

# **Atmospheric Inputs of Heavy Metals to the North Sea: Results for 1999**

A report produced for 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

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December 2000



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# Executive Summary

There is continuing concern within the Oslo and Paris Conventions for the Prevention of Marine Pollution, of which the UK is a participating party, regarding the possible adverse effects of heavy metals and certain other pollutants entering the North Sea and other convention waters. The Government is committed under the terms of the Hague Declaration to reduce the emissions of selected pollutants deemed to enter the North Sea from atmospheric deposition (as defined in the declaration). In the UK, the Department of Environment Transport and the Regions is responsible for managing the sampling and analysis programmes to ensure compliance with the UK's commitments under the Hague Declaration (1990) and the Oslo and the Paris Conventions.

On behalf of the Department of Environment Transport and the Regions, the Scottish Executive; the National Assembly for Wales and the Department of the Environment in Northern Ireland, AEA Technology's National Environmental Technology Centre has continued to operate a long-term measurements programme at three locations near to the east coast of the UK. These sites are at Banchory (Kincardineshire), East Ruston (Norfolk) and High Muffles (North Yorkshire). The concentrations of 10 metals, including Cd, Pb, As, Cr, Ni, Cu and Zn, have been measured in atmospheric particulate material and in rainwater at these locations.

The overall aim of this programme of measurements is to provide a quantitative assessment of pollutant concentrations. These can then be used in the identification of long-term trends and in an assessment of transboundary fluxes. The results can then be used to assess the attainment of commitments made under both the Oslo and Paris Commission (OSPARCOM) and United Nations Economic Commission for Europe (UNECE).

Results have previously been reported of the sampling and analysis programme for the period 1996 to 1998 (Playford and Baker 1999). This report provides an extension to that report to include data for 1999.

The spatial variations (between the three sites) in concentrations of heavy metals, especially for Cd, Pb, As and Cr in atmospheric particulate and rainwater, are consistent with those which would be expected from emission inventory data for the respective areas. The variations for Cu and Zn are less readily rationalised probably because of the nature of their use and the difficulty in sampling at locations remote from localised sources.

Atmospheric concentrations of Pb at all three east coast sites have declined in line with reductions in the estimated UK emissions between the periods 1987-1990 and 1996-1999. Reductions in annual mean air concentrations of 58% - 72% have occurred, compared with a 62% decrease in estimated emissions between the periods 1987-1990 and 1995-1998, emission data for 1999 are not yet available. The reductions in emissions have mainly been brought about by restrictions on the use of Pb additives in petrol together with increased in the use of unleaded petrol over this period.

Concentrations of other trace elements measured in particulate material in air have also decreased between 1987 and 1999. Although emission estimates are generally more uncertain than for Pb, annual mean air concentrations of Cd, Cr and Ni, at East Ruston and High Muffles/Staxton Wold have declined approximately in line with reductions in estimated emissions in the UK since 1987. The percentage reductions in annual mean air concentrations of Cd at these sites were 45% and 78% between the periods 1987-1990 and 1996-1999 respectively. Estimated UK emissions have declined by 44% between 1987-1990 and 1995-1998. Average annual Cr concentrations in air decreased by 22% and 54% at East Ruston and High Muffles/Staxton Wold, compared with a 45% reduction in emissions during the same periods. Corresponding Ni emissions are thought to have reduced by 37%, while annual mean air concentrations decreased by 41% and 47% at East Ruston and High Muffles/Staxton Wold respectively.

No significant decreases in the air concentrations of Cu were observed at any of the sampling sites for the period 1996-1999 compared with the period 1987-1990 even though the reduction in the mean emissions between these periods has been estimated to be about 48%. At Banchory in eastern Scotland a significant increase between 1987-1990 and 1995-1998 has been observed. However, copper is used extensively in agriculture, horticulture, in wood preservation and as a growth promoter in pig farming and for electrical distribution in buildings and for railway electrification. It is therefore likely that these or other possible local sources of copper are contributing to the concentrations observed in the air.

Although significant decreases in concentration of Zn in air particulate has been observed at both High Muffles and East Ruston, significant increases in air concentrations have been observed at Banchory. The observed reduction in air concentrations of Zn at East Ruston between the periods 1987-1990 and 1996-1999 of 33% is in agreement with the estimated reductions in emissions during the same periods of 28%. The change of location from Staxton Wold to High Muffles resulted in a corresponding decrease of 51%. The observed increase in the air concentrations of Zn at Banchory may indicate either local emissions or contamination.

Estimates of the inputs of metals to the North Sea and the annual average deposition at each site have been calculated. In general there is little evidence of any significant trends in the estimated atmospheric inputs of heavy metals to the North Sea. Trends in the estimates of deposition at the individual sampling sites is as has previously been noted generally masked by the variability of the rainfall which significantly influences the calculated deposits.

# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Methods of Sampling and Analysis</b>	<b>2</b>
2.1	SAMPLING LOCATIONS	2
2.2	ROUTINE SAMPLING OF ATMOSPHERIC PARTICULATE MATERIAL AND RAINWATER	2
2.2.1	Sampling of airborne particulate material	2
2.2.2	Sampling of rainwater	3
2.3	SAMPLE PREPARATION AND ANALYSIS	4
2.3.1	Air Filters	4
2.3.2	Rainwater/Bulk Deposition	4
<b>3</b>	<b>Results</b>	<b>5</b>
3.1	AIR CONCENTRATIONS	5
3.2	TRENDS IN AIR CONCENTRATIONS	5
3.2.1	Cadmium in air	7
3.2.2	Lead in air	7
3.2.3	Chromium in air	8
3.2.4	Nickel in air	8
3.2.5	Copper in air	9
3.2.6	Zinc in air	9
3.2.7	Sodium in air	9
3.3	RAIN CONCENTRATIONS	10
3.4	TRENDS IN RAIN CONCENTRATIONS	11
3.4.1	Cadmium in rain	11
3.4.2	Lead in rain	11
3.4.3	Arsenic in rain	12
3.4.4	Chromium in rain	12
3.4.5	Nickel in rain	12
3.4.6	Copper in rain	12
3.4.7	Zinc in rain	13
3.4.8	Mercury in rain	13
3.5	ESTIMATION OF HEAVY METAL INPUTS TO THE NORTH SEA	13
<b>4</b>	<b>Conclusions</b>	<b>15</b>
<b>5</b>	<b>References</b>	<b>16</b>

## Appendices

## APPENDIX 1 MONTHLY DATA (1999)



# List of Tables and Figures

## Tables

1	Sampling Sites
2	Annual Mean Air Concentrations (1994-1999) - Banchory
3	Annual Mean Air Concentrations (1994-1999) - East Ruston
4	Annual Mean Air Concentrations (1994-1999) - High Muffles
5	Precipitation-weighted Annual Mean Rainwater Concentrations (1994-1999) - Banchory
6	Precipitation-weighted Annual Mean Rainwater Concentrations (1994-1999) - East Ruston
7	Precipitation-weighted Annual Mean Rainwater Concentrations (1994-1999) - High Muffles
8	Annual Deposition (1994-1999) - Banchory
9	Annual Deposition (1994-1999) - East Ruston
10	Annual Deposition (1994-1999) - High Muffles
11	Temporal Changes in Air Concentrations - Banchory
12	Temporal Changes in Air Concentrations - East Ruston
13	Temporal Changes in Air Concentrations - High Muffles
14	Annual Total Deposition to the North Sea (1987-1999)

## Figures

1	Location of Sampling Sites
2	Annual Mean Concentrations of Cadmium in Air (1987-1998)
3	Annual Mean Concentrations of Chromium in Air (1987-1998)
4	Annual Mean Concentrations of Copper in Air (1987-1998)
5	Annual Mean Concentrations of Lead in Air (1987-1998)
6	Annual Mean Concentrations of Nickel in Air (1987-1998)
7	Annual Mean Concentrations of Zinc in Air (1987-1998)
8	Annual Mean Concentrations of Sodium in Air (1987-1998)
9	Annual Mean Concentration of Cadmium in Rain (1987-1998)
10	Annual Mean Concentration of Lead in Rain(1987-1998)
11	Annual Mean Concentration of Chromium in Rain(1987-1998)
12	Annual Mean Concentration of Nickel in Rain(1987-1998)
13	Annual Mean Concentration of Copper in Rain(1987-1998)
14	Annual Mean Concentration of Zinc in Rain(1987-1998)
15	Annual Mean Concentration of Arsenic in Rain(1990-1998)

# 1 Introduction

The UK Government has made international commitments concerning the emissions and the resultant deposition to the North Sea and other convention waters under the requirements of the North Sea Conference and the Oslo and Paris Conventions. Under the terms of the Hague Declaration (1990) and the Oslo and the Paris Conventions (OSPARCOM) the UK Government is committed to reduce the emissions of selected pollutants that are deemed to enter the North Sea and other convention waters from atmospheric deposition. These pollutants include certain heavy metals and other compounds. In the UK the Department of Environment Transport and the Regions is responsible for managing sampling and analysis programmes to ensure compliance with the UK's commitments under the Hague Declaration(1990) and the Oslo and the Paris Conventions.

Estimates have previously been made and reported of trace element inputs via the atmosphere into the North Sea (Cambray et al., 1975; Playford et al., 1995; Playford and Pomeroy, 1996, Playford and Baker, 1999). This report continues the reporting of these data and includes estimates for the period 1996 to 1999.

On behalf of the Department of the Environment, Transport and the Regions (DETR) (formerly the Department of the Environment), AEA Technology has operated a network of coastal sampling stations since 1986. This was a requirement of the Paris Commission's Comprehensive Atmospheric Monitoring Programme (CAMP). The results have been reported previously for the period 1986-1991(Playford et al., 1995) for the period 1992-1995 (Playford and Pomeroy, 1996) and for the period 1996-1998 (Playford and Baker). This report extends the previous report to include sampling data for 1999 and emission data for 1998. In addition where there have been minor changes in the previously reported emission data these are reflected in the discussion presented here.

The overall aim of this programme of measurements is to provide a quantitative assessment of pollutant concentrations. These can then be used in the identification of long-term trends and, together with other data, in an assessment of transboundary fluxes. The results can then be used as input into discussions at both OSPARCOM and UNECE.

The objectives of the present study were as follows:

- to maintain the existing measurement programme
- to provide data for the UK's submission to OSPARCOM
- to liaise with technical organisations associated with the Oslo and Paris Commission to ensure, where practicable, standardisation of procedures and interpretation of results
- to provide DETR with an interpretation of the sampling and analytical results
- to provide estimates of the atmospheric inputs of pollutants to the North Sea based on UK data

This report provides a summary of the above activities.

## 2 Methods of Sampling and Analysis

### 2.1 SAMPLING LOCATIONS

Three sampling sites were established in 1986 along the North Sea coast of the UK. The three sampling stations are located at sites at Banchory (Kincardineshire), East Ruston (Norfolk) and High Muffles (North Yorkshire) as shown in Figure 1. Details of the sampling sites are given in Table 1.

The sampling stations were selected to provide representative locations for collecting samples of air particulate and deposition for estimating the atmospheric input of heavy metals into the North Sea. The sites were chosen to be as far as practicable from local sources of emissions such as centres of population, local industrial pollution and motor traffic but at the same time to be typical of the region. It is important to note that the results obtained from three sampling stations along the North Sea coast can only provide an estimate of UK mean concentrations and may not be fully representative of the whole of the United Kingdom.

The stations were also sited so as to be sufficiently distant from the immediate influence of sea spray. The analysis of samples in the presence of high sea salt concentrations is more difficult. There was also the possibility of contamination of the samples by the resuspension of material from the sea surface. It has been shown previously that sea spray may be significantly enriched with trace metals relative to bulk sea water (Cambray et al, 1975). Therefore, it was decided to locate each sampling station, ideally, at least 10 km from the coast to reduce the direct input of sea spray while still being representative of the area as a whole. The East Ruston station is situated at about 8 km from the coast.

### 2.2 ROUTINE SAMPLING OF ATMOSPHERIC PARTICULATE MATERIAL AND RAINWATER

Simple methods of sampling were used in order to obtain continuous and trouble-free operation at remote locations with limited operator attention. Atmospheric particulate material and rainwater are sampled continuously. All samples are collected at 1.5 m above ground level to reduce contamination by soil splashing during heavy rainfall. Sample collectors (described below) are changed on a monthly basis by local site operators. The samples are sealed prior to their despatch to the National Environmental Technology Centre (NETCEN). Each sampling station is subject to an annual calibration visit.

#### 2.2.1 Sampling of airborne particulate material

Samples of airborne particulate material were collected by drawing air through a filter paper (Whatman 40, 6 cm diameter) held in a polypropylene duct. The inlet nozzle faced downwards

to avoid the intake of rain. A plastic backing disc (1.5 mm mesh) prevented the collapse of the filter paper. The volume of air sampled, about 300 m<sup>3</sup> per month, was measured by an ordinary domestic gas meter. Previous wind tunnel tests of the air sampler have suggested that the upper cut-off diameter for particle collection is about 10 µm in normal ambient conditions. The air was drawn through the filter by a diaphragm pump operated by a small induction motor (240 volt AC, 50 watts).

