ISSN 1366-7300

ENVIRONMENTAL CHANGE RESEARCH CENTRE

University College London

RESEARCH REPORT
No. 79

SUMMARY OF RESEARCH UNDER DETR CONTRACT "ACIDIFICATION OF FRESHWATERS: THE ROLE OF NITROGEN AND THE PROSPECTS FOR RECOVERY" EPG/1/3/117

WORK PACKAGE 3: METALS

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April 2001

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Contents

Metals – key points

Scoping study

1) A scoping study was completed to provide an overview of current knowledge on UK temporal and spatial trends in trace metals, monitoring and the potential for setting critical loads.

2) Decreasing trends in emissions have been identified most clearly in the UK's longest running metal monitoring programme, the Rural Network, with decreasing concentrations in chromium, nickel, copper, arsenic, vanadium, zinc and lead deposition.

3) Atmospheric transport and deposition in the UK are heavily influenced by meteorological conditions and assessment of depositional trends must take these into account. Similarly, future climate change could potentially have a major impact on inputs to freshwaters, particularly with respect to the release of catchment stored metals.

4) Several methods are available for assessment of metal deposition trends, including terrestrial mosses, sediment trap samples, dated lake sediments and analysis of standing waters.

5) In the definition of metals critical loads there is still much to be done, including the provision of a unified critical loads methodology; the selection of suitable receptor organisms and setting of critical limits; and the collection of suitable model input data.

Metal deposition and cycling at Lochnagar

1) Mercury data from Lochnagar suggest that atmospheric deposition has increased over the last three years. However, a longer dataset is needed to follow, and confirm, this trend.

2) Mercury deposition concentrations are greater than their equivalent lake water concentrations and this suggests that Hg is bound and stored in catchment soils, which implies that it could be released via soil erosion as a result of, for example, future climate change.

3) Other trace metals show a decline in deposition at Lochnagar, and all except Pb show a decline in lake water concentrations.

4) Most terrestrial plant species followed similar decreasing trends to those of atmospheric deposition, particularly *Hylocomium splendens* and *Pleurozium schreberi.*

5) Other terrestrial and aquatic plants showed less agreement with depositional trends, while epilithic diatoms on artificial substrates showed limited usefulness primarily due to the low amounts of material produced.

6) Sediment traps show very good potential for monitoring lake metal trends and suggest catchment inputs may be very important.

Task 3.1: Atmospheric Deposition of Heavy Metals: an assessment of monitoring in the UK with reference to critical loads and forthcoming legislation

P.A. Henderson

CRITICAL LOADS ACIDITY AND METALS

Atmospheric Deposition of Heavy Metals: an assessment of monitoring in the UK with reference to critical loads and forthcoming legislation.

A scoping study produced for the Department of the Environment, Transport and the Regions (DETR) as part of the Critical Loads Acidity and Metals programme (contract no. EPG 1/3/117 [AQ 17/8/307])

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July 1999

Contents

List of Tables, Figures and Appendices

Chapter 1: Introduction

1.1 Aims of the study

This study forms part of the DETR-funded Critical Loads Acidity and Metals (CLAM) programme (contract no. EPG 1/3/117 (AQ 17/8/307)) and will look specifically at heavy metal pollution which is seen to travel via the atmosphere outwith the source locality. Pollution which has an impact on areas which may be, in many cases, thought to be pristine or undisturbed. This pollution can often disrupt fragile ecologies.

The main areas which will be covered in following sections are;

- Introduction to research related to heavy metals in the environment.
- Review of UK atmospheric metals research over the last 5-10 years - short-term and long-term programmes.
- Review of recent European/Scandinavian atmospheric metals research.
- Review of other (worldwide) atmospheric metals research.
- Comparison of UK data with other countries data.
- Uses of indirect methods other than direct monitoring to assess trends in metal pollution (e.g. sediment profiles, ice cores, moss surveys, computer models).
- A discussion of metals monitoring with special reference to lake systems.
- Future monitoring in the UK.
- Discussion of relevant National / European air quality legislation.
- The role of Critical Loads in defining future policy.
- Future scenarios affecting atmospheric heavy metals deposition (e.g. climate change).
- Conclusions and recommendations for monitoring and critical loads.

1.2 Background

Heavy metals are emitted to the atmosphere from both natural and anthropogenic sources. Large amounts of naturally-derived heavy metals are emitted into the atmosphere from sources including forest fires, seasalt inputs, windblown dust, volcanoes and biogenic processes. Additionally, the geological presence of these metals is acted upon by various physical, chemical, biological and meteorological processes to bring them into the atmosphere (Pacyna, 1998).

In order to assess the extent of anthropogenic atmospheric trace metal pollution it is first necessary to understand and attempt to quantify naturally-derived levels. Pacyna (1986) compiled natural annual metal emission data, including amounts of Cd, Cu, Ni, Pb, Zn and Hg released to the atmosphere. Of natural sources; windblown dust and volcanic emissions release the largest amounts of trace metals with Arnold *et al* (1981), suggesting that as much as 10 x 10^9g yr^{-1} of cadmium is released from the Mount Etna volcano alone. Table 1 shows total worldwide metal emissions from natural and anthropogenic sources.

Through calculation of the percentage of anthropogenic emissions relative to the total we can gain a greater understanding of the uncertainties which surround emission source apportionment between natural and anthropogenic. Only atmospheric lead is shown to be almost entirely anthropogenic in origin (94.1-99.7%). In contrast, anthropogenic chromium is only 39.3-61.5% of the total emitted to the atmosphere with soil-derived dust accounting for over 50% of the total (Pacyna, 1998)

The large variability in values of natural versus anthropogenic emission (e.g. anthropogenic Hg; 52.1-100%) points to a lack of knowledge relating to emission source apportionment, with only upper and lower lead estimates being similar (Pacyna, 1998)

Clearly, there have always been natural emissions of trace metals to the environment but emissions through human activities, mostly on fine particles, are the major cause of recent concentration increase, resulting in alterations to the geochemical cycles of these metals and potential negative effects on diagnostic environments (Pacyna *et al*, 1995). To show the relative anthropogenic accumulation, an enrichment factor (EF) of an element x can be estimated using the formula;

$$Efx = (x / Ref)_{aerosol} / (x / Ref)_{reference\ material}$$

Where x / Ref is the concentration ratio of an element (x) to a reference material.
Values obtained from this equation near unity suggest that metals are derived through crustal erosion, much larger values (e.g. >100) imply that there are other forces responsible for enrichment and these could be either anthropogenic or other natural.

Source	Hg	Cd	Pb	Cu	Cr	Zn	Ni	Se	As
Total natural	0-4.9	0.1-3.9	0.9-23.5	2.2-53.8	4.5-82.8	4.0-85.9	2.9-56.8	0.7-18.1	1.1-23.5
Total anthro-pogenic	0.9-6.2	3.2-12	287.5-376.0	19.7-50.8	7.2-53.7	70.4-193.5	24.2-87.2	1.7-5.8	12.0-25.6
Total	0.9-11.1	3.3-15.9	288.4-399.5	21.9-104.6	11.7-136.5	74.4-289.4	27.1-144.0	2.4-23.9	13.1-49.1
% anthro-pogenic	52.1-100	75.5-97.0	94.1-99.7	48.6-90.0	39.3-61.5	66.9-94.6	60.6-89.3	24.3-70.8	52.1-91.6

Table 1 Worldwide emissions of trace elements from natural and anthropogenic sources and % anthropogenic emissions of total
Data of natural emissions from Nriagu, 1989 and data for anthropogenic emissions from the early 1980s by Nriagu and Pacyna, 1988. (values x 10^3 t year^{-1}).

Anthropogenic atmospheric heavy metal pollution has been present since pre-industrial times. For example, Lead from Roman and Greek smelting activities has been identified in Arctic ice (Hong *et al*, 1994) and concentrations of the metals; Cu, Zn and Pb have been enriched in some Welsh lake sediments during Roman times due to forest clearance (Jones, 1984). The problem has, however, been greatly exacerbated since the time of the industrial revolution (e.g. Hamilton-Taylor, 1979; Martin, 1985 and Jones *et al*, 1991). In addition, there have been subsequent increases in the atmospheric levels of metals since World War II (Hermanson, 1991). Other workers (e.g. Candelone *et al*, 1995; Birch *et al*, 1996; Von Gunten *et al*, 1997 and Callender and Van Metre, 1997) have noticed a decline in deposited levels since the late 1970s.

Toxic heavy metals including Pb, Hg, Cd, Cu and Zn have all been produced as by-products of various industrial processes including the production of primary nonferrous metals, fertilizer manufacture and combustion of fossil fuels (Nriagu, 1979) and by other non-industrial sources such as the release of lead as toxic alkyl-lead compounds from petrol engines.

Metals can be emitted into the atmospheric environment as either a point or diffuse source, and in this respect, the location of the area or site in question must be considered when trying to identify contributing sources. This becomes especially important when trying to develop pollution control legislation, as atmospherically-transported pollution can travel across international boundaries.

Although there are significant amounts of naturally-derived heavy metals in the atmosphere, the inputs from the large scale industrialization in Europe have been enormous. Estimated total atmospheric emissions of trace elements from anthropogenic sources in Europe for 1979 are shown in Table 2.

Atmospheric pollution has been seen to have a detrimental effect on health, most noticeably perhaps, in episodes such as the sulphurous London smogs of 1952 which had a devastating effect on public health. Atmospheric contamination has also led to large-scale problems of environmental pollution with issues such as acid deposition. The creation of acidic rainfall chiefly through emissions of SO_X and NO_X compounds and the resultant ecological effects have been well documented (e.g. Cosby *et al*, 1985; Battarbee *et al*, 1985; Jones *et al*, 1989; Lee *et al*, 1992; CLAG, 1995).

The examples given above have received much deserved media and scientific attention. What faces us in the future is determining the often more subtle effects of lower concentrations of more toxic compounds on both public health and ecology. Future environmental policy must be shaped to try and reduce any harmful effects from atmospheric pollution and this must be implemented at a national and regional level.

	Total Emissions for 1979 (Tonnes)
Pb	123×10^3
Cd	2.7×10^3
Zn	80.0×10^3
Cu	15.5×10^3
Cr	18.9×10^3
Ni	16.0×10^3
* Hg	0.4×10^3

*Table 2 Emissions of Pb, Cd, Zn, Cu, Cr, Ni from all anthropogenic sources in Europe for the year 1979 (adapted from Pacyna, 1984) *Hg data from Pacyna (1983)*

1.3 **Fate of heavy metals after emission**

Metals are released into the atmosphere in either gaseous or particulate form. Gaseous metal containing compounds may exist as either the molecular or elemental form. For example, mercury may be present as elemental vapour (Hg°) or as one or more molecular forms such as the volatile inorganic salt; $HgCl_2$ or the monoalkyl derivative; CH_3HgCl. Lead may also appear in the vapour phase as trialkylead (Harrison, 1986).

The number of heavy metal containing compounds is potentially very large and most are associated with particulates. Upon chemical transformation in the atmosphere a small number of different primary compounds will give rise to a much larger number of secondary compounds. A primary exhaust lead component, PbBrCl has a size of ~0.015μm and will rapidly coagulate in the presence of $(NH_4)_2SO_4$ aerosol to form $PbSO_4$. However, the contribution from this process is unknown and it may only account for a few percent of the total lead.

After emission, metals are subject to the effects of various physico-chemical influences. These factors contribute to the length of residence time in the atmosphere and hence to their ability to travel and affect areas outwith their source location. Metals emitted into the atmosphere which are associated with particulate matter will undergo a number of physical processes including diffusion and condensation of atmospheric water and other vapours. Smaller particles will also coagulate and eventually sediment out of the atmosphere. This so called dry deposition is one method for the removal of particles from the atmosphere and for particles greater than 1 μm obey the principles of Stokes' Law. The other main method of particle deposition is wet deposition in association with precipitation and atmospheric moisture.

The dispersion of heavy metals after emission is also very much related to meteorological conditions at the moment of their emission into the atmosphere and, in particular, to wind velocity and precipitation (Rovinskii *et al*, 1994). In a study carried out in areas adjacent to metallurgical processes it was found that 10-30% of emitted trace elements were deposited within a local zone, up to 10 km from source (Bobovnikova *et al*, 1980). Another study by Chan and Lusis (1985) found that deposition 40 km from a copper smelter was below 2.6% for metals including nickel, lead, cadmium and zinc during periods of no precipitation. However, in periods of precipitation the percentage deposition increases dramatically to 36% for nickel, 92% for zinc, 100% for copper and 9.7% for cadmium. Particles in the atmosphere act as cloud condensation nuclei, therefore heavy metals associated with these particles will ultimately be removed with precipitation. In addition to this, there is also 'incloud' washout when aerosol particles are entrained in rain droplets by diffusion processes (Rovinskii *et al*, 1994) Deposition of metals through precipitation can be defined by washout factors and this will be explained later (see 1.6.1).

In addition to the effects of physical and meteorological processes, particles will also react with atmospheric gases and are subject to chemical transformations within the atmosphere. Biggins and Harrison (1979) used laboratory experiments to determine the chemical transformations of inorganic lead compounds and found that they did not proceed with tropospheric UV light wavelengths, with sulphur dioxide and with ammonia. The main reaction appeared to be with sulphates and most importantly, with ammonium sulphate. In the case of organic compounds of lead, Harrison and Laxen (1978) have indicated that the major reaction route for tetra-alkyl lead compounds is through direct photolytic breakdown or reaction with ozone, triplet atomic oxygen (O_3P), or hydroxyl radicals.

It has been shown above, through the example of emitted lead from automobiles, that speciation is very important to the reaction pathways and fate of atmospheric heavy metal compounds. In addition, the potential toxicities and effects on plant and animal communities are changed markedly between different chemical species of the same element. The issue of heavy metal toxicities, with some examples of the toxic effects on specific biota are covered in more detail in 1.8.

1.4 **Main sources of atmospheric heavy metals in UK/Europe**

Various sources of metals to the atmosphere emitted were mentioned in 1.2. In addition, other sources such as steel secondary production plants, technological processes related to coal, oil, municipal waste and wood combustion, chlorine, glass and cement production, are all large industries in developed countries and major anthropogenic sources of heavy metal (Rovinskii *et al*, 1994).

Atmospheric pollution is able to cross local, regional and national boundaries. Bartnicki (1996) has given national emissions of the metals As, Cd, Pb and Zn from each European country for 1985 and calculated the exchange of metals between countries using the Heavy Metal Eulerian (HMET) model. The author has determined that approximately 30% to 90% of the metals emitted from each country are deposited in other countries. In the case of the United Kingdom, the flux (emission - deposition) of cadmium for 1985 was 1.76×10^{-2} tonnes, for zinc it was 1.28 tonnes and for lead it was 6.44 tonnes (the second highest for a European country after USSR).

Emissions data should however not be considered as being completely reliable, Pacyna (1994) has suggested an accuracy of $<25\%$ for lead, 50% or less for Hg and Cd and 100% for the rest. Generally, the reliability of emissions data for Europe and North America decreases in the following order;

Pb $>$ Hg and Cd $>$ remaining heavy metals.

It is possible to apportion sources of metals emissions or at least to differentiate between types of emission through determining the relative proportions of metal isotopes deposited. Martin (1985) used the ratio of $^{206}Pb/^{207}Pb$ to differentiate sources of lead deposited in lake sediment assuming that ^{206}Pb is mainly radiogenic and that ^{207}Pb is anthropogenic. The lake sediment $^{206}Pb/^{207}Pb$ ratio decreases from 1.167 at 60 years BP to 1.149 in the surface (1978) layer indicating a decrease in radiogenic lead in favour of anthropogenically-derived lead deposited over this time period. At about 40 cm (c.a. 1800) the ratio has increased to 1.192 representing more radiogenic lead deposition before the onset of the Industrial Revolution.

Metals can also be used as markers element in particulate pollution, Fung and Wong (1995) have used heavy metals as marker elements on particulates to apportion pollutant loadings from various urban sources by first sampling and analysing scrubber effluent and then ambient air samples.

Table 3 gives emissions of the five heavy metals species (Cd, Pb, Zn, Cr and Cu) from the ten largest emitters of lead in Europe (lead emission is used here as a measure of industrial size and development of a country). From the data presented, there does not appear to be a relationship between emission and deposition. For example, France is the fourth largest emitter of cadmium from the list of ten European countries, but is a net importer of deposited cadmium. There is more cadmium deposited in France than is emitted, providing evidence of trans-boundary pollution. Similarly, countries which emit more than is deposited in their country also substantiate the evidence for long-range transboundary transport of metals as this material will always be transported and deposited elsewhere. In the majority of cases however, European countries are net exporters of heavy metals.

1.5 **Typical selected heavy metal concentrations in UK ambient air**

Pb: 183 ng m^{-3} urban <---------------> 33.4 ng m^{-3} rural
Hg: 0.14 ng m^{-3} urban <---------------> 0.047 ng m^{-3} rural
Cd: 2.0 ng m^{-3} urban <---------------> 0.76 ng m^{-3} rural
Cr: 5.6 ng m^{-3} urban <---------------> 0.95 ng m^{-3} rural
Zn: 87.0 ng m^{-3} urban <---------------> 30.0 ng m^{-3} rural

The above data has been summarised from the AEA-Technology trace element survey (Lee *et al*, 1994) and shows mean concentrations of heavy metals in air from 1986-1989 measured at the following urban sites; Lambeth, Brent, Manchester (Rusholme and Bradford), Trafford (Altrincham and Flixton) and the rural sites; Chiton and Wraymires (part of the UK Rural Network, see 2.2.1[1]).

Urban concentrations are typically between three to ten times higher than rural concentrations in the UK and concentrations were found to comparable with other urban data from Europe (e.g. Fidalgo *et al*, 1988) and North America (e.g. Marshall *et al*, 1986).

		Cd	Pb	Zn	Cr	Cu
1	USSR	816 (7.9×10^{-2})	43,842 (10.31)	21,282 (4.29)	7,147	6,535
2	France	170 (-5.5×10^{-3})	10,545 (3.46)	6,127 (1.39)	1,095	450
3	United Kingdom	99 (1.76×10^{-2})	10,098 (6.44)	3,488 (1.28)	1,134	580
4	Italy	124 (1.74×10^{-2})	9,365 (3.01)	4,420 (1.18)	1,055	385
5	German FR	328 (4.03×10^{-2})	9,308 (1.83)	11,689 (1.75)	2,135	1,552
6	Spain	126 (7.44×10^{-2})	5,534 (1.79)	3,255 (2.04)	571	565
7	Poland	207 (8.63×10^{-2})	4,568 (0.45)	4,725 (1.58)	1,161	1,313
8	Belgium	171 (7.5×10^{-3})	3,986 (1.33)	4,736 (0.36)	642	613
9	Netherlands	88 (0.3×10^{-3})	2,427 (1.13)	3,067 (-3.5×10^{-2})	255	105
10	Yugoslavia	65 (4.08×10^{-2})	2,423 (0.51)	2,013 (0.79)	205	287

Table 3 European country emissions and heavy metal fluxes of heavy metals from all sources (anthropogenic) for 1979.
in tonnes (year^{-1}*) (after Pacyna, 1998) Numbers in parentheses are metal flux values (after Bartnicki, 1996) for 1985.*

1.6 **Deposition of heavy metals**

The need to understand the movements of pollutants once they have entered the atmosphere is paramount if effective pollution control legislation is to be implemented. Monitoring at source, and emission inventories are part of the overall information required to identify pollutant emissions but this must also be substantiated with research into the movement and deposition of atmospheric metals. There is a need to collect data on the amounts of metals deposited and distribution patterns, and this requires active monitoring.

Deposition characteristics of lead from automobiles can be used as an example of the dispersive effects of ‘near-ground’ pollution sources. Huntzicker *et al* (1975) estimated, that of the 24 tons of lead which are consumed in the Los Angeles area each day, 6 Tons are retained within the vehicle, and the rest, 18 Tons, is emitted to the atmosphere. Furthermore, of the total lead consumed, 40 per cent becomes near fallout (on or near roads), 8 per cent is deposited within the metropolitan area and 24 per cent is more widely dispersed. Having an atmospheric residence time of one or two weeks, this material can travel many hundreds of miles before being deposited.

Up to a quarter of lead consumed by automobiles can be subject to long-range transport (depending on climatic conditions) and this is from a near-ground source. Industry accounts for the largest percentage of anthropogenic emissions of heavy metals, for example, 65% of cadmium and 58% of zinc emitted comes from the nonferrous metal industry alone (Pacyna, 1996). Emissions from industrial chimneys create gaseous plumes which lead to the deposition of pollution downwind of the source. Over recent decades taller chimneys have been built to discharge the emissions above inversion layers. This has the effect of reducing pollution to the immediate area but leads to an increase in long-distance tropospheric transport of pollutants (Alloway and Ayres, 1997a)

1.6.1 **Meteorological effects**

Meteorological conditions play an important role in the removal of pollutants from the atmosphere (see 1.2). The 'washout factor' (W) as defined by Chamberlain (1960) assesses the removal of an element by rainfall;

$$W = \frac{\text{concentration of an element in rainfall } (\mu\text{g kg}^{-1})}{\text{concentration of an element in air } (\mu\text{g kg}^{-1})}$$

Cawse (1974 and 1987) used washout factors derived from the soluble fraction of rainwater (W_{sol}) due to the relatively large contribution from dry deposition. High values of W_{sol} (e.g. $>$1000) are associated with pollutants present at the rain forming altitude (~3 km) and include Cu, Mg and Mn. Low values of W_{sol} (~500) are typical of emission sources close to the ground and include the elements; As, Pb and V. Intermediate values (500-1000) include the elements Cd, Ni and Zn. (Baker, 1997). Clearly, both the elemental solubility and type of emission source affect the value of washout factor and these variables can go some way to explain deposition patterns of heavy metals. In addition to meteorology, landscape topography can also affect deposition rates, for example the deposition of heavy metals and acidifying pollutants in a forested region can be substantially higher than over open land due to the high surface roughness (De Vries and Bakker, 1998)

1.6.2 **Long-range transport and deposition**

It has been known since the 1960s that pollutants can travel great distances. Traces of lead have been found in Greenland and Antarctica snow strata (Murozumi *et al*, 1969) and mid-1960s lead concentrations in Greenland ice layers were found to be 200 times greater than they had been

5500 years previously, with the most marked rise seen after 1950. Clearly this lead originated in Europe and the United States and can be associated with a rise in leaded-petrol consumption at this time. More recent work on Greenland snow and ice cores further substantiate the evidence for the long-range trans-boundary pollution of the Northern Hemisphere (Candelone *et al*, 1995). It has also been argued that, in the case of mercury, much of the long-range contamination observed at remote locations was due to natural emissions (e.g. Rasmussen, 1994). The complexity of the global mercury cycle has led to much debate as to the main cause of atmospheric mercury contamination. However, despite uncertainties in current understanding, there is a broad and consistent database indicating that over large regions of the globe, human-related Hg emissions have increased relative to natural sources since the onset of the Industrial Revolution (Fitzgerald *et al*, 1997)

There have been many studies carried out to identify long-range atmospheric transport of heavy metals (e.g. Berg *et al*, 1996; Yaaqub *et al*, 1991 Rovinskii *et al*, 1994) and also studies to model the movement of atmospheric pollutants (e.g. De Caritat *et al*, 1997).

