinity of industrial processes included in this study were in the range 0.01 - 0.05 μg/m^3.

Based on the results of the monitoring programme alone, measured concentrations of Pb indicate that no single industrial sector is likely to lead to exceedences of the 2004 annual mean objective. Moreover, all sites (with the possible exception of the IMI Refiners Ltd site) fall below the Lower Assessment Threshold of 0.25 μg/m^3 set by the EU as an indication of the likelihood for mandatory assessment and the National objective for 2008.

Comparisons between the weekly measured values and the bulked 24-hour measurements showed good agreement ($r^2 > 0.95$) between the two sampling regimes for Pb, Cd, Ni and As. For Hg, the agreement was considerably less ($r^2 < 0.1$) due to the low levels observed and the increased uncertainty related to measurements made at this level. The results show that, where monitoring is required, a sampling regime of 7 days can offer a cost-effective approach to study whilst maintaining the relationship between results based on a monitoring regime of fixed 24-hour periods.

The results of the current programme highlight possible exceedences of the proposed Limit Values for As, Cd and Ni at a number of monitoring locations:

For As, one site showed an annual mean concentration greater than the proposed Limit Value (6 ng/m^3). An annual mean of 8.36 ng/m^3 was recorded at IMI Refiners Ltd. In addition, the UAT was breached at Walkers Galvanizing plant in Walsall (an annual mean of 4.22 ng/m^3 was found). The proposed LAT was breached at a number of additional sites, which include: White Rose Environmental; Wolverhampton Municipal Waste Incinerator; Corus Engineering Steels Ltd; Paramount Batteries and Bruhl UK Ltd. Annual mean As concentrations at each site were all greater than 2.4 ng/m^3.

For Cd, the proposed Limit Value of 5 ng/m^3 was exceeded at two sites where annual mean concentrations of 7.37 ng/m^3 and 7.73 ng/m^3 were measured. These sites were IMI Refiners

Ltd. in Walsall and Britannia Zinc Ltd. in Avonmouth, respectively. In addition, an annual mean value of 3.50 ng/m^3 was observed at Sidney Smith iron foundry.

Results of the analysis for annual mean Ni concentrations indicate one marginal exceedence of the proposed Limit Value (20 ng/m^3). This was 20.6 ng/m^3 at the INCO nickel refinery in Swansea. Moreover, the LAT was breached at the Bruhl UK Ltd. works in Sandwell (annual mean 13.4 ng/m^3). All other sites showed annual mean Ni concentrations below the LAT.

For Hg, a Limit Value of 50 ng/m^3 has been proposed.. The results of the current work highlight that particulate phase concentrations of Hg are generally very low (around the limit of detection of the analytical technique), and of the order 0.06 ng/m^3. In contrast, results of vapour-phase Hg ($Hg_{[vap]}$) measurements highlight that concentrations can be greatly elevated in the vicinity of certain industrial processes. For example, the highest mean $Hg_{[vap]}$ concentration was found in the vicinity of a chloroalkali plant, 24.1 ng/m^3, compared to typical values of 3 ng/m^3 found at other sites located in the vicinity of steel, cement, and power generation sectors. Moreover, concentrations of $Hg_{[vap]}$ found at Sutton Coldfield crematorium were not significantly elevated above those measured in the locality of sites falling outside the chloroalkali sector.

5.2 Recommendations and future monitoring requirements

The requirements for further monitoring in the UK have been assessed through analysis of the results of the current work against the proposed Limit Values, having given due consideration to sector types. Where available, annual emissions rates (kg/annum)[14] have been used as an indicator to identify similar installations within sectors that may additionally lead to exceedences of existing and proposed Limit Values. Additionally, internal confidential reports have been made available from the Department of Trade and Industry and DEFRA which provide additional support for the sector analysis for Pb.

Comparison of results have been made against the proposed Upper and Lower Assessment Threshold (UAT and LAT) values for each of the three pollutants in order to determine the future work required at each of the sites. These are shown in Table 1.1 in Section 1 of this report.

The following sections provide further details regarding the future monitoring requirements for each metal in turn:

5.2.1 Lead

Results of the current assessment show no direct exceedences at any of the sites of the Limit Value of 0.5 µg/m^3. Moreover, only one site showed an annual mean Pb concentration, which approached the Air Quality

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[14] Environment Agency for England & Wales Pollution Inventory: http://216.31.193.171/asp/introduction.asp

Strategy objective of 0.25 μg/m^3. Further details regarding sector breakdown are provided below:

Copper and Copper Alloy
The highest concentration of Pb was measured at IMI Refiners Ltd, Walsall (Site 2) of 0.237 μgm^{-3} which approaches the LAT value for Pb. This site falls within the Copper and Copper Alloy production sector and has an emission rate of ~4738 kg/yr. The only other site falling within this sector is Site 1 (A Cohen & Co). This site is authorised under LAPC by Greenwich Borough Council and does not show any potential exceedence of the Limit Value of 0.5 μg/m^3 or the more stringent AQS objective of 0.25 μg/m^3.

Steel Industry
The second highest concentration was measured at Corus Engineering Steels Ltd, Rotherham (0.146 μgm^{-3}) and does not represent a risk of exceeding the more stringent AQS objective for 2008. This site falls in the Steel Industry sector and has an emission rate of 14540 kg/yr. Other processes in Steel Industry sector have lower emission rates than Corus Engineering Steels Ltd at Rotherham so exceedence at these sites is unlikely at any other site in the UK. For example, annual emission rates at Corus UK Ltd, N. Lincolnshire (Site 6) and Corus UK Ltd, Llanwern (Site 8) are 720 kg/yr and 7,178 kg/yr, respectively. Both sites have recorded lead concentrations well below the Limit Value and UK AQS objectives for 2005 or 2008.

Corus UK Ltd's sites at Teeside and Port Talbot were not included in the current work. However, based on annual emissions alone the sites are unlikely to represent a problem with compliance on the basis of the results of the current work. Annual emissions of Pb at these sites are lower (~12,500 kg/yr) than Corus Engineering Steels Ltd at Rotherham.

Other sectors
Results for other sectors indicated that the LAT (0.25 μg/m^3) was not approached at any other site. Consequently, no further consideration is required.

Discussion:
The concentration measured at IMI Refiners is marginally below the LAT (0.25 μgm^{-3}) and the more stringent objective for 2008. The annual mean Pb concentrations measured during the course of the study has shown a significant decreased (95%) in ambient concentration over

previous years' data[15] gathered in response to the previous EU Directive (82/884/EEC now amended). Such a decrease has been the result of the phased closure of plant since January 2000 resulting in reduced production capacity estimated to be approximately 1/5th that of previous years. Thus, in direct response to the Limit Value, the site is unlikely to exceed the limit value. However, from the national perspective, monitoring has been undertaken for a number of years in response to the aforementioned Directive (82/884/EEC). Consequently, it may be of national interest to obtain a longer-term data set to determine more accurately the impact of the phased closure of the plant. Thus, it is recommended that monitoring be continued at this site in order to obtain a longer-term data set.

In addition to Site 2, monitoring is undertaken in accordance with Council Directive 82/884/EEC at Brookside Metal Co. Ltd in Willenhall, West Midlands. This site has not been included in the current survey. However, results for 1999/2000 indicate that ambient concentrations of Pb in the vicinity of Brookside Metal Co. Ltd. currently exceed the Limit Value of 0.5 $\mu g/m^3$. The annual Pb emission rate (in 1999) at this site is 950 kg/yr. Consequently, it is recommended that further monitoring be undertaken in the vicinity of this site on the PM_{10} fraction using a Partisol 2000 unit rather than the current M-Type sampler used in accordance with the Directive.

In addition to IMI and Brookside sites, current problems[16] in complying with the AQS objective of 0.25 μgm^{-3} may exist at the Britannia Recycling (secondary lead) plant in Wakefield (annual emission rate of 398 kg/yr in 1999), and the Dens Metals plant in Dundee (no emissions available). Recorded concentrations of Pb reported were 0.39 μgm^{-3} (TSP sample) at Britannia Recycling, whilst for Dens Metals, data showed highly variable concentrations between 0.1 μgm^{-3} and a number of peaks of over 2.5 μgm^{-3}. However, the report details proposals adopted by both sites with respect to adopting techniques that could be considered as Best Available Techniques (BAT) and abatement strategies that would result in lower levels of Pb and compliance with the AQS objective for 2008. In order to assess the effectiveness of such measures it is recommended that monitoring be undertaken at these two locations.

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[15] UK Non-Automatic Air Quality Networks: Lead and Multi-element Monitoring. Annual Report 2000. Stanger Science and Environment Report No. SSE/AQ/020440101/YB/1759

[16] Confidential Report to DTI and DETR dated October 2000

Information provided by the Department of Trade and Industry[17] during the initial consultation process for the current work has highlighted a number of possible sites with the copper and copper alloy sector that may represent problems in compliance with the AQS objectives for 2004 and 2008. A number of these sites have been included in the current work (A. Cohen & Co Ltd, IMI Refiners Ltd and Cerro Extruded Metals Co. Ltd). For other sites listed, emissions data is unavailable from the Pollution Inventory indicating that all other processes listed in the consultation correspondence are Part B LAPC authorised processes. On the basis of results of the current work at Site 1 (A. Cohen & Co Ltd), a LAPC authorised process, annual emission rates at these additional sites are unlikely to be significant and present problems in complying with the Limit Value and/or the 2008 AQS objective.

5.2.2 Arsenic

One site shows a clear exceedence of the proposed 6 ng/m^3 Limit Value: IMI Refiners Ltd (Site 2). In addition, a number of sites show a breach of the proposed LAT and UAT values. Site 15 (Walkers Galvanizing) showed a marginal exceedence of the UAT. However, data capture at this site is low (28%) and is likely to have a strong influence on the annual mean increasing the level of uncertainty surrounding this measurement.

A number of sites show breaches of the proposed LAT value. These include:
- White Rose Environmental (Site 22);
- Wolverhampton MWI (Site 30);
- Corus Engineering Steels Ltd (Site 7);
- Paramount Batteries (Site 10), and
- Bruhl UK Ltd (Site 26).

For Site 30, only 9 months monitoring data was obtained providing added uncertainty with respect to the measured annual mean concentration of As. These sites are outlined below according to the relevant industrial sector in which they fall. Table 5.2 summarises the assessment of annual means against LAT and UAT values for As.

Copper and Copper Alloy
IMI Refiners (Site 2) falls within the Copper and Copper Alloy sector. Results indicate a clear exceedence of the proposed 6 ng/m^3 Limit Value for As. The annual As emission rate for Site 2 is ~180 kg/yr.

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[17] G.I. Miles letter dated 12 March 1999. DTI - Metals Directorate.

Other Part A Processes in the UK falling within the Copper and Copper Alloy sector have lower annual emissions rates when compared to IMI Refiners Ltd. For example, Brookside Metal Co. Ltd, has an annual emission rate of 42 kg/yr. Thus, it is expected that other Part A sites within this sector will not cause a problem in complying with the proposed Limit Value for As, where regulated under Integrated Pollution Control (IPC).

Additionally, Sites 1 (A Cohen & Co Ltd) and 14 (Cerro Extruded Metals) were included in this sector as Part B processes regulated under LAPC. Results indicate that the LAT is not breached at either site indicating that, for Part B processes of a similar size, such installations are unlikely to represent a problem with compliance of the proposed Limit Value. For Part B processes of a larger size than either Sites 1 or 14, further comparative work may be required in order to fully elucidate the implications for compliance.