The mean filtration efficiency for Whatman 40 paper has been shown to be about 95% for the elements under study in field conditions (Cawse and Peirson, 1972). It must be pointed out that volatile forms of elements such as Pb are unlikely to be sampled with an efficiency as high as that observed for particulate material unless the vapour is adsorbed onto particulates. However, it has been found that only about 10% of total Pb is in such a volatile form even close to a source of emission (such as in the case of a central reservation of a motorway; Colwill and Hickman, 1973). At increased distances from the source it is likely that more of the volatile form will be adsorbed onto particulate material in the atmosphere.

To avoid contamination the complete air filter assembly was returned to the laboratory in a polythene bag. The filter papers were then removed from their holders and prepared for analysis in a laminar air-flow cabinet. The samples were handled with polythene disposable gloves and plastic forceps to reduce the possibility of contamination.

## 2.2.2 Sampling of rainwater

Rainwater was collected using a polythene funnel (15 cm diameter) and a high density polythene bottle. Until recently the collecting funnel was covered with a polypropylene mesh to prevent the ingress of flies, bird droppings, etc. The polypropylene mesh had a square aperture of 710 µm and a mesh count of 9 per cm. This gave an open area of about 44%. The collector retained the bulk deposition, i.e. the wet deposition, plus the dry deposit which falls upon the funnel and mesh and is washed into the bottle by subsequent rain. However, the polypropylene mesh will inevitably have affected the dry deposition collection efficiency of the funnel. During 1997 the funnels at all sampling sites were changed, and a funnel of similar size but with a small replaceable debris filter of about 4 cm in its base installed. The debris filter is replaced on a monthly basis during routine sample changes. No significant changes have been noted in the overall collection efficiency since the installation of the new funnels.

The rainwater collecting bottle was acid washed with 5% v/v acetic acid (AR grade) and then rinsed with demineralised water before use. It was then enclosed in a black polythene bag to inhibit the growth of algae. Although considered desirable for the collection and retention of some elements, samples were not acidified during the sampling period. This was because of the potential risk to site operators and difficulties which would have arisen in the transport of samples. However, samples were acidified on receipt at the laboratory prior to analysis as described below.

## 2.3 SAMPLE PREPARATION AND ANALYSIS

### 2.3.1 Air Filters

DETR's Air and Environment Quality Division requested that samples collected from 1996 to 1998 inclusive be bulked and analysed on a quarterly basis. However, from 1999 it was agreed to revert to monthly analyses to provide data comparable with that provided by other contracting parties within the Oslo-Paris commission.

Monthly air filter samples were digested in nitric acid prior to analysis by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) techniques. The following 10 metals were analysed in the atmospheric particulate material: As, Cd, Cr, Cu, Na, Ni, Pb, Sc, Ti and Zn. The results, obtained in terms of total ng analyte per sample were converted into air concentrations based on the volume of air filtered during the sampling period.

For each monthly batch of samples, a number of samples were prepared and measured in duplicate for quality control (QC) purposes. Independent QC Standards were also prepared and measured by ICP-MS and ICP-AES.

For each element, the limit of detection (LOD) was calculated at the time of analysis. The uncertainty in the measurements made by ICP-MS and ICP-AES were estimated to be  $\pm 10\%$ , for results that were significantly above the LOD. However, higher uncertainties will typically be associated with results falling within an order of magnitude of the LOD.

### 2.3.2 Rainwater/Bulk Deposition

On receipt in the laboratory the volumes of the monthly rainwater samples were measured. The samples were acidified to 0.5% v/v with high purity nitric acid and allowed to stand at least overnight. The monthly samples were then pre-concentrated prior to measurement by ICP-MS and ICP-AES for the 10 metals listed above (section 2.3.1). The results are expressed as  $\mu\text{g l}^{-1}$  of the bulked quarterly sample.

As for the air filter samples, QC Standards and duplicate samples were prepared and measured during the analysis of a batch of rainwater samples. LODs were determined at the time of analysis. The uncertainties associated with the analysis are as described for the air filters (section 2.3.1).

The uncertainties attributable to both sampling and analysis have been shown to be of the order of 10-15% (Playford et al., 1995).

## 3 Results

Monthly mean concentrations of heavy metals and sodium in air and rainwater and quarterly deposition for 1999 are provided in Appendix 1. Deposition data at each site are derived from the rainwater concentrations and the measured rainfall.

The monthly mean concentrations in rainwater, shown in Appendix 1, are precipitation-weighted. Also, the total deposition of each element has been estimated on a monthly basis from rainwater concentrations and the measured rainfall.

For each of the years 1994 to 1999, the annual mean concentrations of the metals in air and rainwater have also been derived. The annual mean concentrations of the metals in air at Banchory, East Ruston and High Muffles, are shown in Tables 2 to 4 respectively. Tables 5 to 7 list the precipitation-weighted annual mean concentrations of the metals in rainwater at the three sites. Tables 8 to 10 provide estimates of the total annual deposition from rainwater concentrations and measured annual rainfall at each location.

### 3.1 AIR CONCENTRATIONS

Since measurements began at Banchory and East Ruston (both 1986) and at High Muffles (1993) (formerly Staxton Wold until 1991) the air concentrations of the anthropogenically-derived metals As, Cd, Cu, Ni, Pb and Zn have tended to be similar at East Ruston and High Muffles (Staxton Wold) and are higher than those recorded at Banchory. During the period 1986-1991 (Playford et al., 1995) the average values at Staxton Wold and East Ruston were generally 3-4 times higher than those at Banchory. These observations were again apparent, but to a slightly lesser extent during the period 1996 to 1998 when air concentrations of many of the seven heavy metals at East Ruston and High Muffles were ~2 to 3-fold greater than those at Banchory (Tables 2 to 4). Slightly higher annual average air concentrations of some of the metals were observed during 1999 compared to 1998.

### 3.2 TRENDS IN AIR CONCENTRATIONS

Measuring trace levels of metals in air is subject to uncertainty as despite the care taken in preparing and handling the sampling material random contamination may occur most frequently during analysis. Occasionally it was evident when calculating the annual means (section 3) that these values were being unduly influenced by one or several single quarterly values that were considerably higher or lower than the mean of all the quarterly values. An approach has been developed (see below) to decide whether results are likely to be outliers. If it was considered that such results were anomalous these figures were rejected for the purpose of examining trends in the air concentrations.

To provide a consistent assessment of the validity of the data, the following rules were employed. For the monthly data obtained between 1987 and 1995, the mean and standard

deviation of the monthly results for the entire sampling period were calculated. Any results which exceeded the sum of the arithmetic mean plus three standard deviations were considered unreliable. This method was also verified by considering the distribution of the reported results. To calculate a distribution an interval of 1/20 of the maximum reported results was used. Although it is unlikely that a normal distribution would be obtained using such a method it was considered that it was reasonable to assume that the distribution would be continuous and therefore any result which was remote from its nearest neighbour by more than two intervals was considered suspect. While better validation methods exist for larger data sets, this empirical approach seems to provide satisfactory screening and identification of outliers with the relatively small dataset currently available. All 'less' than values were considered actual values for the calculation of the means.

The quarterly data for the period 1996 to 1998 were also tested for anomalous results by comparison with the 'valid' monthly data compiled as described above. For each metal any quarterly datum that fell outside the range of the 'valid' monthly data was rejected. The vast majority of the quarterly data were found to be within the acceptable ranges. However, with monthly sampling and quarterly analysis individual monthly samples which are anomalous will be much less apparent since one high or low concentration in a batch of three may be 'masked' by two 'normal' results. The removal of one full quarter's results which appear anomalous also has a greater impact on the annual calculation since it effectively removes 25% of the available data. The return to monthly sampling will enable obviously anomalous results to be identified once again. However, it will be necessary to establish current 'mean' values before such a method can be used on the 1999 data. For the 1999 data only those monthly data which exceed the annual mean by about a factor of 10 have been considered anomalous.

Sampling was necessarily re-located from Staxton Wold to nearby High Muffles in 1991. For the purposes of examining the trends in air concentrations of heavy metals all data from these two locations are referred to in this report as being from High Muffles.

The annual mean air concentrations of Cd, Pb, Cr, Ni, Cu, Zn and Na, at Banchory, East Ruston and High Muffles for the period 1987-1999 are shown in Figures 2 to 8 respectively. Measurements of As in air only commenced at the beginning of 1993 and are therefore excluded from this examination of trends in air concentrations. In each of these time-series plots a regression against time is also shown. Linear regression has been used to indicate the direction of any trend in the data. Since data from Staxton Wold may not be directly comparable to that obtained at High Muffles no trend line is shown for these sites.

The National Atmospheric Emissions Inventory (NAEI) has compiled emissions inventories for several heavy metals in the UK (Salway et al., 1996). Estimates of annual emissions to the atmosphere from the UK of Cd, Pb, Cr, Ni, Cu and Zn are also shown in Figures 2 to 7 respectively. Data are available up to 1998 using a consistent methodology (Goodwin et al., 2000).

The changes in average air concentrations of these seven elements between 1987 and 1999 have been quantified in Tables 11 to 13. For each metal the annual mean air concentration for the periods 1987-1990 and 1995-1999 are listed for Banchory, East Ruston and High Muffles. The percentage reduction in annual mean concentration between these periods has also been calculated at each of these sites (Tables 11, 12 and 13, respectively). Thus, average air

concentrations over the first four and last four years of this measurement programme are compared.

### 3.2.1 Cadmium in air

The mean concentrations of Cd in air for the period 1996 to 1999 varied from 0.08 ng m<sup>-3</sup> at Banchory, 0.14 ng m<sup>-3</sup> at High Muffles, to 0.22 ng m<sup>-3</sup> at East Ruston. This is as would be expected for pollutants derived from regional-scale transport. Concentrations of pollutants emitted from centres of UK population and industrial sources would be higher in westerly flow at the southern sites. Similarly, concentrations of such pollutants in easterly flow would also be higher at the southern sites, since air masses would have passed over densely populated or industrial areas of Europe. This is especially true at East Ruston which is on the North Norfolk coast. Elevated concentrations at High Muffles are probably attributable to the proximity of the industrial Midlands.

A downward trend in air concentrations of Cd was apparent at Banchory and East Ruston. A strong decline occurred at High Muffles/Staxton Wold (Figure 2) but this may be an indication of a difference between the two sites. The reductions in annual mean air concentrations between 1987-1990 and 1996-1999 were 45% at Banchory, 52% at East Ruston and 78% at High Muffles/Staxton Wold (Tables 11 to 13). The relatively high reduction in annual mean concentrations observed following the move of the sampling station from Staxton Wold to High Muffles may indicate that they may have been influenced by a local source of cadmium at Staxton Wold. The percentage reduction in annual mean estimated total emissions of Cd in the UK between 1987-1990 and 1995-1998 was 44%. The inclusion of another years data in the correlation of measured air concentrations with estimated annual emissions to the atmosphere indicates an improved correlation compared to the previous report. The correlation coefficients during the period 1987-1998 are East Ruston ( $r = 0.765$ ,  $p < 0.02$ ), Banchory ( $r = 0.755$ ,  $p < 0.02$ ) and at High Muffles ( $r = 0.732$ ,  $p < 0.1$ ).

### 3.2.2 Lead in air

As for Cd, the spatial variation in Pb concentrations followed the order East Ruston > High Muffles > Banchory. UK emissions of Pb resulted predominantly from the use of petrol for road transport and as such emission estimates are probably better quantified than those of most of the other pollutants discussed in this report. Air concentrations of Pb in rural areas would be expected to be largest in and around areas with highest traffic density generally in southern Britain, (Stedman 2000). A downward trend in air concentrations was apparent at all three locations (Figure 3). The decreases in average air concentrations between 1987-1990 and 1996-1999 were similar at the three sites; 58% at East Ruston and 72% at High Muffles and 64% at Banchory (Tables 11 to 13) and these compare well with a reduction in estimated UK emissions of 62% between 1987-1990 and 1995-1998.

Estimated UK emissions of Pb to the atmosphere were found to correlate significantly with annual mean air concentrations of Pb at all three sites over the period 1987 to 1998. The correlation coefficients were; at Banchory ( $r = 0.915$ ,  $p < 0.001$ ), East Ruston ( $r = 0.910$ ,  $p <$



0.001) and High Muffles ( $r = 0.922$ ,  $p < 0.01$ ). The downward trends in annual air concentrations at all sites clearly follow the estimated reductions in emissions (Figure 3).

The reduced concentrations measured in more recent years at East Ruston and High Muffles have resulted primarily from the reduction of the lead content of petrol in the UK together with the increased use of unleaded petrol (Goodwin 2000).

Examination of the Pb/Cd ratio in emission estimates and air concentrations is interesting. During the period 1987 to 1998 this ratio in emissions was in the range 80-150, mean 107. The ratio in air particulate sampled during the same period at the three east coast sites was; Banchory (20-72, mean 51), East Ruston (50-75, mean 64) and High Muffles (25-79, mean 54). This suggest that either the spatial pattern of cadmium and lead sources are significantly different so that these rural sites are more affected by local cadmium rather than lead sources which seems unlikely or the depositional behaviour of the two metals is quite different or cadmium emissions are underestimated nationally. This issue may be resolved later in the HAPs programme by exploring more detailed mapping approaches to estimating the influence of spatial variation in emissions on rural lead and cadmium concentrations.