1.6.3 **UK deposition monitoring**

Long-term monitoring of heavy metals has been undertaken at four rural sites in the UK since 1972 (Cawse *et al*, 1994), and in addition, there has been multi-element analysis at a single site in southeast England over a 1 year period (Yaaqub *et al*, 1991) and a 15 month trace metal monitoring of the atmosphere over the southern North Sea (Chester *et al*, 1993). Long-term monitoring of atmospheric multi-element metal pollution has been carried out at three UK coastal locations for inclusion into the Paris Commissions study into the trans-boundary pollution entering the North Sea (AEA, 1998), and at over 30 lowland sites in England and Wales for over two years to assess the extent of atmospheric heavy metal deposition to agricultural land (Alloway, 1998). Smaller single site deposition of heavy metals have been monitored at Auchencorth Moss, Southern Scotland (Smith *et al*, 1997) as part of the LOIS (Land Ocean Interface Study. see also Neal *et al*, 1997a; Neal *et al*, 1997b, Jarvie *et al*, 1997; Langan *et al*, 1997). There are also deposition data from Lochnagar, northeast Scotland recorded as part of the MOLAR project (MOLAR, 1996) and for a PhD project (e.g. Yang, 1999). The above studies will be looked at in more detail in chapter 2.

1.7 **Environmental impact of heavy metals**

1.7.1 **Environmental compartments involved in the uptake/release of heavy metals**

After metals are deposited from the atmosphere to the earth surface they are associated with either particulate matter or dissolved in water. Through this association, metals often become available to living organisms. The uptake of metals involves crossing a biological membrane and this is most readily achieved by the metal divalent ions (e.g. Cd^{2+}, Hg^{2+} and Pb^{2+}) and these species are common in natural systems (AMAP, 1998). Free ions will be taken up directly by animals, ingested as water or taken into the body via dermal adsorption which increases with increasing pH (Gerhardt, 1993). In the case of plants, metal ions will be absorbed through the surface of roots and adsorbed though the leaves of terrestrial and aquatic plants.

Once the metals have become incorporated into the living tissue of the organism (e.g. liver, kidneys, bone, roots, leaves) they are subject to being ingested by other species and consequently are able to move up the food-chain. These processes are termed bioaccumulation and biomagnification and will be explained in 1.8.

Metals associated with particulates differ in that bioavailability depends upon their association with the inorganic or organic material they are bound to and this is affected by the physico-chemical characteristics of their environment. Generally, metals intimately associated with soil or sediment matter are made unavailable for uptake until there is a change in environmental conditions.

1.7.2 **Incorporation of metals into aquatic ecosystems**

Metals deposited into aquatic ecosystems either become incorporated into the sediment if they are in the solid phase and associated with particles, or they exist in the ionic phase dissolved in water. Figure 1 is a schematic representation of transfers and fates of heavy metals in a lake system. The diagram also serves to illustrate metal inputs and outputs to and from the system. The action of incorporating metals into the sediment provides an ideal method of reconstructing trends in past atmospheric pollution inputs (e.g. Hamilton-Taylor, 1979) after correction for background/natural concentrations. Therefore, sediments are often used as surrogate measures of historic changes in the trace metal content of various environmental compartments (Hermanson, 1991) and this concept will be expanded in later chapters.

1.7.3 **Retention and release of metals from sediments/soils**

Trace elements which are in the solid phase will exist in one of the following arrangements;

I. Dispersed in a silicate crystal lattice structure
II. Formation of a metallic compound (e.g. PbS)

III. Dispersed in a hydrated oxide (g. Fe and Mn oxides)
IV. Precipitated as an insoluble compound (e.g. carbonates)
V. Held onto surfaces by ion-exchange or specific adsorption.

For metals which have been deposited atmospherically, the most likely arrangement will be V. The metals are not permanently fixed but are subject to being bound or mobilized depending on immediate environmental conditions.

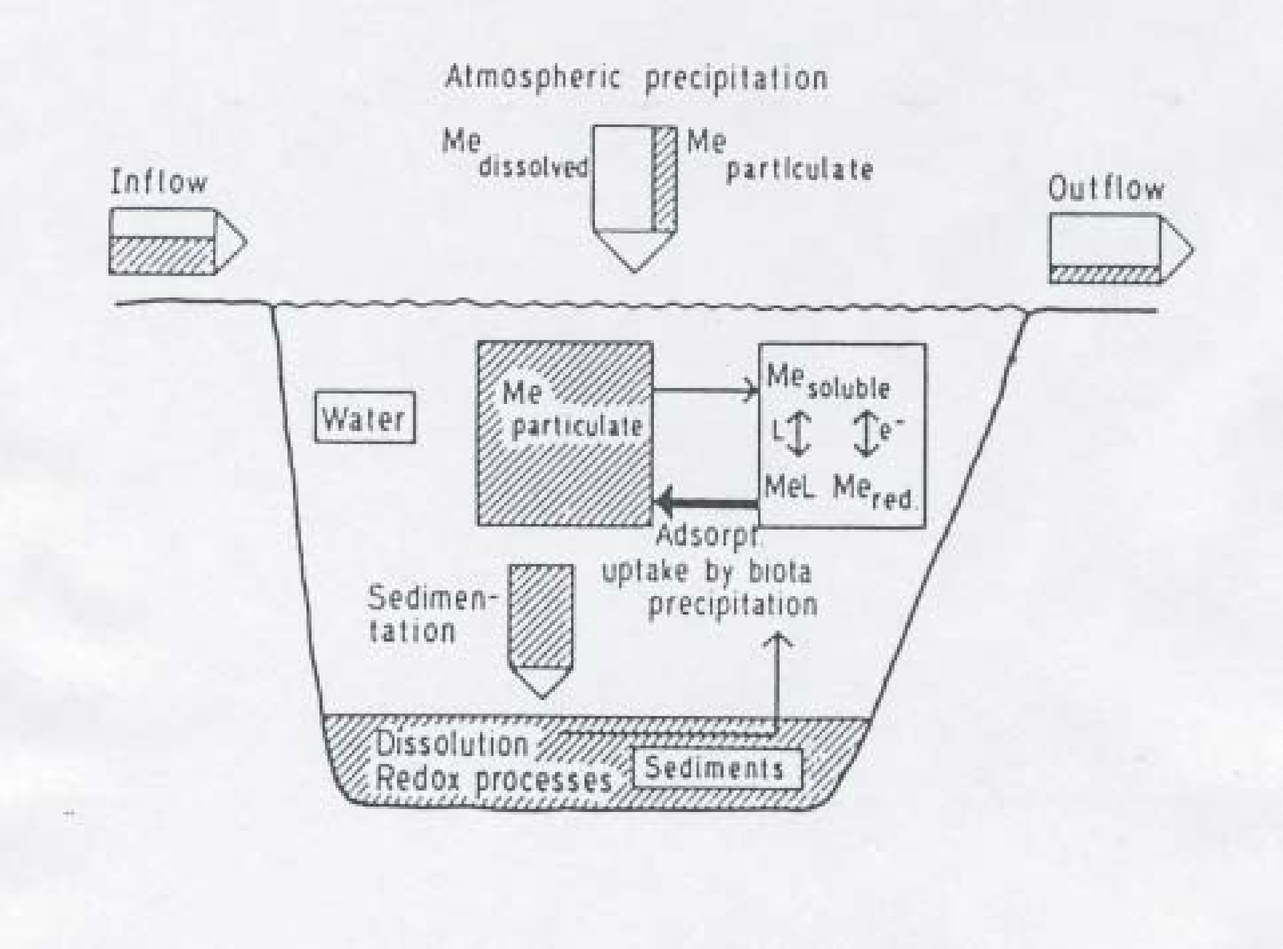


Figure 1 Transfers and fate of heavy metals in a lake system (after Sigg, 1985).

As soils and sediments are diverse mixtures of inorganic and organic material, the nature of their relationship with metals is affected by the following variables;

- Cation Exchange Capacity (CEC)
- pH (acidity/alkalinity)
- Water hardness
- Mineralogy of the sediment/soil (e.g. surface area, mineral structure)
- Organic matter content
- Presence of adsorbing precipitates (e.g. carbonates and oxides).

There is a relationship between adsorption of heavy metals and organic matter content in sediments. Metal concentrations and CEC are positively correlated with organic matter content. Lin and Chen (1998) have shown that the ability of metals to be adsorbed onto sediments increases in the order Zn >Pb >Cu >Cr.

In addition to the physical and chemical characteristics of the environmental media, the speciation of the metal is also extremely important in determining uptake and release and this in turn is affected by the chemistry of the immediate environment (e.g. pH, redox).

1.7.4 **Uptake and release of metals from biological compartments**

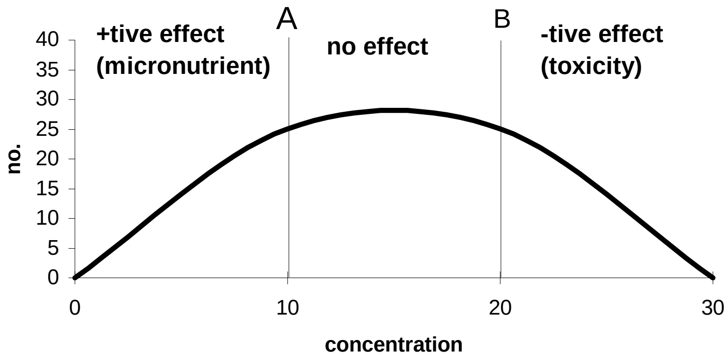
It has been stated previously that metal species become bound up with the inorganic and organic fractions of the soil and sediment. Metals are also interrelated with the biota in an intimate manner. In the water column, for example, metal ions may adversely affect phytoplankton if they are present in high concentrations However, these organisms will eventually settle to the sediment surface (after adsorbing metal ions), and in doing so will reduce the residual concentrations and act as a natural regulator (Sigg, 1985). Sigg also proposes that biological surfaces are better scavengers of heavy metals than inorganic surfaces in situations where the majority of the inorganic fraction is made up of minerals of low surface area such as quartz, feldspars and chlorite (this will be a common occurrence in lake systems). Even if inorganic surfaces have a partial covering of humic substances they will still have a lower affinity for metal ions than biological surfaces (Balistieri, 1981). Eventually, the organic fraction will be mineralized and the adsorbed heavy metals will be released back into the wider environment where they will be available to be adsorbed on to another particle surface. The free metal ion could also be mistaken for a micronutrient and physiologically assimilated into the organisms cells. It is at this point that the toxic effects of the heavy metal species become apparent.

1.8 **Toxicities of heavy metals.**

Of the heavy metals of interest to this study, only cadmium, mercury and lead are toxic non-essential elements at any concentration. The others; chromium, copper, nickel and zinc are micro-nutrients required by some, but not all, organisms in concentrations <0.01% (see Hunter *et al*, 1997) At concentrations greater than this these micronutrients become toxic (see Gerhardt, 1993). It has been shown that components of mixtures below their “no effect” concentration can contribute significantly to the toxicity of the mixture (Hermans *et al*, 1985), in this case the compounds have similar nodes of action and concentration additivity would be expected.

Figure 2 shows graphs of biological response to increasing heavy metal concentration. The top graph shows the response to an essential heavy metal micronutrient, such as Zn, Cu and Cr. The initial positive effect of increasing concentration reaches a critical concentration (A) after which there is no further benefit but also no negative effects. As concentration is increased beyond this point, a second critical point (B) is reached, after which further increases in concentration have a negative effect. The biological response of increasing concentration of non-essential heavy metals such as Pb, Hg and Cd is shown in the bottom graph in Figure 2. Increasing the concentration of the heavy metal initially has no effect, the organism can tolerate increases in concentration until the critical point (A) is reached. At this point, subsequent increases in concentration with have a negative effect on the organism. The response graphs shown in Figure 2 are simplistic and do not consider the possible additivity effects of two or more metals in the system (see Jak, 1998). However, they do illustrate the fact that several heavy metals are essential to living organisms and they also show that there is a threshold concentration above which living organisms can neither use or tolerate heavy metals. It is the 'no effect' area of the graphs, A-B (top) and <A (bottom), which must be quantified in order that critical limit values may be set.

The presence of two or three heavy metal species acting together on a component of the ecosystem may lead to synergistic or antagonistic effects (Kraak *et al*, 1993). Upon further additions of differing metal species these effects probably cancel each other out, but it has been shown by Jak (1998) that multiple additions of metals will exhibit additive toxicity in zooplankton communities. Jak (1998) also states that ecological implications are induced by direct toxic effects on the species level, so that protection of the most sensitive species will ensure protection of functioning and structure of the ecosystem. This has implications in defining critical loads for metals and will be developed later.



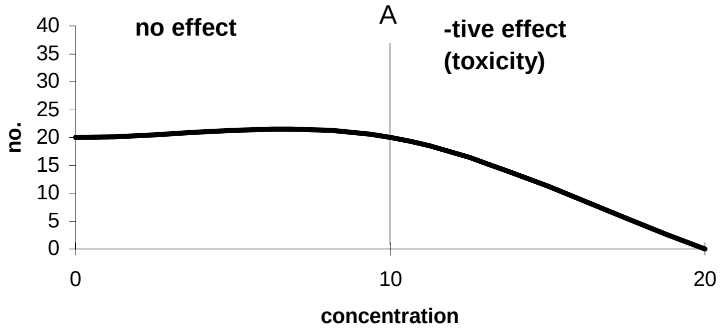


Figure 2 The biological response of increasing concentrations of essential heavy metal micronutrients (top) and of non-essential heavy metals (bottom)

The ability of an organism to accumulate heavy metals to concentrations one or more orders of magnitude greater than concentrations in their food is defined as bioaccumulation and is the net accumulation of metals from biotic and abiotic sources. In contrast to many organic compounds, metals in their elemental form cannot be metabolised and so, from animals, the only method of removal is by excretion. Metals therefore have the potential to accumulate in the body, potentially leading to acute and chronic effects. The bioaccumulation factor (BAF) is an expression of the relationship between the concentration of a metal in the tissue of an organism and that in the surrounding air or water. This ratio depends on rate of uptake and rate of loss and is largely dependent on bioavailability and tissue type (AMAP, 1998). Bioaccumulation, however, is not consistent between individuals of the same species as other factors such as feeding habits and physiological condition also have an effect. In addition, metals can biomagnify by progressive accumulation through successive trophic states, again this is not a straightforward matter and depends upon feeding habits. Muir *et al* (1992) investigated biomagnification in the Arctic foodchain (often through five stages) and found significant Cd biomagnification between cod and birds, seals and whales but low values between polar bears and ringed seals because polar bears prefer to eat seal blubber which is low in cadmium. The cadmium had largely accumulated in the seals liver and kidneys. It is always important to determine metal concentrations in the same organs of different animals when trying to observe biomagnification.

Taylor (1983) reviewed over 40 studies of biomagnification in marine and freshwater foodwebs and found no tendency towards higher concentrations in the predators, indeed concentration factors for the invertebrates were higher (<100) than those of the predators (<20). Although there is no evidence of biomagnification in the foodwebs studied by Taylor (1983), a metal transfer to predators is possible and may lead to harmful levels in the tissue and to toxic effects (Dallinger *et al*, 1987).

In contrast to the synergistic effects observed by Jak (1998), metal species which are initially toxic may be modified within an organism into a relatively benign form through interactions between metals or through biotransformation (AMAP, 1998). The following is a list of factors influencing metal toxicity to organisms (after Bryan, 1976).

Forms of metal in water	Inorganic/ organic	Soluble	Ion Complex ion Chelate ion Molecule
		Particulate	Colloidal Precipitated Adsorbed
Presence of other metals or poisons	Joint action No interaction Antagonism		More-than-additive Additive Less-than-additive
Factors influencing physiology of organism and possibly form of metal in water		Temperature pH Dissolved oxygen Light Salinity Water hardness	
Condition of organism		Stage in life history (egg, larva etc.) Changes in life cycle (e.g. molting, reproduction) Age and size Sex Starvation Activity Additional protection (e.g. shell) Adaptation to metals	
Behavioural response		Altered behaviour	

1.8.1 **Selected specific toxic effects of heavy metals on biota**

A number of environmental physico-chemical parameters can influence the toxicity of individual metals on specific species. The following information should be viewed as a guide to the potential toxic effects of metals only and is not exhaustive. Toxicity information for Hg, Cd and Pb is taken from AMAP (1998). Data for Cr, Cu, Ni and Zn are from several sources and referenced individually.

Metal	Species	Exposure	Toxic effect
Hg	**Plants**		
	Macro algae (*Laminara hyperborea*)	High conc. inorganic Hg	reduced gametophytic germination
	Red algae (*Plumaria elegans*)	acute	50% growth reductions
	Water cabbage (*Pistia stradiotes*)	various levels	increasing levels of free amino acids, decreasing chlorophyll content, protein, RNA and enzyme act.
	Invertebrates		
	Larval Shrimp (*Palaemonetes vulgaris*)	acute	reduced post-larval survival, delayed molting, extended development time
		high	reduced cardiac activity and oxygen consumption,

	Adult crabs (*Carcinus maenus*)		perhaps also loss of ability to osmoregulate
	Fish	sublethal	depressed olfactory response and osmoregulatory imbalance
	Rainbow trout (*Salmo gairdneri*)	sublethal	reduction in haemoglobin, body weight and body protein
	Roach	inorg. Hg	various symptoms, however unrepresentative of other birds
	Birds		
	Gallinaceous spp.	sublethal org. Hg	impaired co-ordination, ataxia, degeneration of cerebellum
	red-tailed hawk (*Buteo jamaicensis*)	sublethal org. Hg	neurological impairment, reproductive effects and weight loss. Concs. above 30 μg g^{-1} in liver/kidney and 2-3 μg g^{-1} in eggs may result in a detrimental effect in birds.
	Birds (general)		
	Mammals		
	General	various	neurotoxin (severe behavioural disturbance), damages reproductive capacity
	mammalian liver/kidney	25-60 μg g^{-1}	general risk concentration
	Humans	High (methyl Hg)	severe symptoms; neurological disorders, deafness, numbness of limbs, eventual death (e.g. Minamata disease)
Cd	**Plants**		
	Floating macrophytes (*Lemna minor* and *Salvina natans*)	high	Growth red^n and loss of Chlorophyll-A
	White pine (*Pinus strobus*) and Red maple (*Acer rubrum*)	high	inhibition of needle expansion interveinal chlorosis, leaf stunting, wilting, death
	Invertebrates		
	Shrimp (*Palaemonetes pugio*)	40 μg g^{-1} (body burden)	Inhibits molting growth red^n and reproductive impairment
	Nematodes	sublethal	growth of alevins inhibited
	Fish		development of fractured vertebrae
	Atlantic Salmon (*Salmo salar*)	sublethal	inhibition of enzyme activity, hypoglycemia
	Minnow (*Phoxinus phoxinus*)		renal damage
	Other species	various chronic	
	Birds		
	Wild pelagic seabirds	60-480 μg g^{-1} (body burden)	cell necrosis, mitochondrial swelling, tubulorrhexis
	Other	95-240μg g^{-1} (kid)	renal damage and lung emphysema
	Mammals		
	Humans	100-200 μg g^{-1} (kid)	renal damage
	Rats	188μg g^{-1} (liver)	liver cell morphology damage

Pb	**Terrestrial plants** (e.g. lettuce, carrot)	>0.005 mg L^{-1}	red^n in respiration/photosynthesis/growth rate
	Invertebrates		
	Mussels (*Mytis edulis*)	high	Storage of Pb in membrane-bound vesicles
	Oyster (*Crassostrea gigas*)	>0.01 mg L^{-1}	reduced larval development
	Fish General	Chronic	Sublethal effects on morphology and enzyme activity
	Birds Mallard ducks (*Anas platyrhynchos*)	high	lethargy, weakness, anorexia, anaemia
	Mammals General	sublethal	hematopoietic, nervous, gastrointestinal, renal,
Zn	**Invertebrates**		
	Freshwater snail (*Leptoxis praerosa*)	sublethal concs.	physiological changes (Reed-Judkins *et al*, 1998)
	Snail (Biomphalaria	0.5 mg L^{-1} (pH 7.3)	

	glabrata)	1.0 mg L^{-1} (pH 7.3) 1.5 mg L-1 (pH 7.3)	reduction of fecundity and growth rate delayed hatching of embryos 60% of juveniles / 20% of adults died within 33 days (Munzinger and Guarducei, 1989)
	Fish		
	Rainbow trout (*Salmo gairdneri*)	671 μg L^{-1} (pH 4.7) 97 μg L^{-1} (pH 5.7) 66 μg L^{-1} (pH 7.0)	LC$_{50}$ (96 hr) LC$_{50}$ (96 hr) LC$_{50}$ (96 hr) (Cusimano *et al*, 1986)
Cr	**Plants**		
	Floating macrophytes (e.g. *Lemna* and *Spirodela*)	10 mg L^{-1}	growth inhibition (e.g. Jana, 1988)
	Insects		
	Mayfly (*Ephemerella subvaria*)	2 mg L^{-1}	LC$_{50}$ (96 hr)
	Caddisfly (*Hydropsyche betteni*)	64 mg L^{-1}	LC$_{50}$ (96 hr) (Warnick and Bell, 1969)
Cu	**Plants**		
	Diatoms (*Synedra tenera*)	<100 μg L^{-1}	frustule deformation
	(*Fragilaria crotonensis*)	“	death
	(*Cyclotella comensis*)	“	death (Ruggiu *et al*, 1998)
	Invertebrates		
	Freshwater snail (*Leptoxis praerosa*)	sublethal concs.	physiological changes; altered cellulolytic enzyme activity (Reed-Judkins *et al*, 1998)
	Chironomid (*Chironomus decorus*)	0.74 mg L^{-1} (water pH 7-7.8) 5.80 mg Kg^{-1} (in sediment)	LC$_{50}$ (48 hr) LC$_{50}$ (72 hr) (Kosalwat and Knight, 1987)
Ni	**Plants**		
	Blue-green algae (*Anabaena cylindrica*)	>600 μg L-1	unaffected (Spencer and Green, 1981)
	Insects		
	Mayfly (*Ephemerella subvaria*)	4 mg L^{-1}	LC$_{50}$ (96 hr)
	Stonefly (*Acroneuria lycorias*)	33.5 mg L^{-1}	LC$_{50}$ (96 hr) (Warnick and Bell, 1969)

1.9 **Air quality legislation**

In the United Kingdom, as a requirement of the 1995 Environment Act, it is the responsibility of the Secretary of State to prepare and publish a National Air Quality Strategy. This Strategy is being developed to control and improve the quality of air and has been developed from two main themes; firstly from the principles advocated at the United Nations Conference on Environment and Development at Rio de Janeiro, 1992 (the “Earth Summit”) and secondly, the recent improvements in understanding of air pollution and measures required to tackle it.

For metals, lead is seen as a priority pollutant in the Strategy, due mainly to widespread concern over public health and the relative ease with which levels can be reduced. Other heavy metals may be included in the future revisions of the Strategy through requirements of the EC Air Quality Framework Directive (96/62EC).

Earlier air quality legislation introduced in the UK , such as the Clean Air Acts of 1956 and 1968 and the Control of Pollution Act (1974) did much to reduce pollution from smoke and sulphur dioxide in industrialized urban areas of the UK. However, until the UK entered the EU in 1973, air pollution measures tend to have been carried out by using ‘best practicable means’. Indeed, the Royal Commission in 1976 recommended that air quality standards advocated by the EC should be rejected in favour of non-mandatory air quality guidelines. It was not until 1980 that the UK accepted the introduction of EC air quality standards (Elsom, 1992) Air quality standards give clear targets that a country should try to achieve and require a proactive approach by member states and need a nationwide monitoring scheme to assess compliance. In addition to air quality standards, the EC has defined stricter air quality standards (‘guide values’) which are non-mandatory but may indicate the future direction of policy. The UK has decided that legislation in place at the moment (including the 1990 Environmental Protection Act and, the 1995 Environment Act) are sufficient to provide the required compliance.

On a European level, member states of the EU must take steps to implement legislation which is adopted by a qualified majority in the Council of Ministers which effectively removes the power of veto for individual states (Elsom, 1992) This should ultimately provide a unified approach to atmospheric protection on a European level and reduce trans-boundary pollutants. However, for less-developed states in Eastern Europe, and in Asia there is much to be done to reduce emissions.