Galvanizers

Walkers Galvanizing (Site 15) is authorised under Local Authority Pollution Control (LAPC) Process Guidance Note 2/2. Information from DEFRA[18] indicates that there are 70 other processes authorised under this process guidance note in England and Wales. Results of the current work indicate a breach of the UAT for As. However, data capture at this location was low (only 28%), thus providing further uncertainty with respect to the accurate determination of the annual mean. Data loss analysis indicates that the loss of 50% data capture may provide an under-estimate of the 'true' annual mean in the range of 15 – 20%. As a result, it is recommended that monitoring be continued at this site in order to obtain a better estimate of the annual mean concentration. Moreover, it suggested that an additional site of similar nature and size be included in order to more accurately determine compliance of the non-ferrous Part B processes falling within this sector under the LAPC regime.

Clinical / Municipal Waste Incinerators

Annual mean As concentrations for both incinerators indicate breaches of the LAT. Annual mean As concentrations at the two sites are around 3.2 ng/m^3. For Site 30, additional uncertainty exits with respect to measurements made on less than one full year's of data highlighting that further work may be required. Both sites included in the current work are authorised under LAPC Process Guidance Note 2/5. Information provided by DEFRA indicates that there are 9 other processes in

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[18] DETR. Annual LAPC statistical survey 1998/99.

England and Wales which are authorised under this Process Guidance Note. At this stage it is not feasible to comment on the likelihood of these sites exceeding the proposed Limit Value as emissions data is not readily available in order that a comparison can be made.

A recent new Directive (2000/76/EC) has been published on the incineration of waste which aims to prevent (or where that is not practicable, to reduce as far as possible) negative effects on the environment caused by incineration and co-incineration of waste. The Directive aims to achieve this through stringent operational conditions and technical requirements and through the setting of emissions limits for a number of pollutants, including heavy metals. As a result, it is unlikely that once the directive is in force that As emissions from incineration will present a problem with respect to compliance with the proposed Limit Value. However, further work may be required in order to clarify the current situation and the likely impact of the Directive on future ambient concentrations.

Steel Industry

Site 7 has the highest measured value of the sites in the steel sector and shows a breach of the LAT. Pollution Inventory estimates indicate that of all the sites falling within this sector, Site 7 has the highest emission (~ 128 Kg/yr). The two other sites (Corus UK Ltd, Scunthorpe (Site 6) and Corus UK Ltd, Llanwern (Site 8)) within this sector that were assessed as part of this study. Both have lower emissions of As than Site 7 (~45 kg/yr for Site 6 and ~27 Kg/yr for Site 8) and corresponding lower measured concentrations. Thus, this sector is not thought to represent a problem in complying with the proposed Limit Value based on the results of the current work. Corus UK Ltd’s sites at Port Talbot and Teeside were not included in the current work. Both have annual emissions of As of around 25 kg/yr. Based on the results of the current work and using annual emissions as an indicator for compliance it is unlikely that either of these sites will present problems in complying with the proposed Limit Value.

Results of the current work indicate that further monitoring is required at Site 7 in order to fully elucidate compliance with the proposed Limit Value for As given the breach of the proposed LAT.

Lead Acid Battery sector

Paramount Batteries (Site 10) breaches the LAT for As. However, no such breach is observed at Site 9 (Tungsten Batteries Ltd). No emissions data is available with respect to the two sites as a result of LAPC authorisation. It is recommended that further work be undertaken to clarify the potential for high levels of As in the vicinity of plants within this sector.

Iron Foundry Hot blast cupola and Cold blast cupola
Sites 26 and 27 within this sector show annual mean concentrations of As that breach and approach the LAT, i.e. Site 26 breaches the LAT with an annual mean value of 2.67 ng/m^3 whilst Site 27 approaches the LAT with an annual mean value of 2.3 ng/m^3. These 2 sites are authorised under LAPC Process Guidance note 2/5. Information provided by DEFRA indicates that there are 50 other processes in England and Wales which are authorised under PGN 2/5.

Results of the current study indicate that installations within this sector may require further work in order to clarify the likelihood of high concentrations in the vicinity of processes within this sector.

Lead Production / Recycling
The Lead Production / Recycling sector does not appear to represent a problem with regards to compliance against the proposed Limit Value for As. Results for Site 3 (Britannia Zinc) indicate that there is unlikely to be a problem at the site which has the highest emissions to air (~610 Kg/yr) within the sector. . The annual mean As concentration at this site was 1.89 ng/m^3 does not represent a breach of the LAT. All other sites within this sector have lower emission rates. Results of the current study show that at least two of these sites, Site 4 and Site 5, record lower ambient levels of As which reflect the lower emissions rate.

Power Generation
The power generation sector represents the most significant source of As to air in the UK[19]. Results of the current work show that, of the sites included, none showed an exceedence of the proposed 6 ng/m^3 Limit Value. Moreover, concentrations measured were below the LAT.

The Pollution Inventory for England and Wales (Part A processes only) indicates that there are a number of power generation sites which release larger quantities of As than those sites included in the current study. These include (1999 values): Kingsnorth (816 kg/yr), Ferrybridge (663 kg/yr), Fiddlers Ferry (610 kg/yr) and Cottam (580 kg/yr) power stations. Of the sites included in the current work, Longannet power station (Site 18) has the highest annual emission of As (470 kg/yr).

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[19] A review of arsenic in ambient air in the UK. A report prepared on behalf of the DETR, Scottish Executive, The Department of the Environment Northern Ireland and the National Assembly for Wales. February 2000. Stanger Science and Environment. Report SSE/AQ/1465.

Results show that this site does not pose any problems with compliance of the proposed Limit Value for As (even when additional uncertainty due to low data capture is taken into consideration): in part, by virtue of its geographic location that means the plume-grounding occurs in the Firth of Forth.

Based on the current results for Longannet further consideration is required with respect to Kingsnorth, Ferrybridge, Fiddler's Ferry and Cottam power stations. Geographically, areas of population exist in downwind locations of Fiddler's Ferry and Ferrybridge power stations. Cottam and Kingsnorth power stations are located in rural and coastal area, respectively, indicating that the plume grounding may not occur in areas of population. In order to fully elucidate the implications of the emissions to air associated with operations at these sites for the proposed Limit Value for As, it is recommended that further sites be established at Fiddler's Ferry and Ferrybridge power stations.

For Scotland and Northern Ireland, an initial assessment of power generating processes has been made[20]. Detailed consideration is limited by available emissions data. However, for Northern Ireland, Belfast West power station has a similar emission rate to Kilroot (Site 20), a site that does not currently cause concern with respect to exceeding the proposed Limit Value. It is therefore unlikely that Belfast West will result in exceedence of the proposed Limit Value based on emissions alone. For Scotland, information obtained from the Scottish Power Environment Report for 1999 – 2000[21] indicates that one additional power station emits As in Scotland. Cockenzie power station emits smaller quantities of As (~120 Kg/yr) when compared to Longannet (~470 Kg/yr). Consequently, on the basis of the results of the current work it is unlikely to cause any exceedence of the proposed Limit Value for As, or any problems with respect to proposed UAT or LAT values.

Other sectors:

Other sectors included in the current monitoring programme showed annual mean As concentrations that were lower than the proposed LAT. Consequently, it is unlikely high concentrations will be experienced in the vicinity of processes within these sectors.

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[20] personal communication SEPA and DoE(NI)

[21] http://www.scottishpower.com/aboutus/

Discussion:

Further monitoring for As is recommended in the vicinity of IMI Refiners Ltd in Walsall where a clear exceedence of the proposed Limit Value has been found. Other sites within the Copper and Copper Alloy sectors are unlikely to require further monitoring based on annual emissions alone. In addition, further work it is recommended that further work be undertaken in the vicinity of Walkers Galvanizing (Site 15) and an additional galvanizing plant of a similar nature.

The proposed LAT value for As was found to be breached in the vicinity of the two incinerator plants included in the current work. Available information indicates a further 9 incineration plants in England and Wales which may require further work. However, it is anticipated that the current control measures recently introduced through the waste incineration directive (2000/76/EC) will reduce emissions from these plants significantly so as not to warrant further monitoring. It is advisable that monitoring be continued at both plants in order to accurately determine the effectiveness of legislated control measures.

For As, breaches of the proposed LAT were also found in the vicinity of the two sites falling within the iron foundry sector. These sites are authorised under LAPC by local authorities throughout England and Wales – separately by SEPA in Scotland and by The Chief Inspector and District Councils in Northern Ireland. Further work is required to identify plants of a similar nature to those included in the current work where further monitoring may be required.

Additional sites falling under the power generation sector with annual mean emission rates higher than those included in the current work have been identified at Fiddler’s Ferry, Ferrybridge, Kingsnorth and Cottam power stations. Due to the geographic location of Fiddler’s Ferry and Ferrybridge power stations, and proximity of areas of population, it is recommended that additional sites be established at these two locations. For Scotland and Northern Ireland, other power stations identified have lower annual mean emission rates than those sites in the power-generation sector included in the current work.

Table 5.2. Analysis of results against proposed Lower Assessment Threshold criteria for Proposed Limit Values for As (uncertainty of ± 30%).

Site (code)	Measured (ngm^{-3})	Industrial Sector	Proposed Limit Value set at 6 ng/m^3		
			UAT (3.6 ng/m^3)	UAT< > LAT	LAT (2.4 ng/m^3)
IMI Refiners Ltd	8.36	Copper and Copper Alloy	Breach of proposed LV and UAT		Breach of LAT
Walkers Galvanizing (15)	4.22	Galvanising	Breach UAT		
White Rose Environmental (22)	3.31	Clinical Waste Incinerator		Sites fall between LAT and UAT	
Wolverhampton MWI (30)	3.11	Municipal Waste Incinerator			
Corus Engineering Steels Ltd, Rotherham (7)	3.01	Steel Industry			
Paramount Batteries (10)	2.91	Lead Acid Battery			
Bruhl UK Ltd (26)	2.67	Iron Foundry (Hot blast cupola)			

5.2.3 Cadmium

Two of the sites assessed as part of this study exceed the proposed Limit Value of 5 ngm^{-3}: IMI Refiners Ltd (Site 2) and Britannia Zinc Ltd (Site 3). In addition, two sites breach the LAT value of 2 ng/m^3 (Site 27 and Site 15). Table 5.3 summarises the assessment of annual means against LAT and UAT values for Cd.

The following provides further information with respect to sector breakdown and recommendations for future monitoring:

Copper and Copper Alloy
Within this sector, IMI Refiners Ltd (Site 2) showed a clear exceedence of the proposed Limit Value. Cadmium emissions from Site 2 are ~76kg/yr. Within the non-ferrous metal sector of the Pollution Inventory Britannia Zinc and Britannia Refined Metals are shown to have higher annual emission rates for Cd than IMI Refiners Ltd. These sites are given further consideration below. However, for copper and copper alloy processes it appears that IMI Refiners has the highest annual emission rate which may lead to exceedances of the proposed Limit Value. Consequently, it is recommended that further monitoring be undertaken at this site.

Lead Producer / Recycling
Site 3 (Britannia Zinc Ltd) was the only other site within the current study to show a clear exceedence of the proposed Limit Value for Cd. The site falls within the Lead Producer / Recycling sector for which two other sites (Site 4 and Site 5) were also included. Neither of these two sites showed an exceedence of the proposed Limit Value, or any breach of the LAT. The annual emissions of Cd from Site 3 are ~ 1252kg/yr. The Pollution Inventory for England and Wales indicates that other sites within this sector have substantially lower emission rates. It is therefore unlikely that similar sites will breach the lower assessment threshold.