### 3.2.3 Chromium in air

Figure 4 indicates a downward trend in air concentrations. The percentage reductions in annual mean concentrations of Cr between the periods 1987-1990 and 1996-1999 were 22% and 54%, at East Ruston and High Muffles respectively (Tables 12 and 13). These reductions may be compared with the 45% reduction in average annual estimated emissions in the UK between 1987-1990 and 1995-1998. However, at neither East Ruston nor High Muffles was there any indication of a significant correlation with the estimated UK emissions data. A significant increase (63%) in average air concentrations was recorded at Banchory between 1987-1990 and 1996-1999 (Table 11). However, it is apparent that a few uncharacteristically high Cr values were reported during 1999 and the annual average air concentrations at this site were generally somewhat lower than those measured at the other two sites in previous years.

### 3.2.4 Nickel in air

At East Ruston and High Muffles, where average air concentrations of Ni are similar, downward trends in air concentrations have been observed over the last thirteen years (Figure 5). The rate of change in the annual means is also very similar at these sites, i.e.  $-0.129$  and  $0.144 \text{ ng m}^{-3} \text{ y}^{-1}$  at East Ruston and High Muffles respectively. The percentage reductions in annual mean concentrations between the periods 1987-1990 and 1996-1999 at East Ruston and High Muffles were 41% and 47%, respectively (Tables 12 and 13) compared with a corresponding reduction in estimated UK emissions of 37%. The main sources of Ni emissions to the atmosphere in the UK are coal and heavy fuel oil combustion (Salway et al., 1996, Goodwin et al., 1999). Estimated annual emissions correlated weakly with annual mean air concentrations at High Muffles ( $r = 0.764$ ,  $p < 0.05$ ) and East Ruston ( $r = 0.707$ ,  $p < 0.05$ ) with no significant correlation evident at Banchory.

### 3.2.5 Copper in air

At both Banchory and High Muffles increases were observed between the periods 1987-1990 and 1996-1999. Only at East Ruston was a reduction (10%) observed between periods. Overall there would appear to be little indication of any significant changes in average concentrations of Cu have occurred over the last thirteen years (Figure 6).

During the period covered by this report significant seasonal variations in the concentrations of copper are observed at all three sampling sites. Copper is used extensively in agriculture and horticulture as a relatively cheap fungicide; in wood preservation and as a growth promoter in pig farming and for electrical distribution in buildings and for railway electrification. It is therefore likely that these or other uses of copper are contributing to the concentrations observed in the air.

### 3.2.6 Zinc in air

A downward trend in annual mean air concentrations of Zn was observed at both East Ruston and High Muffles (Figure 7). A substantial decrease in the annual mean air concentration of Zn at High Muffles was apparent (Figure 7), i.e. 51% between 1987-1990 and 1996-1999 (Table 13). However, it was between these two periods that the sampling site was moved from Staxton Wold to High Muffles which might have had an effect on the concentrations observed. At East Ruston the decrease in average air concentrations was less the corresponding reduction was 33% (Table 12) which was more comparable to the 28% reduction in estimated UK emissions between 1987-1990 and 1995-1998. However, in neither case was there any strong correlation between estimated emissions and air concentrations.

At Banchory, the annual mean air concentrations of Zn have increased significantly over the last ten years (Figure 7). The annual mean concentration in air has more doubled during the period 1987-1990 and 1996-1999 (Table 11), and local contamination or emission source must be suspected. Zinc is an extremely widely used material for rust-proofing of steel and in the production of tyres and it is difficult to avoid possible contact with zinc coated materials. It is therefore difficult to exclude the possibility of contamination as the cause of the increase at Banchory.

### 3.2.7 Sodium in air

As would be expected no significant changes in the annual mean air concentrations of Na were apparent over the last thirteen years at any of the three locations (Figure 8). The percentage reductions in the annual means between 1987-1990 and 1996-1999 were 13%, 4% and 30% at Banchory, East Ruston and High Muffles (Tables 11,12 and 13, respectively). Inputs of marine-derived aerosols are the main source of Na at all three sites. Variations in average air concentrations at each site are likely to result from variations in meteorological conditions and their varying distance from the sea and possibly to reductions in emissions of crustal metals from coal fuels. Clarification on this last point may be possible once a base metal emission inventory has been developed.

The decrease in concentrations recorded at High Muffles probably results from the comparison of data from Staxton Wold for 1987-1989 and data from High Muffles for 1995-1999. Although both sampling sites are in the same general area Staxton Wold was only about 10 km from the sea and High Muffles is about 20 km from the sea which would have reduced the sea-salt component measured in the air samples.

### 3.3 RAIN CONCENTRATIONS

In Tables 5 to 7 the precipitation-weighted annual mean concentrations in rainwater of the nine metals measured during 1999 may be compared with those recorded during 1994 to 1998 at Banchory, East Ruston and High Muffles, respectively.

As noted previously (Playford et al., 1995; Playford and Pomeroy, 1996) the annual mean rainwater concentrations of many of the elements are quite variable at a given site (Tables 5 to 7). This can be partly explained by the variability of rainfall which is to some extent negatively correlated with the measured concentration. The rain samplers are bulk collectors. For some elements dry deposition may contribute a significant proportion of the total deposition. In other cases where the element has only a small proportion of the total deposited as dry deposition the concentrations would be expected to remain more consistent.

In the earlier years of this measurements programme (up to 1991) the results reported for Banchory were found to be consistently lower than those for either East Ruston or Staxton Wold (Playford et al., 1995). However in more recent years (1992-1995) for some of the metals these differences have become less pronounced (Playford and Pomeroy, 1996). In most cases this appears to be mainly due to a decrease in the concentrations reported at the other two sites (High Muffles and East Ruston) rather than an increase in concentrations at Banchory.

The average Pb concentrations (1994-1999, excluding 1996) at East Ruston and High Muffles were  $3.4 \mu\text{g l}^{-1}$  and  $3.6 \mu\text{g l}^{-1}$  respectively compared to  $2.0 \mu\text{g l}^{-1}$  at Banchory. Similarly, the corresponding Ni concentrations were  $0.83$  and  $0.52 \mu\text{g l}^{-1}$  at East Ruston and High Muffles respectively, compared to  $0.38 \mu\text{g l}^{-1}$  at Banchory. Average Cu concentrations in rainwater at East Ruston, High Muffles and Banchory were  $1.9 \mu\text{g l}^{-1}$ ,  $1.7 \mu\text{g l}^{-1}$  and  $1.0 \mu\text{g l}^{-1}$  respectively. Average Zn concentrations in rainwater at East Ruston ( $15.0 \mu\text{g l}^{-1}$ ) and at High Muffles ( $17.4 \mu\text{g l}^{-1}$ ) were 50-70% greater than those measured at Banchory ( $10.2 \mu\text{g l}^{-1}$ ) during the period 1994 to 1999.

The differences between rainwater concentrations at Banchory and the other two locations were not as apparent for As, Cd and Cr over the period 1994-1999. For example, the average annual means for Cd were  $0.10$ ,  $0.10$  and  $0.08 \mu\text{g l}^{-1}$  at Banchory, East Ruston and High Muffles respectively.

### 3.4 TRENDS IN RAIN CONCENTRATIONS

Large monthly and quarterly variations were apparent in the measured rain concentrations observed at all stations during the sampling programme. The variation in precipitation-weighted annual mean rain concentrations (Figures 9-15) is generally much greater than that observed in the corresponding air samples. Although there appears to be a limited negative correlation with rainfall for most substances the calculated coefficients of correlation are generally small and it may be misleading to over-generalise. What is apparent is that dry deposition which is deposited onto the funnel during periods of low rainfall will have an influence on the measured concentrations. However, since it is assumed that any dry deposit will be washed into the collecting bottle by subsequent rainfall it is possible that the 'subsequent' rainfall could actually occur during a subsequent sampling period. If this were the case, dry deposition which was deposited during a period without rainfall could eventually be washed into a sample during a period with high rainfall. This would effectively mask the effect of dry deposition making the calculation of correlation coefficients of concentration relative to rainfall meaningless.

The direct measurement of the effect of dry deposition on the observed concentrations is possible using wet only samplers. However, such measurements are generally more complex to undertake and the reliability of such sampling methods is not always good. It is also very difficult to accurately regulate the sampling between wet and dry periods and to determine when each sampler should be exposed.

In the current programme the use of annual deposition-weighted averages, rather than individual monthly or quarterly measurements, probably provides a better indication of changes since this will also 'average' the effects of dry deposit.

#### 3.4.1 Cadmium in rain

The precipitation-weighted annual average rain concentrations for Cd since 1987 are shown in Figure 9. Data from Staxton Wold may not be directly comparable to that obtained at High Muffles and for this reason no trend line is shown. However, from the limited data available for High Muffles (1994-1999) the trend in concentrations appears similar to that observed at East Ruston. At East Ruston a decrease in rain concentrations during the period 1990 to 1999 is observed although the annual variations are large. Data prior to 1990 were generally below the LOD and have therefore not been included. Following the introduction of more sensitive analytical techniques (ICP-MS) it was possible to reduce the limits of detection for Cd and concentrations above the improved LOD are now routinely observed. At Banchory although the calculated trend line indicates a slight decrease during the same period the annual variations are of a similar magnitude to the estimated decrease and the trends may not be significant.

#### 3.4.2 Lead in rain

The precipitation-weighted annual average rain concentrations for Pb since 1987 are shown in Figure 10. As discussed previously no trend line is shown for Staxton Wold and High Muffles. However, as for Cd, with the limited data available at High Muffles(1994-1999) the apparent trend is similar to that observed at East Ruston. At both East Ruston and Banchory a small decrease in rain concentrations during the period 1990 to 1997 is observed although the annual

variations are large and are of a similar magnitude to the estimated decrease. The continued decrease in estimated concentrations observed between 1997 and 1999 is also reflected in total deposition despite the fact that the rainfall at all sites during 1998 and 1999 increased by about 10% to 20% percent compared to 1997.

### **3.4.3 Arsenic in rain**

The precipitation-weighted annual average rain concentrations for As since 1987 are shown in Figure 11. The data for East Ruston indicate a small decrease in rain concentrations during the period 1990 to 1999. However, the data from Banchory seems to indicate little change in rain concentrations during the period 1990 to 1999. The decrease observed at all sampling sites between 1997 and 1999 appears to result more from an increase in concentrations observed during 1997 than any general change in the estimated long-term trends. At both East Ruston and Banchory the concentrations observed are consistent with the general trends previously reported (Playford and Baker, 1999).

### **3.4.4 Chromium in rain**

The precipitation-weighted annual average rain concentrations for Cr since 1987 are shown in Figure 12. The data for all sampling locations indicate little change in rain concentrations during the period 1990 to 1999. The concentrations at all three of the current sampling locations show very good agreement during the period 1994 to 1997. The main source of chromium in emissions in the UK is coal combustion with small amounts discharged from other industrial combustion processes. The concentrations in rain appear to be generally similar at all stations during 1990-1999.

### **3.4.5 Nickel in rain**

The precipitation-weighted annual average rain concentrations for Ni since 1987 are shown in Figure 13. Concentrations calculated for East Ruston and Banchory indicate a small decrease in rain concentrations during the period 1990 to 1997. In addition, although the amount of data are far more limited the results for High Muffles for the period 1994 to 1999 also appear to suggest a similar reduction at this site. Nickel emissions in the UK are mainly attributable to the coal and fuel oil combustion and the decrease in rain concentrations observed since 1990 is good agreement with the estimated reductions in total UK emissions during the same period. The results for 1999 indicate that the mean precipitation weighted rain concentrations was very similar at all stations.

### **3.4.6 Copper in rain**

The precipitation-weighted annual average rain concentrations for Cu since 1987 are shown in Figure 14. The data for all sites all sites appears to suggest a general decrease in concentration of copper in rain. However, the annual mean concentrations can be very variable from year to year and with the current data available it is impossible to be certain of an overall reduction in rain concentrations. Copper is used extensively in domestic, industrial and analytical equipment and is also used in agriculture and horticulture in some anti-fungicide preparations. It is therefore difficult to rule out the possibility that a contribution from one or more of these sources is

influencing the variations in concentrations observed. Emissions from coal combustion generally accounts for more than half of the total copper emissions in the UK.

### 3.4.7 Zinc in rain

The precipitation-weighted annual average rain concentrations for Zn since 1987 are shown in Figure 15. The measured concentrations at East Ruston and Banchory indicate that there is little decrease in the concentrations observed at either of these sampling locations and the annual variations in measured concentrations, particularly at Banchory, are relatively small. However, the higher concentrations observed at High Muffles appear to be accompanied by correspondingly larger variations in annual concentrations. This may reflect the increased concentrations and variations which will result from the proximity of High Muffles to the industrial areas of Northern England. The main emissions of zinc in the UK are iron and steel production, non ferrous metals manufacture, waste incineration road transport and coal combustion. It is interesting to note that the annual mean concentrations for both 1998 and 1999 are similar at all three sites. The very high annual mean concentration at High Muffles during 1997 appears to have resulted mainly from an unusually high concentration measured during the first quarter of 1997 which may be an outlier.