Recently, at Aarhus, Denmark on 24 June 1998, the United Nations Economic Commission for Europe (UNECE) agreed various protocols to reduce air pollution. Included in this agreement was the Heavy Metals Protocol, specifically meant to address emissions of atmospheric cadmium, lead and mercury but also with provisions for adding other metals and controls in future. The Metals Protocol will need to be taken into account when setting any objectives for heavy metals (Cd, As, Ni, Hg) covered by the forthcoming Air Quality Daughter Directives. (DETR, 1999). However, in order that any agreed reductions in metal emissions can be successfully achieved there is a need for a European metals-based atmospheric monitoring and modelling programme.

The EMEP programme (Co-operative Programme for Monitoring and Evaluation of Long Range Transmission of Air Pollutants in Europe) has provided partner states with regular information on the emissions and the spatial distribution and temporal variation of concentrations and depositions of air pollutants, as well as on the quantity and significance of long range transport across boundaries (EMEP, 1997). This has been a useful tool in assessing compliance with protocols designed to reduce emissions of acidifying compounds and photochemical oxidants. The Sofia Protocol (1988), includes agreed emission reductions of NO_X and later the Oslo Protocol (1994), included further agreements on reductions in sulphur emissions. The EMEP programme and the developed LRTAP (Long Range Transport of Atmospheric Pollutants) model has been essential in ensuring compliance with agreed reductions of acidifying compounds.

Modelling of atmospheric metals transport and deposition over the EMEP network has been carried out using the Heavy metals model (HMET) developed by the Meteorological Synthesizing Centre - West (MSC-W) of EMEP. The HMET model can be used to model the transport and wet/dry deposition of As, Cd, Pb, Zn and Hg. Rovinskii *et al* (1994) have developed another numerical model which uses EMEP data to study the transport and deposition over the EMEP area. The uses and results of selected European modelling programmes will be discussed in Chapter 2.

1.10 **The basis of the Critical Loads concept**

A Critical Load is the term given to the amount of pollutant deposition an ecosystem can sustain without damage (CLAG, 1995). The term was first used in the acidification debate of the 1980s to quantify the effective load of acid deposition to a site to a point where noticeable changes occurred. The data produced as a result were used, in conjunction with other European data, to calculate sulphur emission reduction targets which were agreed in the 'Oslo Protocol' in June 1994.

The principles of critical loads are relatively straightforward. Datasets of information obtained through sampling/analysis and databases on environmental media such as soils, geology, freshwater and vegetation are amassed and then used in combination with data relating to the effect of the individual pollutant on that medium. Computer models of the pollutant impact can then be made to assess the extent of damage and to highlight vulnerable areas. In this way, critical loads can be used as a predictive tool and to illustrate potential detrimental impacts of pollution.

The critical loads approach and methods could be successfully applied to metals in the future. However, receptor organisms and effects-based critical limits for specific organisms needs to be further refined as does the question of additive toxicities (UN ECE, 1998).

1.11 **Related research**

Currently, as part of a DETR-funded project, Imperial College London are undertaking a project which is concerned with the development of a critical loads methodology for toxic heavy metals (contract no. EPG 1/3/85 (AQ 17/8/267). The aims of this project are to;

1. To critically review existing critical load methodologies for toxic heavy metals (Cd, Pb, As and Zn) and assess their applicability to the UK.

2. To collate datasets on the distribution of metals in stream sediments and to review factors which influence the environmental pathways in different soil types. Eventually incorporating these factors into a national GIS
3. Use field data and experimental studies to assess critical concentrations of each metal in soils and freshwater.

To develop a GIS system in which UK data on land cover, climate, soil properties, metal deposition and current metal concentrations in soil and stream sediments can be overlain to map critical loads.

(DETR, 1999c)

The above project will seek specifically to develop the critical loads concept for heavy metals in a UK context with the aim of eventually mapping critical loads. In addition, this project is also part of the NERC-funded Environmental Diagnostic programme. The programme however does not currently include the toxic heavy metals; nickel and mercury which are to be included in the forthcoming EC Air Quality Daughter Directive. This is unfortunate as it is likely that critical load based control strategies will be used in subsequent emission reduction legislation.

The main aim of this study differs from that of the critical load methodologies project in that this study will specifically focus on reviewing UK monitoring in rural upland areas to identify potential deposition trends with respect to impacts upon freshwaters. Furthermore, as upland areas are dominated by atmospheric inputs of heavy metals and, as these areas often have a shallow soil cover it is thought that freshwater lakes and streams will be important receptors of deposited metals in these locations. This study will attempt to identify the most suitable means of monitoring heavy metal deposition in upland and remote areas for inclusion into a critical loads methodology. There are, however, areas of commonality between both projects including assessment of deposition trends and heavy metal toxicities.

Chapter 2: Review of Atmospheric heavy metal monitoring: results and modelling

2.1 **Types of monitoring programmes.**

2.1.1 **Active monitoring of atmospheric deposition.**

There are three main methods of monitoring metals in atmospheric deposition:

1. Sampling of airborne dust/aerosol particulates
2. Sampling of rain (wet + dry deposition)
3. Sampling of dry deposition

(1) involves drawing air with the aid of a pump though a filter paper (e.g. Whatman 40, 6 cm), held in a duct. The inlet nozzle should face downwards to avoid the intake of rain and the pump flow rate should be set to ensure that only particles of smaller than 150 μm are drawn into the duct. A plastic backing mesh (1.5 mm) is placed behind the filter paper to prevent collapse of the paper The volume of air drawn through is registered by a gas meter
(2) involves collection of rainwater at intervals (e.g. weekly, monthly) in a polythene funnel and acid-washed bottle. The filter should be covered with a terylene mesh to exclude insects etc. and the collection bottle should be enclosed in a black bag to inhibit growth of algae. The sample collected is total deposition (wet+dry)
(3) involves mounting a filter paper (e.g. Whatman 541) horizontally in a perspex frame. Cover from the rain is provided by a large sheet of perspex (~1 m^3) about 12 cm above the filter paper.
(above sampling methods from Cawse, 1974)

More complex automated sampling devices can be used to monitor selected components of air with a higher time resolution than more traditional methods. An example is the Versatile Air Pollution Sampler (VAPS). VAPS can be used to discriminate between particle size of the sample, capturing both fine and coarse particle fractions for analysis. The greater flexibility of sample discrimination with systems such as VAPS can be extremely useful in development of source-receptor modelling. A description of the VAPS system and usage in monitoring aerosol and acidic gas samples for a source apportionment study is given by Pinto *et al* (1998).

A fully-automated gas-phase Hg monitoring device utilising exchangeable adsorbant traps with fluorescence spectrometry has been used by Lee *et al* (1998). The system gives good detection limits comparable with other methods (Edinghaus *et al*, 1996) and high time resolution.

For real-time detection and monitoring of hazardous air pollutant metals, Seltzer and Meyer (1997) have developed the use of an Inductively Coupled Argon Plasma (ICAP) continuous emission monitor. This system has applications in industrial emissions monitoring and in heavily polluted urban areas, and at present will only provide a limit of detection (LOD) between 0.1 and 20 μg m^{-3}. Although having a better LOD than previous continuous emissions monitoring systems the LOD is still around three orders of magnitude higher than what would be required in rural air monitoring programmes.

The choice of sampling method should be selected to fulfill the requirements of the work. The methods outlined above provide a continuous record with sampling frequencies as long or short as required. It is however relatively labour intensive and expensive to maintain. Furthermore, continuous deposition monitoring of certain elements can be troublesome in rural locations if element concentrations are very low (Berg *et al*, 1995)

2.1.2 **Passive biomonitoring of metals**

Other methods of monitoring include the sampling and analysis of biological materials to provide indirect records of atmospheric deposition. The assumption being, that certain plant/animal species will adsorb and accumulate metals in proportion to that in atmospheric deposition (which have been deposited), and thus can act as living indicators of pollution. Various species groups have been used for biomonitoring purposes including mosses, lichens, tree bark and needles and peat.

Certain moss species are particularly good because they obtain their nutrients directly from precipitation and from the impaction of airborne particulates. Mosses also have a high capacity to retain metals from solution and a carpet of living moss tissue, which is built up over a 3-5 year period, reflects an integrated measure of atmospheric deposition during that period (Berg *et al*, 1996). This means that the concentrations of heavy metals in mosses may be assumed to correlate closely with heavy metal deposition (Herpin, *et al*, 1996). Metals are also strongly concentrated in mosses when compared with metal levels in precipitation, especially the very low concentrations found in precipitation from rural areas, and as such, the problem of low analytical detection limits can be reduced (Steinnes, 1995). For critical evaluations and interspecies comparisons for the use of moss as a biomonitor of heavy metals see Steinnes (1995) and Wolterbeek *et al* (1995).

The following is a list of moss species which have been used as heavy metal biomonitors;

- *Hylocomium splendens* (e.g. Berg *et al*, 1995; Markert *et al*, 1996(a); Herpin *et al*, 1996; Berlekamp *et al*, 1998, Rose and Harlock, 1998)
- *Pleurozium schreberi* (e.g. Rose and Harlock, 1998; Bowman and Harlock, 1998; Brumelis *et al*, 1997; Berg *et al*, 1996)
- *Isothesium stoloniferum* (e.g. Pott and Turpin, 1998)
- *Hypnum cupressiforme* (e.g. Markert *et al*, 1996(b))
- *Sphagnum papillosum* (e.g. Gstoettner and Fisher, 1997)
- *Sphagnum auriculatum* (e.g. Vasconcelos and Tavares, 1998)
- *Fontinalis antipyretica* (e.g. Bruns *et al*, 1997)

Moss samples, taken from a herbarium, have also been used to retrospectively infer deposition concentrations of heavy metals. Herpin *et al* (1997) analysed moss taken from several locations in Germany between 1845 and 1974 to determine a record of deposition for As, Cd, Cr, Cu, Pb, Ni, V and Zn.

Lichens are also sensitive and useful heavy metal biomonitor species because, like mosses, they obtain their nutrients from the atmosphere and have a widespread coverage in rural areas (see Nash and Gries, 1995; Jeran *et al*, 1996; Poblet *et al*, 1997 and Loppi *et al*, 1997). However, as the annual growth increment is usually easier to distinguish for mosses, they are considered superior to lichens if any time resolution in the measurement is desirable (Steinnes, 1995).

Other compartments such as eggshells (Ormerod and Tyler, 1994) and mammal species (Sawicka-Kapusta and Zakrzewska, 1998) have also been used to determine the occurrence of heavy metals in the environment, although not specifically from atmospheric deposition.

2.1.3 **Monitoring using sediment trapping methods**

It was stated in section 1.7.2 that deposition of metals into lake systems would provide, through time, a historical record of pollution inputs. This principle can be adopted and used in routine deposition monitoring through the use of traps submerged in lakes to capture sedimenting material (e.g. Hamilton-Taylor *et al*, 1984).

2.1.4 **Surface water monitoring**

The concentrations of chromium in surface waters and rainfall has been compared by Neal *et al* (1996) and it was found that there was a delayed response between deposition to catchment (via rainfall), and removal from catchment. In rural locations with no direct source heavy metal inputs, any increases above background will be due to atmospheric inputs. Steinnes and Henriksen (1993) have found that Zn concentrations in water from small Norwegian lakes correlated well with atmospheric inputs (determined by analysis of *Hylocomium splendens*).

Surface water samples can be used to determine atmospheric metal inputs but background concentrations, storage of metals within the catchment soils and vegetation and also of hydrologic flow regimes which affect the water chemistry must be taken into account.

2.2 **Review of UK monitoring**

2.2.1 **Long-term programmes (> 2 years)**

1. **A study of atmospheric trace elements in Great Britain 1972-present.** A long-term survey at three rural sites in the UK managed by the National Environmental Technology Centre (NETCEN), part of AEA Technology. Sites are located at; Chilton (Oxon.), Styrrup (Notts.), Windermere (Wraymires, Cumbria). Four other sites were also monitored until 1978, they were; Trebanos (West Glamorgan) Leiston (Suffolk), Collafirth (Shetland) and Plynlimon (central Wales). Particulates and rainwater are collected monthly at each site and are bulked to provide quarterly analysis for 35 elements in the particulate fraction (including the heavy metals Cd, Cr, Cu, Hg, Ni, Pb, V and Zn) and 25 elements in the soluble form (including the heavy metals Cd, Cr, Cu, Hg, Ni, Pb, V and Zn) in addition to pH and sulphate and nitrate. (see Cawse, 1974; Cawse *et al*, 1994 and Baker, 1997).

2. **Multi-element network** (Cd, Cr, Cu, Se, Mn, Ni, Pb, Zn (at all five sites) and V (at Westminster only)) at five urban locations throughout the UK - Strathclyde (Glasgow and Motherwell), Greater London (Brent and Westminster) and West Yorkshire (Leeds). Samples are collected on 0.8μm pore filter paper over a 1 week period, at a flow rate of 3 litres min^{-1}. The M-E network is managed by NETCEN (AEA Technology) and has been operating since 1976. (See 11.) Originally, a total of 16 elements including arsenic, cobalt, germanium, beryllium, molybdenum, antimony and titanium were monitored as part of the multi-element network. However, as concentrations found were generally below the limit of detection and limits of detection were well within the occupational exposure limits (OELs) of these elements, monitoring was ceased.

Annual mean heavy metal concentration in air from the five multi-element sites, in addition to one other in Central London are available via the DETR website at http://www.environment.detr.gov.uk/airq/aqinfo.htm or directly from the AEA Technology (NETCEN) website at http://www.aeat.co.uk/netcen/airqual/. Data available through the World Wide Web includes the years 1980-1998.

3. **North Sea Network** (priority parameters; Hg and Cd. Grey List; Cr, Pb, Cu, Ni and Zn determined in precipitation (wet+dry deposition) and gas/aerosol). Designed to assess the atmospheric inputs to the North Sea, to meet the UK commitments to the Paris Commission (OSPARCOM 1996 and OSPARCOM, 1997). The three sampling locations are situated on the east coast of Britain, they are; Banchory (Aberdeenshire), High Muffles (North Yorkshire) and East Ruston (Norfolk), and a further site located at Lough Erne, Northern Ireland. These sites and the network are managed by NETCEN. Particulates in air samples are collected by drawing air at a rate of 6 litres min^{-1} through a filter paper (Whatman 40, 6 cm dia.), held on a polypropylene duct with the inlet facing downwards. The network is managed by NETCEN and has been running since 1986.

4. **Industrial Areas (Pb monitoring)** There are three areas currently monitored with a total of eight sampling locations. The areas are Newcastle Upon Tyne (Elswick works) and Walsall (IMI and Brookside). Selection was made after small, short term studies prompted further investigation. The monitoring has been ongoing since 1985 and 1988 (with start date depending on location) until present and is managed by NETCEN.

5. **Lead in Petrol** (Pb monitoring in air) Initiated in 1983-84 at eight sites (two rural, three urban and three kerbside) to monitor the effect of the reduction in use of leaded petrol. There are currently seven sites operational and they are located at; Eskdalemuir (rural), Cottered (rural), North Tyneside (urban), Newcastle (urban), Cardiff (kerbside), Manchester (kerbside) and Kensington, London (kerbside). Again, the network is managed by NETCEN.

Information regarding the above networks is given in AEA (1996). Further information relating to the above monitoring networks (1-4) is shown in Appendix 1.

6. **LOIS (Land-Ocean Interface Study)** LOIS was set up to study the interaction between the land and sea, specifically the catchment area of the east coast of Britain draining into the North Sea. There has been some work on atmospheric deposition of metals for LOIS carried out at Auchencorth Moss, Southern Scotland by Fowler *et al* (1996) which monitored one rural site during 1995. The Auchencorth Moss work has been the only atmospheric heavy metal deposition data used in LOIS and will be described in 2.2. LOIS is funded in the UK by the

National Environmental Research Council (NERC) and forms part of a larger worldwide research project; LOICZ (Land-Ocean Interaction in the Coastal Zone) instituted by the International Geosphere-Biospere Programme (IGBP).

7. **OSPARCOM** (Oslo and Paris Commission) under the Comprehensive Atmospheric Monitoring Programme (CAMP). Heavy metals data for precipitation, aerosol and gas and wet and dry deposition have been collected from three coastal sites in the UK. This monitoring is analogous to that described in (3) The North Sea Network and is carried out by NETCEN.

8. **Dissolved Cr pollution in rainfall and surface waters in Mid-Wales during the mid-1980s** (Neal *et al*, 1996) Monitoring programme in Wales since 1983. Initially recording bulked weekly rainfall and stream water data but also throughflow and stemflow from 1984-1992 to allow a more thorough assessment of atmospheric inputs to the catchment.

9. **Atmospheric concentrations of trace elements in urban areas of the UK** (Lee *et al*, 1994) Airborne aerosol trace metal (including the heavy metals; Cd, Cr, Hg, Ni, Pb and Zn) concentrations monitored at seven sites. Monitoring began from early to late 1970s until 1989 at Walsall, Lambeth, Brent, Manchester City-North, Manchester City-South, Altrincham, Flixton, Wraymires (rural), Chilton (rural). The latter two sites are part of the UK rural network and are included to highlight differences between urban and rural data.

10. **Environmental Change Network (ECN)** (Lane, 1997) A network of 42 freshwater (26 river and 16 lake) sites throughout the United Kingdom, including 2 river and 3 lake sites which are also part of the Acid Water Monitoring Network (AWMN), see 3.3 and Patrick *et al* (1991). A large number of chemical and biological parameters are measured from samples taken monthly from rivers and quarterly from lakes. Included in these parameters are the following heavy metals Ni, Hg, As, Pb and V (total; $\mu g\ L^{-1}$) and Cd, Zn and Cu (dissolved; $\mu g\ L^{-1}$). The ECN sites have widespread UK geographical coverage and it would be expected that some of the rural, more remote ECN sites far from point sources would be able to identify inputs of atmospheric heavy metal pollution. pH data is available at each site and this is of interest when used is conjunction with heavy metal data. (ECN, 1999). Determination of specific heavy metals varies between sites, however, the list of determinands is as follows; Cd (dissolved), Hg (total), Hg (dissolved), Pb (total), Pb (dissolved), Cu (total), Cu (dissolved), Ni (total), Ni (dissolved), V (total), V (dissolved) and As (total). Length of sampling period is also variable with the earliest data available from 1994. See Appendix 2 for information on the locations of ECN sites.

11. **Multi-element survey: Summary and trend analysis 1976/7 - 1988/9**. McInnes (1992) A report on 12-years of the UK multi-element survey as described in (2) above.

12. **Bulk deposition monitoring for Cd, Cu, Ni, Pb and Zn at two sites in Northern England**. (Lawlor, pers. comm.) A deposition monitoring study carried out by the Institute of Freshwater Ecology Windermere at Great Dunn Fell on the Pennines and at the River Duddon in the Lake District. This work is ongoing, but due to end in April 1999. At the moment, however, no data are available.

13. **Atmospheric deposition monitoring at Lochnagar, northest Scotland**. An AWMN, ECN and MOLAR site also sampled as part of a PhD project (Yang, 1999) at UCL. Atmospheric deposition samples have been routinely analysed since July 1996 for heavy metals (Cd, Pb, Co, Cu and Zn), in addition to intensive research on heavy metal budgets within the catchment. Ensis Ltd. manage research at Lochnagar. (see also 2.8 for further details).

14. **A survey of heavy metal deposition in England and Wales**. (Alloway, 1998 and Alloway *et al*, 1998) Deposition monitoring of heavy metals at sites in England and Wales carried out between March 1995 and August 1997 for the Ministry of Agriculture, Fisheries and Food (MAFF). The aim of the project was to assess inputs of heavy metals to land from various sources, including sewage sludge, animal manures, fertilizers and lime, agrochemicals and irrigation water, in addition to atmospheric inputs. The objectives of the atmospheric component of this research were:

- to determine the extent of the deposition of selected heavy metals from the atmosphere as part of an inventory of inputs to agricultural land;
- evaluate regional and temporal variations in deposition;
- investigate any links between measured deposition and soil composition at monitoring sites;
- attempt to identify the sources of significant depositions of elements at selected sites.

Deposition sampling was carried out using ‘inverted frisbee’ collectors at 36 locations throughout England and Wales with a bias towards lowland arable and grazing compared with upland rough grazing and forest (see Appendix 3 for locations of sites and annual average total metal deposition). Samplers were located 1.8 m above ground level and in pairs (duplicates) each fitted with a bird deterrent. Of the 36 sites, one site at Avonmouth, near Bristol was selected within 2.5 km of a large Pb-Zn smelter (a known pollution ’hotspot’), the other sites were selected to meet criteria ensuring that they can be considered as being remote and rural. The deposited material was collected monthly and comprised wet + dry deposition. A total of 23 elements were determined, including the heavy metals; As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, V. Aliquots of filtrate were analysed using ICP-OES and hydride generation/cold-vapour AAS for As and Hg. Membrane filters containing the insoluble residue were dissolved in *aqua regia* and aliquots analysed using ICP-OES and hydride generation/cold vapour AAS techniques.

2.2.2 UK Short-term Programmes (not exceeding 2 years) and biomonitoring

1. **Trace elements in daily collected aerosols at a site in Southeast England** (Yaaqub *et al*, 1991) 13 components of aerosol samples, including the five heavy metals; Pb, Zn, Cd, Ni and Mn were analysed in daily samples collected over a 1 year period from March 1987 to March 1988 at Hemsby, a rural site 50 km from Norwich, Norfolk. The study has identified primary and secondary pollution sources and has highlighted the three main sources of metals as being anthropogenic, crustal and marine.

2. **The atmospheric distributions of trace metals over the North Sea for a 15-month period** (Chester *et al*, 1993) Aerosol and rainwater samples were collected on board the *RMS* Challenger over a 15-month period from August 1988 until October 1989 at various locations on the ship's track throughout the southern North Sea. The results of the study show that there are three main source components namely; anthropogenic, crustal and marine and concluded that in the North Sea atmospheric deposition is a major source of metals and that both 'dry' and 'wet' deposition sources are important. In addition, air masses moving over the North Sea from continental Europe are richer in some trace metals (e.g. Zn and Pb) than air masses which have crossed the UK. However, during the study period air masses were predominantly moving from west to east over the British Isles in prevailing UK conditions. (see also; Chester and Bradshaw, 1991 and Ottley and Harrison, 1993)

3. **Gas-phase mercury in the atmosphere of the United Kingdom** (Lee *et al*, 1998) Total gas-phase mercury was measured over a period of 10 months (June 1995 to April 1996) at Harwell, a rural site in central southern England. An automated mercury vapour analyser (cold-vapour atomic fluorescence adsorption technique) which could analyse with a time resolution down to five minutes and had a limit of detection below 0.2 ng m^{-3} was used. A background concentration of 1.5 ng m^{-3} was observed (a low value not larger than a rural location in Ireland). A diurnal cycle in concentrations was also seen indicating a specific surface source emitting ~15 ng m^{-3}. The role of two fossil fuel plants located in the 30° wind sector was suggested but not confirmed using meteorological data and sulphur dioxide as a marker.

4. **Spatial distribution of trace metals in lake sediments and catchment mosses in the UK, 1994** (Rose and Harlock, 1998). Indicator mosses (*Hylocomium splendens* and *Pleurozium schreberi*) were sampled during 1994 and analysed for the trace metals; Cd, Cu, Pb, Ni, V and Zn. A total of 75 lake sites were selected (66 in Great Britain and 9 in Northern Ireland). The above study was part of the Fly Ash and Metals in Europe (FLAME) project, funded by EU

COPERNICUS. Lake surface sediment samples were also taken from each site and analysed for heavy metals.