Iron Foundry
Site 27 (Sidney Smith - Iron Foundry cold blast cupola) breaches the UAT. No information is available for emissions from Site 27 as authorised under LAPC (process guidance note 2/5). However, information obtained from DEFRA indicates that there are 51 other processes authorised under this process guidance note. At this stage it is not feasible to comment on the likelihood of these sites exceeding the proposed Limit Value or the UAT as emissions data is not readily available. However, in light of the mandatory nature of further work required where the UAT is breached, it is recommended that further

work be carried out in the vicinity of Site 27 together with a sector analysis of the likelihood of other hotspots in the vicinity of these types of processes.

Incineration

Neither of the two incineration sites included in the current work showed exceedence of the proposed Limit Value or breaches of the LAT. A recent new Directive (2000/76/EC) has been published on the incineration of waste which aims to prevent (or where that is not practicable, to reduce as far as possible) negative effects on the environment caused by incineration and co-incineration of waste. The Directive aims to achieve this through stringent operational conditions and technical requirements and through the setting of Limit Values for a number of pollutants, including heavy metals. For Cd, it is envisaged that emissions of Cd across the EU will fall from 16 tonnes per year in 1995, to around 1 tonne per year in 2005. Consequently, this sector is unlikely to be a problem with respect to compliance against the proposed Limit Value.

Other sectors:

Other sectors included in the current monitoring programme showed annual mean Cd concentrations that were lower than the proposed LAT. However, for Site 15 (Walkers Galvanizing) a low data capture was obtained for the estimate of the annual mean concentration which is shown to approach the LAT. Consequently, it may be necessary to undertake further work at this site. With respect to all other sectors no further consideration is required on he basis of the results of the current work.

Discussion:

Further monitoring work is required at Site 2 (IMI Refiners Ltd); Site 3 (Britannia Zinc Ltd), Site 27 (Sidney Smith) and possibly Site 15 (Walkers Galvanizing). With respect to Site 27 further desktop work is required in order to clarify the UK position with respect to iron foundries. By necessity, this work will require identification of local authorities throughout the UK that have authorised processes under Process Guidance Note 2/5.

Table 5.3. Analysis of results against proposed Lower Assessment Threshold criteria for Proposed Limit Values for Cd (uncertainty of ± 30%).

Site (code)	Measured (ng/m^3)	Industrial Sector	Proposed Limit Value set at 5 ng/m^3		
			UAT (3 ng/m^3)	UAT < > LAT	LAT (2 ng/m^3)
Britannia Zinc Ltd (3)	7.73	Lead Producer / Recycle	Breach of proposed LV and UAT		Breach of LAT
IMI Refiners Ltd (2)	7.37	Copper and Copper Alloy			
Sidney Smith (27)	3.50	Iron Foundry – cold blast cupola	Breach of UAT	Site falls between LAT and UAT	

5.2.4 Nickel

One site showed a direct exceedence of the proposed Limit Value for Ni (20 ng/m^3): INCO Europe (Site 13). In addition, one site (Bruhl UK Ltd (Site 26)) showed a breach of the proposed LAT (10 ng/m^3). Table 5.4 summarises the assessment of annual means against proposed LAT and UAT values for Ni.

Further consideration to the individual sectors is provided below:

Non-ferrous metals
Site 13 (INCO Europe Ltd) showed a direct exeedence of the proposed Limit Value. However, data capture at this site was low (~40%) which provides additional uncertainty regarding the estimate of the annual mean when compared to a mean based on a full years' data. Results suggest an under-estimation of the annual mean by approximately 15% when compared to an annual mean based on 100% data capture. The site falls within the non-ferrous metals sector with annual emissions in the region of 1374 Kg/yr. Within the non-ferrous sector IMI Refiners Ltd has the second highest annual emission rate of Ni at 345 Kg/yr (1999 value) and does not show a breach of the LAT. Thus, the results of the current work indicate that further work is required at Site 13 but, in general, other processes within the non-ferrous metals sector are unlikely to lead to elevated concentrations.

Iron Foundry (hot blast cupola)
Results for Bruhl UK Ltd (Site 26) show a breach of the LAT indicating that further work is advisable in the vicinity of this plant.

No information is available for emissions from Site 26. The site is authorised under LAPC Process Guidance Note 2/5. Information provided by DEFRA indicates that there are 51 other processes in England and Wales which are authorised under Process Guidance Note 2/5. At this stage it is not feasible to comment on the likelihood of these sites exceeding the proposed Limit Value or breaching the LAT or UAT values. Thus, it is recommended that monitoring be continued at Site 26 in order to clarify the current UK position with respect to this site and a more detailed sector analysis performed.

Other sectors
Other sectors included in the current monitoring programme showed annual mean Ni concentrations that were lower than the proposed

LAT. Consequently, no further consideration is required on the basis of the results of the current work.

Discussion:

Further monitoring work for Ni is required at Sites 13 and 26. In addition, it is recommended that further desktop work be undertaken in order to identify additional sites falling within the iron foundry (hot-blast cupola) sector. By necessity, this work will require information to be gathered from local authorities throughout the UK which have authorised processes under Process Guidance Note 2/5.

Table 5.4 Analysis of results against proposed Lower Assessment Threshold criteria for Proposed Limit Values for Ni (uncertainty of ± 30%).

Site (code)	Measured (ng/m^3)	Industrial Sector	Proposed Limit Value set at 20 ng/m^3		
			UAT (14 ng/m^3)	UAT < > LAT	LAT (10 ng/m^3)
INCO Europe (13)	20.6	Nickel Refinery	Breach of proposed LV and UAT		Breach of LAT
Bruhl UK Ltd (26)	13.4	Iron Foundry (hot-blast cupola)		Site falls between LAT and UAT	

5.3 Summary of Future Monitoring Requirements

The following represents a summary of the individual recommendations for further monitoring on the basis of the results of the current work.

Sector	Sites	Metals
Current sites requiring further work		
Non-ferrous metal production	IMI Refiners (Site 2) Britannia Zinc (Site 3) INCO Europe (Site 13)	Pb, As, Cd Cd Ni
Iron Foundries	Sidney Smith (Site 27) Bruhl UK, Ltd (Site 26)	As, Cd As, Ni
Incineration:	White Rose Environmental (Site 22) Wolverhampton MWI (Site 30)	As As
Steel Industry	Corus Engineering Steels Ltd (Site 7)	As
Lead Acid Battery	Paramount Batteries (Site 10)	As
Galvanizing	Cerro Extruded Metals (Site 14) Walkers Galvanizing (Site 15)	As As, Cd
Chloroalkali	ICI Chemicals and Polymers	Hg [Vapour and particulate]
Sites not previously included		
Non-ferrous metal production	Britannia Recycling (Wakefield) Brookside Metal Co Ltd	Pb Pb
Non-ferrous foundry	Dens Metals (Dundee)	Pb
Power Generation	Fiddler’s Ferry Ferrybridge	As As
Galvanizing (Part B)	Identified through LAPC Registers	As
Incineration	Identified through LAPC Registers	As
Iron Foundries	Identified through LAPC Registers	As, Cd, Ni

6 Report Statement

We confirm that in preparing this report we have exercised all reasonable skill and care.

Unless specifically assigned or transferred within the terms of the agreement, the consultant asserts and retains all Copyright, and other Intellectual Property Rights, in and over the report and its contents.

Appendices

Appendix A: List of Consultees and Contacts

Department for Environment, Food and Rural Affairs (formerly DETR)
Air and Environment Quality Division
Ashdown House
123 Victoria Street
London SW1E 6DE

Department of Trade and Industry
Metals Directorate
151 Buckingham Palace Road
London SW1W 9SS

The National Assembly for Wales
Cathays Park
Cardiff CF1 3NQ

Scottish Executive
Environment Group
1H Victoria Quay
Edinburgh EH6 6QQ

Department of the Environment in Northern Ireland
Calvert House
23 Castle Place
Belfast BT2 2AA

Environment Agency
Rio House
Waterside Drive
Aztec Way
Almondsbury
Bristol BS12 4UD

Galvanizers Association
Wren's Court
56 Victoria Road
Sutton Coldfield
West Midlands B72 1SY

Federation of British Cremation Authorities
41 Salisbury Road
Carshalton
Surrey SM5 3HA

Scottish Environmental Protection Agency
Erskine Court
Castle Business Park
Stirling FK9 4TR

Bristol City Council
Health and Environmental Services
The CREATE Centre
Spike Island
Smeaton Road
Bristol BS1 6XN

CRE Group Ltd
Stoke Orchard
Cheltenham
Gloucestershire GL52 7RZ

PS Analytical
Arthur House
Crayfields Industrial Estate
Main Road
Orpington
Kent BR5 3HP

ETI Group Ltd
Stoke Orchard
Cheltenham
Gloucestershire GL52 7RZ

Appendix B: Micro-scale environmental considerations

Site location	Guidance notes for installation
Rooftop	• if not previously identified, locate the nearest flat-roof building immediately downwind of the process stack • supplied support frames for equipment are not required • equipment housing to be bolted to stone paving slabs in order to minimise damage to the roof surface and spread the load of the equipment • bolt-endings underneath the paving slab to be covered by rubber feet to protect the roof-top • exact location of the equipment on the roof-top is away from any immediate influences of walls and/or other building structures. • under no circumstances must a monitor be positioned near a vent outlet or stack emanating from a building. • electricity cables are to be kept as short as possible utilising the nearest available electricity supply
Ground	• supplied support frames for equipment are required • sites requiring security cages will be identified • electricity cables are required to be run from supply to the equipment in such a way as not to put individuals at risk, i.e. avoid obvious paths • the exact location of the equipment at the site is to be located away from any immediate influences of walls and/or other building structures. Where the installation of equipment adjacent to a wall or boundary is unavoidable, it is important that the equipment is sited on the exposed side of the wall. • under no circumstances must a monitor be positioned near a vent outlet or stack emanating from a building.

Appendix C: Local Site Operators

The table below provides information on the organisations appointed by Stanger Science and Environment to undertake the duties of local site operator and the site(s) under their control during the programme.