### 3.4.8 Mercury in rain

The sampling and analysis of rainwater for mercury has been undertaken at only one sampling site at Chilton in Oxfordshire. Sampling of mercury in rainwater requires all collection equipment to be manufactured from glass and the collection vessel to be pre-treated with concentrated hydrochloric acid before use. The routine use of concentrated acids at the normal North Sea sites, which are often operated by non-technical staff, was not considered viable because of safety and transport considerations. Generally the concentrations of mercury in rainwater were close to the analytical limits of detection ( $1-3 \mu\text{g l}^{-1}$ ) and not significantly above reagent blanks analysed at the same time as the samples. Mercury emissions in the UK have fallen by about 75% since 1970 (Goodwin et al, 2000). The main sources of mercury emissions are waste incineration, non-ferrous metal production and coal combustion. Another major source, the use of mercury cells in chlorine production has declined in recent years.

Measurements of total gaseous mercury (TGM) concentrations were made for a period of about a year at Harwell in Oxfordshire using a cold vapour atomic fluorescence absorption technique (Lee, et al 1996). Measurements of TGM have recommenced at the Chilton site again during 2000.

## 3.5 ESTIMATION OF HEAVY METAL INPUTS TO THE NORTH SEA

Cambray et al. (1975) estimated the total deposition of trace elements by rain to the North Sea. These estimates were based on the mean concentrations of elements in bulk deposition observed at land-based stations around the North Sea and an assumed average rainfall rate over the sea of  $438 \text{ mm y}^{-1}$ . The mean rainfall rate was derived from a limited number of measurements carried

out at sea, compared with similar measurements carried out at adjacent land-based measuring sites. These suggested that the rainfall observed at sea was of the order of 55% of that observed on nearby land. Barrett *et al.* (1990) estimated a similar figure for total rainfall over the North Sea of 435 mm y<sup>-1</sup> derived from satellite observations.

Assuming the area of the North Sea to be 5.25 x 10<sup>5</sup> km<sup>2</sup> and the mean rainfall over the sea to be 438 mm y<sup>-1</sup>, the total deposition has previously been calculated for every complete year between 1987 and 1998. These data, together with that estimated by Cambray *et al.* (1975) for the period June 1972 to May 1973 were reported by Playford and Baker (1999). The total deposition has similarly been estimated for 1999. These results are shown in Table 14.

The estimated inputs using the above method do not take into account any concentration gradients from land to sea, that can occur due to removal processes or dilution. All sampling is currently undertaken on a monthly basis (quarterly between 1995 and 1998), it is therefore impossible to separate onshore from offshore winds that would enable direction dependent corrections to be established and applied.

The method of calculation used by OSPARCOM to estimate inputs of pollutants to the North Sea differs somewhat from that used in this report. The OSPARCOM methodology incorporates data from many more sites in Europe and uses weighting factors to make some allowance for the reduction in concentration which is likely to occur with distance from the coast. The weighting factors for each station are derived from model calculations. However, our estimates are a useful measure of the upper bound of UK inputs to the North Sea. These show that the UK inputs of Cd, Pb, Ni and Zn have more than halved over the period 1994 to 1999 and that aerial inputs of many other anthropogenic elements have declined.

## 4 Conclusions

The major conclusions of this work are:

- Measurements of heavy metals in air particulate and rainwater have been continued at three sites near to the North Sea coast of the UK. These provide an effective measure of the aerial inputs of anthropogenic elements from the UK to the North Sea.
- The upper bound of the input of UK-derived Pb and Cd by deposition from the atmosphere to the North Sea in 1999 was 400 and 13 tonnes year<sup>-1</sup> respectively, compared with 3500 and 98 tonnes year<sup>-1</sup> respectively in 1987, the first full year when measurements were undertaken in the current sampling programme.
- The decrease in the concentrations of Pb in air is consistent with the reduction in the Pb content of leaded petrol and the increasing use of unleaded motor fuel in the UK.
- Concentrations of other trace elements measured in air particulate have decreased since measurements began in 1986. For Cd, Cr and Ni, annual mean air concentrations at East Ruston and High Muffles/Staxton Wold have declined in line with reductions in estimated emissions in the UK between 1987 and 1998.
- The greater uncertainty in estimated depositions caused by the variability in rainfall results in large variations in the measured monthly and quarterly concentrations. This in turn makes the observation of trends less reliable than those for air concentrations.
- The relative concentrations of heavy metals, in both air and rain, observed at each station are generally consistent with those which would be expected given their respective locations in the United Kingdom, our understanding of the spatial distribution of emissions and concentrations of other anthropogenic pollutants.
- The uncertainties attributable to both sampling and analysis have been shown to be of the order of 10-15%. However, a careful assessment of the data is necessary to identify samples which may have suffered contamination during the sampling period.

Overall the sampling and analytical programmes have confirmed that during the periods 1972 to 1973 and 1987 to 1999 there have been significant decreases in the inputs of the measured trace elements to the North Sea. These decreases are generally in agreement with estimated decreases in UK emissions during these periods.



## 5 References

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**TABLE 1**  
**SAMPLING SITES**

	<b>BANCHORY</b>	<b>EAST RUSTON</b>	<b>HIGH MUFFLES</b>
<b>Location</b>	Kincardineshire	North Norfolk	North Yorkshire
<b>National Grid Reference</b>	NO 677 986	TG 341 279	SE 776 939
<b>Latitude</b>	57° 05' N	52° 48' N	54° 20' N
<b>Longitude</b>	02° 32' W	01° 28' E	0° 48' W
<b>Elevation</b>	120 m above sea level	5 m above sea level	265 m above sea level
<b>Distance from coast</b>	26 km	8 km	21 km
<b>Mean annual rainfall (1994-1997)</b>	820 mm	641 mm	712 mm
<b>Land use within a 10 km radius</b>			
Crops and fallow	26 %	77 %	27 %
Grassland	34 %	10 %	51 %
Rough Grazing	31 %	10 %	19 %
Woodland	2 %	1 %	2 %
Other land	7 %	2 %	1 %

**TABLE 2**  
**Annual Mean Air Concentrations (ng m<sup>-3</sup>) (1994-1999)**  
**BANCHORY**

<b>Year</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>1994</b>	0.20	0.11	0.41	2.1	424	1.4	5.2	20.8
<b>1995</b>	0.41	0.06	0.33	1.9	627	0.71	4.4	16.2
<b>1996</b>	0.32	0.09	0.54	2.6	618	0.61	4.3	14.3
<b>1997</b>	0.44	0.06	0.40	2.7	639	0.95	3.4	26.9
<b>1998</b>	0.31	0.05	0.31	2.0	490	0.49	2.2	19.9
<b>1999</b>	0.27	0.11	1.04	1.2	410	0.16	2.2	14.7

**TABLE 3**  
**Annual Mean Air Concentrations (ng m<sup>-3</sup>) (1994-1999)**  
**EAST RUSTON**

<b>Year</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>1994</b>	0.51	0.41	0.51	4.3	1070	2.1	13.9	32.5
<b>1995</b>	0.87	0.23	0.80	4.2	1073	2.0	15.1	37.8
<b>1996</b>	0.89	0.22	0.86	3.9	846	1.7	13.3	18.4
<b>1997</b>	0.64	0.17	0.51	2.4	888	1.6	11.7	11.0
<b>1998</b>	0.65	0.19	0.36	2.5	927	1.4	12.1	30.2
<b>1999</b>	1.27	0.29	0.79	3.5	923	0.7	17.5	18.4

**TABLE 4**  
**Annual Mean Air Concentrations (ng m<sup>-3</sup>) (1994-1999)**  
**HIGH MUFFLES**

<b>Year</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>1994</b>	0.45	0.15	0.69	2.9	755	1.9	11.0	20.1
<b>1995</b>	0.76	0.14	1.2	2.7	672	1.8	12.2	20.4
<b>1996</b>	0.75	0.15	1.0	3.0	653	1.6	7.7	25.6
<b>1997</b>	0.40	0.13	0.87	6.3	652	1.3	8.1	24.7
<b>1998</b>	0.49	0.10	0.45	3.8	567	1.2	6.6	39.2
<b>1999</b>	0.62	0.16	0.19	4.9	593	0.7	9.1	39.9

**TABLE 5****Precipitation-weighted Annual Mean Rainwater Concentrations ( $\text{mg l}^{-1}$ ) (1994-1999)****BANCHORY**

<b>Year</b>	<b>Rainfall (mm)</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Ti</b>	<b>Zn</b>
<b>1994</b>	680	0.26	0.07	0.23	1.2	3011	0.64	3.1	2.4	22.6
<b>1995</b>	909	0.13	0.08	0.65	0.75	2699	0.71	2.0	0.92	10.2
<b>1996</b>	845	Not derived due to loss of samples during analysis								
<b>1997</b>	880	0.31	0.25	0.29	1.2	2583	0.20	2.8	2.4	5.2
<b>1998</b>	1040	0.09	0.04	0.60	0.85	1841	0.16	0.90	1.4	11.3
<b>1999</b>	917	0.14	0.06	0.23	1.0	1980	0.30	0.89	0.6	4.6

**TABLE 6****Precipitation-weighted Annual Mean Rainwater Concentrations ( $\text{mg l}^{-1}$ ) (1994-1999)****EAST RUSTON**

<b>Year</b>	<b>Rainfall (mm)</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Ti</b>	<b>Zn</b>
<b>1994</b>	764	0.22	0.20	0.24	2.0	3186	1.3	4.3	1.5	23.0
<b>1995</b>	598	0.29	0.10	0.52	2.2	3874	1.7	5.4	2.6	30.7
<b>1996</b>	568	Not derived due to loss of samples during analysis								
<b>1997</b>	634	0.27	0.06	0.47	3.4	3488	0.50	3.9	2.6	9.8
<b>1998</b>	706	0.15	0.07	0.36	1.3	2663	0.52	2.2	1.7	9.3
<b>1999</b>	914	0.12	0.04	0.28	1.3	2720	0.34	1.9	0.9	6.1

**TABLE 7****Precipitation-weighted Annual Mean Rainwater Concentrations ( $\text{mg l}^{-1}$ ) (1994-1999)****HIGH MUFFLES**

<b>Year</b>	<b>Rainfall (mm)</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Ti</b>	<b>Zn</b>
<b>1994</b>	747	0.42	0.11	0.29	2.1	2752	0.96	5.3	1.1	28.7
<b>1995</b>	617	0.32	0.13	0.64	2.9	3216	0.97	4.9	0.77	16.8
<b>1996</b>	693	Not derived due to loss of samples during analysis								
<b>1997</b>	791	0.33	0.05	0.16	1.3	2383	0.18	3.9	1.2	28.3
<b>1998</b>	997	0.20	0.05	0.33	1.0	2183	0.35	2.6	0.61	10.3
<b>1999</b>	951	0.24	0.07	0.37	1.4	1467	0.31	2.5	0.83	7.4

**TABLE 8**  
**Annual Deposition ( $\text{mg m}^{-2}$ ) (1994-1999)**  
**BANCHORY**

Year	Rainfall (mm)	As	Cd	Cr	Cu	Na	Ni	Pb	Ti	Zn
1994	680	174	50	158	844	$2.05 \times 10^6$	436	2141	1658	15362
1995	909	113	65	573	538	$1.90 \times 10^6$	597	1586	719	8787
1996	845	Not derived due to loss of samples during analysis								
1997	880	273	222	253	1016	$2.27 \times 10^6$	176	2463	2109	4604
1998	1040	97	44	624	884	$1.90 \times 10^6$	165	936	1489	11779
1999	917	131	54	208	3355	$1.81 \times 10^6$	271	819	519	4180

**TABLE 9**  
**Annual Deposition ( $\text{mg m}^{-2}$ ) (1994-1999)**  
**EAST RUSTON**

Year	Rainfall (mm)	As	Cd	Cr	Cu	Na	Ni	Pb	Ti	Zn
1994	764	169	155	180	1499	$2.43 \times 10^6$	986	3281	1182	17570
1995	598	174	60	311	1334	$2.32 \times 10^6$	1030	3200	1525	18379
1996	568	Not derived due to loss of samples during analysis								
1997	634	171	41	298	2125	$2.21 \times 10^6$	320	2443	1628	6236
1998	706	106	51	257	879	$1.90 \times 10^6$	367	1523	1167	6548
1999	913	408	40	765	1153	$2.48 \times 10^6$	306	1688	821	5603

**TABLE 10**  
**Annual Deposition ( $\text{mg m}^{-2}$ ) (1994-1999)**  
**HIGH MUFFLES**

Year	Rainfall (mm)	As	Cd	Cr	Cu	Na	Ni	Pb	Ti	Zn
1994	747	315	85	220	1538	$2.05 \times 10^6$	720	3988	826	21409
1995	617	197	76	354	1311	$1.85 \times 10^6$	577	2714	441	8236
1996	693	Not derived due to loss of samples during analysis								
1997	791	260	42	129	1047	$1.89 \times 10^6$	146	3049	973	22402
1998	997	198	47	330	1006	$2.20 \times 10^6$	350	2544	605	10218
1999	951	226	67	350	1347	$1.40 \times 10^6$	299	2336	787	7008