5. **The analysis of trace metals in surface waters from Scotland and Wales** (Rose *et al*, 1997) A spatial study of trace metal in 188 lakes sampled over 1995/6 to determine concentrations of Hg, As, Se, Be, V, Cr, Co, Ni, Cu, Zn, Mo, Ag, Cd, Sb, Ba, Tl, Pb and Bi. Principal components analysis (PCA) was used to determine any patterns in the data.

6. **Measurement of heavy metals in wet + dry deposition at Auchencorth Moss, Southern Scotland from December 1994 until February 1996** (Fowler *et al*, 1996) A 14-month study determining concentration fluxes of Pb, Cd, Cu, Cr, Zn and Ni (in addition to other atmospheric pollutants) atmospherically deposited to an area of blanket bog. The site was selected to be representative of Northwestern Europe and ecosystems which were subject to low concentrations of the major pollutants.

7. **Monitoring of atmospheric heavy metal deposition in Europe using bryophytes: UK Survey.** (Parry and Williams, 1998) This national heavy metal monitoring programme commissioned by the DETR was carried out by Imperial College London. Samples of terrestrial mosses (*Pleurozium schreberi* and *Hylocomium splendens*) were taken from over one hundred locations in England, Scotland and Wales over the period November 1997 - April 1997. The methodology used followed that of the European surveys of metal distribution (Berg *et al*, 1995b) and the data produced comprises the UK component of the Atmospheric Heavy-Metal deposition to Europe programme carried out every five years. The total area of mainland England, Scotland and Wales (231,000 km^2) was divided into 200 squares, each measuring 34 x 34 km, providing coverage equal to one sample per 1.2 km^2. Due to the uncertainties surrounding the extent and abundance of these species in the UK, various agencies such as English Nature, Scottish Natural Heritage and the Forestry Commission were contacted to help identify sites. Of the 206 sites visited, 95 sites had no suitable mosses, leaving just over one hundred samples in the survey. Appendix 6 shows information on the sample type and locations of sampling. After collection, moss samples were digested using nitric acid and analysed using ICP-MS for the following metals; V, Cr, Fe, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Pb, Bi. Results were then sent to the co-ordinator of the European programme.

2.3 **European monitoring/survey of atmospheric heavy metals**

The following are examples of active atmospheric heavy metal deposition monitoring [2.3.1] that has been carried out in Europe with programmes running over the past 10-20 years. In addition, examples of heavy metal biomonitoring [2.3.2] studies carried out in Europe and Scandinavia over the past twenty years are given. The following lists some of this work which has been published within the last five years and gives a brief description of each;

2.3.1 **Active monitoring of metals**

1. **MOLAR Deposition and surface water monitoring at six lake sites throughout Europe** (MOLAR, 1996) Rainfall samples and lake surface water samples are collected and analysed for heavy metals (Pb, Cd, Hg, Cu, Co, Cr, Ni, Mn, V, As and Zn) using ICP-MS. Bulk deposition collectors are sampled every two weeks and surface water samples are taken quarterly. Metals data for rainfall have been collected from October 1996 to December 1997 and for lake waters from July 1996 to April 1998. The site at Lochnagar, however, continues to be routinely monitored. Work package 2 of the MOLAR programme is concerned with measuring and modelling major element and pollutant fluxes in mountain lakes and their impact on fish. The sites where the above determinands are measured are; (1) Lochnagar (Scotland), (2) Lago Redo (Spanish Pyrennes), (3) Gossenkollesee (Austrian Alps), (4) Jorisee (Swiss Alps), (5) Starolesnianske Pleso (Slovakia) and, (6) Ovre Neadalsvatn (central Norway). For further information and data from Lochnagar see 2.8.

2. **Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea** (Mignon *et al*, 1997) An assessment of atmospheric inputs from October 1992 to September 1993. Rainwater and aerosol samples were sampled. In addition, a new method for sampling total deposition (an acidified water trap for total fallout) was used in an attempt to quantify accurately dry deposition values and also dry deposition velocities. An estimation of total annual metallic inputs to the Ligurian Sea has also been made.

3. **A heavy metal monitoring programme in Denmark** (Bak *et al*, 1997) A monitoring programme initiated in 1990 to assess the concentrations of heavy metals (As, Pb, Cd, Cu, Cr, Hg, Ni and Zn) in arable soils. Inputs from various types of land use and from atmospheric deposition are considered. It was found that differences are not found between soils with different land use, atmospheric deposition etc. that renders it possible that the heavy metal content of soil in general is determined by anthropogenic sources. However, it is thought that elevated levels of As, Cd, Cu, Pb and Hg in soil are affected by anthropogenic sources which are most likely to be atmospheric in remote areas without arable agriculture. It was concluded that levels in arable soils and on natural soils do not give rise to concern and that they are low compared with Danish soil quality criteria.

4. **Monitoring of heavy metals in protected forest catchments in Sweden**. (Aastrup *et al*, 1995) Part of a long-term integrated monitoring programme running since the early 1980s which

has included deposition monitoring of Hg, Pb, Cd, Zn and Cu. It has been the aim of this work to assess the fate and effects of pollution on mature ecosystems. The findings suggest that storage of Pb and Hg within the ecosystem is large when compared with the flux and that present day inputs have little effect on the flux. The flux is largely governed by biogeochemical conditions.

5. **Annual atmospheric deposition of 16 elements in eight catchments of the central Barents region** (Chekushin *et al*, 1998) Snow and rainwater samples were used to calculate total yearly deposition rates of 16 metals (including Cd, Cr, Cu, Ni, Pb) at eight catchments in Finland, Norway and Russia through 1993 and 1994. From this study yearly deposition rates have been estimated for each metal.

6. **Czech air quality monitoring and receptor modelling study** (Pinto *et al*, 1998) Analysis of ambient aerosol samples collected at two sites in the Czech Republic from February 1992 through February 1994 and source-characterisation work. Trace elements from Al to Pb were determined in samples and used to develop a source-receptor model. During the period of the study, there were several periods of air stagnation in the Teplice valley leading to very high concentrations of airborne metals (e.g. Pb 456 ng m^{-3}, Zn 616 ng m^{-3}).

7. **Pattern recognition of particulate-bound pollutants sampled during a long-term urban air monitoring scheme** (Armanino *et al*, 1996). Daily collection of ambient atmospheric particulate samples in Bologna, nothern Italy from October 1991 until March 1993. Heavy metals; Pb, Cr, V, Ni and Cd were determined for each sample. An urban study which statistically showed the link between traffic and metal pollution (principal component analysis) and the resulting drop in concentrations upon traffic limiting measures (multivariate plots).

2.3.2 **Biomonitoring surveys of heavy metals**

1. **Long-term changes in concentration and deposition of atmospheric mercury over Scandinavia** (Iverfeldt *et al*, 1995) A comparison of present-day total gaseous Hg levels in air and the total Hg in precipitation with historical data for a site in southwest Sweden. A decrease in yearly average air concentrations and median levels from 1980-1984 to 1990-1992 was observed. Higher concentrations were found in winter and were associated with an increased usage of fossil fuels and an increased mixing height in the atmosphere. Overall decreases in Hg concentrations over Sweden were probably thought to be a result of lower European continental emissions.

2. **A comparison of heavy metal deposition in selected Eastern European countries using the moss monitoring method, with special emphasis on the 'Black Triangle'** (Markert *et al*, 1996) Analyses of moss samples to compare heavy metal pollution (Cd, Cr, Cu, Fe, Ni, Pb and Zn) in Germany, Poland, the Czech Republic and the Slovak Republic. *Pleurozium schreberi*, *Scleropodium purum*, *Hypnum cupressiforme*, *Hylocomium splendens*, *Polytricum formosum* and *Dicranium scoparium* were used. The levels obtained highlighted the technical development of the countries concerned with respect to implementation of emission reduction measures. The study reveals an increase in heavy metal concentrations and higher than average levels in the eastern parts of the countries compared.

3. **Environmental indicators for long-range atmospheric transported heavy metals based on national moss surveys** (Berg *et al*, 1996) A study which uses data from Norwegian national moss surveys of 1977, 1985 and 1990 to look at deposition patterns of Pb and Cd across the country. Samples of *Hylocomium splendens* were taken from 500 sites and analysed by AAS. Long-range atmospherically transported metals were characterised by high concentrations in the south decreasing rapidly with increasing distance from the coast. 1990 Pb levels in the south showed a 30-40% decrease when compared with 1977 levels.

4. **The German heavy metal survey by means of mosses** (Markert *et al*, 1996) *Pleurozium schreberi*, *Scleropodium purum*, *Hypnum cupressiforme* and *Hylocomium splendens* were collected at 539 sites and analysed by ICP-AES and AAS for the elements As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn. The survey illustrated deposition patterns across Germany ranging from more heavily polluted industrialised areas to the relatively unpolluted rural areas. However, expected correlations between the effect of traffic (Pb) and the concentration in moss could not be demonstrated with any certainty.

5. **The distribution of heavy metals in a transect of the three states; the Netherlands, Germany and Poland, determined with the aid of moss monitoring** (Herpin *et al*, 1996) A survey involving the collection of *Pleurozium schreberi*, *Scleropodium purum*, *Hypnum cupressiforme* and *Hylocomium splendens* at 806 sampling locations across three countries and determining levels of Cr, Cu, Fe, Ni, Pb, V and Zn. Specific industrial source characterization was achieved and a steep east-west concentration gradient was found. Information was put into the GIS-system; 'ARC-Info' and contours of concentration were identified which suggested trans-boundary pollution.

6. **Atmospheric metal pollution (Cr, Cu, Fe, Mn, Ni, Pb and Zn) in Oporto city derived from results for low volume aerosol samplers and for the moss *Sphagnum auriculatum*.** (Vasconcelos and Tavares, 1998) A comparitive urban study over two months which sampled for heavy metals using active means of low-volume aerosol monitoring and using bags of exposed moss (exposed weekly). The study showed a positive correlation between both methods, and that exposed *Sphagnum auriculatum* provided a quantitative estimation of the different concentrations of heavy metals in urban atmospheres. During the initial stages of biomonitoring, specific calibration using mechanised monitoring was used. The relative order of the mean concentrations was Fe (1.8 mg m^{-3}) > Zn > Pb > Cu > Cr > Mn > Ni (20 ngm^{-3}). Aerosol concentrations of Pb were also monitored over a longer time period (1991 and 1997) with results showing a 50% decrease from 1996 due to the use of unleaded petrol.

7. **The use of moss, lichen and pine bark in the nationwide monitoring of atmospheric heavy metal deposition in Finland** (Lippo *et al*, 1995) A nationwide biomonitoring programme assessing the usefulness of different monitoring species. Concluded that mosses and lichens can be used to locate source and the extent of the area affected but that accumulation in mosses and lichens was higher than in bark. Despite this, all three media proved to be suitable for use as bioindicators.

8. **The spatial distribution of trace metals in lake sediments and catchment mosses: Ireland**. (Bowman and Harlock, 1998) Moss samples (*Hylocomium splendens* and *Pleurozium schreberi*) were sampled from 36 sites throughout Ireland during 1994 and analysed for the trace metals; Cd, Cu, Pb, Ni, V and Zn. Metal concentrations were found to be of a similar order to those considered to be a European background and unusually high recorded levels could be explained by contamination from catchment geochemistry. Metal moss concentrations were generally in accordance with surface sediment samples collected as part of the survey. The above study was part of the Fly Ash and Metals in Europe (FLAME) project, funded by EU COPERNICUS. Also, as part of FLAME, similar work was carried out in the; (1) **Czech Republic** (Fott *et al*, 1998). Moss samples from only ten locations were taken in the Czech

Republic due to the low occurrence of *Hylocomium splendens* and *Pleurozium schreberi*. Results from these sites, however, did show that the greatest concentrations of metals were seen to the west of Prague and that the lowest concentrations were in the east of the country. (2) **Estonia** (Alliskaar and Punning, 1998). Moss samples were taken at 43 sites and analysed for metals. Results showed that the deposition of atmospheric particulates is of local origin around pollution sources and that Estonia receives a large proportion of its pollution from long-range transport which carries pollutants over the country. (3) see 2.2.2 [4] **UK** research.

2.4 **Example Arctic monitoring programmes**

1. **Regional atmospheric deposition patterns of Ag, As, Bi, Cd, Hg, Mo, Sb and Ti in a 188,000 km^2 area in the European Arctic as displayed by terrestrial moss samples - long range atmospheric transport vs. local impact** (Reimann *et al*, 1997) Moss samples (*Pleurozium schreberi* and *Hylocomium splendens*) taken from northern Finland, northern Norway and northern Russia were collected in summer 1995 and analysed using ICP-MS. The study revealed a sharp concentration gradient from areas of heavily polluted industrialisation in northern Russia (Nickel smelter), towards almost pristine conditions 150-200 km from source.

2. **Post-industrial revolution changes in large-scale atmospheric pollution of the Northern Hemisphere by heavy metals as documented in Central Greenland snow and ice**. (Candelone *et al*, 1995) A study using metals data form snow and ice cores from Summit, Greenland to assess the extent of metals deposition in the Arctic since the onset on the Industrial Revolution. Data has been extrapolated to determine the cumulative deposition flux (in tonnes) for the Greenland ice cap.

See also the work of Steinnes (1995) and Jaffe (1995) for information on metals deposition to subarctic areas and Landers *et al* (1998) for mercury deposition to arctic and boreal ecosystems.

2.5 **Examples of monitoring programmes in America/Asia.**

1. **Airborne lead in the Springfield, Missouri area during a 19-year period** (Sheets *et al*, 1997) Continuous sampling of urban air particulates from 1975-1993 at nineteen locations in Springfield, Missouri. Particulates were collected on glass-fibre filters using high-volume air samplers. The nitric acid-soluble lead was determined using AAS and by differential pulse polarography. Results showed a significant decrease of levels over this period (~90%) which correlated well with decreasing national trends in total lead emissions to the atmosphere.

2. There have been a number of heavy metal surveys utilising lichens as a bioindicator species, for example;

- Distributions of airborne heavy metals as measured in the lichens *Ramalina stenospora* and *Parmotrema praesorediosum* in Baton Rouge, Louisiana. (Walther *et al*, 1990). Metal concentrations in the two lichen species were used to construct contours and metal distribution plots across the study area to prove the effect of an industrial area on air metal concentrations.

- Heavy metal concentrations in a lichen of Mt. Rainier and Olympic National Parks, Washington, USA. (Frenzel *et al*, 1990). Observing uptake of heavy metals in lichen (*Alectoria sarmentosa*) which were emitted from nearby sources.

- Chemical element concentrations in four lichens on a transect entering Voyageurs National Park (Bennet and Wetmore, 1997). Disproved a hypothesis that lichens could not detect chemical pollution over a 24 km transect entering a National Park. Hg, Cd and Cr were measured in samples taken over a three year period. Pollution was detected and the decrease was curvilinear away from the source.

3. **Apportionment of air pollution sources by receptor models in Hong Kong**. (Fung and Wong, 1995) A one year (1986/87) ambient air particulate sampling programme at five locations in Hong Kong. Elemental profiles of these particulates and of coal and fly-ash from nearby industry were used to build a source-receptor model for the area and to apportion pollution to specific sources. Using particle metals data sources were attributed to Zn, Pb and Cd.

2.6 General deposition and airborne concentration trends from UK research

2.6.1 Urban areas

Concentrations of heavy metals in urban air have been measured in the UK multi-element network since 1976 at five locations. Over this time, airborne concentrations of the nine elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) have shown an overall decrease throughout the network and a decrease at most individual sites. Table 4 shows WHO guideline values for some metals monitored as part of the survey and the periods of exceedence. Nickel showed a reduction of 36% and vanadium and zinc, a reduction of 80% (McInnes, 1992). Of all the elements, lead has shown the most consistent reductions with between 9 and 18 per cent of the 13 year average concentration per year at the five sites, this main reduction was seen after 1986/7 following the reduction of the maximum permitted lead content in petrol to 0.15 g L^{-1} (MacInnes, 1992).

Annual average air concentrations of cadmium and lead from two sites in the multi-element network are shown in Figure 3. Lead exceeds the lower guideline level in central London in 1984/5 prior to the reduction in petrol lead and cadmium is seen to exceed the lower guideline value in London in 1988/9. For all years shown Figure 3, annual average concentrations of the two metals are greater in London than in Glasgow. Despite there being only five data points for each element, lead concentrations are seen to be decreasing over time and this is better seen by looking at more recent data from the network (available via NETCEN [http://www.aeat.co.uk/netcen/airqual/index.html] and Environment Agency [http://www.environment-agency.gov.uk/] websites). Cadmium in central London shows no decreasing trend and, in fact, increased between 1976 and 1988. Conversely, in Glasgow there has been a clear decreasing trend with concentrations decreasing by one order of magnitude between 1976 and 1988, attributed to the demise of heavy steel making industry in the area.

Element	Guideline Values (upper-lower)	Exceedance
Pb	0.5 - 1.0 μg m^{-3}	Lower : several sites until 1985/6 Upper: 1976/7 only - Brent & Glasgow
Cd	10 - 20 ng m^{-3}	Lower : exceeded C. London Upper: not exceeded
V	1.0 μg m^{-3} (max. 24hr value)	Highest monthly average of 100 ngm^{-3} suggests possible 24 hr exceedence

Table 4 WHO - Guideline values for elements monitored in the UK Multi-element survey and periods of exceedence
(adapted from McInnes, 1992)

The WHO guidelines referred to in Table 4 and shown in Figure 3 are large levels which act as guide values, above which there could be associated human health risks. For the purposes of this report the main points of interest are the concentration trends, not the absolute values, as they relate to more subtle potential effects on ecosystems. Current definitions of critical limits are based on mass per unit weight for terrestrial and aquatic ecosystems (de Vries *et al*, 1998) and hence there are no comparable data for airborne concentrations.

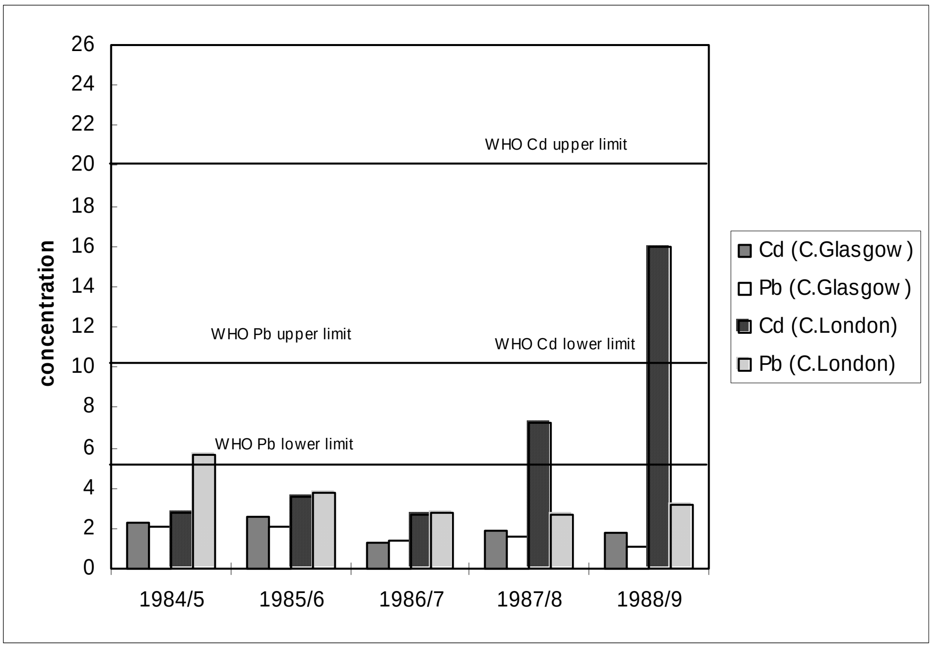


Figure 3 Annual average concentrations of cadmium (x10^{-9} g m^{-3}) and lead (x10^{-7} g m^{-3}) in ambient air samples from Glasgow and London from 1984/5 - 1988/9.
(adapted from McInnes, 1992)

There has been a programme of metals monitoring at seven urban sites throughout England since the early 1970s (see Lee *et al*, 1994 and 2.2.1 [9]). The results of this long-term survey suggest that levels at all urban sites are greater than those from the rural sites by a factor of between three and ten times and that levels were highest at Walsall when compared with other urban sites due to the presence of a smelter in the vicinity. The elements that showed the greatest enrichment over the period of the study were Cd, Pb and Hg, moderate enrichment was seen in Ni, V and Zn and virtually no enrichment was seen in Cr. The following conclusions can be drawn from percentage changes in the concentrations of airborne metals between 1975-1978 and the years 1986-1989;

- Elements which showed clear reductions of >60% included the heavy metals; Pb, As, Cd and V.
- Elements which showed a significant long-term decline at three or more of the six urban sites included Cd, Ni, V and Zn.
- Elements which showed only small reductions (<40%) over the period of the study included Cr. This and other elements showing little or no significant decrease are mainly crustal or marine in origin.
- None of the elements monitored in the survey exceeded the occupational exposure limit divided by 40 (a commonly used unofficial guideline value).

In conclusion, the figures from annual average urban and rural concentrations suggest that in UK air there has been a substantial reduction in many elements which come primarily from combustion-related sources. It was recommended by Laxen (1998) that arsenic and mercury determinations are added to the network in view of the forthcoming EU air quality framework and daughter directives and also to consider monitoring at industrial sites if they exceed, or are at risk of exceeding, limit values. These measures would seem appropriate but it is also important that existing metals are continually monitored in the future in order that long-term trends can be identified.

Monitoring of metal concentrations in aerosols from urban areas is carried out mainly in the context of public health issues and to monitor emissions relating to legislation introduced to reduce emissions from industrial and domestic sources. In the interests of this report, rural areas remote from sources of metals emissions are of more relevance as these areas often contain fragile ecosystems which are likely to be affected by even very small inputs of heavy metals. Urban data however, are useful because, as in the case of the multi-element survey it can show trends in pollutant emissions and deposition. It is only in recent years that the technology has existed to enable analysis of nanogramme levels in water and air and so has made monitoring of deposition and aerosols possible in rural locations. Time series data from rural areas is therefore often shorter than from urban areas.

2.6.2 **Rural areas**

2.6.2.1 **Seasonality**

One of the major sources of atmospheric heavy metals is from combustion of coal (e.g. As and Hg) and oil (e.g. Zn and V) leading to higher wintertime emission levels in northern Europe. In addition, winter climatic conditions often lead to the development of atmospheric inversions trapping pollutants in the lower atmosphere. Data from OSPARCOM (1996 and 1997) for the monitoring site at Banchory, northeast Scotland shown in Figure 4 and Figure 5 do appear to show yearly trends (even over two years ignoring precipitation data for August 1994 Pb). The data, however, do not show greater concentrations of lead in winter, in fact there appears to be a maxima in early summer and late autumn. There is little seasonal variation in the use of petrol and higher winter concentrations (of lead) are ascribed to the higher frequency of stable atmospheric conditions (Lee *et al*, 1994). However, higher lead concentrations derived from coal burning would be seasonal. If this is the case, conditions must have been such as to create precipitation maxima in early summer and late autumn in the years 1994/5.