Site Code / Company Name	**Local Site Operator**
1: A Cohen & Co Ltd.	London Borough of Greenwich Public Services Riverside House Woolwich High Street London SE18 6DN Contact: Colin Perryman
2: IMI Walsall 15: Walkers Galvanizing	Walsall Metropolitan Borough Council Environmental Health and Consumer Services Pollution Control Division Challenge Building Hatherton Road Walsall WS1 1YG Contact: Mick Clews
Site 3: Britannia Zinc Ltd	Bristol City Council Health and Environmental Services The CREATE Centre Spike Island Smeaton Road Bristol BS1 6XN Contact: David Muir
Site 4: Midland Lead Refiners Site 6: Corus UK Ltd Site 11: Associated Octel Company Ltd. Site 16: Castle Cement Site 21: Drax Power Station - National Power plc Site 23: ICI Chemical and Polymers Plc Site 26: Bruhl UK Ltd. Site 27: Sidney Smith Site 28: FE Mottram Ltd	CES Maunsell House 160 Croydon Road Beckenham BR3 4DE Contact: James Richer

Site Code / Company Name	Local Site Operator
Site 5: Britannia Refined Metals Ltd	Britannia Refined Metals Ltd Botany Road Northfleet Gravesend Kent DA11 9BG Contact: Frank Boyes
Site 7: Corus Engineering Steels Ltd	Rotherham Metropolitan Borough Council Environmental Health Elm Bank House 73 Alma Road Rotherham S60 2BU Contact: Andy Hawkins
Site 8: Corus UK Ltd, Llanwern	Newport County Borough Council Environmental & Public Protection Division Civic Centre Newport South Wales NP9 4UR Contact: Clive Badger
Site 9: Tungsten Batteries Ltd.	Harborough District Council Council Offices Adam and Eve Street Market Harborough Leicestershire LE16 7AG Contact: Norman Proudfoot
Site 10: Paramount Batteries	Barnsley Metropolitan Borough Council Environmental Health Services Wellington House 36 Wellington Street Barnsley S70 1WA Contact: Caroline Petty
Site 12: Esso Petroleum Company Ltd	Southampton City Council Environmental Health Service Southbrook Rise 4 - 8 Millbrook Road East Southampton SO15 1YG Contact: Paul Wells

Site Code / Company Name	**Local Site Operator**
Site 13: INCO Europe Ltd	City and County of Swansea Environmental Health The Guildhall Swansea SA1 4PE Contact: Andrew Pritchard
Site 14: Cerro Extruded Metals	Sandwell Metropolitan Borough Council Dept. of Environmental Services PO Box 42 Lombard Street West Bromwich West Midlands B70 8RU Contact: Robert Lloyd
Site 17: Sutton Coldfield Crematorium	Birmingham City Council Environmental Services Department Regulation Division PO Box 5248 581 Tyburn Road Birmingham B24 9RF Contact: Bob Appleby
Site 18: Longannet Power Station	Fife Council Environmental Health Service 5/7 Comley Park Dunfermline Fife KY12 7HU Contact: Dougie Nelson
Site 19: Coolkeeragh Power Station	Derry City Council Environmental Health Department Council Offices 98 Strand Road Derry BT48 7NN Contact: Philip O'Doherty
Site 20: NIGEN Ltd	Carrickfergus Borough Council Environmental Health Department Town Hall Carrickfergus Co. Antrim BT38 7DL Contact: John MacIntyre

Site Code / Company Name	**Local Site Operator**
Site 22: White Rose Environmental	Leeds City Council Environment Department 155 Kirkstall Road Leeds LS4 2AG Contact: John Tubby
Site 24: Glacier Vandervell Ltd	East Ayrshire Council Pollution Control Western Road Kilmarnock KA3 1LL Contact: Michael Rooney
Site 25: Belfast Harbour Estate	Belfast City Council Health & Environmental Services The Cecil Ward Building 4 - 10 Linehall Street Belfast BT2 8BP Contact: Alastair Curran
Site 29: Cliff Hill Quarry	Stanger Science and Environment Ward Street Ettingshall Wolverhampton WV2 2PJ Contact: Alan Lloyd
Site 30: Wolverhampton MWI	Wolverhampton Metropolitan Borough Council Dept. Environmental Protection Civic Centre St Peter's Square Wolverhampton WV1 1RG Contact: Bob Gudger

Appendix D: LSO Record Sheet - Partisol 2000

Site Code: ____________ Process Name: ______________________

Operator(s): ______________________________

Date/Time of attendance: ______________________________

PM_{10} Inlet cleaned: Yes ☐ No ☐

Date of PM_{10} inlet cleaning: ______________________________

Parameter	**Filter Identifier**			
Filter ID				
Record				
Start Time				
Start Date				
Finish Time				
Finish Date				
Volume				
Valid (hrs)				
Temp (^oC)				
Pressure				
Total				

Appendix E: LSO Record Sheet - Partisol Plus (Model 2025)

Site Code: ______________ Process Name: ______________________________ Operator(s): ____________________

Date/Time of Attendance: ______________________________ PM_{10} inlet cleaned: Yes ☐ No ☐

Date of PM_{10} inlet cleaning: ____

Filter ID	Measured Parameter											
	Stat	Rec:	Actual Sample Start	Actual Sample Stop	Valid Elapsed Time	Total Elapsed Time	Volume	Flow	FltT	AmbT	Pres	%RH

Appendix F: Sampling and Analysis - Technical Details

Partisol 2000 and Partisol-Plus 2025 units were employed for the sampling of PM_{10} in the current assessment. Common elements for each of the sampling regimes are summarised below:

1. Sampling was undertaken on the PM_{10} fraction collected onto cellulose nitrate filters (47mm diameter)[22]
2. Flow rates were maintained at 16.7 l/min
3. Site attendance and operational duties were performed by appointed local site operators (LSOs)
4. Sampling data were provided by appointed local site operators to Stanger Science and Environment on pro-forma sheets (as shown in Appendices D and E). Parameters recorded were filter identifier, dates of exposure, volume sampled (m^3), total number of hours sampled, the number of valid hours (where performance criteria were met), ambient temperature and pressure.
5. PM_{10} inlets were cleaned every 4 weeks to prevent the build-up of particulate matter and contaminants.
6. Each filter was given a unique reference known as a filter identifier. Filter identifiers enable the user to name/classify specific filter cartridges and/or filter magazines so that the interval data (i.e. the sampling period) is filter-specific.
7. Filters with unique identifiers were dispatched from the laboratory and returned to the laboratory within 47mm diameter individual storage containers[23].
8. LSOs were informed of the importance of storage and told to never touch filters with fingers.

Further details regarding the two sampling regimes are provided below:

'Weekly' Sampling - Partisol 2000

Rupprecht & Patashnick Partisol 2000 units were employed at all 30 sites within the project. Sampling was undertaken on the particulate PM_{10} fraction for a period of up to 7 days (normally covering the period from Wednesday 12:00 hours - Wednesday 12:00 hours).

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[22] Gelman Science - GN Metricel Membrane Disc Filters, 0.8 µm, 47mm plain (Product Code 64679)

[23] R & L Slaughter - 55mm contact plate (Product Code 402/0076/00)

Inter-Comparison Data Partisol 2025

Rupprecht & Patashnick Partisol-Plus Samplers (Model 2025) were used at 5 of the 30 sites in order to ascertain the effectiveness of the 7-day sampling regime as a cost-effective method of meeting compliance with the first Daughter Directive.

The Partisol-Plus units have an innovative filter storage and exchange system, which permits the operation of the device for up to 16 days of daily sampling between site visits.

Partisol 2025 samplers were operated using an edited version of the default "BASIC" setting which stipulates a fixed 24-hour sampling period prior to filter exchange taking place. Sampling was commenced at 12:00 - 12:00 hours in order to minimise any differences that would occur between the two sampling regimes due to local site operation (normally undertaken around mid-day).

Analysis of Particulate-phase Pb, As, Cd, Ni, Hg, (and V)

The following section describes briefly the two analytical techniques used in the programme for the determination of particulate phase metal concentrations. It does not attempt to produce a detailed review of the techniques, which has been carried out previously[24]. Details regarding the method of analysis for vapour-phase Hg concentrations are given.

Inductively-coupled plasma is a very high temperature excitation source that desolvates, vaporizes, excites, and ionizes atoms. The sample is nebulized (sprayed as a very fine vapour) and enters the torch with a flow of argon gas. The argon keeps the torch from melting and is also the plasma itself. A strong radio frequency (Rf) generator in the coils around the torch produces a magnetic field, which generates the argon plasma. The temperature in the plasma approaches 10,000 Kelvin in the quartz "torch". Metal atoms in the plasma are excited to higher energy levels and when they "relax" or return to the ground state, they emit light. The light given off (in the case of ICP-AES) by these atoms is separated into the separate wavelengths by a grating and is detected by a photo-multiplier tube. The atoms give off narrow bands (discrete wavelengths) of emitted light, particular to a given element. In this way, the presence of a particular element can be established. The amount of light given off is also proportional to the amount of that element in the sample, so the concentration of a given element in a sample can be accurately determined.

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[24] Handbook of Air Pollution Analysis (1977). Second Edition. Eds. Roy M. Harrison & Roger Perry, Pub. by Chapman and Hall.

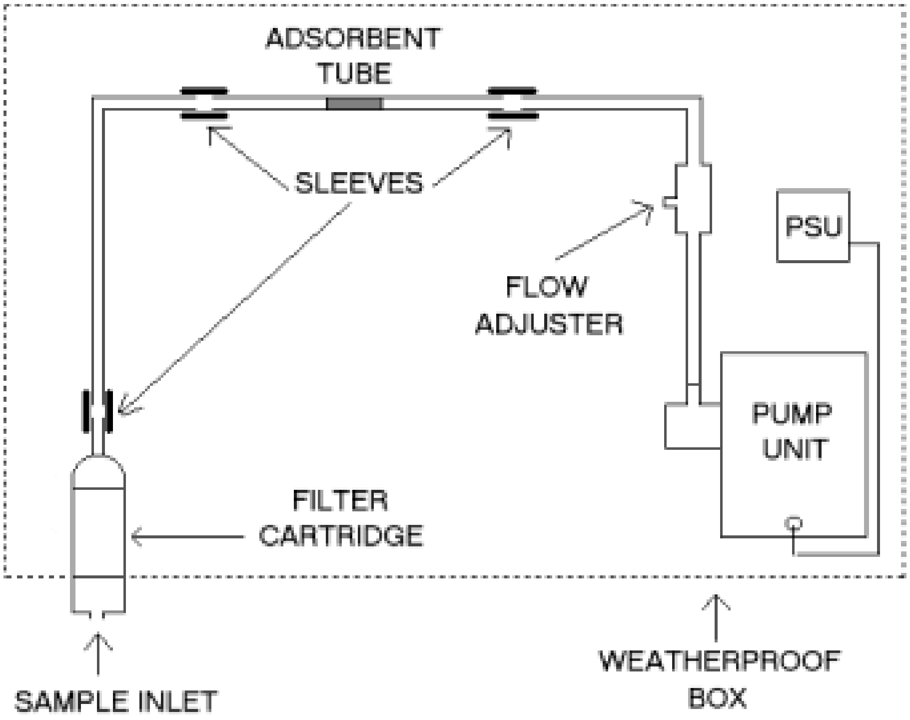
For ICP-MS the same principal of operation applies except in that atoms are measured through mass.

Calibration with reference solutions, based on the linear relationship between concentration and measured pulse rate, allows a quantitative analysis of the sample analyte.

Sampling and Analysis Vapour-phase Hg

Weekly active sampling for vapour-phase mercury was carried out onto adsorption tubes using a low volume pump at a flow rate of 100 ml/minute. Particulate phase was removed prior to adsorption using a 25 mm 0.8 µm cellulose ester filter. This is housed in an open-ended cassette mounted on the end of the sampling line (Figure F.1). Vapour-phase mercury is trapped onto gold-coated silica where it forms an amalgam.