**TABLE 11**  
**Temporal Changes in Air Concentrations**  
**BANCHORY**

	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>	<b>Na</b>
<b>Mean (ng m<sup>-3</sup>)</b>							
<b>1987-1990</b>	0.14	0.32	1.2	0.67	8.4	9.2	623
<b>1996-1999</b>	0.08	0.52	2.1	0.56	3.0	18.9	540
<b>% change</b>	-45%	63%	75%	-17%	-64%	107%	-13%

**TABLE 12**  
**Temporal Changes in Air Concentrations**  
**EAST RUSTON**

	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>	<b>Na</b>
<b>Mean (ng m<sup>-3</sup>)</b>							
<b>1987-1990</b>	0.46	0.83	3.6	2.3	33	29	933
<b>1995-1998</b>	0.22	0.65	3.0	1.3	14	19	890
<b>% change</b>	-52 %	-22 %	-17 %	-41 %	-58 %	-33 %	-4 %

**TABLE 13**  
**Temporal Changes in Air Concentrations**  
**HIGH MUFFLES**

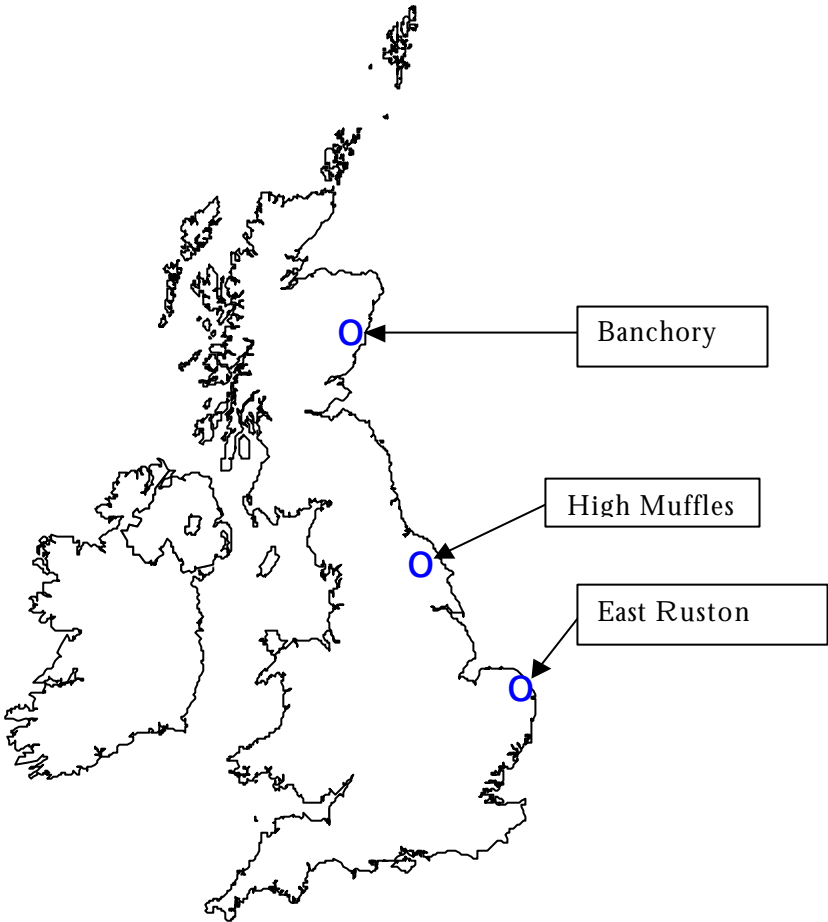
	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>	<b>Na</b>
<b>Mean (ng m<sup>-3</sup>)</b>							
<b>1987-1990</b>	0.62	1.4	4.1	2.7	28	66	883
<b>1995-1998</b>	0.14	0.7	4.5	1.4	7.9	33	615
<b>% change</b>	-78 %	-54 %	10 %	-47 %	-72 %	-51 %	-30 %

**TABLE 14**  
**Annual Total Deposition to the North Sea (1987-1999)**  
**(tonnes year<sup>-1</sup>)**  
**(By method of Cambray et al., 1975)**

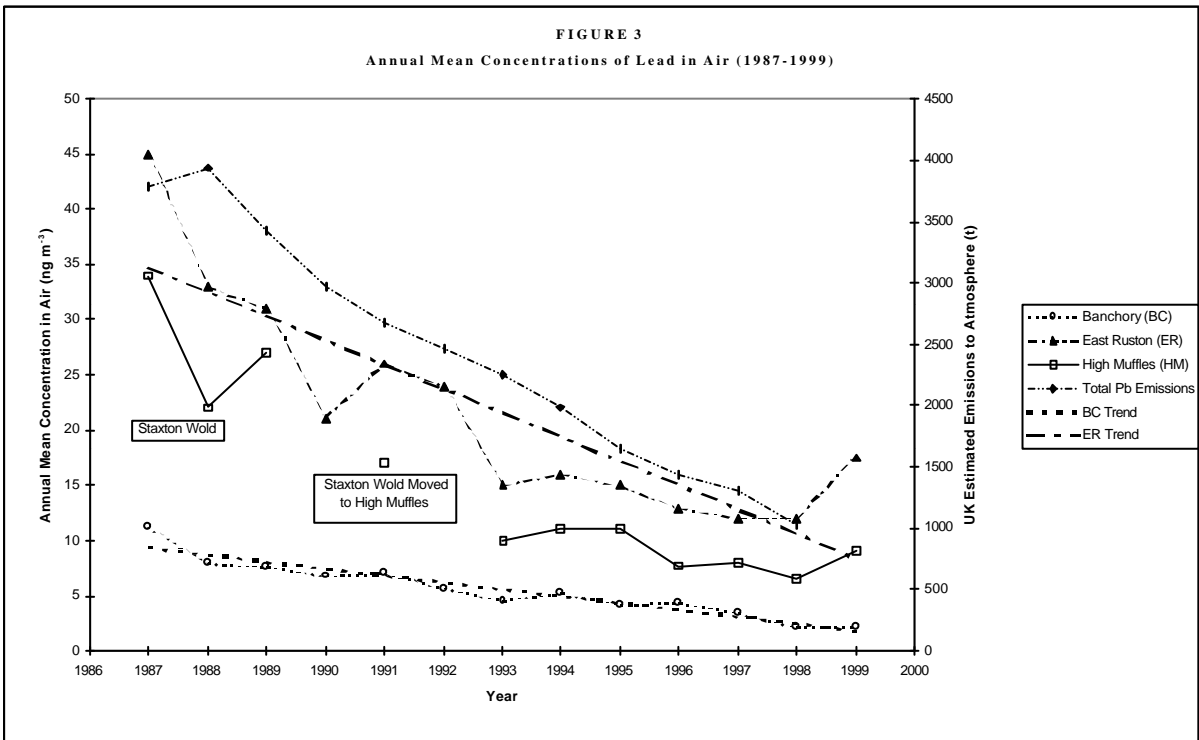
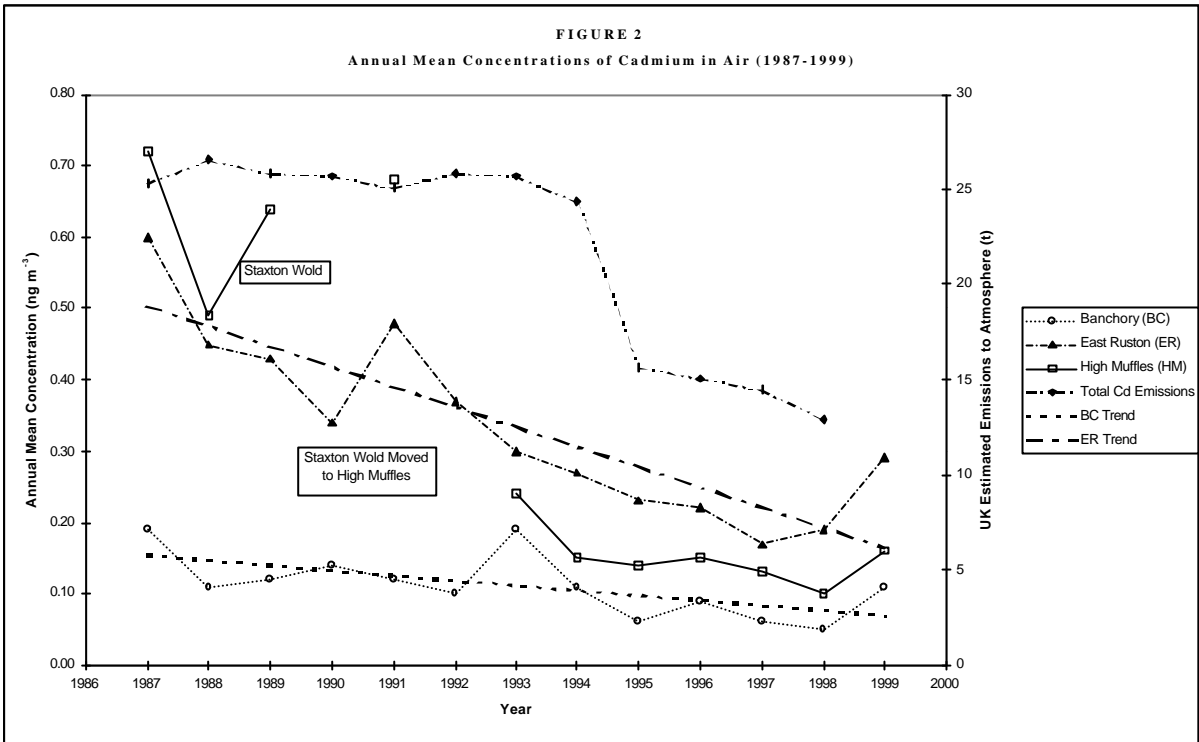
Element	Annual Total Deposition to the North Sea t y <sup>-1</sup>													
	1972-73	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
<b>As</b>	<b>1500</b>			210	200	140	57	57	69	56	Not	70	34	38
<b>Cd</b>		98	100	77	67	59	31	34	29	23	derived	28	12	13
<b>Cr</b>	<b>840</b>	280	320	260	150	130	180	48	59	130	due to	71	99	67
<b>Cu</b>	<b>6900</b>	970	930	1100	590	1400	350	330	400	380	loss of	450	240	280
<b>Ni</b>	<b>1400</b>	360	340	440	340	450	250	150	220	250	some	67	79	72
<b>Pb</b>	<b>8100</b>	3500	3500	3000	1400	2400	880	760	980	880	samples	810	430	400
<b>Ti</b>		770	970	1100	500	800	630	240	390	310	during	480	280	180
<b>Zn</b>	<b>38000</b>	5400	5300	6100	4900	5800	2800	2700	5700	4100	analysis	3300	2300	1400