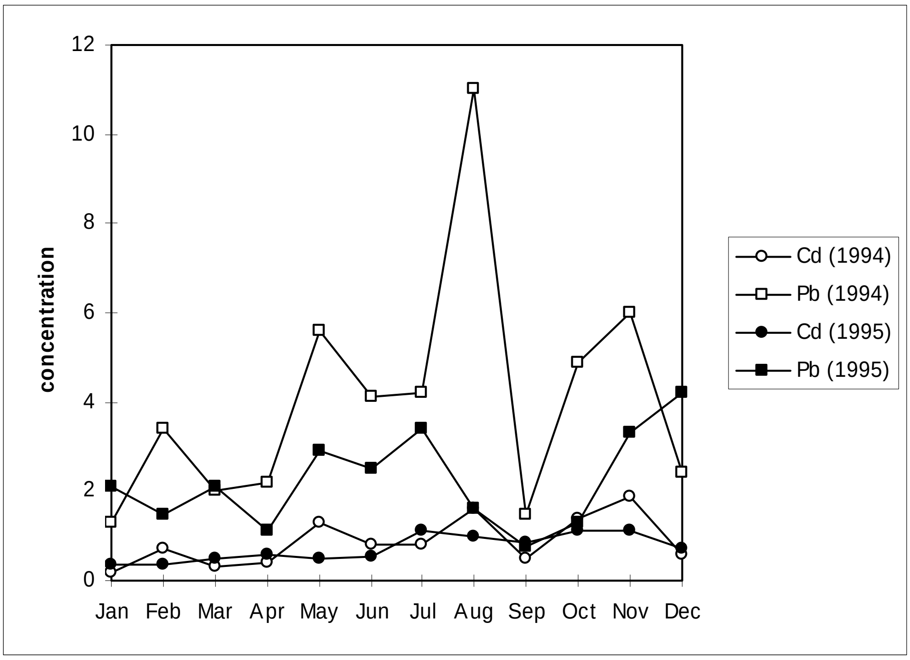


Figure 4 Monthly concentrations of cadmium (x10^{-7}g L^{-1}) and lead (x10^{-6} g L^{-1}) in precipitation at the CAMP monitoring site; Banchory, 1994 and 1995.
(after OSPARCOM, 1997)

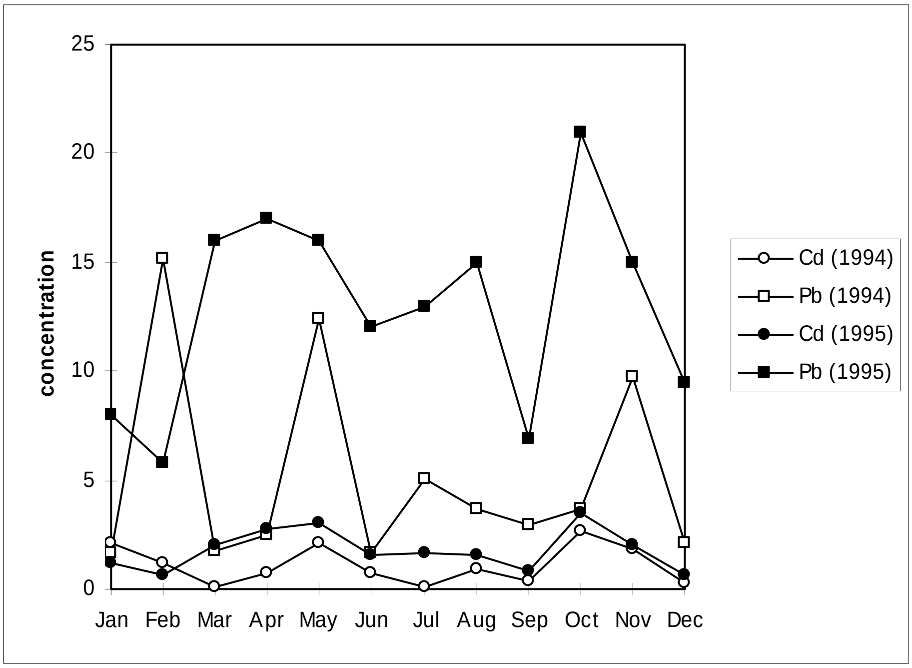


Figure 5 Monthly concentrations of Cd (x10^{-10}ng m^{-3}) and Pb (ng m^{-3}) in aerosol and gas at Banchory; 1994 and 1995
(after OSPARCOM, 1996 and 1997).

Aerosol concentrations are generally higher during 1995 than 1994 at Banchory especially in the summer months and must be related to emission characteristics and also to meteorological conditions. Importantly, the summer of 1995 was dry and warm throughout the UK with a settled area of high pressure. This allows the accumulation of pollutants through reduced atmospheric dispersion and limited removal by precipitation (Yaaqub *et al*, 1991) and possibly explains the high aerosol concentrations between March and September of that year.

The two years of OSPARCOM data presented in Figure 4 and Figure 5 do not provide sufficient information to observe trends in seasonal deposition (see also Fowler *et al*, 1996) but they do serve to illustrate the need for long-term collection of data to observe decreases brought about through emission controls. A long-term dataset will also enable meteorological effects to be considered.

The MAFF-funded monitoring of atmospheric deposition at 35 sites in England and Wales from April 1995 to September 1997 (Alloway, 1998 and Alloway *et al*, 1998) gives some information on the effects of seasonality on deposition of heavy metals. Collated monthly deposition data from each of the 35 monitoring sites (excluding Avonmouth) is shown for the two years of the programme.

There are no clear reproducible seasonal trends observed for deposition over the two complete years of monitoring. However, there is a relationship between increased rainfall and deposition, as would be expected. This is most evident in the case of cadmium, lead, arsenic and zinc. Mercury behaves differently; a period of low precipitation from May to September in 1995 is associated with increased deposition in June and July. For each of the priority heavy metals namely, As, Cd, Cr, Cu, Ni, Pb and Zn a long period of dry weather in the summer of 1995 (May to September) has resulted in relatively low deposition over this period. These results are similar to data produced at the CAMP monitoring site at Banchory (OSPARCOM, 1996 and 1997). Clear deposition relationships between sites are seen in periods of stable atmospheric conditions, at other times localised weather conditions appear to determine deposition characteristics at specific locations. In the case of data collated from over 30 sites (Alloway *et al*, 1998) this results in no seasonal trends being observed as variable conditions throughout the country lead to differing deposition patterns perhaps disguising trends at individual locations.

2.6.2.2 **Short-term active monitoring and biomonitoring**

Shorter monitoring programmes are often single site and/or single element based, used to determine the effect of a point source (e.g. Fung and Wong, 1995) and are often used to refine or develop analytical or monitoring methods (e.g. Pinto *et al*, 1998). Below are several UK monitoring programmes which yield meaningful monitoring results.

(1) Trace elements in aerosols over southeast England

A one year daily study of trace elements in aerosols was carried out by Yaaqub *et al* (1991) in southeast England. This work concentrated mainly on source apportionment and found highest levels of elements in air coming from the east. High resolution work such as this makes it apparent that meteorological conditions are extremely important factors in determining precipitation and aerosol metal concentrations when emissions levels are constant. The development of high pressure systems over Europe allows the accumulation of aerosols because of reduced vertical mixing. When this air is moved west the continuing relative stability of the air and relative absence of wet removal processes can lead to high aerosol concentrations. Thus, any subsequent precipitation can remove high concentrations of pollutants. Transport from the west is dominant in the UK as a whole and is generally associated with frontal systems bringing wind and rain which efficiently remove pollutants from the atmosphere resulting in lower aerosol concentrations. In addition, as rainfall events are more frequent there is less time for atmospheric build-up of pollutants so concentrations in precipitation tend to be lower. Davies *et al* (1991) have determined high pollutant loadings in precipitation associated with easterly trajectories in northeast Scotland similar to the OSPARCOM data mentioned earlier.

Mercury is not routinely monitored as part of the multi-element network (McInnes, 1994) or the rural network (Cawse, 1994 and Baker, 1997); and although monitored for CAMP (OSPARCOM, 1996 and 1997) as a priority pollutant, results are sporadic. Indeed, mercury has been omitted from inclusion into the transport and deposition model EUTREND used for the prediction of metals deposition to the OSPARCOM North Sea area because the model is inadequate to describe the complex atmospheric behaviour of mercury (van Pul *et al*, 1998).

(2) Atmospheric gas-phase monitoring of mercury

A one year study of atmospheric gas-phase mercury has been carried out at Harwell, a rural site in central southern England (Lee *et al*, 1998). This is the first UK survey of this kind and yielded the following results:

- Mean annual concentration of gas-phase mercury was 1.68 ng m^{-3} between June 1995 and April 1996.
- Hourly mean concentrations: maximum 20.5 ng m^{-3}, minimum 0.26 ng m^{-3}.
- Mean concentrations of clean air indicated a background of approximately 1.5 ng m^{-3}.
- Mean concentrations from the most polluted easterly sector were approximately 2.2 ng m^{-3}.
- Diurnal patterns of total gaseous mercury (TGM) showed elevated concentrations at night under stable nocturnal boundary layers.

- Emission calculations indicated a flux of around 15 ng m^{-2} day^{-1}.

Conclusions of this study were that TGM measurements were not greatly different from those made in rural Ireland, or in other parts of continental Europe. It was also stated that more data on atmospheric concentrations were required in order to calculate UK flux budgets.

(3) Short-term intensive monitoring of atmospheric and wet deposition concentrations of heavy metals

A short-term study of both aerosol and wet deposition has been carried out by Fowler et al (1996) to determine deposition fluxes to a moorland area in southern Scotland. The area was selected as it was thought to be representative of northwestern Europe impacted by low levels of air pollutants. The concentrations of heavy metals in aerosol and rain throughout 1995 are shown in
Figure 6. The high concentrations of aerosol lead are in agreement with the data from 1995 monitoring at Banchory, northeast Scotland (OSPARCOM, 1997) but not with those from 1994 which were 2 - 3 times lower. Rainfall lead is in agreement with Banchory data from 1995 with values in the range 1.5 - 4 mg L^{-1}. The 1994 rainfall lead data at Banchory however are much higher suggesting different meteorological regimes between the two years, if it is assumed that deposition patterns are approximately analogous throughout eastern Scotland. If the variability in rainfall lead concentrations is observed for the other heavy metals, the presentation of one year of data cannot be used to make assumptions on deposition for previous or subsequent years even at the same location. Also, although long-term trends may be observed suggesting the decrease of atmospheric concentrations of heavy metals (Cawse *et al*, 1994 and Baker 1997) related to emission reductions, consistent annular patterns of deposition may not be evident.

Of additional interest, Fowler *et al* (1996) have observed consistent diurnal patterns in modelled dry deposition velocities of aerosol species. The velocity maxima occurs between 1200 GMT and 1500 GMT and ranges from 2.5 mm s^{-1} for PM2.5 particles and 11 mm s^{-1} for the PM10 particles, during this time the fluxes exceed nocturnal values by about 50%.

(4) Single-site monitoring of rain water and surface water in Wales

The previous studies mentioned dealt with aerosol and gaseous-phase metals and aerosol and wet deposition. Neal *et al* (1996) have monitored rainfall and surface waters for chromium since 1983, again to assess atmospheric inputs. (Although this study can be considered long-term it has been included in this section because it is concerned with a single element and samples are only taken from various sites in mid-Wales). A large pollution event was identified in 1987 and was seen in rainfall, throughflow and stemflow chromium concentrations where levels of Cr increased from 1984/85 values of c.a. 2 µg L^{-1} to c.a. 6 µg L^{-1} in 1987. The large increase in concentrations to the streams in the catchments, during the peak years of 1986/87, approached and in some cases surpassed values which are thought damaging to sensitive aquatic organisms. It should be noted however that these peak values were anomalous and are set against a long-term declining background trend possibly due to more rigorous emission controls. Neal *et al* (1996) have recommend that long-term trace metal monitoring programmes are maintained in order to assess the extent of monitoring required to satisfy the forthcoming demands for critical loads information in this field.

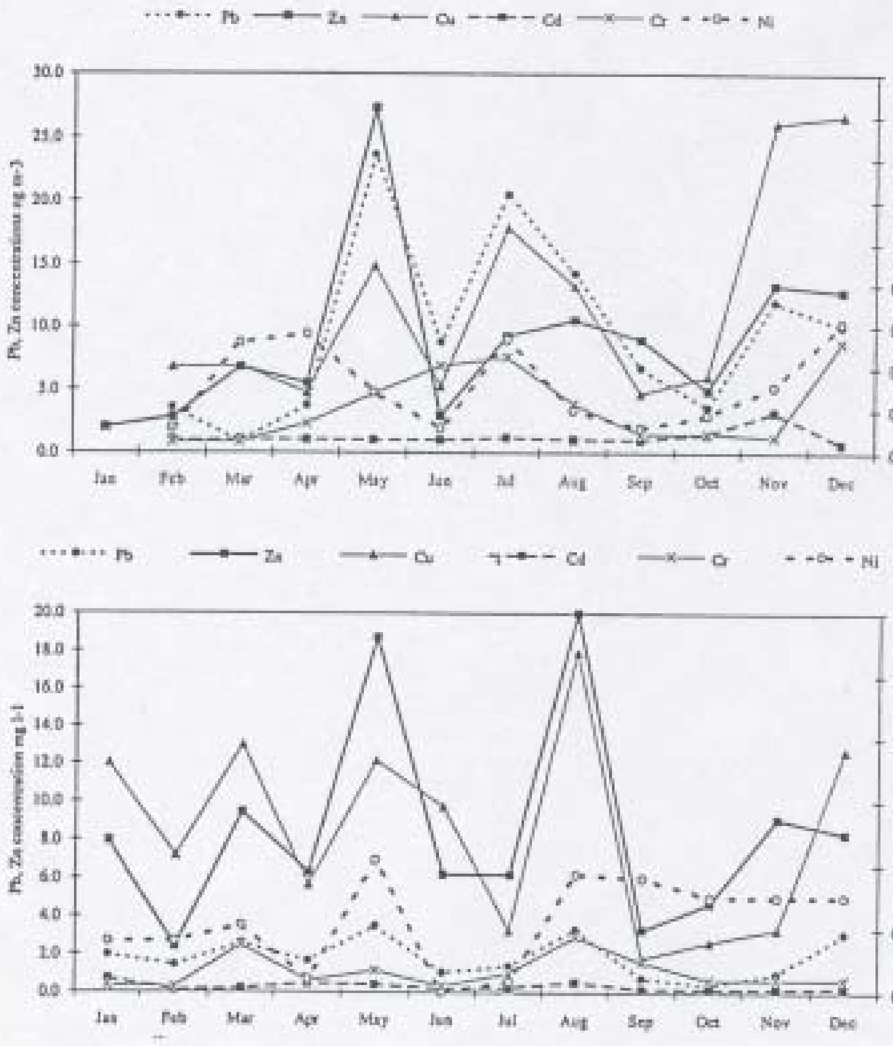


Figure 6 Concentrations of heavy metals in aerosol (top) and wet deposition (bottom) at Auchencorth Moss, southern Scotland during 1995. (after Fowler et al, 1996).

(5) Multi-site survey of surface water concentrations in Scotland and Wales

Trace metal concentrations in UK surface waters were also determined by Rose *et al* (1997). Although this study made no attempt to quantify atmospheric inputs directly, the results show spatial differences between lake waters in Scotland and Wales over the period 1995/6. General conclusions were:

- At all sites Hg, As, Se, Be, Bi, Pb and Ag were below ICP-MS limits of detection.
- The South-central area of Wales and Anglesey showed highest concentrations possibly due to mining and smelting activities.
- Southern and southwest Scotland showed elevated concentrations as did sites on Orkney and Wales. Sites in the northwest and Hebrides showed lower concentrations.

PCA analysis proved inconclusive as only information on geographical location was available. The authors proposed that information on lake and catchment characteristics and other water chemistry might also be required to explain the data more fully. In addition, it was recommended that sediment cores should also be taken from the lakes to put the data into a temporal context.

For studies such as that of Rose *et al* (1997), with a single sample from each location, it is possible that inferences can be made as to the spatial distributions of trace metals. However, without detailed information on specific catchments it is hard to make conclusions about sources and trends. In terms of monitoring, a programme of this nature would require two to three decades of data to enable identification of trends. It has been seen that even with long datasets on water quality that trends in heavy metal concentrations may still not be statistically apparent (see Robson and Neal, 1996).

(6) Biomonitoring of atmospheric heavy metals in England, Scotland and Wales using mosses.

Information on the UK heavy metal biomonitoring survey is given in 2.2.2 [7] and in Appendix 6. Mosses (either *Hylocomium splendens* and/or *Pleurozium schreberi*) were successfully sampled at 111 sites out of a possible 206 and achieved reasonably good geographic coverage of the UK mainland despite the restricted number of samples. However, areas which favour the growth of the moss species used, such as acid heaths and moorland, are more commonly found in the west and north of the UK and tend to have been sampled more successfully.

Figure 7 shows concentrations of the heavy metals As, Cd, Ni, Pb and Zn in *Pleurozium schreberi* samples from locations approximately on a south to north transect over the UK. Overall, the highest levels of heavy metals (except nickel) were found at May Moss in Yorkshire. Indeed, concentrations of Cd (1.12 mg kg^{-1}) and Pb (36.43 mg kg^{-1}) at this location were the highest observed anywhere in the UK. The highest levels of arsenic (8.10 mg kg^{-1}) were found at Rodborough in southwest England; nickel (9.41 mg kg^{-1}) at Mortimer Forest in the West Midlands and zinc (849.67 mg kg^{-1}) at West Williamson SSSI in Dyfed, southeast Wales. From assessing the concentrations at locations shown in Figure 7, the lowest metal levels were found at Loch Lomond and in the Pengelli Forest.

From the complete survey, results indicate that the concentration ranges are broadly similar to those found in other parts of Northern Europe and values are quite close to those seen in Norway (e.g. Berg *et al*, 1996). Furthermore, the results for the UK show that highest deposition concentrations are found in the midlands and north of England and this is in good agreement with moss monitoring data from the FLAME project (Rose and Harlock, 1998) which identified the English midlands and the north of England as having the highest moss metal concentrations in the UK(see 3.1.4).

An interesting comparison can be made between the Pengelli Forest results shown in Figure 7 and results from another sampling site in Dyfed; West Williamson SSSI, which is situated approximately 40 km further north, also shown in Figure 7. The data from these sites are shown in Table 5. Although the sites are only 40 km apart, the mosses show very different heavy metal concentrations. For each of the five heavy metals, moss concentrations are higher at the West Williamson SSSI site than at Pengelli Forest, with approximately three times the concentration of arsenic, cadmium and lead, and over twelve times higher for nickel. The largest difference is seen for zinc, with almost fifty times the concentration observed at West Williamson SSSI. The large discrepancy between concentrations at sites which are relatively close together cannot be accounted for by meteorological patterns as these will be similar over a distance of 40 km. Furthermore, the differences cannot be due to different patterns of long-range transport and deposition when they are located only 40 km apart. More probably, the differences are due to relatively high emissions from various localised sources in the Milford Haven area, approximately 10 km west of the West Williamson SSSI.

There are a number of large Part A authorised processes in the south Dyfed area associated principally with the petrochemical industry in Milford Haven (EA, 1999). Although there are no significant authorised discharges of zinc (or other heavy metals) to the atmosphere there are appreciable quantities of atmospherically discharged particulate matter from a number of fuel and power production plants. From 1995/6 data (EA, 1999), there are several hundred tonnes of particulate material released from three main combustion sources around Milford Haven each year and this particulate matter may be a large source of heavy metals to the surrounding area. West Williamson SSSI is located 10 km east of Milford Haven and the location will receive inputs of atmospheric deposition during prevailing wind patterns. The site at Pengelli Forest however, due to it’s location, is likely not to receive inputs directly from these, or other large industrial point sources.

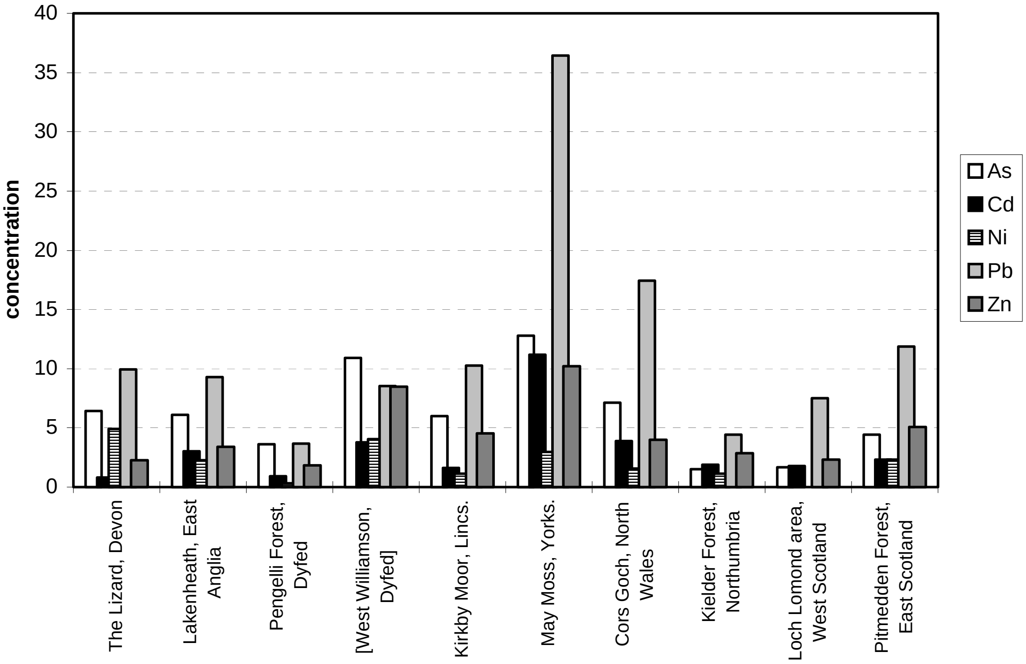


Figure 7 Concentrations of heavy metals in Pleurozium schreberi *samples from selected locations in the UK moss monitoring programme 1996/7.*
concentrations of Zn expressed as 10^{-2} *g* kg^{-1} *(except for West Williamson;* 10^{-1} *g* kg^{-1}*), Pb and Ni in mg* kg^{-1} *and As and Cd expressed as* 10^{-4} *g* kg^{-1} *(after Parry and Williams, 1998)*

	OS Grid ref.	As (mg kg^{-1})	Cd (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
Pengelli Forest, Dyfed	SN 132 390	0.36	0.09	0.33	3.68	18.20
West Williamson SSSI, Dyfed	SN 030 060	1.09	0.38	4.04	8.51	849.67

*Table 5 Concentrations of heavy metals in terrestrial moss (*Pleurozium schreberi) *samples from two sites in Dyfed, southwest Wales in 1997.*
(after Parry and Williams, 1998)

Data from the UK moss monitoring survey has been sent to the co-ordinator of the European programme and all the results of the current five year European-wide survey will be published in a final report. It is unfortunate that, out of a potential 206 sites, suitable mosses were only found at just over half the locations. This has the effect of lowering the resolution of the data and reducing the quality of final deposition maps. Moss monitoring methodologies were developed and applied initially in Scandinavia (e.g. Ruhling and Tyler, 1970) where there is generally good geographic coverage of both *H. splendens* and *P. schreberi*. There is a problem in applying these techniques directly to areas where there is poor coverage of bioindicator moss species and there is much work being done to address this problem through investigation into using other moss species (Parry, pers. comm.). It has been demonstrated previously that it is possible to have two sites relatively close together exhibiting very different heavy metal deposition concentrations due to the effect of localised emissions. Care should be taken firstly in identifying representative sites and secondly in interpreting these results before inclusion into deposition maps. In order that an accurate picture of long-range transport and deposition can be made, as many sites as possible are required. The less sites there are, the more difficult it will be to identify anomalous values which will affect overall patterns. Another possible shortcoming in the UK survey regards time of sampling; samples were collected from November to April (the winter season) instead of summer collection which is recommended by the European moss monitoring protocol (Ruhling, 1994).