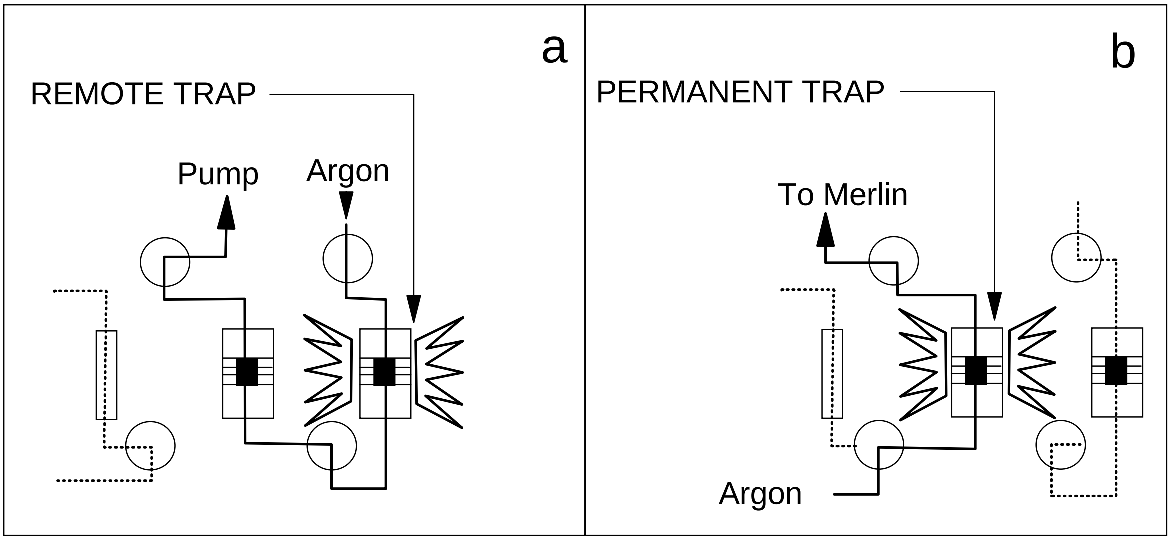
Figure F.1: Schematic diagram of vapour-phase absorbent tube configured on Partisol 2025



Determination of Mercury in Air

The Sir Galahad utilises amalgamation in conjunction with atomic fluorescence detection for the determination of mercury in gas samples. Gas samples are passed over a gold tube where the mercury is trapped. Gold tubes have been shown to collect all forms of mercury from air samples at flow rates up to 5.0 l min^{-1} and at temperatures up to 200^{o}C. Once the sample has been passed over the tube, it is inserted into the Sir Galahad where the trap is flushed with a stream of argon to remove any residual gases. The tube is then heated to approximately 900^{0}C for 1 minute, still in a stream of argon, causing the mercury to desorb. It is then flushed onto a fixed gold tube in the Sir Galahad where it is collected. From there it is thermally desorbed into an atomic fluorescence detector where the mercury is detected. Figure F.2 shows the schematic of the analysis sequence.

Figure F.2. Schematic diagram for remote trap analysis



The Sir Galahad is calibrated using the vapour injection technique. Known volumes of the vapour from a calibration vessel containing elemental mercury at a known temperature are injected using a gas tight syringe. The software calculates the concentration of mercury in the vapour according to a range of temperatures. The calibration range of 0 - 1000 µl of Hg^{0} vapour is required to produce a linear regression co-efficient, r, greater than 0.999 and an intercept less than 2% of the top calibration standard prior to analysis of adsorption tubes taking place. If not, the instrument is re-calibrated until these conditions are met.

Once calibrated, the stat transfer efficiency of the instrument is checked. This test is to confirm that mercury is quantitatively trapped on the remote sampling tube then desorbed onto the fixed calibration trap and from there into the detector. To carry out this test, a gold tube is taken and analysed in the Sir Galahad until a repeatable blank value (below 200 pg) is obtained. Once achieved, a known amount of mercury is added to the tube. The tube is then analysed on the Sir Galahad and the recovery calculated. This recovery must be 95 - 105%.

Appendix G: Operational and Equipment Performance

Monitor Performance

Typical problems encountered in monitor performance included:

1. Water-logging of temperature probe connections resulting in temperature error status codes and incorrect volume measurements
2. EPROM lock-outs resulting in software crashes (Partisol 2000)
3. Failure in the automatic filter exchange mechanisms of the Partisol 2025 units. These were more frequent than expected during the early stages of the programme. Discussions with ETI Group Ltd and the manufacturers (Rupprecht & Patashnick) highlighted that a previous filter cassette design with non-chamfered edges were released to the UK through failures in the QA/QC procedures at the manufacturer.

Operational Difficulties

Local site operators experienced a number of operational difficulties during the year of monitoring. These included:

1. Problems with access to sites where private individuals and/or organisations were required to provide assistance
2. Fuel shortages during the month of September due to nation-wide action by hauliers. This resulted in sampling period of greater than 7 days at many sites
3. Disruption to the power supply due to adverse weather conditions was experienced at Site Code 18: Scottish Power Longannet Power Station. The site is very exposed to the high winds on the Firth of Forth which resulted in overhead power cable failures on a number of occasions during the winter of 1999/2000
4. A limited number of weeks were lost due to misalignment of filters within the hub unit of the Partisol 2000

Appendix H Problems in ICP-AES Analysis

Problems regarding the accuracy of measurements made for As and Hg were encountered in the early stages of analysis using ICP-AES by CRE Group Ltd. These concerns were raised through a routine UKAS audit of the analytical laboratory that identified the following issues:

- Low recovery rates of Hg (60 - 80%) from certified reference material of known concentration
- Potential carry-over from the microwave digestion of Hg to subsequent samples leading to erroneously high measurements
- High and variable concentrations of arsenic in blank (unexposed) filters

As a consequence, analysis was stopped. Further investigations were undertaken in order to determine where problems in analysis for As and Hg were occurring. These are outlined in further detail below:

Recovery of Hg and As

Analysis was undertaken using in-house spiked filters to determine recovery and repeatability of analysis for Hg and As. These were compared with repeatability and recovery studies using certified reference material obtained from the Laboratory of the Government Chemist. Results of the in-house repeatability studies showed recoveries of 97 - 111% and good reproducibility. On the basis of acceptable recovery of Hg and As from in-house spiked filters, UKAS agreed that CRE Group no longer had to externally resource reference filters.

Investigations for Potential Carryover

ICP-AES analysis was undertaken on a series of 20% nitric acid blanks. Results indicate that As levels were consistently below the limits of detection (350 ng/sample). However, for Hg analysis, results displayed a negative drift indicating possible increasing levels of contamination. A further investigation was undertaken which involved spiking a series of filters with Hg followed by microwave digestion. Having analysed the spiked filter, subsequent ‘blank’ extracts and solutions were analysed for Hg for evidence of carryover. The results of this investigation highlighted that there was a problem in carryover occurring within the ICP-AES nebulizer system and not within the microwave extraction system.

High and variable background concentrations

Investigations regarding the 'high and variable' concentrations of As in unexposed filters centred on consultation with the filter supplier, Gelman Sciences. Analysis by an independent laboratory[25] produced low levels of As around the limits of detection. Gelman Sciences confirmed that the possibility of contamination of filters with As through their manufacturing process was negligible.

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[25] Harwell Scientifics Ltd., 551 Harwell, Didcot, Oxfordshire OX11 0RA

Conclusions

As a result of the investigations surrounding the problems experienced by CRE Group Ltd with the ICP-AES UKAS accreditation was withdrawn for As and Hg analysis. Specifically, the investigations highlighted that a problem with the ICP/nebuliser system was the likely cause for carryover rather than the microwave digestion system. Moreover, independent analysis of blank (unexposed filters) ruled out the occurrence of high background levels of contamination. The results of these investigations were reported to UKAS on 13 March 2000.

Due to the withdrawal of UKAS accreditation for As and Hg from CRE Group's UKAS Schedule, analysis of extracts for these two elements was sub-contracted to Harwell Scientifics Ltd using ICP-MS. Harwell Scientifics Ltd have UKAS accreditation for ICP-MS analysis. However, prior to undertaking this analysis, a sub-sample (20%) of the existing extracts (approximately 250 in all) was chosen for analysis for Pb, Cd and Ni in order to compare with previously reported ICP-AES results. As and Hg were also included in order to clarify the problems in analysis previously reported by CRE Group Ltd. This was undertaken in order to seek equivalence between the two analytical techniques. Extracts to be included in this cross-comparison were identified by Stanger Science and Environment in order to provide concentrations over a wide range (high and low) of previously reported values and across different filter batches.

Results of the comparisons between ICP-AES and ICP-MS for Pb, Cd, Ni, As, Hg (and V) were subjected to a Student t-test. The results are summarised in Table H.1. Both laboratories estimate uncertainty budgets of ± 20 - 25% on values (see section 3.4 for further details).

Results of the cross-comparison confirmed previously identified problems with As and Hg. That is, bias existed between the techniques with respect to these two elements. For both elements, the calculated value of 't' is greater than the value of 't' obtained from distribution tables at the 95% confidence limits, although for As, only marginally. In contrast, results for Pb, Cd and Ni indicate that no significant bias between the two techniques is evident. For V the sample size of comparison is small (n = 3), although results still indicate that there is little difference between the results of the two techniques.

As a consequence of the results of the comparison between the two laboratories the following instructions were given with respect to further analysis of historical samples and future sample returns. The instructions were mutually agreed between CRE Group Ltd and Stanger Science and Environment in order to provide an appropriate balance between the necessity to adhere to an accreditation schedule, and the commercial outlay of bringing in an additional laboratory incurring costs not previously envisaged. They included:

1. Harwell Scientifics Ltd to re-analyse all previously reported extracts (approximately 250) for As and Hg

2. Harwell Scientifics Ltd to undertake all further analysis for As and Hg until CRE Group provide further evidence of satisfying UKAS auditors
3. CRE Group Ltd to continue with digestion of samples with a proportion of the extracts forwarded to Harwell Scientifics Ltd for the above As and Hg analysis
4. CRE Group Ltd to continue with ICP-AES analysis for Pb, Cd, Ni (V included in the case of Site Code 20

Table H.1 Comparison of ICP-AES and ICP-MS results for Cd, Ni, Pb, Hg, As and V (ng/m^3) alongside Student 't' test results.

Statistic	**Determinant**					
	Cd		**Ni**		**Pb**	
	ICP-AES	**ICP-MS**	**ICP-AES**	**ICP-MS**	**ICP-AES**	**ICP-MS**
Mean	2.97	2.18	6.38	5.53	239	172
StDev	8.77	4.92	8.39	6.73	843	487
'n'	33	33	38	38	44	44
Pooled StDev	7.11		7.60		689	
t $_{[Calculated]}$	0.45		0.48		0.46	
t $_{[95\%\ Confidence\ Limits]}$	2.00		2.00		2.00	
	Hg		**As**		**V**	
	ICP-AES	**ICP-MS**	**ICP-AES**	**ICP-MS**	**ICP-AES**	**ICP-MS**
Mean	3.50	0.45	16.39	6.27	2.22	1.47
StDev	2.68	0.76	26.55	15.07	1.63	0.84
'n'	28	28	38	38	3	3
Pooled StDev	1.97		21.59		1.29	
t $_{[Calculated]}$	5.79		2.04		0.70	
t $_{[95\%\ Confidence\ Limits]}$	2.05		2.00		3.182	

CRE Group Ltd purchased its own ICP-MS in the summer of 2000. Familiarity with ICP-MS analysis for ambient metals was achieved and added to their UKAS Schedule in September 2000. Consequently, a backlog of samples covering all monthly dispatches from mid-July 2000 onwards were analysed by CRE Group Ltd rather than Harwell Scientifics Ltd.

Prior to undertaking this analysis, a further comparison between the two laboratories was carried out on 11 samples previously reported for As and Hg using ICP-MS analysis at Harwell Scientifics Ltd. This comparison was carried out in order to observe any bias between the two laboratories undertaking ICP-MS analysis. The results were subjected to statistical analysis using the Student ‘t’ test (shown in Table H.2).

Table H.2 Comparison of ICP-MS results for As and Hg (ng/m^3) alongside Student 't' test results.

Statistic	**Determinant**			
	As		**Hg**	
	CRE Group	**Harwell Scientific**	**CRE Group**	**Harwell Scientific**
Mean	1.35	1.31	-0.04	0.14
StDev	0.63	0.62	0.02	0.11
'n'	11	11	11	11
Pooled StDev	0.62		0.08	
t	0.17		-5.11	
t $_{[95\% \text{ Confidence Limits}]}$	2.20		2.20	

Results of the cross comparison of ICP-MS techniques between the two laboratories highlight that there is no bias between the two laboratories with respect to ICP-MS analysis for As. For Hg, bias is shown to still exist. Assuming that the extract solutions have not changed between the time of the original analysis and the follow-up analysis undertaken by CRE Group Ltd, the bias shown in Table H.2 appears to be in the measurement methods between the two laboratories. That is, CRE Group Ltd utilise a 3-point calibration (blank, 1.25 ppb and 2.5 ppb), whilst Harwell Scientifics Ltd use a single point (50 ppb) calibration. For both laboratories, the limit of detection reported for Hg are similar (5 – 6 ng/filter) providing further evidence that the bias for Hg exists as a result of differences in measurement method. Moreover, the concentrations recorded for Hg are low resulting in a high measurement uncertainty. Thus, the bias appears to exist as a consequence of differences in the approach to calibration and the increased uncertainty associated with measurements at such low levels.