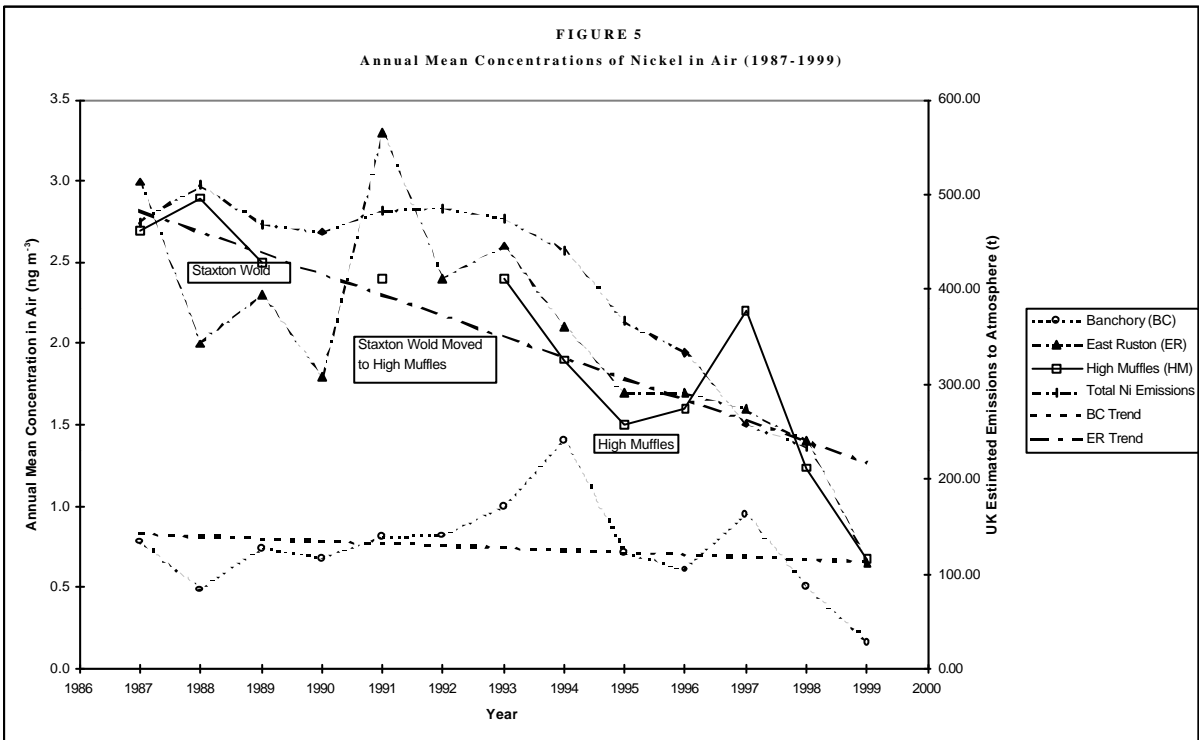
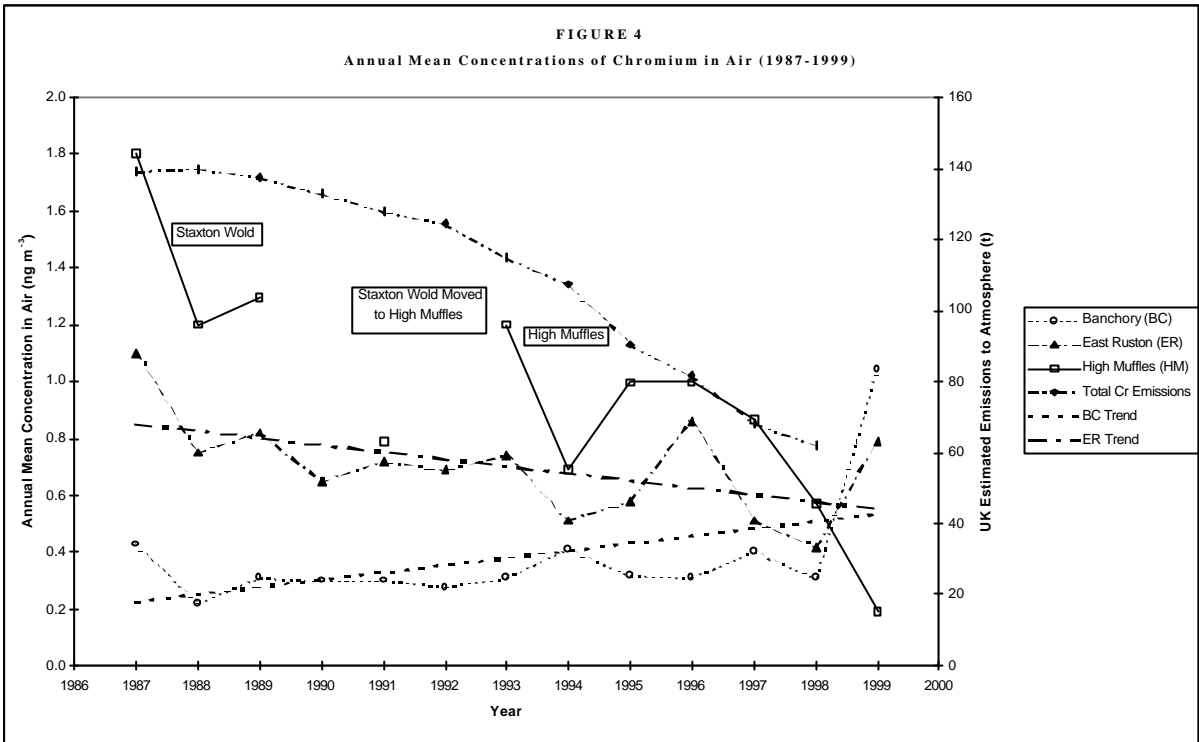
# LOCATION OF SAMPLING SITES

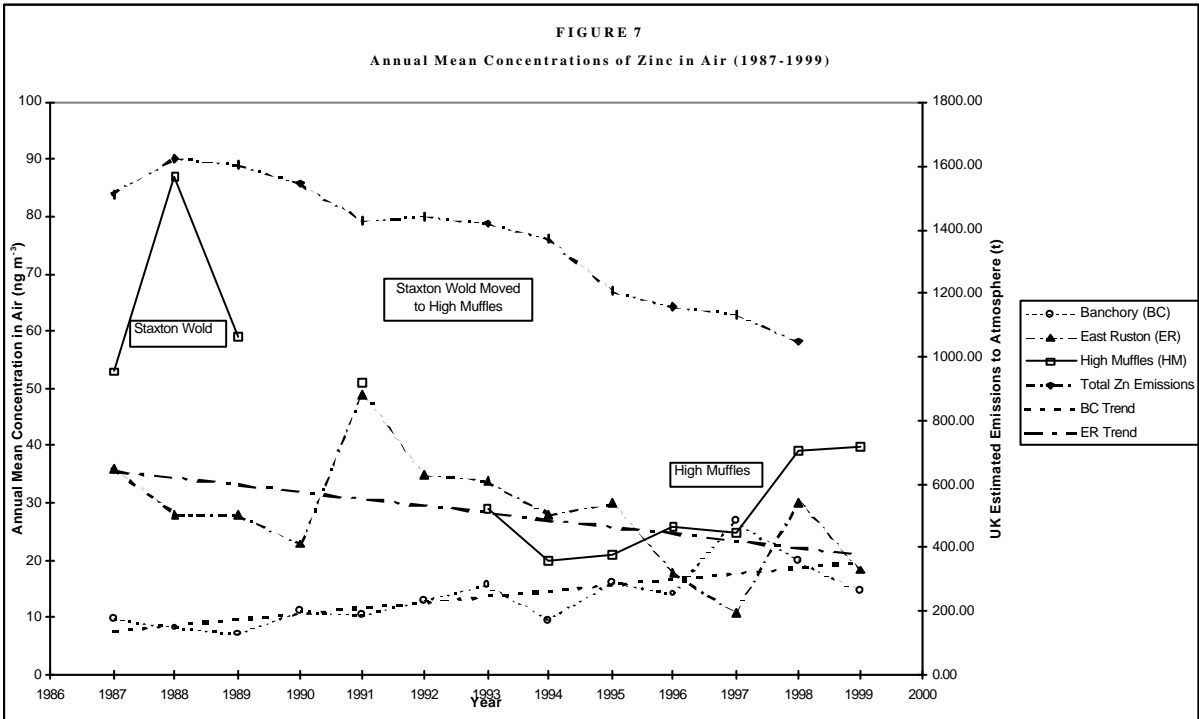
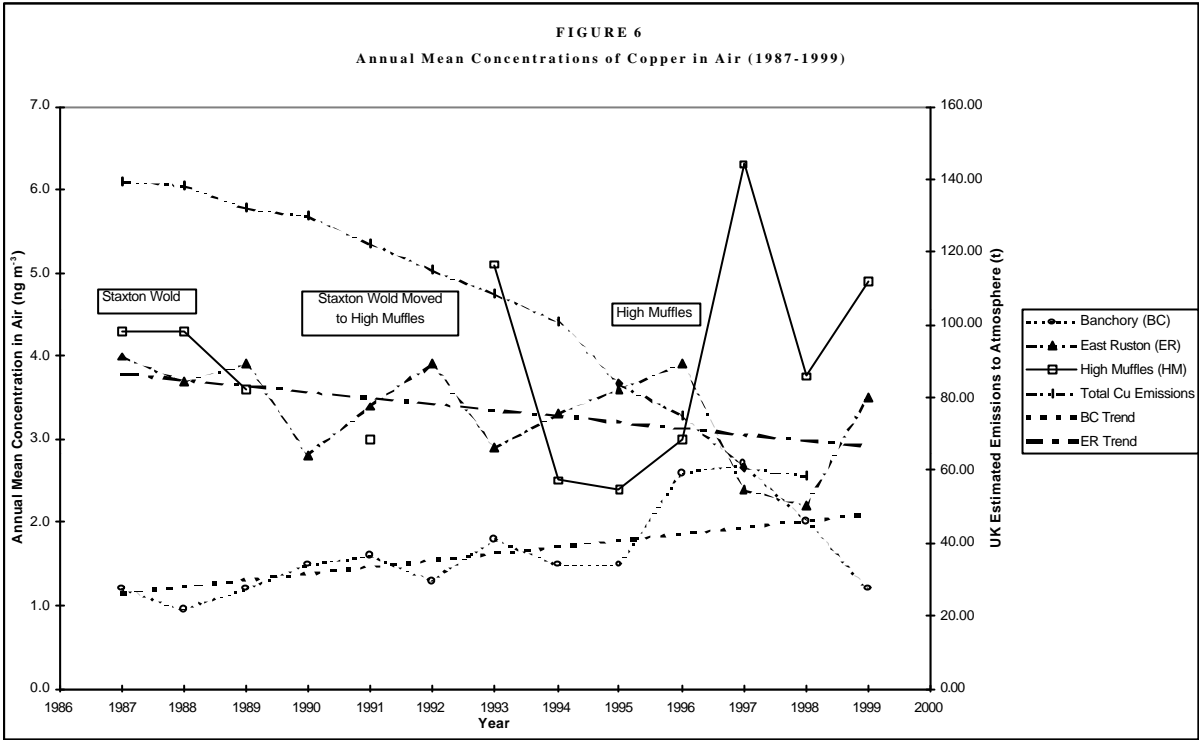
## FIGURE 1