2.6.2.3 **Long-term monitoring**

(1) Bulk deposition and stream water in mid-Wales

Further to the work of Neal *et al* (1996), long-term multi element analysis of upland stream water and bulk deposition has been carried out at Plynlimon, mid-Wales and is described in Robson and Neal (1996). Data have been collected from 1983 to 1993 on chromium, copper and zinc. With such a large amount of data points, there is ‘noise’ evident in the scatterplots. Two techniques were used to try and identify trends in data, statistically by using the seasonal Kendall test and graphically by using LOWESS. The seasonal Kendall test is commonly used for testing monotonic trend in environmental data and the LOWESS technique (a locally weighted regression smoothing scatterplot technique) to graphically observe trends. Of the heavy metal species in rainfall, zinc is the only one to indicate a possible trend, chromium and copper do not. Zinc concentrations increase between 1984 and 1987 and then level off. However, LOWESS curves suggest that the underlying changes are not monotonic and should not be considered a long term trend. In order to examine any downtrend in zinc it is necessary to collect another five or ten years worth of data. For streamwater chemistry; copper, zinc and chromium show possible trends but upon smoothing the data with LOWESS, any long term trends were shown to be unlikely. Zinc and chromium show concentration increases which are directly related to increases in rainfall zinc and chromium. The relationship between rainfall and streamwater chemistry is not seen with copper.

It is suggested by Robson and Neal (1996) that with environmental data there are cyclical variations in bulk precipitation inputs which means that trends cannot be established with ten years of data and that monitoring programmes of this nature should be continued over several decades. (see also Evans *et al*, in press)

There are large amounts of variability in deposition data due to many factors, not least to meteorological conditions. With such a large number of samples, it is inevitable that there is going to be a high degree of scatter, which can only really be resolved by increasing the length of monitoring and partially through the use of powerful statistical techniques.

(2) UK Rural network: England

The foremost collection of long-term atmospheric particulate material and bulk deposition heavy metals data in the UK is that collected by AEA Technology (Cawse *et al*, 1994 and Baker, 1997) from 1972 until present at three rural English locations.

During the first twenty year period of the survey, there has been decreasing trends in the concentrations of many elements in air (see Figure 8 below) with decreases ranging from 3 to 11% per year. There are no clear relationships evident between elements or sites but overall decreases over the twenty years are of the order; As/Pb > Zn > V > Cr > Ni > Cu at the three monitoring stations. The main decreases were seen in the first ten years (1972-1982) which are in agreement with a reported decline in black smoke levels in urban areas. Distinct reductions in the concentrations of lead were most evident after 1986 following restrictions in leaded petrol and led to a further decrease of around 60% at rural locations. According to urban airborne particulate data from the 1970s (McInnes, 1979), concentrations of Cr, Ni, Cu, Zn, Pb and As exceeded the rural values by up to three times.

For wet and dry deposition, elements with high enrichment factors (generally the toxic heavy metals) were highly soluble. Classification of elements according to the efficiency of removal from the atmosphere by rain (washout factors) showed high values for pollutants such as Zn, Ni and Cu, present at rain forming altitudes and low values for pollutants at ground or low level sources such as Pb. As soluble metals are generally more biologically available than insoluble metals, comparison between rural and industrial areas showed an increase of available metals between two and four times in the industrial areas. The difference is even more pronounced in highly industrial areas with increases between one and two orders of magnitude.

Emissions data from various sources from 1970 to the early 1990s are presented in
Table 6 and emission values for arsenic, cadmium and zinc over the same period are shown graphically in Figure 9. The overall percentage reductions in emissions for lead over this period is 60.8, for Zn, 67.6 and for Cd, 59.8. Reductions of around 7-8% per year over the same time period

for heavy metals in air as shown by Cawse *et al* (1994) correspond with the reductions in emissions. UK heavy metal emission data for 1996 (AEA, 1999) is also given in Table 6. Unfortunately, the last available compilation of European emissions data (Pacyna, 1996) dates from the early 1990s. Using these data, UK emissions account for only two to three percent of total European emissions. Using more recent European data, it is likely that the proportion of UK emissions would increase.

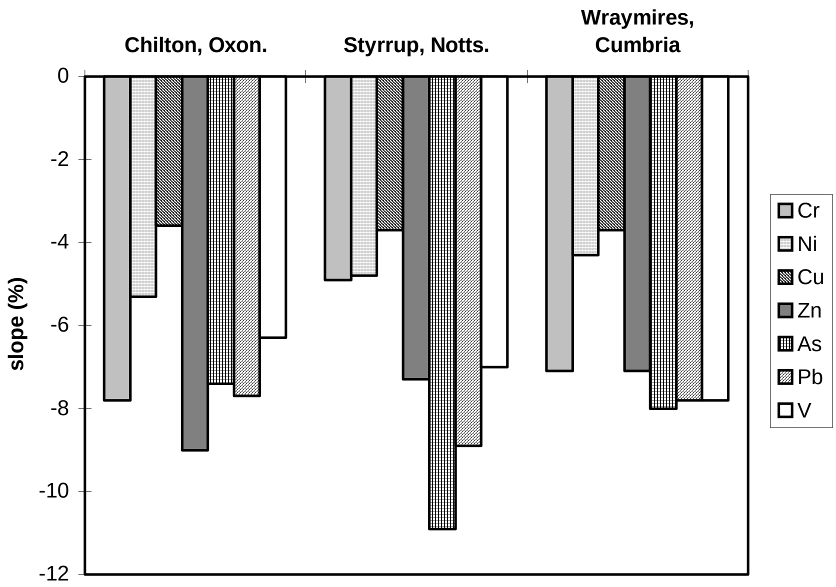


Figure 8 Trends in heavy metal concentrations in air, 1972-1991, at the UK rural network sites. Slope is expressed as percent per year of the mean annual air concentration for the 20 year period (adapted from Cawse et al, 1994).

Current annual mean concentrations of heavy metals in air and rainwater at Chilton, Oxfordshire and Wraymires, Cumbria are comparable to those measured at other rural locations in the UK, but are lower than those observed at urban sites (see Lee *et al*, 1994). Urban concentrations were 3 to 4 times higher for Cr and Pb and 2 to 3 times higher for As, Cu, Ni and V. Cd and Zn were 1.5 to 3 times higher at urban sites. (Baker, 1997).

Lead, which at present is the only heavy metal with a defined EC directive limit, has had a measured concentration in air over the past five years of only 11% of the new limit value of 0.5 μg m^{-3}. The main source of this ground level atmospheric lead, indicated by Pb/Br ratios, is still vehicle emissions. Of the other heavy metal species (e.g. As, Cr, Ni and V) the main source is from combustion of fossil fuels for domestic and industrial power generation. The reductions in emissions from these sources, which has been brought about by changes in methods of energy production and legislation, has had a positive impact on air quality and this can be seen in the rural network data.

The Rural Network has been operational since 1972 and has provided long term data on metal concentrations in air and bulk deposition samples at three locations in England. An overview of changes in mean deposition of Pb, V and Zn at Chilton, Styrrup and Wraymires compared with changes in their estimated total emissions to the atmosphere in the UK from 1972 to 1995 can be seen in Appendix 4. This graphically shows a decrease in deposition, especially for Pb and V associated with emission reductions over a period of 24 years and highlights the usefulness of a rural network remote from emission sources in detecting these changes.

(3) UK Environmental Change Network (ECN) data

Information regarding the ECN programme is given in 2.2.1 [10]. Heavy metals data is available for river sites R01-R22, data for R07 and R10 is unavailable (see Appendix 2 for river locations) and for lake sites; Scoat Tarn, Llyn Llagi, Loch Lomond, Lochnagar, Loch Davan and Loch Kinord. Much of the data commonly show very low concentrations and in rural areas are often below the detection limits of the techniques used.

Figure 10 and Figure 11 illustrate some time series data for total lead concentrations in water samples from the River Tweed and Lower Clyde respectively. The data for the River Tweed is weekly and can be seen to fluctuate by as much as two to three times between samples. Data for the River Clyde is at a lower resolution but a large variability is also apparent. Presumably inputs from both point and diffuse sources will match this variability observed in the river water samples as will catchment hydrological conditions prior to sampling. Both the Tweed and Clyde (at these sampling locations) will be subject to localised inputs, in addition to atmospheric inputs. The Clyde data shows the largest concentrations (2-20 μg L^{-1}) as it is the more urban location. Concentrations in the Tweed are lower at 0-6 μg L^{-1}. Trends however cannot easily be established on these variable datasets over such a short period of time. There is a need to continue frequent monitoring at the ECN sites to establish a long-term database in order that trends, if any, may be observed.

Water heavy metals data for the Environmental Change Network is also collected from a number of lake sites in the UK. Figure 12 shows temporal metals concentrations of dissolved Cu in Scoat Tarn, northeast England and total Hg in Loch Lomond, west-central Scotland. Straight baselines on each graph represent samples which were below the limit of detection; 0.01 μg L^{-1} for dissolved copper and 0.007 μg L^{-1} for total mercury. Large variability in concentration is observed for both metals at each site.

	1970 (a)	**1975** (a)	**1979** (b)	**1985** (c)	**1987** (a)	**early 1990s** (d)	**1996 (UK only)** (e)
As	-	-	6500	4936 (-24.1)	-	2575 (-47.8)	51 (2)
Cd	2227	1948 (-12.5)	-	1123 (-42.3)	998 (-11.1)	895 (-10.3)	19 (2)
Cr	-	-	18900	-	-	-	-
Cu	-	-	15500	-	-	-	-

Ni	-	-	16000	-	-	-	292
Pb	148319	161652 (+8.9)	123000 (-23.9)	85382 (-44.1)	74030 (-13.3)	58090 (-21.5)	1357 (2)
V	-	-	34500	-	-	-	-
Zn	101785	81826 (-19.6)	80000 (-2.23)	41603 (-48.0)	38113 (-8.4)	32990 (-13.4)	1119 (3)

Table 6 European emissions of heavy metals over the period: 1970s to 1990s and UK emissions for 1996 in tonnes yr^{-1}
Data values in parentheses % change w.r.t. last available data for European data and for UK data, % of total European emissions. (Data sourced from (a) Olendrzynski et al (1996); (b) Pacyna (1984) (c) Bartnicki (1996); (d) Pacyna (1998); (e) AEA (1999).

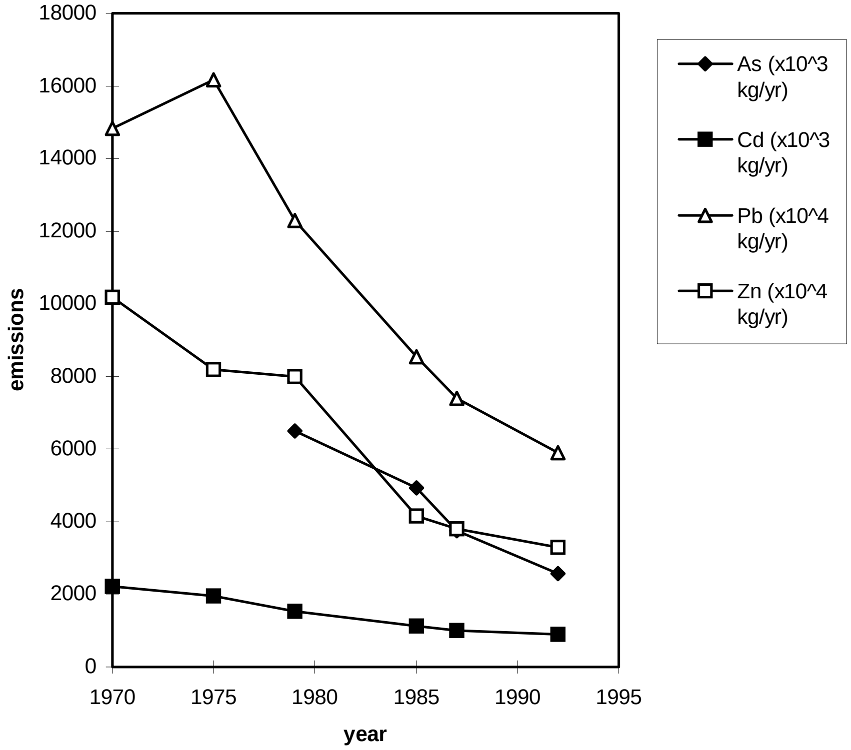


Figure 9 Total European anthropogenic emissions of As, Cd, Pb and Zn from 1970 to the early 1990s (after Olendrzynski et al, 1996; Pacyna, 1984 Bartnicki, 1996; Pacyna, 1998)

In the case of total Hg in Loch Lomond lake water, concentrations seem to naturally tend towards values below the detection limits with episodes of relatively high inputs creating elevated concentrations. During the period covered by the ECN data, there have been three main observed increases in Hg concentration and these must be related to either direct inputs or releases from the catchment and/or sediment. As a comparison, mercury concentrations at the outflow from Lochnagar, northeast Scotland during 1997/98 has been typically 0.01-0.02 μg L^{-1} (Yang *et al*, 1999) and is more consistent than the data from Loch Lomond with no large peaks in concentration observed.

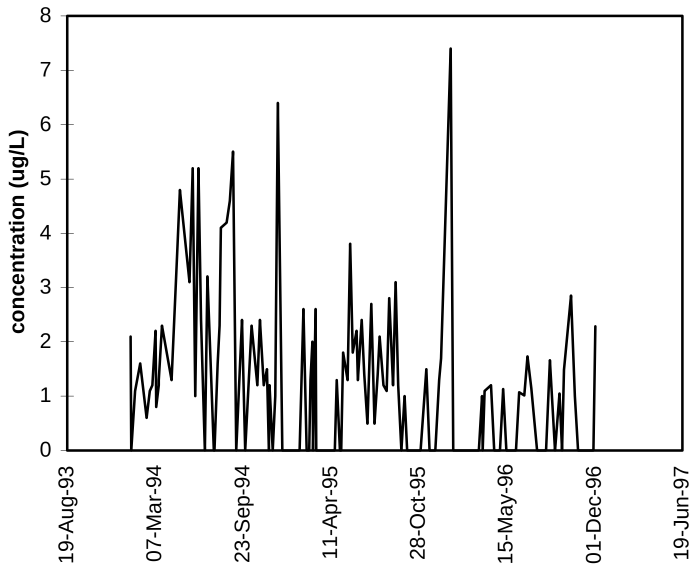


Figure 10 Total Pb in the River Tweed (at Galafoot) January 1994 to November 1996 (after Lane, 1997)

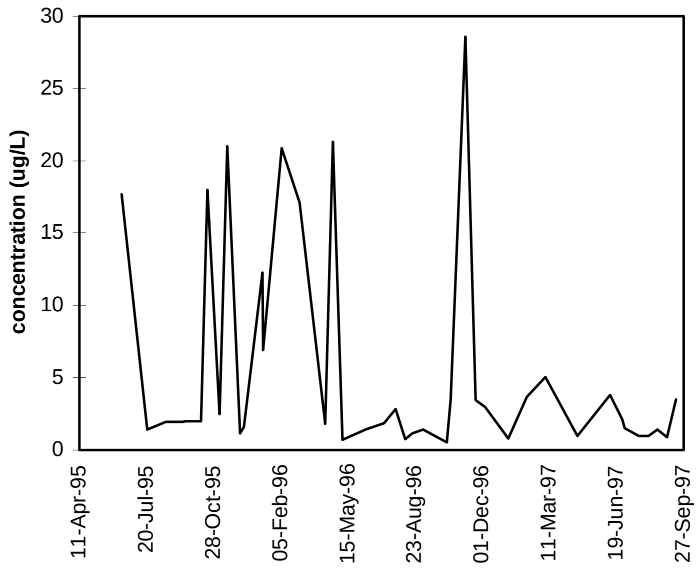


Figure 11 Total Pb in the Lower Clyde from July 1996 to September 1997 (after Lane, 1997)

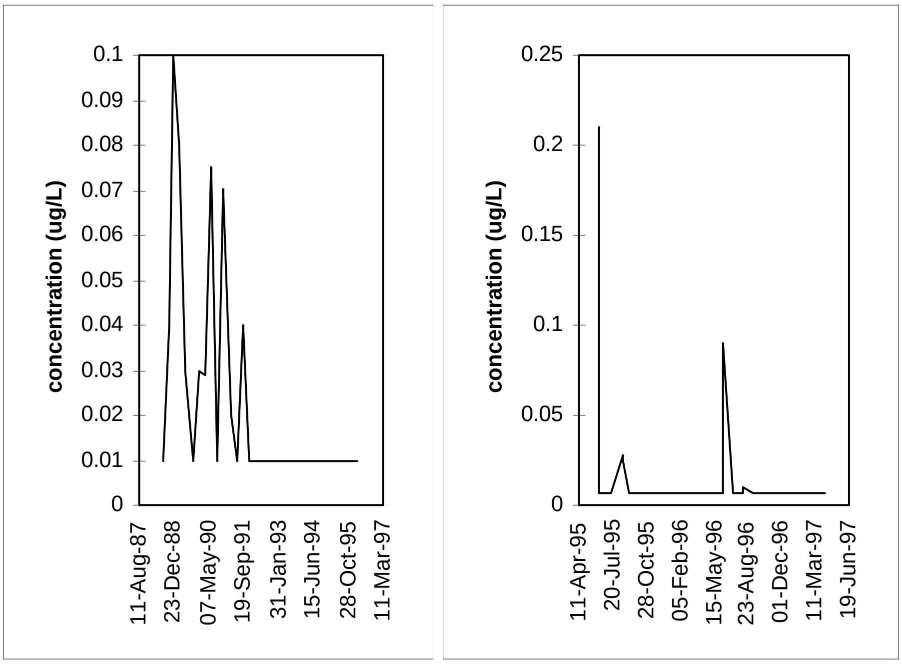


Figure 12 Temporal heavy metal concentrations in lake water from two ECN sites.

(a) Dissolved Cu at Scoat Tarn (left) and; (b) Total Hg at Loch Lomond. Baseline indicates values below limit of detection (after Lane, 1997).

(4) MAFF-funded deposition monitoring of heavy metals in England and Wales to lowland agricultural soils.

Information regarding the above project is given in 2.2.1 [14] and in Appendix 3. Results presented here represent data from March 1995 to August 1997, however, deposition monitoring continued for a further year and effectively ended in August 1998. Monthly deposition samples (wet+dry) have been collected at 36 locations in England and Wales principally to assess the magnitude of atmospheric inputs of heavy metals to agricultural land in comparison with other localised inputs.

Heavy metals deposited atmospherically were found to make up significant proportions of the total heavy metal input to agricultural land. Figure 13 shows the proportions of atmospherically deposited heavy metals to agricultural land in England and Wales. These results illustrate the high importance of atmospheric heavy metal deposition in agricultural areas even where there are other significant inputs, including those from fertilizers and applications of sewage sludge. Metals such as mercury and lead are predominantly atmospheric in origin and proportions of these metals from direct inputs are comparatively low. In contrast, atmospheric inputs of other metals are lower and are proportionally higher in direct inputs from other sources such as applications of animal manures (e.g. copper) and industrial by-product waste (e.g. chromium).

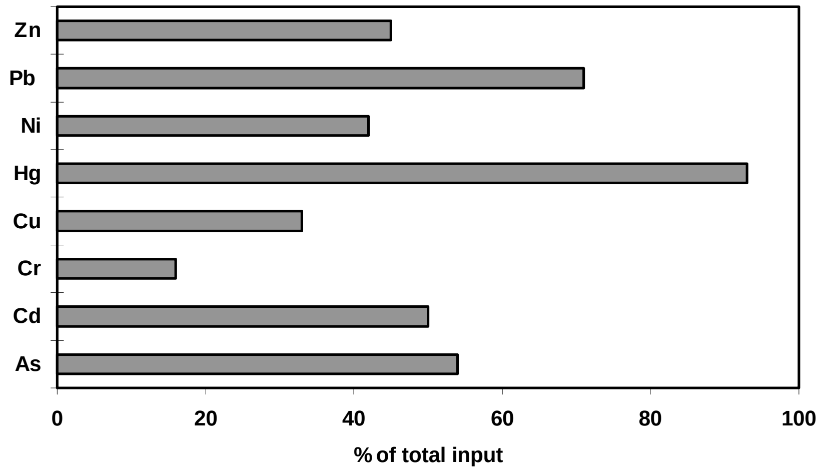


Figure 13 Proportion of atmospherically deposited heavy metal input to agricultural land in England and Wales.

(after Alloway et al, 1998)

There have been clear variations in deposited concentrations identified between sites and most have been attributed to specific sources. Examples of these variations include;

- sites with high annual average deposition values for several elements (see Appendix 3) e.g. Boxworth (As, Hg), Ruthin (Cr, Cu), Sonning (Cr, Ni).
- relatively high values of deposited zinc (315-385 g ha^{-1}) seen at Gleadthorpe, Rosemaund, Northallerton, Usk and Monmouth thought to be associated with local industrial sources.
- higher deposited lead values observed at North Wyke, Devon than at Brentwood, Essex (2 km from the M25 motorway). This is unexpected and can only be attributed to the nearby A30 trunk road at North Wyke (the distance from the sampling location to the road is not known but could be as little as 50 m).

By interpolation, deposition data has been used to model soluble metal concentration, mass deposition, residual metal deposition and total metal deposition on a 20 km x 20 km grid square for all of England and Wales. For total metal deposition, modelled deposition trends for the main heavy metals are as follows;

- Zn - highest values of between 0.5-0.65 kg/ha/yr are seen on the west coast with the lowest values of between 0.2-0.35 kg/ha/yr in the Midlands, southern and eastern England.
- Cu - highest values in central England of >0.125 kg/ha/yr.

- Pb - highest values in south-west England (> 0.095 kg/ha/yr) with further high values (0.055-0.075 kg/ha/yr) seen in several locations throughout England and Wales. Lowest values (0.015-0.035 kg/ha/yr) are seen in the far north of England, south-west Wales and in the Wash.
- Cd - highest values (0.004-0.006 kg/ha/yr) seen in south and north Wales. Lowest values (0.001-0.002 kg/ha/yr) are seen in north-west England, East Anglia and south-central England.
- As - highest values (0.006-0.01 kg/ha/yr) in north Wales and the Pennines and lowest values (0.0015-0.003 kg/ha/yr) in southern England.
- Cr - highest values (0.008-0.012 kg/ha/yr) in east-central England with lowest values (0.0025-0.0045 kg/ha/yr) predominantly in the south of England.
- Ni - highest values (0.015- >0.018 kg/ha/yr) in Wales and Cumbria and lowest values (0.005-0.008 kg/ha/yr) in south and east England.
- Hg - highest values (0.0015- >0.0025 kg/ha/yr) in north Wales and Cumbria/ Northumberland and lowest values in central and southern England (0.0005-0.001 kg/ha/yr).

The above results appear to contrast with those of the UK Multi-Element Network (McInnes, 1979 and 1992) and the UK Rural Network (Cawse *et al*, 1994 and Baker, 1997). These networks have indicated deposition concentrations to urban areas as being generally 3x higher than in rural areas. However, mapping data presented by Alloway *et al* (1998) does not show this, as major urban sources are not taken into consideration. More importantly, and of interest to this review, are the modelled upland deposition data where the highest deposition values for As, Hg, Ni and Zn were obtained for the upland areas of England and Wales. Interpolations in upland areas >300 metres have not been made, yet elevated deposition levels are shown in deposition maps. The MAFF-funded study is primarily to look at heavy metal inputs to lowland agricultural soils and is not relevant for applying to upland areas through the use of models.

As part of this study however, two additional deposition collectors were sited at differing heights at Great Dun Fell, Cumbria to assess altitudinal variations in deposition. The lower site had much higher deposition of As (x11), Cr (x5), Cu (x11) than the higher site, 365 m above. Deposition of Cd, Pb and Hg was similar at both sites. There was little evidence for the expected increases in deposition with increasing altitude due to the meteorological seeder-effect, but deposition at the lower site was found to be generally much higher than deposition at the lowland agricultural sites. These results suggest that increasing altitude can result in higher levels of deposition, although Alloway *et al* (1998) have suggested that the Lower Great Dun Fell site may be affected by a disused metal mine.