UKAS accreditation was given to CRE Group Ltd for the measurement of metals sampled in ambient air. This accreditation included Hg. Consequently, CRE Group Ltd was instructed to proceed with analysis using ICP-MS for As and Hg for all field samples taken from mid-July 2000 onwards. Table H.3 summarises the UKAS accreditation for analysis undertaken throughout the whole of the programme.

Table H.3: Summary of UKAS accreditation schedules for particulate phase ICP-AES and ICP-MS for Pb, As, Cd, Ni, and Hg for relevant monthly dispatches.

	UKAS Accredited Laboratory / Analytical Method		
	CRE Group Ltd	**CRE Group Ltd**	**Harwell Scientifics**
Determinants	**ICP-AES**	**ICP-MS**	**ICP-MS**
Pb, Cd, Ni	December January February March April May June	July (weeks 3 and 4) August September October November	July (weeks 1 and 2)
Hg, As		July (weeks 3 and 4) August September October November	December January February March April May June July (weeks 1 and 2)
V[26]	December January February March April May June	July (weeks 3 and 4) August September October November	July (weeks 1 and 2)

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[26] UKAS accreditation for Vanadium not included in ICP-AES analysis

Appendix I: Comparative sampling data

The following section provides data for the comparison of analytical measurements made using weekly sampling regimes versus bulked-daily samples obtained from 24-hour sampling. It provides details with respect to the comparison of both period mean concentrations (for those above the limit of detection) and the relationship between the two sampling regimes as determined through linear regression.

Table I.1 Comparison of period means (paired values > LOD) for weekly and bulked-daily sampling regimes.

Site	Weekly	Bulked-Daily	% Difference (over bulked-daily)
Pb (μg/m^3)			
All sites	0.0682	0.0662	+2.9%
Site 2	0.0740	0.0670	+9.4%
Site 3	0.1192	0.1272	-6.7%
Site 5	0.0370	0.0331	+10.5%
Site 8	0.0408	0.0321	+21.3%
Site 18	0.0072	0.0057	+20.8%
As (ng/m^3)			
All sites	2.53	2.77	-9.5%
Site 2	5.05	5.19	-2.8%
Site 3	2.13	2.64	-23.9%
Site 5	1.33	1.57	-18.0%
Site 8	1.50	1.58	-5.3%
Site 18	0.60	0.60	0%
Cd (ng/m^3)			
All sites	5.15	5.50	-6.8%
Site 2	6.84	7.18	-5.0%
Site 3	9.38	10.48	-11.7%
Site 5	0.53	0.50	+5.7%
Site 8	1.37	1.02	+25.5%
Site 18	0.24	0.23	+4.2%
Ni (ng/m^3)			
All sites	3.67	3.14	+14.4%
Site 2	5.93	5.37	+9.4%
Site 3	2.56	2.02	+21.1%
Site 5	3.06	2.99	+2.3%
Site 8	3.19	1.52	+52.3%
Site 18	1.23	0.96	+21.9%
Hg (ng/m^3)			
All sites	0.60	0.66	-10.0%
Site 2	0.48	0.47	+2.1%
Site 3	0.58	1.07	-84.5%
Site 5[27]	N/a	N/a	N/a
Site 8	1.04	0.32	+69.2%
Site 18[27]	N/a	N/a	N/a

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[27] No paired values measured above LOD

Figure I.1(a) Relationship between Lead (Pb) weekly and bulked-daily sampling across all co-located sites.

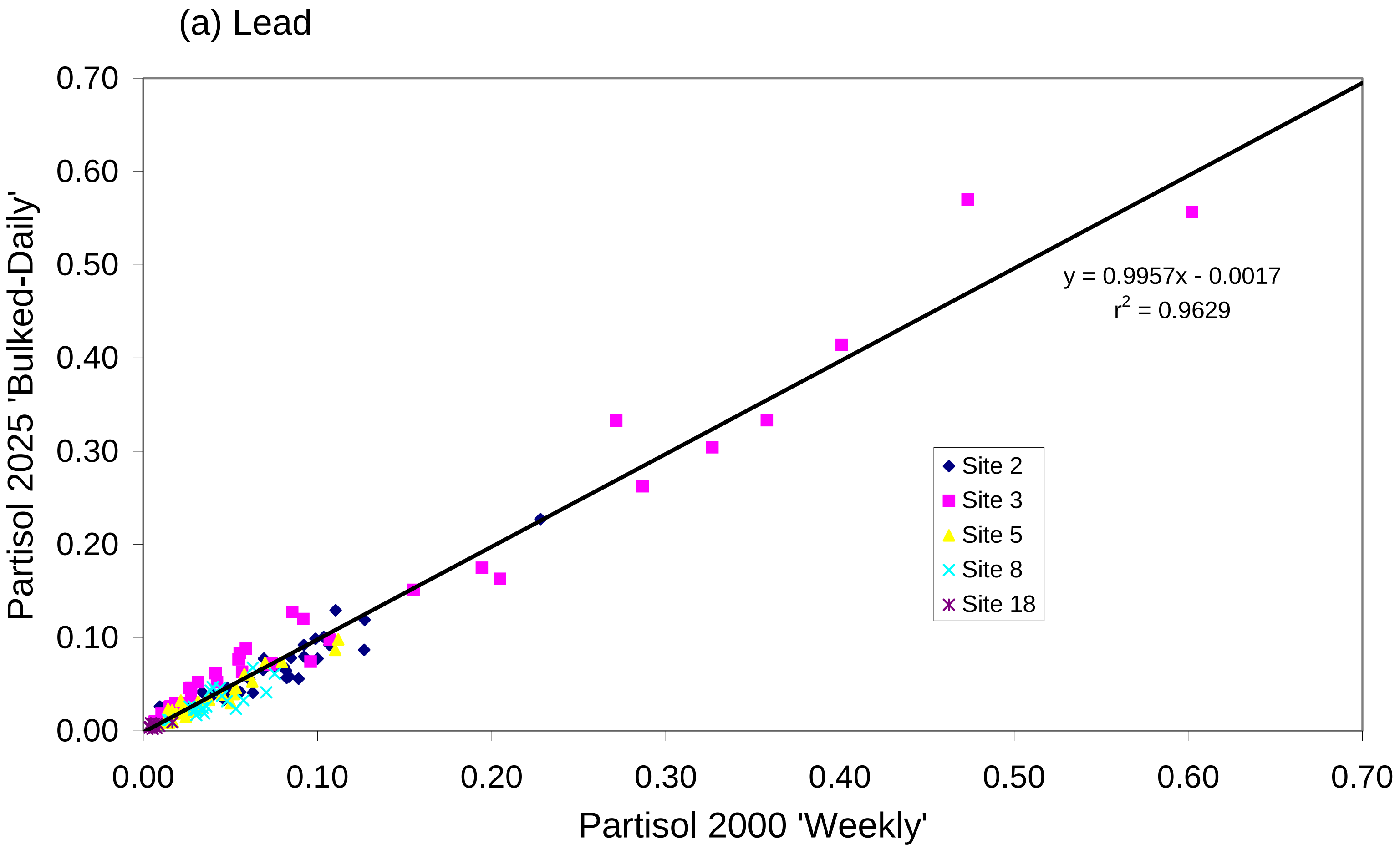


Figure I.1(b) Relationship between Arsenic (As) weekly and bulked-daily sampling across all co-located sites.

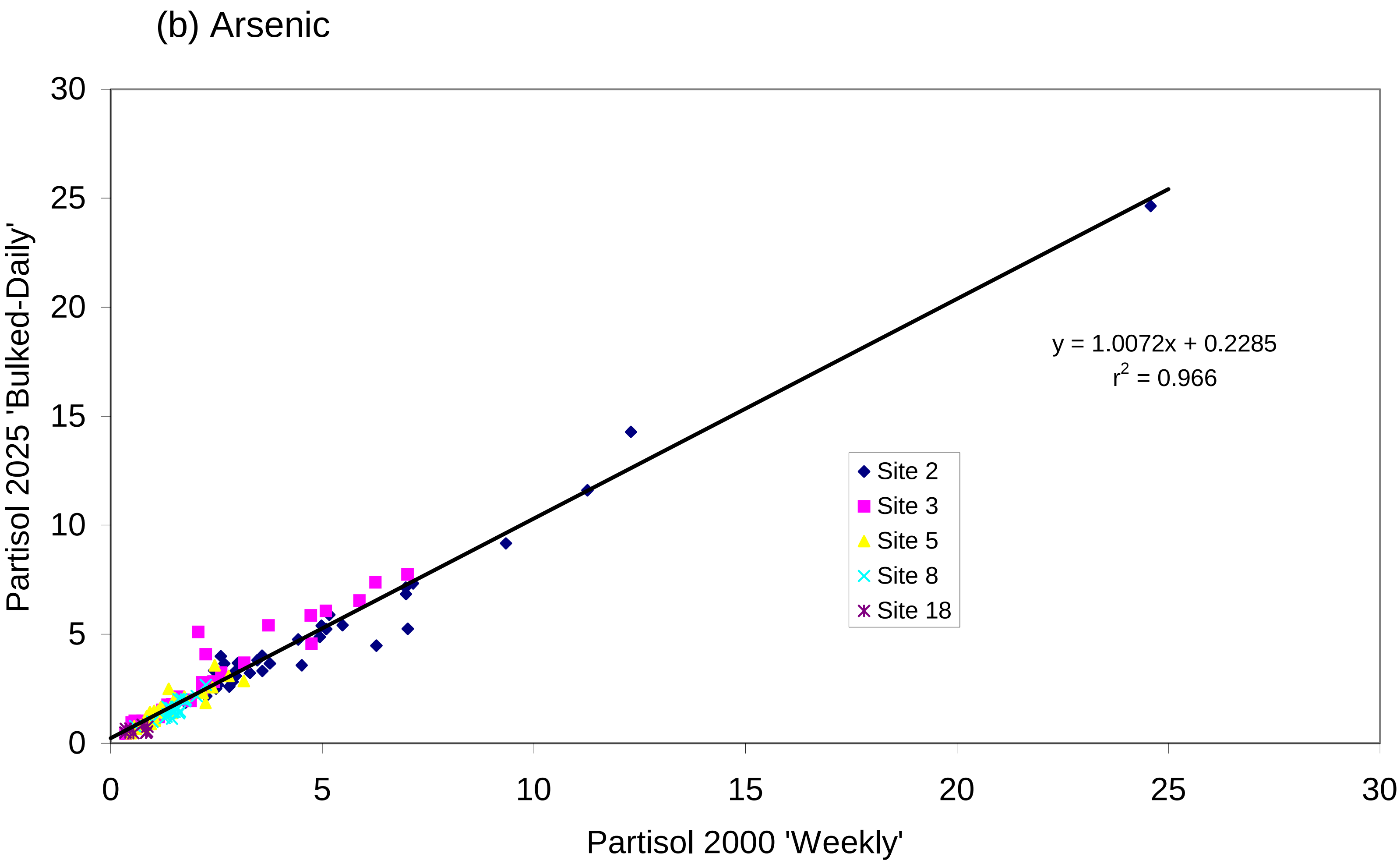


Figure I.1(c) Relationship between Cadmium (Cd) weekly and bulked-daily sampling across all co-located sites.