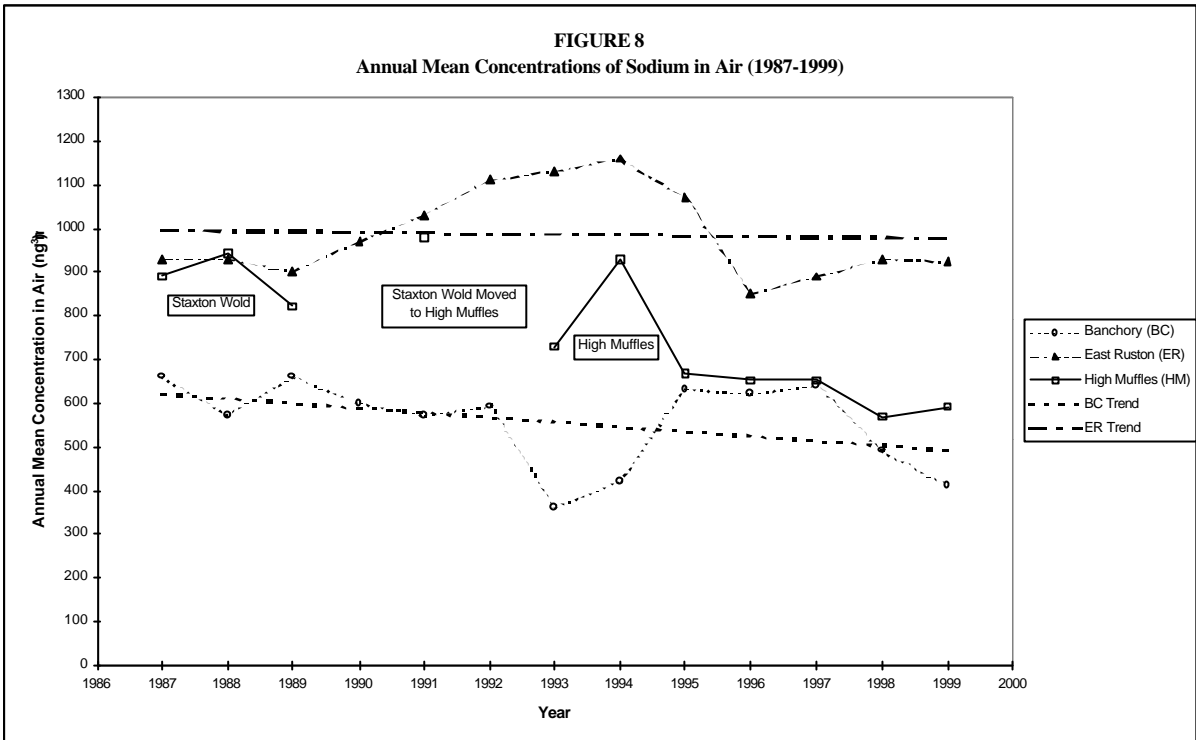


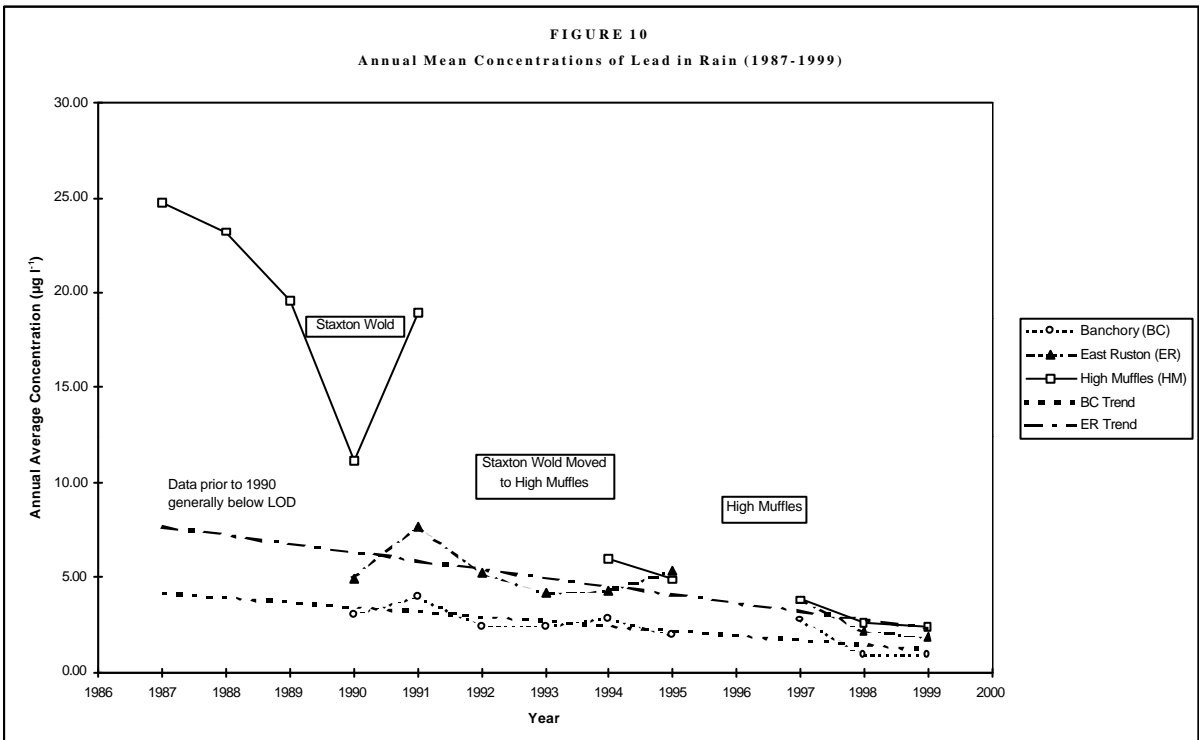
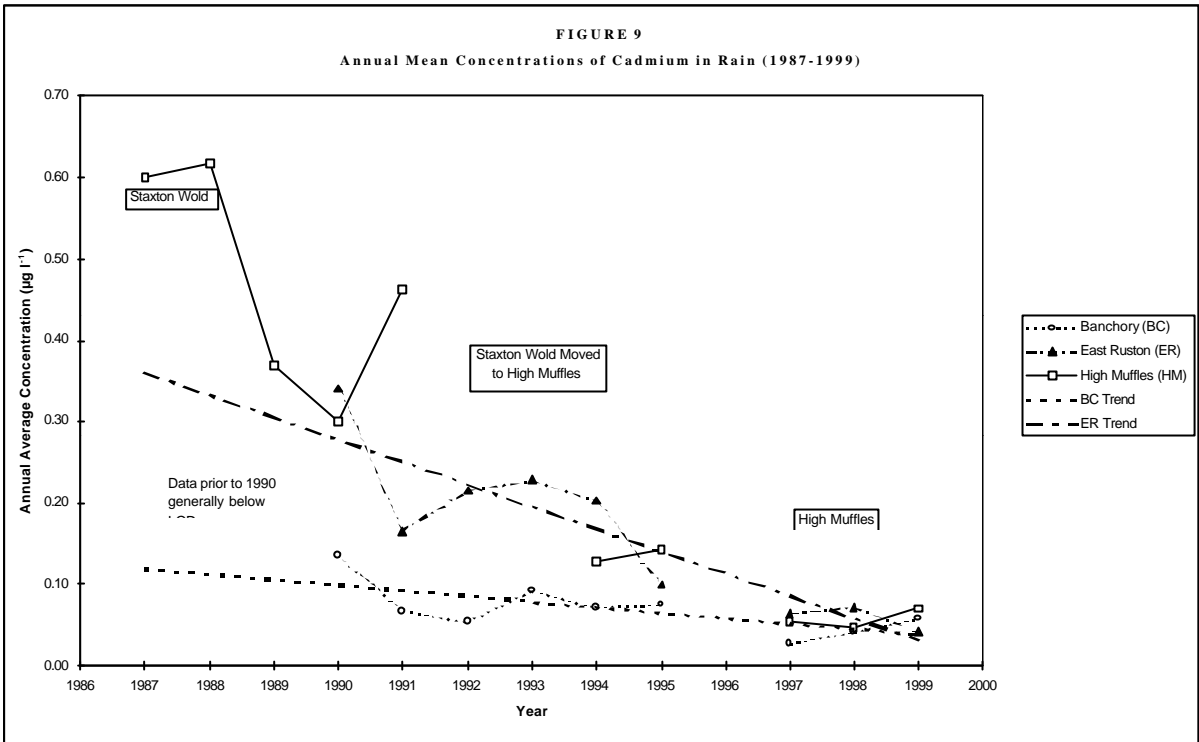


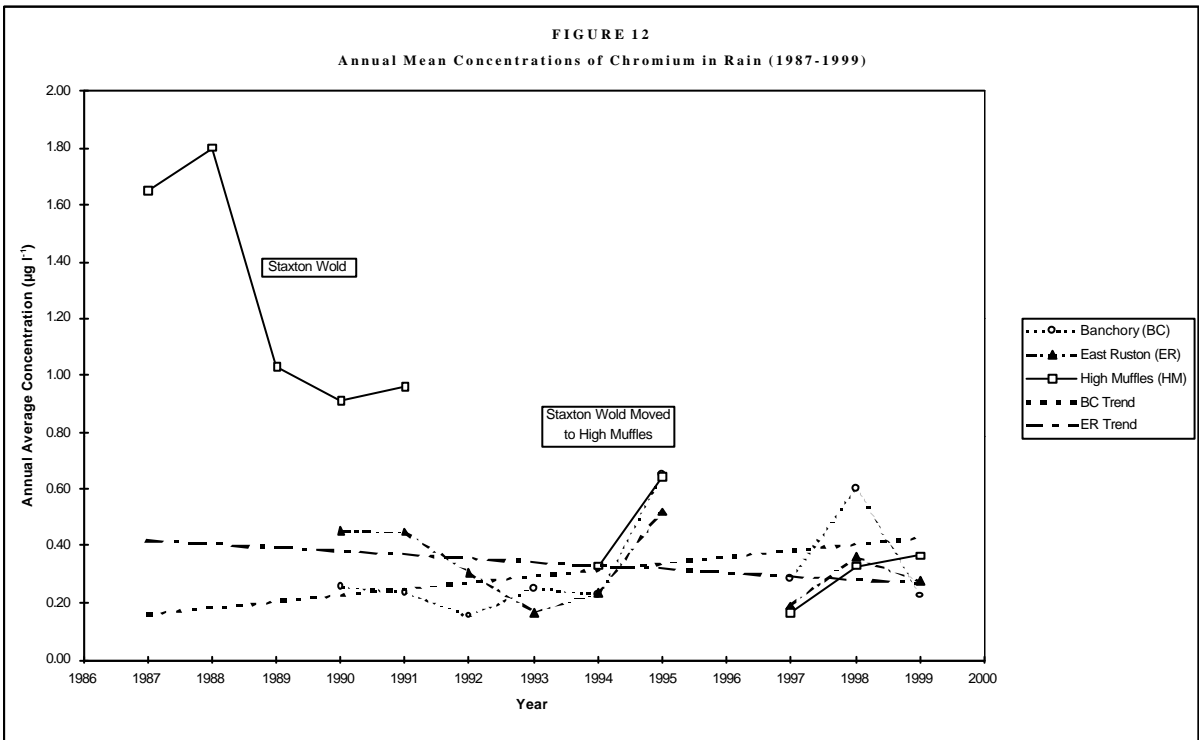
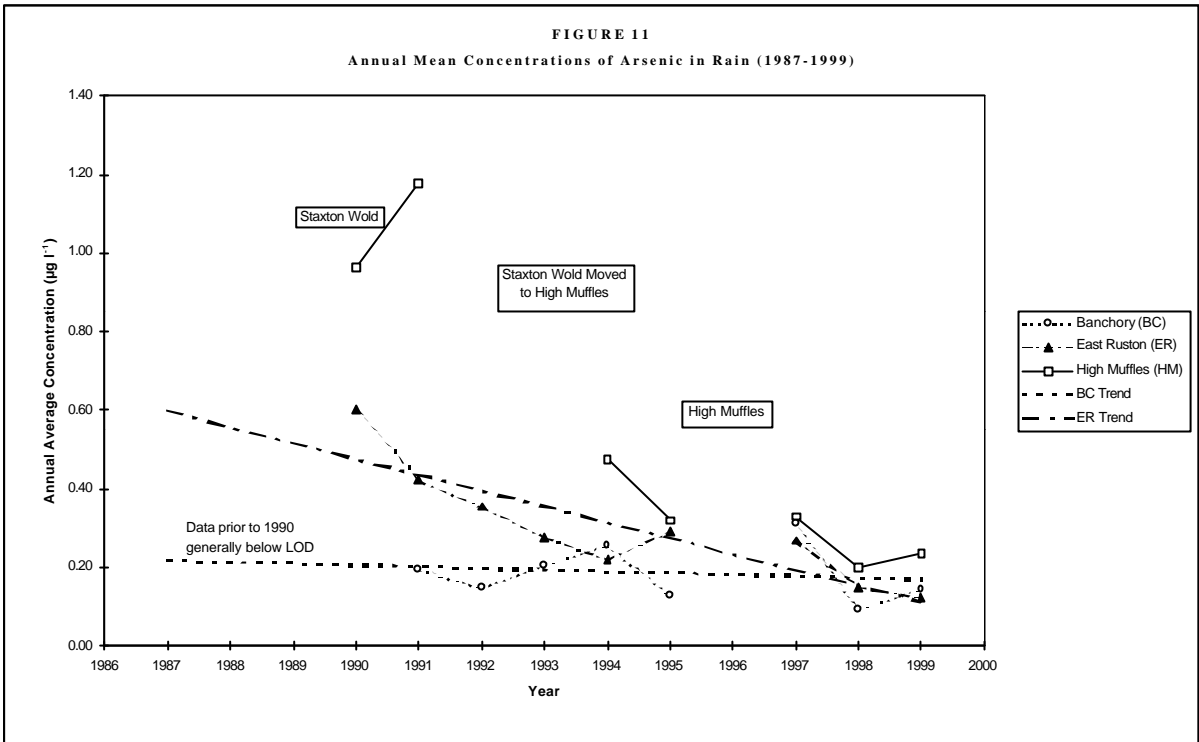