Table 7 shows metals deposition data collected at the Great Dun Fell (lower) site in Cumbria during 1997 and at the UK Rural Network site at Wraymires, Cumbria during 1996. Unfortunately the data represent different years and monitoring at Great Dun Fell was only carried out for four months in the spring/summer and were extrapolated to provide values for a whole year, thus creating considerable errors due to seasonal variations. Also, only the soluble fraction of the rainwater was analysed for the Rural Network, it is not known, but assumed, that wet+dry deposition concentrations were measured at Great Dun Fell. Despite the differences in sampling protocol, both sites are upland, are only around 50 km apart and should be subject to similar weather patterns therefore providing an opportunity to compare deposition concentrations.

The data presented in Table 7 highlight the variability in deposition patterns locally and between years, and also the effect of different monitoring protocols. Only the results for zinc are in good agreement, the others, especially lead, which is one order of magnitude different, do not yield similar results. It is difficult to draw meaningful conclusions from extrapolated data and great care must be taken in modelling deposition on short-term data which may be heavily influenced by meteorological conditions. Alloway *et al* (1998) admit that only data collected over a long period can be used with any confidence.

	Pb	Cd	Hg	Zn	Ni	As
Wraymires, Cumbria (Lake Dist.)	36.9	3.87	1.54	282	71.6	2.71
Great Dun Fell, Cumbria (Pennines)	382	0.8	0.8	262	21	165

Table 7 Heavy metal deposition data (in g/ha/yr) for Wraymires (1996) and Great Dun Fell (1997), both Cumbria.
Wraymires data (after Baker, 1997) for the soluble fraction of rainwater only and Great Dun Fell data extrapolated from four months data (April-August 1997).

In conclusion, the general order of abundance of the most important elements (on the basis of mean annual deposition) observed throughout the MAFF monitoring programme in England and Wales is shown below:

Zn >>> Cu > Pb, Ba > Ti >> Cr, Ni, V > Ag > As, Co > Hg > Cd >> Be

The abundance is purely based upon deposition concentrations and it should be remembered that priority metals such as mercury and cadmium are extremely toxic even at low concentrations (Alloway and Ayres, 1997b) and are more toxic than the most heavily deposited metals, zinc and copper.

2.7 **General deposition trends: European/Scandinavian and other.**

Long-term surveys and single moss monitoring studies have played a significant role in monitoring depositions of heavy metals in Europe and Scandinavia (e.g. Rose and Harlock, 1998; Bowman and Harlock, 1998; Herpin *et al*, 1996; Herpin *et al*, 1997; Markert *et al*, 1996a/b; Berg *et al*, 1996; Brumelis *et al*, 1997)

The Norwegian moss monitoring surveys of 1977, 1985 and 1990 (Berg *et al*, 1996) indicate general reductions in atmospheric deposition of lead (30-40%) between 1977 and 1990 in the southernmost part of Norway. Similarly, with cadmium a reduction of c.a. 40% in areas with concentrations above 0.1 ppm is seen in 1990 when compared with 1977.

German moss samples from a herbarium dating from 1845 until 1991 have shown that lowest heavy metal (As, Cd, Cr, Cu, Pd, Ni, V and Zn) concentrations occurred in the samples from the earliest period (1845 to 1901) and thereafter concentrations generally rose steadily between 1945 and 1974, before falling again in 1991 (Herpin *et al*, 1997). Overall, 1991 concentrations are lower than any others included in the survey (with the exception of Ni and V). Despite the possible sampling and herbarium storage techniques affecting concentration levels, this study is an indicator of increasing levels associated with progressive industrialisation followed by a decrease due to improved pollution prevention methods.

The studies of (a) Berg *et al* (1996) and (b) Herpin *et* al (1997) are suggestive of (a) recent reductions and (b) longer term increases followed by more recent reductions in depositions of heavy metals. Although the examples are from only two studies there is evidence from lake sediment cores that these general trends are indicative of what is occurring throughout Europe. Studies in England (Hamilton-Taylor, 1979; Sanders *et al*, 1993); in Scotland (Battarbee *et al*, 1995); in Switzerland (Von Gunten *et al*, 1997 and Birch *et al*, 1996) and in France (Martin, 1985) give a historical record of anthropogenic atmospheric trace metal pollution and will be discussed more fully in Chapter 3.

2.8 **MOLAR and Lochnagar research**

As part of the EU research programme on Mountain Lake Research (MOLAR), heavy metals (Cd, Pb, Co, Cu and Zn) in rainwater (bulk deposition) and in lake water have been determined at six remote lake sites in Europe. Sampling and analysis for these metals was run between July 1996 and April 1998 and some data from the project are shown in Figure 14 to Figure 16. The MOLAR sites are as given in 2.3.1. Although this data may provide some information on the degree of spatial variability throughout Europe, it is not yet a long enough record to draw any meaningful conclusions on temporal trends.

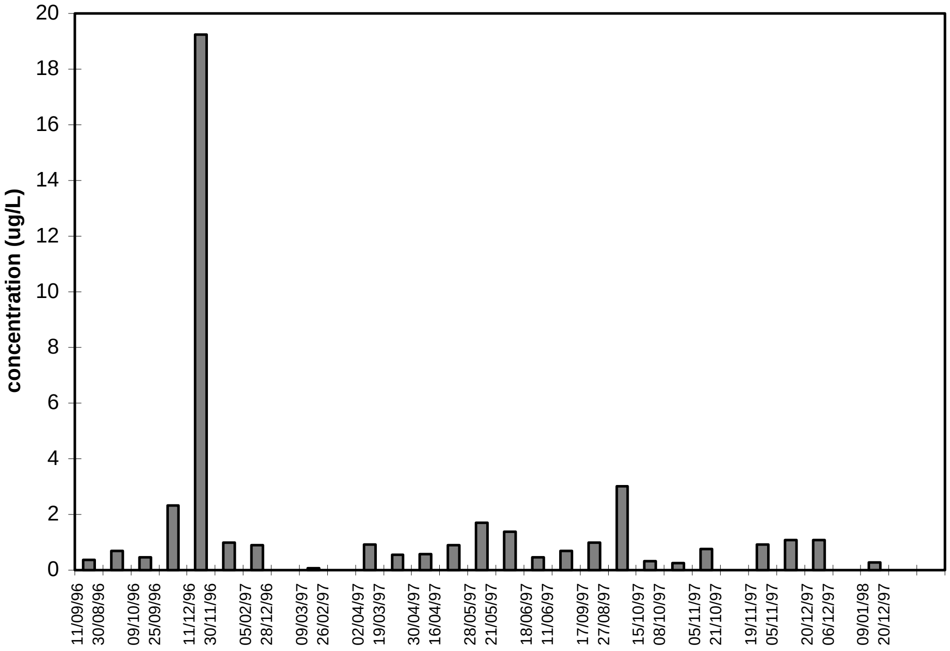


Figure 14 Pb concentration in bulk deposition samples collected from Lochnagar (NE Scotland) over the period August 1996 - January 1998.
Time periods where no data are shown indicate determinands below limits of detection (after Yang, pers. comm.)

The data presented in Figure 14, Figure 15 and Figure 16 show metals deposition data over a period of around 18 months which, although too short to be able to make assumptions about long-term trends, are useful in identifying single time periods with unusually high inputs e.g. Ni concentration of 5.3 μg L^{-1} between 11-09-96 and 25-09-96 and Pb concentration of 19.3 μg L^{-1} between 30-11-96 and 11-12-96. Figure 16 gives mercury deposition and lake outflow water concentrations at Lochnagar between July 1997 and February 1999. Assuming that all mercury is entering directly from the atmosphere and as Lochnagar has a single well-defined outflow, the data shows that there is more mercury entering the catchment than being removed over the sampling period. This suggests some form of catchment and/or lake retention of mercury inputs. Mercury deposition data collected in central London over part of the same time period (Yang, pers. comm.) through funding by Ensis Ltd. is also shown in Figure 16 to illustrate deposition differences between urban and rural areas. Concentrations in the urban central London location are ca. 3 times higher than those of the rural site at Lochnagar over the short sampling period. In addition to deposition data, outflow concentration data at Lochnagar exists for the following metals; As, Cd, Co, Cr, Cu, Ni, Pb, Sb, V and Zn.

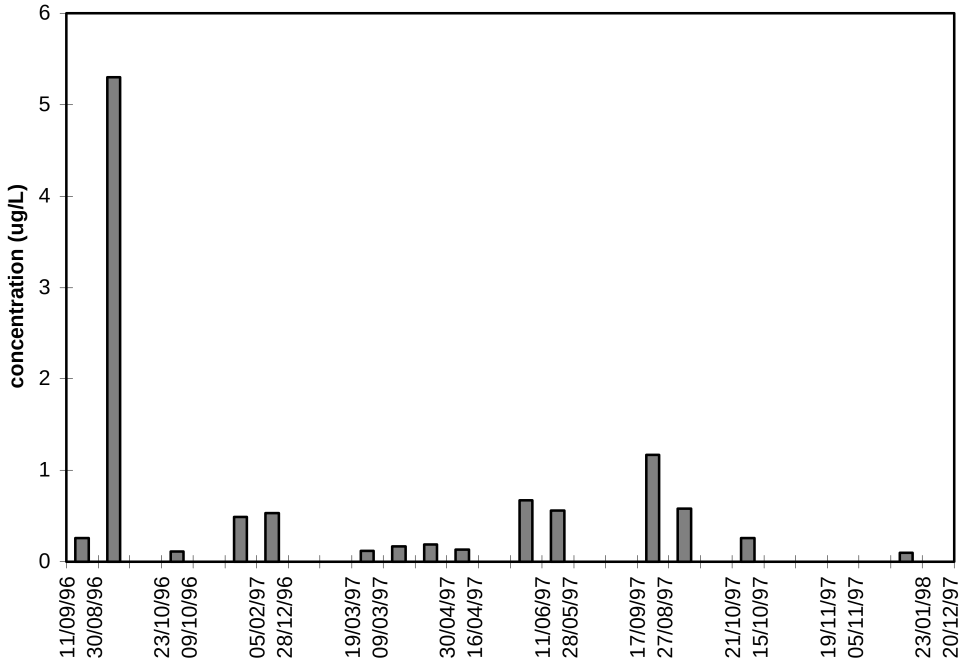


Figure 15 Ni concentration in bulk deposition samples collected from Lochnagar (NE Scotland) over the period September 1996 - January 1998.
Time periods where no data are shown indicate determinands below limits of detection (after Yang, pers. comm.)

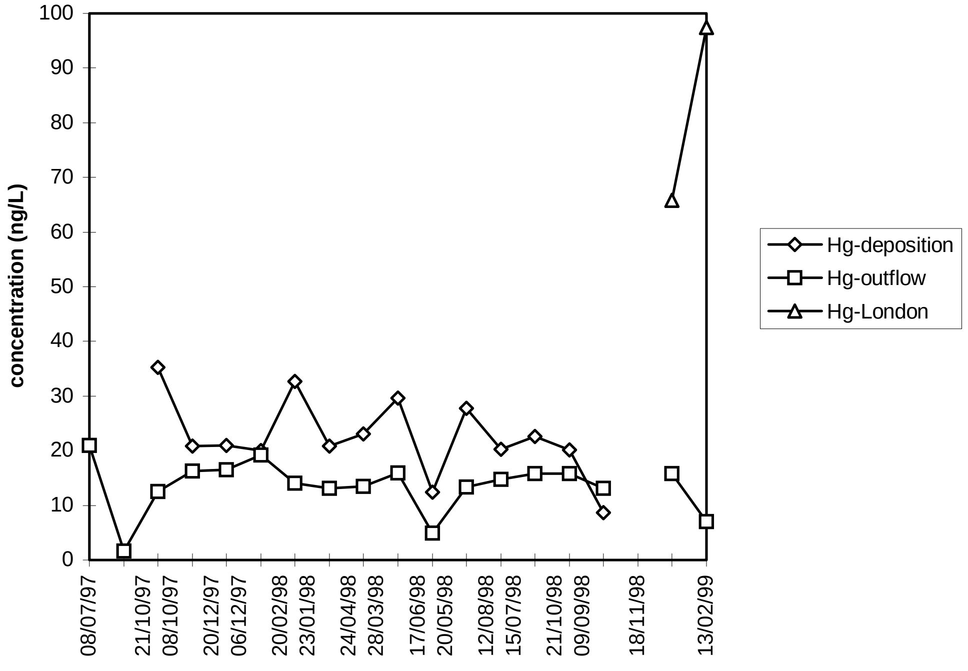


Figure 16 Hg concentration in bulk deposition samples and lake water outflow samples collected from Lochnagar (NE Scotland) over the period October 1997 - February 1999. Hg concentrations in bulk deposition samples from central London 07/01/98 and 14/01/98.
(after Yang, 1999 and Yang, pers. comm.)

The end of the MOLAR research programme will inevitably mean the cessation of sampling and analysis at each of the sites unless continued funding sources can be secured. The UK MOLAR site in northeast Scotland however, will continue to be sampled regularly as part of the DETR-funded Critical loads for Acidity And Metals (CLAM) project. Lochnagar is also a UK Acid Waters Monitoring Network (AWMN) site (Patrick *et al*, 1991) and is one of the UK Environmental Change Network (ECN) sites (Lane, 1997). In addition, Lochnagar is also the focus of PhD research with an intensive study of trace metal storage and the relationships between atmospheric deposition and critical loads. This work will calculate complete trace metal budgets within a lake catchment through analysis of soils, sediment, terrestrial and aquatic vegetation and plankton species. Of the metals determined in this study, special emphasis is placed upon mercury (Yang, 1999).

The MOLAR data highlight the short-term nature of a lot of atmospheric deposition monitoring. The conclusions of Neal *et al* (1996) stating that it is important that the limited number of long-term trace metal monitoring programmes are maintained and that a review to assess the what monitoring programme is required to satisfy international demands for a critical loads programme are further endorsed in this report.

2.9 **European modelling of metals deposition**

In the absence of comprehensive deposition monitoring on a regional and national level there has been a large amount of work undertaken to try and develop models which can provide information on the routes of transport and deposition of environmental pollutants (see also 1.9).

The HMET-model developed by EMEP is formulated in the Eulerian framework. This assumes two-dimensional transport of emitted metals within a single well-mixed homogeneous layer, which during transport are subject to the forces of wind and are removed via wet/dry deposition. The HMET-model has been tested against observations at seven monitoring stations throughout Europe (Bartnicki, 1994) and showed a reasonable agreement with measured levels for deposited As, Pb and Cd. Zn was underestimated by one order of magnitude, but this was thought to be due to underestimations in emissions data. Emission values for the UK and deposition values for the UK predicted by the EMEP model are shown in Figure 17.

The model-predicted UK deposition values are given as 0.013 tonnes Cd yr^{-1}, 0.056 tonnes As yr^{-1}, 2.90 tonnes Pb yr^{-1} and 10.22 tonnes Zn yr^{-1}. There are, however, some limitations in the model, such as the large grid size (150 x 150 km) creating overestimations of metal transport between neighbouring countries and there are also non-linear effects introduced by numerical approximations made in the model (Bartnicki, 1996). Despite their inherent problems, model deposition figures are invaluable in approximating the extent and patterns of deposition over a region-wide area.

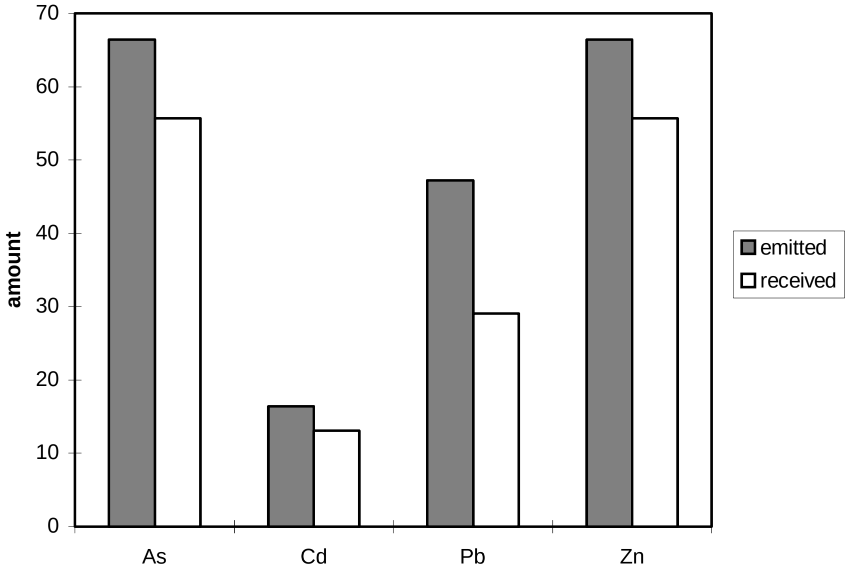


Figure 17 UK emission and deposition values for 1985 for As and Cd (x10^3 kg) and from Pb and Zn (x10^5 kg) the HMET-model
(after Bartnicki, 1996)

Rovinskii *et al* (1994) have used a numerical climatic model to calculate the transport of heavy metals in the atmosphere and their deposition throughout Europe. Emissions data from Pacyna (1983) and the EMEP framework were used. The model-calculated lead concentrations in air and in deposition are shown in Figure 18. They indicate an area of greatest concentration around south-east England, north-west France and northern Germany associated with climatic features of the transport from emission sources. Using this model, the authors observed calculated lead concentrations 1.1 to 5 times higher than the multi-year observations at background monitoring stations. Results were consistently greater for measured data (both aerosol concentrations and wet/dry deposition) from the six sampling stations, than for values derived from the model.

The TRACE (trace toxic air in Europe) atmospheric transport model, developed by the International Institute of Applied Systems Analysis, has been used to model atmospheric, cumulative deposition loads of heavy metals to European soils over Europe during the period 1955-1987. Olendrzynski *et al* (1996) have presented TRACE model calculated depositions for Cd, Pb and Zn over this period of industrial expansion as a cumulative load. This is of particular interest to assess total deposited amounts to land from all sources (e.g. from air, sewage sludge, fertilizer) and is of interest in future policy planning.

Model-calculated 1985 data for zinc and cadmium concentrations in air showed similar concentration patterns over Europe, which would be expected because they are emitted to the atmosphere by the same technological processes, namely coal burning. The largest concentrations were found in the Balkans, northern Spain and in the former Soviet Union and had maximum values of 1.50 ng m^{-3} for Cd and 42.77 ng m^{-3} for Zn. Lead concentration patterns in air showed a more uniform distribution than both Cd and Zn, with highest values centred on western and central Europe associated with large vehicular emissions of lead. The highest lead value was 75.4 ng m^{-3}, but a value of 50 ng m^{-3} (the EC limit value, expressed as an annual average) was exceeded in several countries including Germany and the UK. Total depositions for 1985 indicate Cd maxima occurring in southern Poland (1.47 mg m^{-2}), the Czech Republic and Spain. Deposition patterns for Zn are similar to those of Cd, with maxima of 43.6 mg m^{-2} in southern Poland. For Pb, the maximum value is located at the German-Dutch-Belgian border There are also high values, over 20 mg m^{-2}, in France, the UK and Germany, associated with areas of high traffic densities.

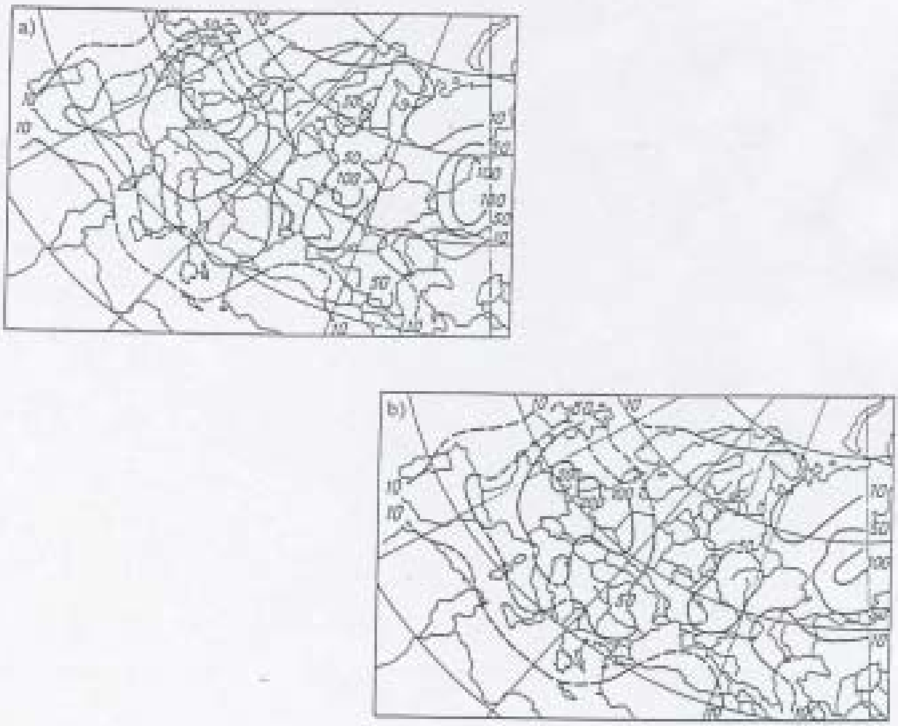


Figure 18 Results of the numerical-climatic model calculated (a) annual mean lead concentrations in air (ng m^{-3}) and (b) the total annual mean lead depositions (mg m^{-2}) onto the underlying surface for Europe. (after Rovinski et al, 1994).

Areas of the highest cumulative deposition, according to Olendrzynski *et al* (1996), over the period 1955-1987 are as follows; for Cd - Southern Poland and the German-Dutch border $>$ 40 mg m^{-2}; Pb - Western Europe (Germany, France and Great Britain) $>$ 500 mg m^{-2}; Zn - southern Poland $>$ 2600 mg m^{-2}. UK data taken from the EMEP grid network show a distinct north-south cumulative deposition gradient, highest and lowest UK values and approximate locations are shown in Table 8. The insensitivities associated with the large grid size (150 x 150 km) are apparent in the case of lead which show the area of the highest deposition extending throughout most of England.

In addition to the models described above, NILU in Norway and the GKSS Research Centre in Germany have developed Lagrangian one-layer trajectory models (sulphur versions adapted for inert particle associated substances) to model trace metals in Europe. Using six-hourly meteorological data, they model inputs to the North Sea / Baltic Sea (GKSS) as monthly and annual averages and to southern Norway (NILU) as daily averages (Pacyna, 1996).

Models created to predict the atmospheric transport and deposition of pollutants have proved to be extremely useful predictive tools. The long-term Lagrangian modelling of acidifying pollutants in the EMEP 150 x 150 km grid has been essential in assessing compliance with the Sofia (1988) and Oslo (1994) Protocols (EMEP, 1997). Long-range atmospheric transport models are low resolution but are necessary to show trends and patterns in transport and deposition on a regional level. To ensure accuracy, however, modellers require high quality emissions data. Pacyna (1994) reported the low accuracy of emissions data and Bartnicki (1996) showed the effect of inaccurate emissions data in the case of zinc transport and depositions over Europe.

	Cumulative deposition from 1955-1987 (in mg m^{-2})	Location
Cd (highest)	20-40	south-central England
Cd (lowest)	1-2	northwest Scotland
Zn (highest)	1500-2640	south-central England
Zn (lowest)	50-100	northern Scotland
Pb (highest)	500-1000	all central and eastern England
Pb (lowest)	50-100	northwest Scotland

Table 8 Highest and lowest cumulative depositions of Cd, Zn and Pb in the UK for the years 1955-1987 (after Olendrzynski et al, 1996)

Assumptions related to the two-dimensional transport of heavy metals and homogeneous dispersal of pollutants vertically within the mixing layer in air are sources of uncertainty in the determination of country budgets. In addition, non-linear effects can be created through the use of models. For example, that when the model is run with emissions from country ‘A’ only, and then with emissions from country ‘B’ only, the sum of the computed depositions should be exactly the same as the one obtained from the model run with both emissions included. However, in practical applications this is not the case and can also give rise to uncertaincies (e.g. Bartnicki, 1996) and should also be considered when using Eulerian models.