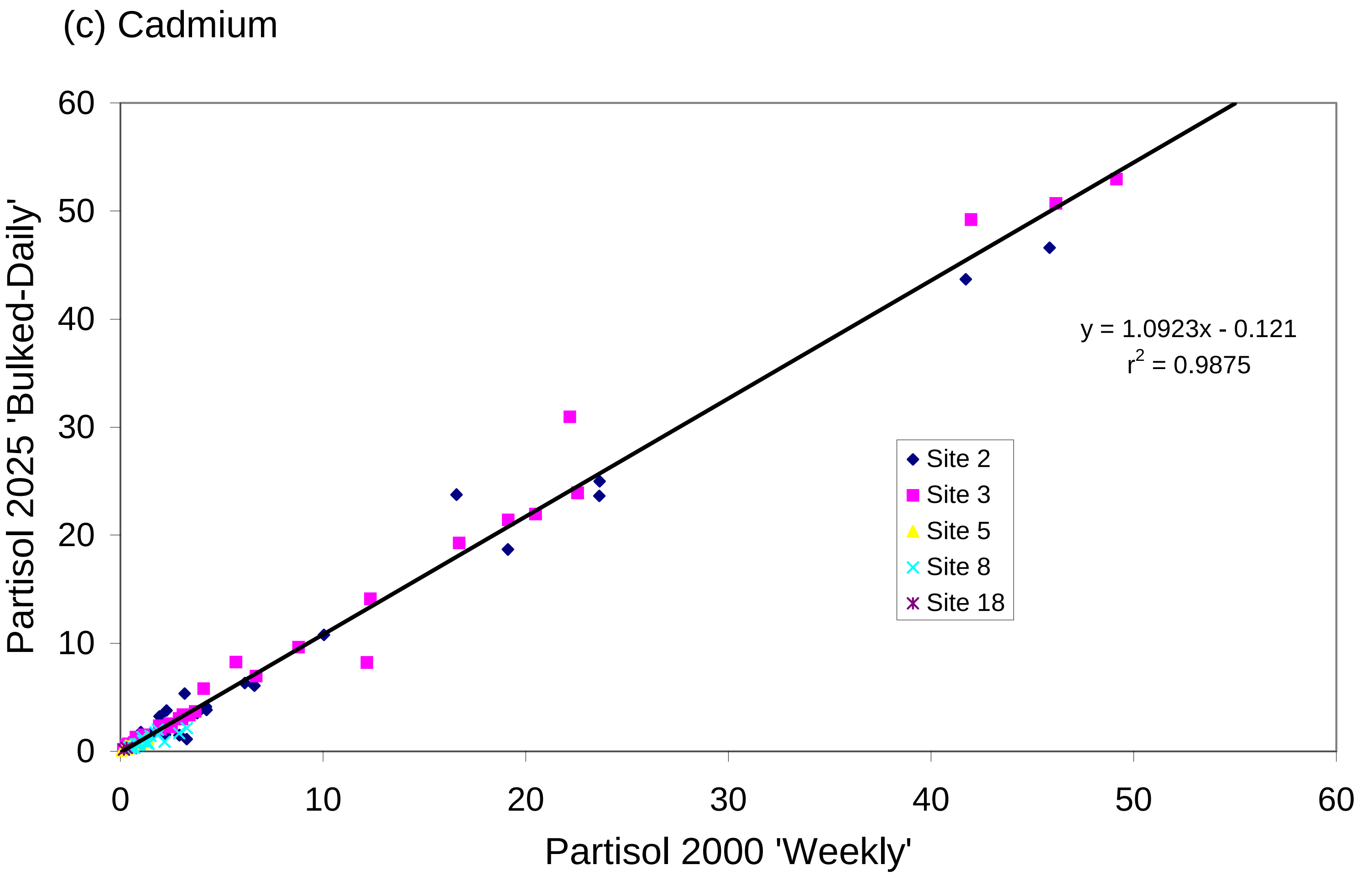


Figure I.1(d) Relationship between Nickel (Ni) weekly and bulked-daily sampling across co-located sites.

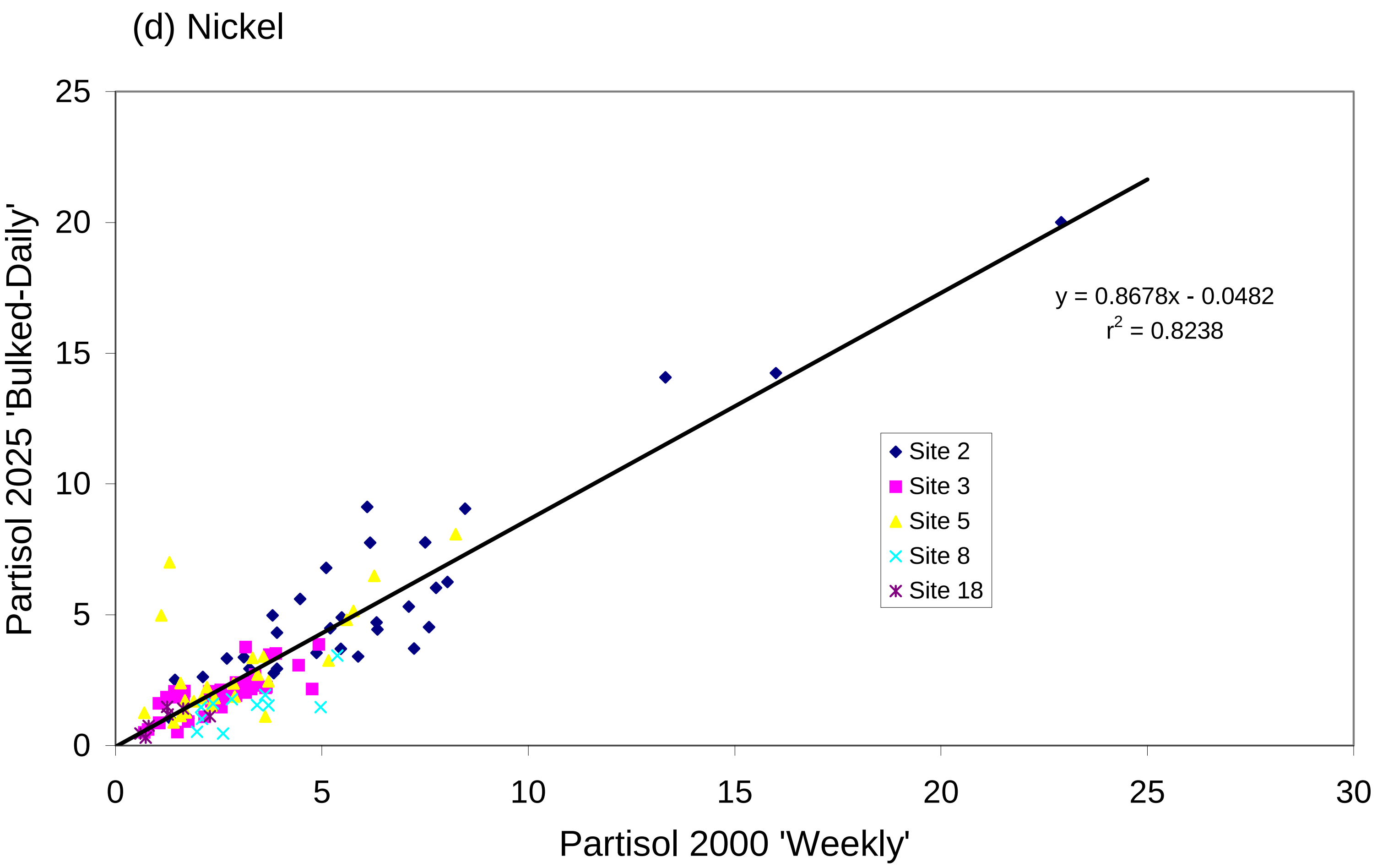
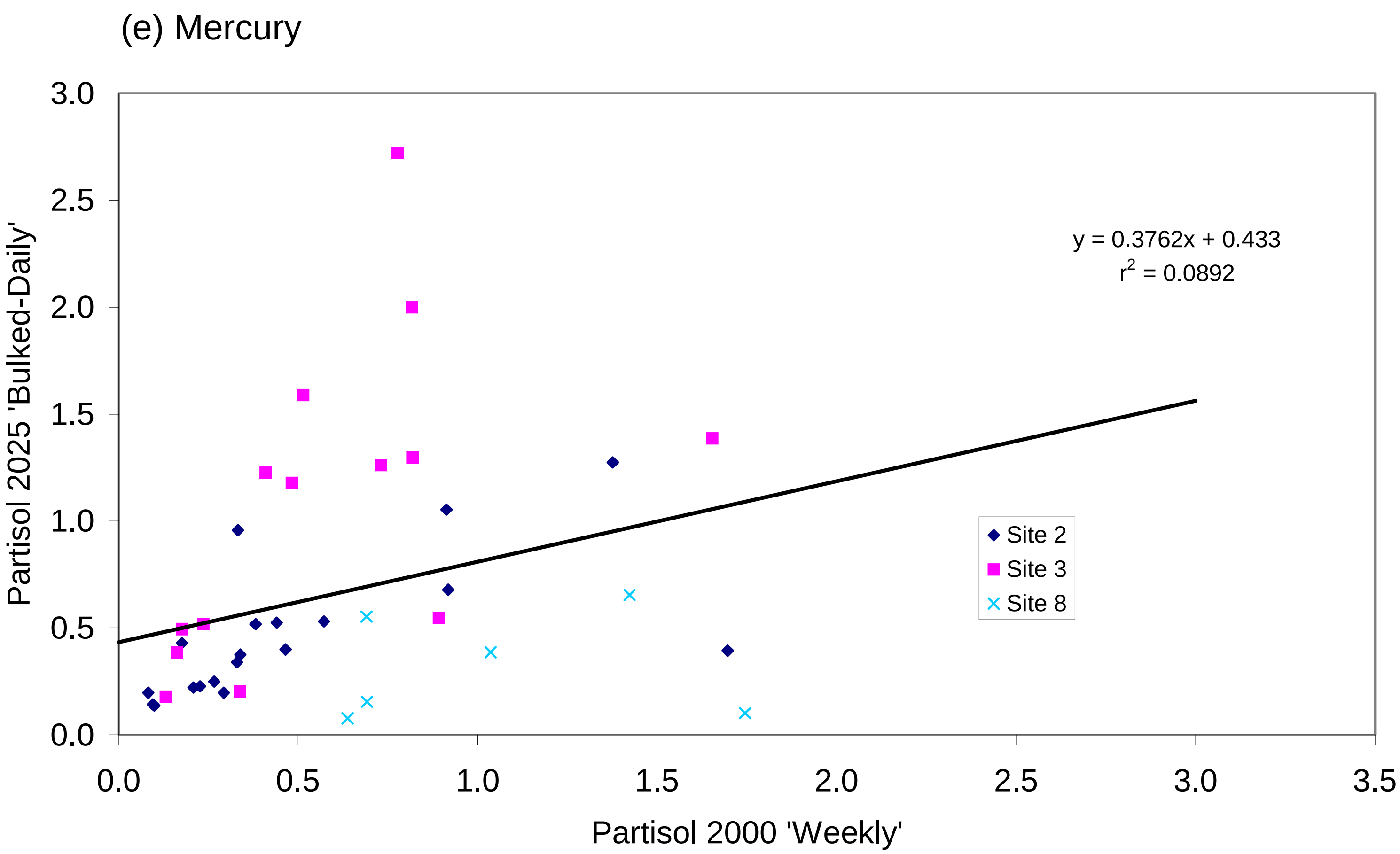


Figure I.1(e) Relationship between Mercury (Hg) weekly and bulked-daily sampling across co-located sites.