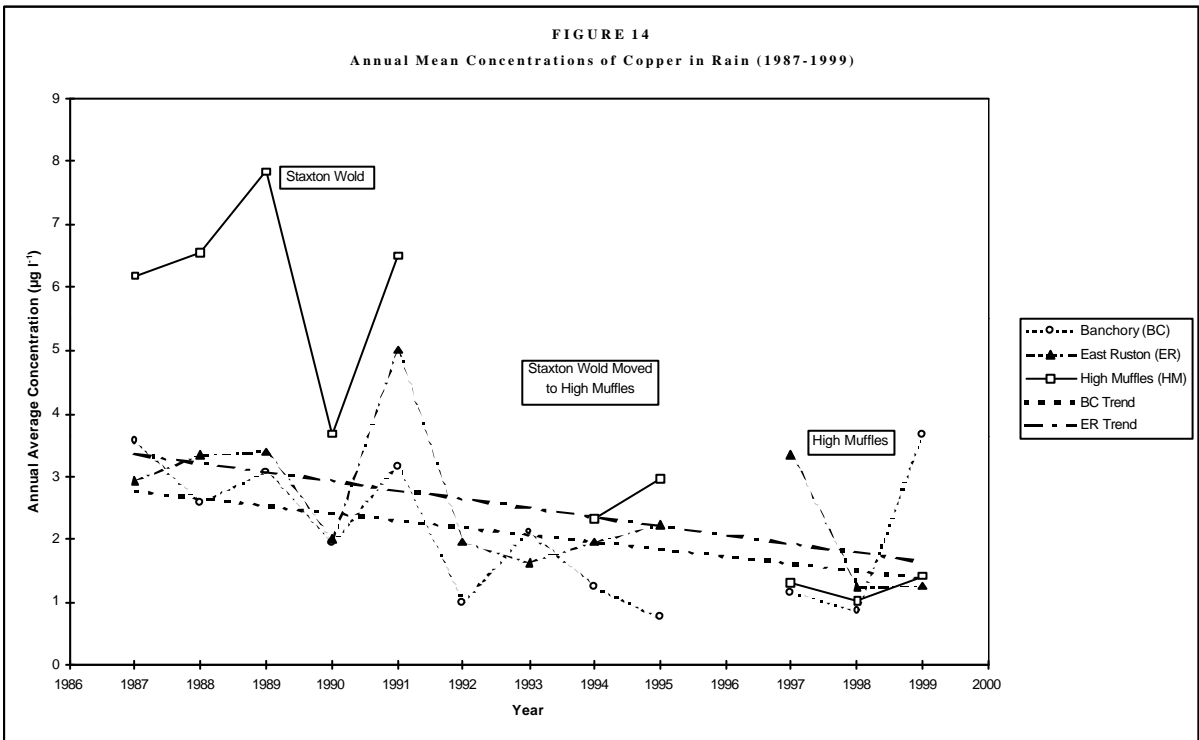
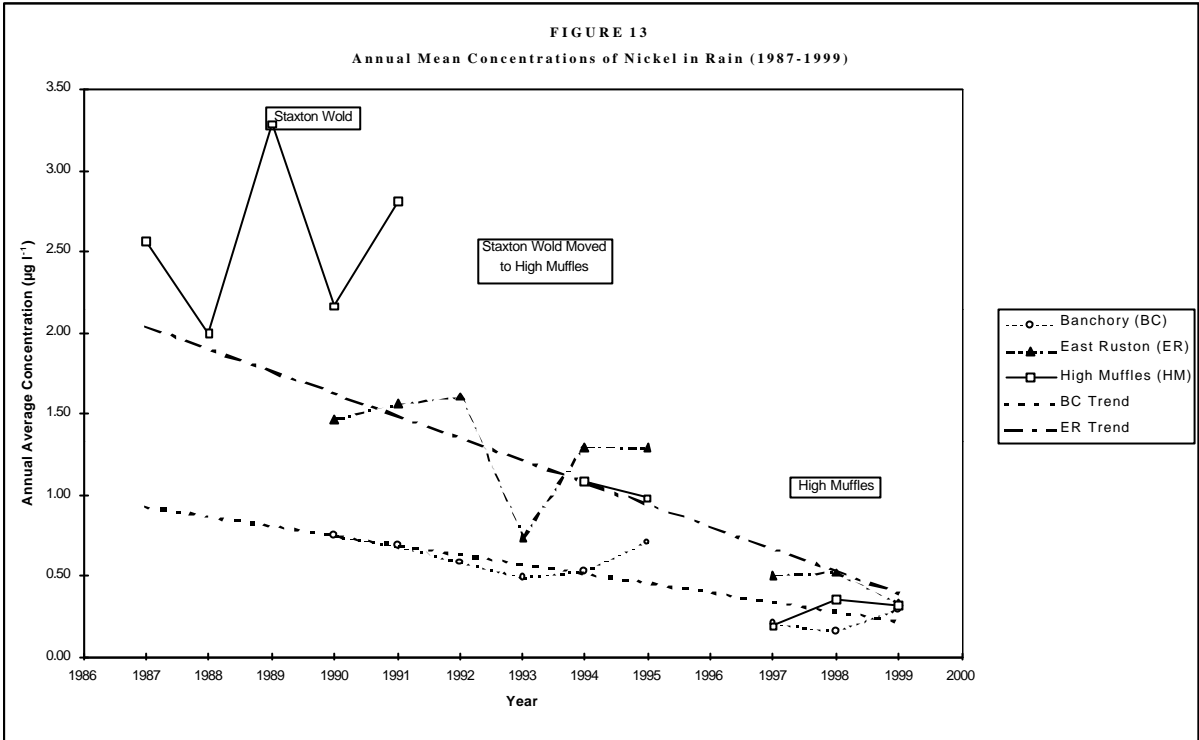


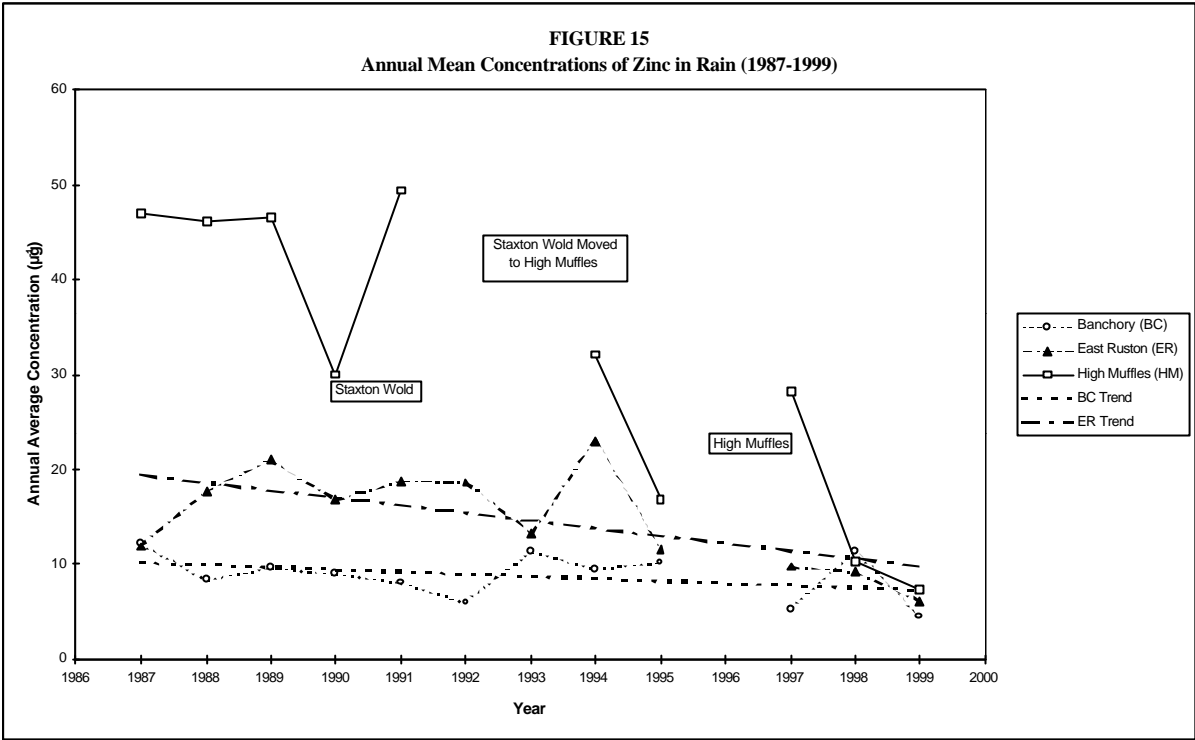
















# **Appendices**

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## **CONTENTS**

Appendix 1 Monthly Data (1999)

# Appendix 1

## Monthly Data (1999)

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## Air Concentrations 1999

<b>Banchory</b>		<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>1999</b>		<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>
January	0.18	0.13	0.36	1.32	657	< 0.17	1.20	0.51	
February					Sample lost				
March	0.10	0.11	0.41	0.98	232	< 0.31	1.86	2.63	
April	0.12	0.13	1.03	0.92	243		1.70	3.40	
May	0.10	0.03		0.77	557	0.51	1.93	10.72	
June	0.83	0.03		0.51	72	0.05	0.25		
July	0.30	< 0.15	0.99	3.43	209	< 0.10	2.29	14.91	
August	0.27	< 0.14	< 0.05	1.85	366	< 0.09	2.62	22.57	
September	0.22	< 0.16	2.18	0.27	136	< 0.11	2.34	14.17	
October	0.16	< 0.12	0.04	2.20	773	< 0.08	4.48	32.56	
November	0.37	< 0.14	3.25	0.47	558	< 0.09	2.32	22.78	
December	0.30	< 0.11	10.39	0.52	705	< 0.07	3.60	23.00	

<b>East Ruston</b>		<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>1999</b>		<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>
January	3.13	0.20	0.47	2.91	719	0.69	8.2	7.5	
February	0.51	0.16	0.82	3.20	461	1.05	1.0	10.7	
March					March/April single sample				
April	0.81	0.24	0.66	2.91	751	1.82	12.8	15.0	
May	0.36	0.19	0.39	1.26	1234	1.84	6.9	18.1	
June	0.39	0.07		1.45	670	1.45	8.1	10.6	
July	0.79	< 0.09	< 0.03	4.11	880	< 0.06	15.0	29.3	
August	0.89	< 0.12	3.49	3.84	699	< 0.08	17.5	22.1	
September	1.62	< 0.48	1.90	5.47	904	< 0.05	28.5	28.5	
October	1.93	0.36	< 0.04	5.36	964	< 0.07	32.1	2.4	
November	1.86	0.47	< 0.05	3.21	1673	< 0.09	27.4	32.5	
December	1.68	0.80	< 0.03	4.27	1201	< 0.05	34.7	25.6	

<b>High Muffles</b>		<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
<b>1999</b>		<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>	<b>ng/m3</b>
January	0.08	0.20	< 0.04	4.80	588	0.68	0.6	7.7	
February	0.51	0.19	0.03	8.82	666	2.16	6.8	18.0	
March	0.70	0.20	0.77	2.59	656	0.89	8.2	12.3	
April	0.68	0.18	0.79	3.18	856	0.82	8.3	9.3	
May	0.55	0.06	< 0.04	2.32	787	1.18	6.3	27.5	
June	0.45	0.04	0.06	3.84	351	1.19	5.3	49.0	
July	0.31	< 0.11	< 0.04	9.15	233	< 0.08	8.0	30.9	
August	0.83	< 0.12	< 0.04	9.13	664	< 0.08	8.7	30.7	
September	0.87	< 0.13	< 0.04	8.71	200	< 0.09	15.7	95.9	
October	0.29	< 0.10	< 0.04	1.46	512	21.19	8.8	208.3	
November	1.37	< 0.12	< 0.04	2.36	911	< 0.08	21.1	31.5	
December	0.87	0.44	< 0.04	1.96	696	< 0.09	11.3	126.1	

## Rain Concentrations 1999

**Banchory**

	Rain mm	As mg/l	Cd mg/l	Cr mg/l	Cu mg/l	Na mg/l	Ni mg/l	Pb mg/l	Zn mg/l
<b>1999</b>									
January	48.6	0.06	0.03	0.34	0.34	2300	0.14	0.76	2.40
February	70.4	0.08	0.04	0.18	0.18	3600	0.17	1.10	2.10
March	31.9	0.09	0.04	1.80	1.80	2300	0.94	0.79	1.90
April	70.0	0.07	0.05	0.15	0.15	2000	0.14	1.10	3.10
May	55.5	0.26	0.10	0.00	0.00	1000	0.71	3.00	4.60
June	82.8	0.62	0.03	0.00	0.00	230	0.65	0.57	0.80
July	52.3	0.07	0.04	0.06	0.06	110	0.20	0.74	2.70
August	42.9	0.09	0.04	0.10	0.10	1500	0.20	0.86	5.30
September	133.0	0.20	0.05	0.10	0.10	340	0.20	1.50	4.10
October	133.0	0.05	0.12	0.41	0.41	4600	0.20	0.32	3.90
November	80.9	0.05	0.10	0.41	0.41	1800	0.30	0.31	3.60
December	115.6	0.03	0.02	0.02	0.02	2500	0.20	0.40	15.00

**East Ruston**

	Rain mm	As mg/l	Cd mg/l	Cr mg/l	Cu mg/l	Na mg/l	Ni mg/l	Pb mg/l	Zn mg/l
<b>1999</b>									
January	116.0	0.08	0.02	0.06	0.60	1500	0.20	1.10	2.50
February	83.0	0.12	0.03	0.37	0.84	4200	0.28	1.70	3.60
March				March/April single sample					
April	88.5	0.25	0.07	0.32	2.00	2000	0.47	2.50	7.00
May	31.8	9.40	0.15	2.50	2.90	2500	0.89	5.10	29.00
June	72.2	0.14	0.04	0.16	1.10	670	0.39	1.40	3.60
July	65.0	0.10	0.04	0.48	1.60	6800	0.50	1.40	14.00
August	127.6	0.09	0.03	0.09	0.82	1400	0.30	1.50	4.60
September	152.0	0.10	0.04	0.10	0.90	1200	0.20	1.90	4.10
October	48.0	0.25	0.09	0.10	1.30	4400	0.31	2.30	8.60
November	41.5	0.10	0.04	0.20	1.10	10000	0.38	1.00	4.50
December	88.0	0.09	0.02	6.10	2.40	2600	0.34	2.40	5.60

**High Muffles**

	Rain mm	As mg/l	Cd mg/l	Cr mg/l	Cu mg/l	Na mg/l	Ni mg/l	Pb mg/l	Zn mg/l
<b>1999</b>									
January	84.7	0.25	0.06	0.09	1.90	1300	0.26	2.80	4.70
February	45.9	0.18	0.06	1.00	2.00	1500	0.37	2.20	3.80
March	178.1	0.18	0.08	0.15	1.10	970	0.27	3.10	4.40
April	71.4	0.13	0.04	0.05	1.90	1500	0.19	1.90	4.30
May	51.3	0.30	0.31	3.50	3.50	1000	1.10	4.70	7.60
June	77.1	0.79	0.04	< 0.00	2.90	510	0.38	2.30	0.80
July	24.6	0.20	0.04	0.20	2.00	370	0.46	2.40	8.80
August	115.9	0.07	0.03	0.10	0.45	220	0.10	1.00	24.00
September	64.5	0.29	0.06	0.20	1.20	630	0.36	3.40	8.80
October	78.1	0.20	0.08	0.32	0.85	2200	0.31	2.20	5.30
November	76.6	0.20	0.06	0.20	0.78	4900	0.33	2.20	4.60
December	82.8	0.20	0.05	0.20	0.66	2700	0.20	1.90	6.80