Appendix J: European Reference Method CEN/TC 264/WG14

Working Group 14 of the European Committee for Standardization (CEN) is currently funded by the DG XI of the European Commission to undertake a Minimum Validation Programme (MVP) for the development of a standard reference method for the determination of Pb, Cd, As and Ni in ambient air. Mercury (Hg) is not considered by WG14 and is therefore not discussed further here. CEN have tasked a separate working group with the development of a standard for assessing levels of Hg and its species in air.

The purpose of the MVP is to perform a field validation of the draft standard and includes all steps covering sampling, sample preparation and analysis of samples. The programme includes 4 discreet components as outlined in Figure J.1.

Specifically, the objectives of the programme are as follows[28]:

1. *To determine the performance characteristics of the complete method, e.g. quantification limits, repeatability and reproducibility for Pb, Cd, As and Ni sampled according to EN 12341 with an LVS device.*
2. *To estimate uncertainty budgets of the sampling step (as far as possible) and overall uncertainty of the complete method.*

The MVP commenced in January 2000 with the undertaking of laboratory trials to determine appropriate digestion techniques (with or without hydrofluoric acid (HF)), and the limits of detection for graphite furnace atomic absorption spectroscopy (GF-AAS) and inductively-coupled plasma mass spectroscopy (ICP-MS). In June 2000, laboratories representing Member States were invited to participate in the programme. The UK Consortium, comprising Stanger Science and Environment, CRE Group Ltd and Harwell Scientifics Ltd, was successful in its bid and is included in this work. Alongside other Member States' laboratories, the second element of the MVP - the 'Preparation for Field Tests' (Figure J.1) was completed in February 2001.

Spain has undertaken the 'Preliminary Field Trials' component of the MVP (the third component) during the period January - February 2001 at a site on the outskirts of Madrid. Exposed filters from the array of instruments were dispatched to each of the four participating Member States laboratories (Austria, Germany, Spain and UK). The results of this analysis have been finalised and accepted by the Working Group. Currently (July 2001) the UK participation in the field trials component of the work is underway at the Avonmouth Site. It is envisaged that this will be complete at the end of July 2001 when the CEN array will be forwarded to Berlin, Germany and later onto Austria. WG14 are due to report to the Commission with respect to its findings by the end of December 2001.

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[28] CEN/TC 264/WG14 N 140rev3 dated 19 February 2001

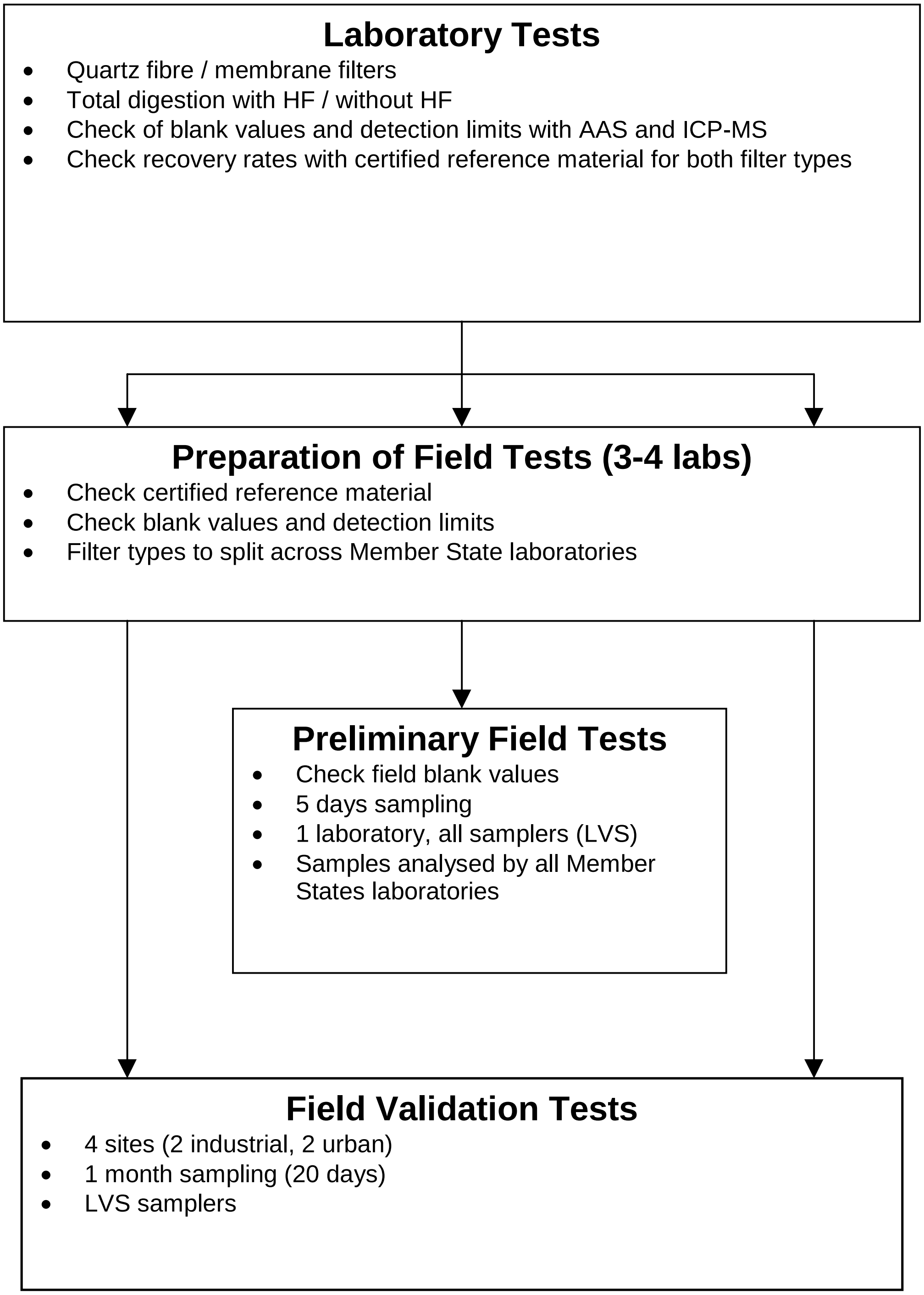
The UK's involvement in WG14 has the potential following benefits:

- Transfer of equivalence to the UK study for sampling ‘PM_{10} metal’ fraction
- Transfer of equivalence to the analytical techniques used in the current study
- The inclusion of ICP-MS as an analytical technique

Site 3: Britannia Zinc Ltd, at the Port of Avonmouth has been identified as a suitable location for inclusion in the CEN WG14 MVP. Concentrations of each pollutant (Pb, As, Cd and Ni) reported here fulfil the requirements of the Working Group with respect to appropriate ranges on which to develop the Reference Method. Moreover, present at the site are both Partisol 2000 and Partisol Plus (Model 2025) units. The inclusion of both units will enable comprehensive comparisons with the CEN LVS array of the Working Group in order to determine equivalence with the proposed reference method for ambient metals monitoring.

The results of separate components of the MVP are subject to reporting at the end of December 2001 when the Field Validation Trials have been completed. Consequently, results of the programme are not are reported here.

Figure J.1 CEN/TC 264/WG14 Minimum Validation Programme



Appendix K: Metal Speciation (As, Ni and Hg)

Trace metal speciation is defined as the distribution of the metal element between different physico-chemical forms. The importance of speciation relates to its impact on

(a) bioavailability and toxicity (including human health concerns), and
(b) transport of the potentially toxic metals in the environment.

Although speciation has a vital role in these areas, it is extremely difficult to measure and measurements undertaken remain (and are likely to remain in the near future) largely for research purposesl. Any speciation scheme undertaken must acknowledge this limitation. With these considerations in mind, there are well-developed methods available for the determination of the speciation of As, Ni and Hg in atmospheric samples, although some method development is necessary.

Analysis of the concentration of metal present as each species will be performed by Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) and Hydride Generation AAS (HG-AAS).

Separate determination of arsenic (III) and arsenic (V)

Separation and determination of As(III) and As(V) can be performed by (i) HPLC-AAS[29], (ii) solid-phase extraction with use of suitable chelating agents[30], or (iii) solid-phase extraction without chelating agents[31].

No speciation schemes for the treatment of air samples have been found after extensive literature searches. The above schemes have been developed and validated for freshwater and drinking water only. Consequently, development work is required in order to test the three methods and verify their suitability for the analysis of air samples in order to develop the optimal methodology.

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[29] A. F. Roig-Navarro, Y. Martinez-Bravo and F. J. Lopez (2001). Simultaneous determination of arsenic species and chromium(VI) by high performance liquid chromatography-inductively coupled plasma mass spectrometry. Journal of Chromatography, 912, 319-327.

[30] C. J. Hsieh, C. H. Yen and C. S Kuo (1999). Determination of trace amounts of As(III) and As(V) in drinking water and As(III) in vapour by GFAAS using 2,3-dimercaptopropane-1-sulfonate as a complexing agent. Analytical Science, 15, 669-673.

[31] S. Yalcin and X. C. Le (2001). Speciation of arsenic using solid phase extraction cartridges. Journal of Environmental Monitoring, 3, 81-85.

Separation of soluble/insoluble Ni and oxides and sulfides of Ni.

Although there will be some overlap of these Ni species, they should be treated separately.

Soluble/insoluble Ni. Collected particles will be dissolved in a suitable solvent (water) at suitable solution conditions, left to equilibrate (approximately 24 hours) and then filtered using a standard 0.45 µm membrane. Analysis of the soluble and insoluble Ni fractions will be performed by graphite furnace AAS, after suitable pre-treatment such as acid digestion.

Ni oxides and sulfides. Collected particles will be sequentially extracted using appropriate extractants as indicated in the literature[32].

Separation of methyl and inorganic mercury

Atmospheric mercury will likely occur in the vapour phase. Mercury speciation measurements would be performed through the use of solid-phase extraction using suitable sorbents. Previously Carbosieve B (methyl mercury), gold wire (elemental mercury) and Chrom W (inorganic mercury) have been used[33], although validation of the exact sorbents would need to be performed. Additionally, verification of the optimal use of sorbents needs to undertaken *i.e.* the use of mixed sorbents or sequential 'train' of sorbents. Subsequent thermal-desorption and measurement by (GC)-HGAAS would allow analysis of the mercury fractions. The use of GC would be required only for the use of mixed sorbents. Particulate mercury, if required, can be sampled by filtration and analysed by AAS after dissolution.

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[32] J. R. Lead, J. Hamilton-Taylor and W. Davison (1998). The effect of sequential extractions of suspended particulate matter on trace metal sorption and microbial cell stability. The Science of the Total Environment, 209, 193-199.

[33] S. Rapsomonakis. Mercury. In: Environmental Analysis using chromatography interfaced with atomic spectroscopy, R. M. Harrison and S. Rapsominakis, Ellis Horwood, Chichester, 1989.

Appendix L: Individual Site Summaries and Site Descriptions

The following individual page summaries provide information for each site included in the current work. Specifically, information is given surrounding the location of the monitoring site in relation to the site of the industrial process, the sector to which the industrial process belongs, metals monitored and the mean concentrations of each metal over the relevant monitoring period.

Figures are given which show the temporal trends in weekly mean values for each metal over the monitoring period.