In addition to using recent meteorological data in model development, models can be scrutinised and refined with the aid of high quality deposition monitoring.

Chapter 3: Assessment of atmospheric heavy metals monitoring approaches

3.1 **Lake systems**

Following emission to the atmosphere, heavy metals are distributed by atmospheric processes that are capable of transporting particle-bound pollutants hundreds or even thousands of miles (e.g. Murozumi *et al*, 1969 and Davies *et al*, 1991). The majority of pollution is derived from urban and industrial areas and these areas are often heavily influenced by local sources, so it is better to study changes in regional loadings of pollutants in the atmosphere in rural locations (Sanders *et al*, 1993). Lakes in remote rural areas give us an opportunity to study the long range atmospheric transport and deposition of heavy metals. Once in the lake, metals are acted upon physically, biologically and chemically and they in turn affect the biology and chemistry of their environment (see 1.7.2/3). A diagrammatical representation of the fate of heavy metals in a lake system is given in Figure 1 which illustrates the dynamics of metal movement into, out of, and retention within the lake. Significantly, there is a high proportion of metals retained after deposition and in the case of rural lakes this will be almost entirely anthropogenic and atmospheric in origin. The retained particulate associated metal fraction will eventually settle out and become incorporated into the sediment. Generally, the distribution of these particles will reflect temporal trends in deposition (Welch *et al*, 1991).

3.1.1 **Sediment cores**

The use of lake sediment cores to reconstruct pollution histories have been discussed briefly in 1.7 and 2.1.3. In the UK, Sanders *et al* (1993) looked at the concentrations of six heavy metals (Zn, Pb, Cu, Ni, Cd and Mn) a sediment core from Esthwaite Water, Cumbria. As atmospheric deposition is a major source of Cd, Cu, Pb and Zn, concentration trends observed in the core may indicate long term changes in atmospheric loadings of these elements. Over the long term (1820-1990) cadmium, copper, nickel, lead and zinc show broadly similar trends, with the lowest concentrations at a depth of between 50 and 60 cm (representing early to mid 1800s), and an increase with time, reaching a maximum at depth of between 10 and 25 cm (representing the 1930s to 1960s). After this there is a gradual decline up until present (Sanders *et al*, 1993). Although all elements show similar trends, the times and duration of maximum increases vary between elements and is presumably related to emission levels, in addition to chemical and biological variables. The use of sediment cores highlight the significance of long-term atmospheric deposition of metals to rural areas of the UK. Similar work on sediment cores by Heft-Adams (1993) has suggested that in the United States, the atmosphere is the most significant source of As, Cd and Pb to the Great Lakes area.

Although sediment cores can provide information on historical pollution inputs to a lake system (e.g. Hamilton-Taylor, 1979 and Von Gunten *et al*, 1997), there is growing evidence that there may be some perturbation of pollution records. This perturbation may be brought about by sediment disturbance during sampling, or post depositional, through natural physical and/or biological mixing. In addition, perturbations may be caused by diffusion of elements along pore water concentration gradients and via diagenic re-mobilisation (Farmer, 1991). Foster and Charlesworth (1996) have gone further, stating that heavy metal distributions within the sediment core are more likely to be a function of post-depositional remobilisation than the history of metal loading to the basin. Clearly, in the interpretation of sediment core heavy metal pollutant profiles due attention should be made to possible pertubatory processes.

3.1.2 **Relationship between historical sediment cores and airborne concentrations**

A comparison of sediment accumulated metals with airborne concentrations of metals between 1970 and 1990 is shown in
Figure 19. The airborne metals concentrations are mean annual average concentrations and represent simplistically what changes there have been from approximately 1970 and 1990, the sediment data in turn represent the same time period. Decreases in airborne particulate metals are reflected in heavy metal concentrations in the sediment profile, with the greatest reductions, in terms of airborne mass and deposited mass, seen for Pb and Zn in both media. It is only with a long term atmospheric monitoring programme that make it possible to observe the correlation between atmospheric levels and sediment deposited concentrations. Unfortunately, the data provided by Cawse *et al* (1994) and Baker (1997) consist of bulked 10 year averages. Shorter term data of a year or six months would enable correlations to be made and this data can only be used as a guide. Esthwaite Water is only ca. 5 km from the Wraymires monitoring site and would provide a good location for high resolution comparative work of this nature although there will be catchment sources to this lake which may be significant and should also be considered. Work carried out on a sediment core from Lake Windermere (approximately 5 km east of Esthwaite Water) by Hamilton-Taylor (1979) mentioned the possibility of comparing the atmospheric deposition data from Wraymires with sedimentary fluxes but this was rejected because the fluxes were averaged over a four year period (1967-1971) and could not be compared directly with deposition data. With the availability of long-term metals deposition datasets such as those from

the rural network and others (e.g. Lochnagar) there is enormous scope to investigate the absolute long term relationship between deposition and accumulation in co-located lake systems.

The ratios of present (surface) to pre-industrial concentrations at Esthwaite Water decrease in the order; Pb (3.8) > Cd > (3.5) > Zn (2.7) > Cu (2.2) > Ni (1.1). demonstrating that although Cd and Pb inputs have declined more than the other heavy metals, their present day inputs are still proportionally greater when compared with background fluxes (Sanders *et al*, 1993). Geochemically-derived and natural atmospheric heavy metals form the background levels at a location, subsequent additions are entirely due to anthropogenic influences and this can be quantified by determining the enrichment factor (see 1.1 and Pacyna, 1998).

The work at Esthwaite Water shows, that of the metals discussed above, Pb and Cd are more inclined to be of man-made origin than natural and, that although levels have been seen to be significantly reduced over the past 15-20 years, they are still enhanced more than the other metals. Increased enhancement of Pb and Cd may not be due only to source but also to their physical characteristics after emission. Cawse (1987) has suggested that Pb and Cd are generally associated with finer aerosols generated through combustion than Cu and Ni and consequently they are distributed further from their source to remote and rural locations.

Other workers have used sediment cores to provide a historical record of anthropogenic atmospheric heavy metal pollution in rural and remote locations, far from point sources. Locations include; the Arctic (Hermanson, 1991), the Swiss Alps (Birch *et al*, 1996), the Scottish Cairngorm mountains (Battarbee *et al*, 1995)

It has been established that lake sediments provide a record of pollutant inputs. However, these inputs will not just be due to atmospheric deposition, in most cases lakes in populated countries will have been directly affected by localised sources. Von Gunten *et al* (1997) highlighted increases of lake sediment copper, cadmium and zinc up until 1960 due to increasing industrialisation around a lake, followed by reductions due to more stringent restrictions on industrial emissions and the introduction of sewage treatment plants. Interestingly, this study did not show increasing lead sediment concentrations between 1900 and 1975, contrary to other research throughout the world (e.g. Callender and Van Metre, 1997) but did reduce with the increasing use of unleaded fuel. Rippey (1982) examined the impact of heavy metals inputs to Lough Neagh, Northern Ireland from a sewage treatment works and found concentration increases with decreasing distance from the pollution source. Foster *et al* (1991) found high catchment-derived heavy metals (Pb, Cu, Ni, Zn and Cd) in sediment at an urban reservoir in the English midlands and Farmer *et al* (1997) have determined large inputs of lead in sediment cores taken from Loch Tay in Scotland, associated with historical lead mining in the area.

In order that lake sediments can be used as a record of atmospheric inputs of heavy metals all other inputs to a lake must first be considered and this can normally be achieved through site inspection and local historical records or from detailed geochemical mapping of the area (see Larsen *et al*, 1996). To conclude, the study of atmospheric heavy metal deposition is best achieved in rural and remote locations.

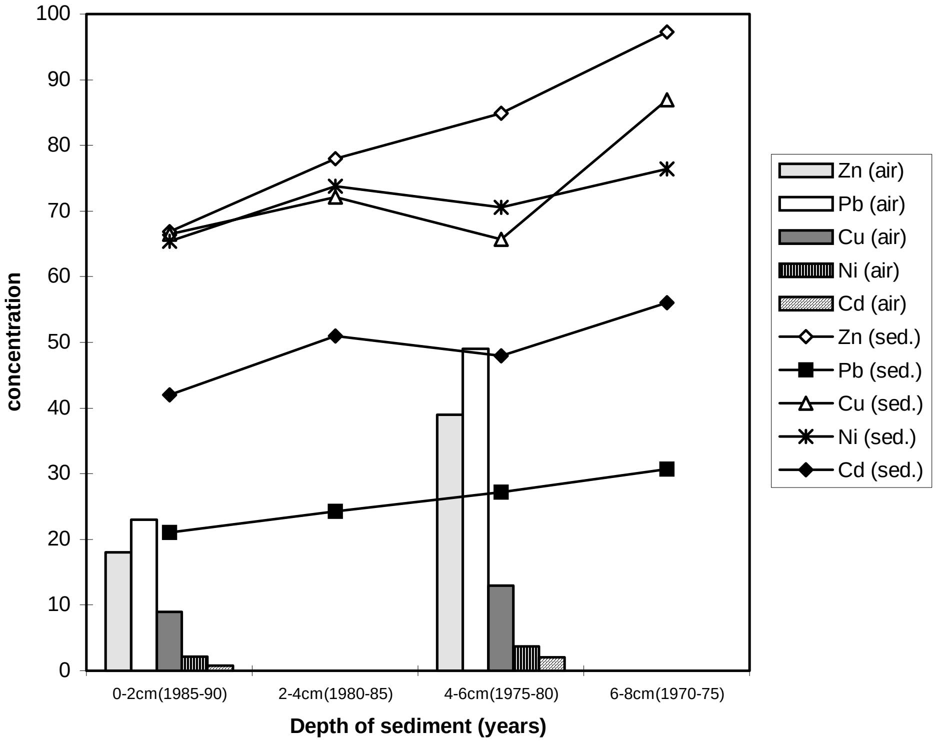


Figure 19 Temporal concentrations of Cd, Cu, Pb and Zn as shown by a sediment core from Esthwaite Water, Cumbria (after Sanders et al*, 1993) and from air particulate monitoring at Wraymires, Cumbria. (Cawse et al, 1994 and Baker, 1997)*
(Air concentrations all in ng m^{-3}*, sediment Cu and Ni in* $\mu g\ g^{-1}$*, Zn and Pb in* $10^{-5}\ g\ g^{-1}$*, Cd in* $10^{-7}\ g\ g^{-1}$*.)*

3.1.3 **Sediment-metal profiles from urban and rural locations**

There is a large amount of published literature relating to the accumulation of heavy metals within lake (and marine) sediments and their uses in establishing a record of past pollutant inputs form both atmospheric diffuse sources and direct point sources. Reference is made below to a number of studies and serve to illustrate heavy metal accumulation within sediment profiles.

Foster *et al* (1991) have revealed that there are high contamination factors for Pb, Cu, Ni, Zn and Cd in a sediment profile at an urban reservoir in the English midlands derived from within the catchment. Vesely *et al* (1993) have shown large elevated concentrations of heavy metals in mountain lake sediments in the Czech Republic, from an area with no known heavy metal ore deposits and with no point sources. Similarly, Rose and Rippey (1996) identified heavy metal pollution in a sediment core from a remote lake, Loch Coire nan Arr, in northwest Scotland. Although being amongst the least polluted areas the UK there is evidence of atmospheric lead, zinc, copper and arsenic contamination in the sediment. The same sediment core, however, showed little or no evidence for nickel, chromium and cadmium contamination. The contamination in the Czech and Scottish lakes is thought to be due mainly to deposition of atmospherically transported heavy metals rather than the within-catchment inputs at the English urban reservoir. Clearly, the impact of diffuse atmospheric heavy metal pollution can be as great as the impact of point source catchment pollution, especially in geologically and ecologically sensitive areas.

Two sediment-heavy metal profiles are shown in Figure 20 and Figure 21 for a lowland site at Banbury reservoir, southeast England and for a remote rural upland site at Lochnagar, northeast Scotland respectively. Actual sediment metal concentrations are seen to be generally of the same order of magnitude between both sites although they are from very different locations. Although sediment concentrations appear similar, the urban site is in fact more polluted due to the dilution effect of a faster sediment accumulation rate. (although without any dating of the Banbury core this cannot be confirmed). Sediment concentrations when taken in isolation (i.e. without information on sediment accumulation rate) may give misleading information on the contamination status of a particular location. In order that the degree of contamination at a particular lake may be assessed and comparisons between lakes made, Rose and Rippey (1996) have developed a method which uses the contamination and dry sediment burden since 1900 to account for the influence of sedimentation rate on the accumulation rate of chemicals in the sediment.

Care must be taken when setting critical limits for sediments. Currently, critical limits in sediments have already been set in several countries such as in Sweden, Norway and the Netherlands (De Vries *et al*, 1998). Unfortunately the ecotoxicological basis for these values and whether they are for sediment or suspended sediment is not made clear. De Vries *et al* (1998) have compiled these data to show critical limit ranges, they are; Cd 0.6-2.4 $\mu g\ g^{-1}$, Cu 36-120 $\mu g\ g^{-1}$, Cr 37-120 $\mu g\ g^{-1}$, Ni 10-180 $\mu g\ g^{-1}$, Pb 15-100 $\mu g\ g^{-1}$ and Zn 123-1050 $\mu g\ g^{-1}$.

3.1.4 **Heavy metals in mosses and surface sediment samples**

Moss species are considered as being good estimators of the extent of atmospheric heavy metal pollution (Berg *et al*, 1995). A comparison of lake surface sediment (0-0.5 cm) and moss (*Pleurozium schreberi* and *Hylocomium splendens*) heavy metal data obtained by Rose and

Harlock (1998) throughout the UK shows broadly similar patterns of spatial distribution. Heavy metal concentrations in surface sediments from the UK generally show the following order;

- English midlands / northeast England > Clyde / Forth valley > London / southeast England > south Wales.

And, heavy metal concentrations in moss samples from the UK generally show the following order;

- English midlands > central Scotland / north England > southeast England / Wales

The moss samples do show similar trends to those of sediment metals. However, moss metals data does not have as good a geographical coverage as sediment data, especially in the south and east of the country due to the absence of the selected species. As direct comparisons were not always possible, mean moss concentrations were taken from eight geographical regions to determine the rankings given above. The use of moss species, such as *Hylocomium splendens*, as a bioindicator has proved an extremely useful tool in areas where it has good geographical coverage, such as Scandinavia (Berg *et al*, 1995). However, in areas including the south-east and midlands of England where it is less prevalent, the limitations of using mosses are evident. See also 2.6.2.2 [6] for a discussion on the UK heavy metal moss monitoring survey of 1996/7 (Parry and Williams, 1998).

The surface sediment (0-0.5 cm) represents recent material carried into the lake from inflow streams and from deposition of atmospheric particulate material over a period of time related to the accumulation rate of the sediment. Thus, the surface sediment can provide a record of modern atmospheric inputs to the catchment. This approach has been used in the FLAME study (Rose and Harlock, 1998; Bowman and Harlock, 1998; Aliksaar and Punning, 1998 and Fott *et al*, 1998) to look at spatial trends in concentration on a nationwide basis. However, for more information on the anthropogenic enrichment of elements, natural ‘background’ metal concentrations need to be determined from geochemical records and/or from analysis of deeper sediments dating from pre-industrial times.

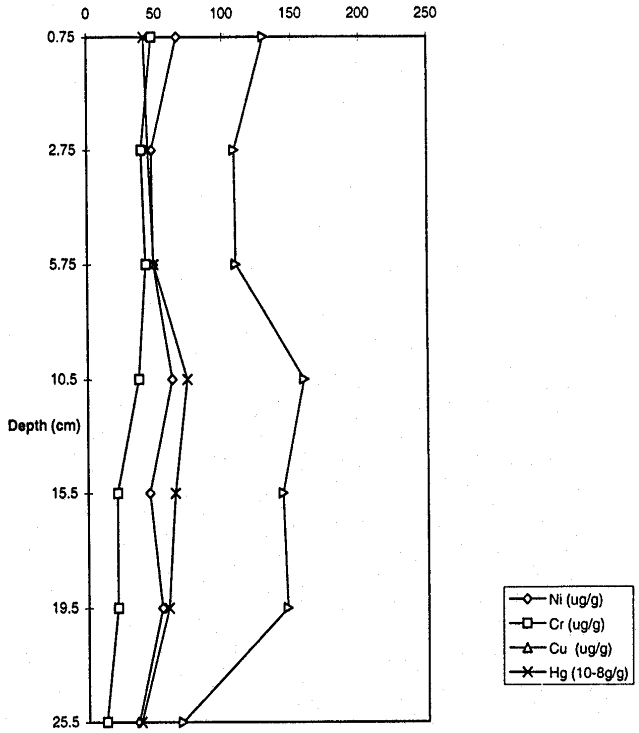


Figure 20 Heavy metal sediment core profile from Banbury Reservoir (core BUNB5), Southeast England (after Yang, pers. comm.)

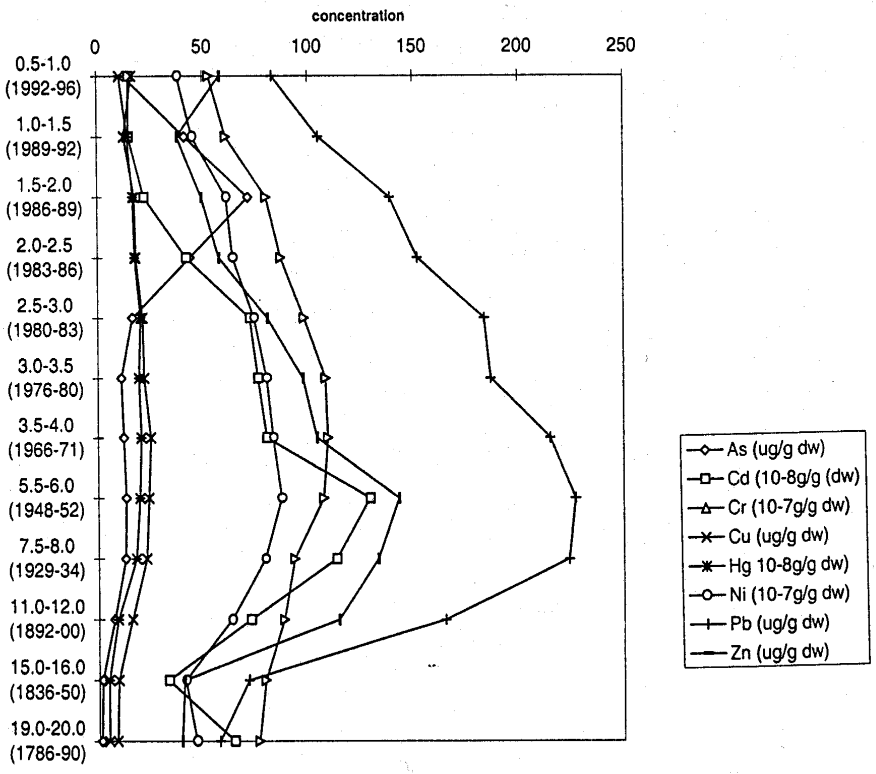


Figure 21 Heavy metal sediment core profile from Lochnagar (core NAG8), Northeast Scotland (after Yang, pers. comm.)

3.2 **Sediment traps**

The depositional fluxes of heavy metals have been measured in Lake Windermere, Cumbria using sediment traps (Hamilton-Taylor *et al*, 1984). Traps were located in a deep water (42m) area of the lake for a period of 1 year (September 1980 to September 1981) and sampled monthly. Findings from this research include;

- Pb - main deposition occurred in November to January, thought to be associated with the major period of mineral accumulation (through high river flows) and also possibly due to re-suspension of sub-littoral sediments.
- Cu - found to be deposited predominantly in March and April (58% of the annual flux). Dissolved Cu concentrations were higher in winter than in summer due to the absence of an efficient scavenging mechanism.
- Zn - some 56% of the annual deposition occurred in January and March, but no conclusions as to processes involved.

The work of Hamilton-Taylor *et al* (1984) has shown that, in addition to changes in river discharge to lakes and deposition to lakes over the period of a year, trap heavy metal fluxes are affected by the lake phytoplankton populations. Of the three metals, copper appears to be the most heavily influenced by the sedimentation and decomposition of diatomaceous material. A trap to surface sediment ratio for Cu of 9.5 suggests that there is large scale recycling of this element at the sediment-water interface surface.

More generally, the workers found that the annual trap to surface sediment flux for Al ($\leq$ 1) indicated the absence of local sediment re-suspension at the deepwater sampling location but that larger ratios for Pb (1.4) and Zn (1.5) suggested possible biogeochemical recycling at the sediment-water interface.

The importance of this work lies in the relationship between heavy metal fluxes and phytoplankton growth over the duration of one year, it demonstrates that even after metals enter the water column they are subject to biological factors which can influence the rate and magnitude of their eventual incorporation into the sediment. Biological factors in addition to chemical (e.g. pH, redox) and physical factors (e.g. temperature, inflow rates) influence the incorporation/release of metals into the sediment. Unfortunately, formalin was used as an *in-situ* biological preservative in this study (although Mn hydroxide was added as a pH buffer) which can lead to lowering of pH and possible solubilisation of metals.

Koelmans (1997) stated that clay and organic matter associated heavy metals captured in sediment traps showed negative trends over the period 1987-1992 in Dutch lakes. In addition, there was a distinct seasonality effect due to algal biomass dilution and it was concluded that trophic state significantly affects trace metal recycling in a similar way to that found by Hamilton-Taylor *et al* (1984) (see also Jak, 1998).

The above two monitoring programmes were designed to observe the effects of phytoplankton populations on trace metal concentrations (Hamilton-Taylor *et al*, 1984) and to monitor the differences in material captured in sediment traps and those at the sediment-water interface (Koelmans, 1987) not specifically to monitor atmospherically-deposited metals over a long period. Hamilton-Taylor *et al* (1984) attempted to compare sediment trap flux data with that of surface sediments (Hamilton-Taylor, 1979) but the resolution of sediment sampled represented a 4-year average and therefore data could not be related directly to sediment trap material (1-year period).

3.3 **The UK Acid Waters Monitoring Network (AWMN)**

The UK AWMN was established in 1988 by the Department of the Environment (DoE) with support from the DoE (Northern Ireland) to provide a long term high quality chemical and biological database, which in conjunction with the existing UK precipitation monitoring network would allow trends in surface water acidity to be assessed (Patrick *et al*, 1991). Selected monitoring sites were in areas considered sensitive to acidification, yet were chosen to minimise the effects of anthropogenic catchment-based impacts. A map of AWMN sites and their grid references are given in Appendix 5.

The Network has been operational for eleven years and over this time there has been a large amount of biological, chemical and hydrological data collected from each of the 22 lake and stream sites (see AWMN, 1995). In addition, there is an archive of environmental samples from the AWMN at the Environmental Change Research Centre (ECRC), University College London (UCL), which includes sediment trap samples, aquatic macrophyte and moss samples, terrestrial moss samples. In addition, sub-samples of quarterly AWMN water samples are stored at the Institute of Hydrology, Wallingford, Oxon.

3.3.1 **AWMN Sediment trap samples.**

The use of sediment traps to monitor deposition to lake systems has been referenced in 2.1.3 and also previously in this section. Yearly sediment trap samples, representing annual deposition have been taken from 11 lake sites since 1990, the samples have been dried and are stored at the ECRC, UCL. The sediment traps used consist of an array of three tubes (5 cm diameter) into which

PVC cylinders are placed and secured. The tubes are attached to a triangular plastic frame with inherent buoyancy which is then suspended on a anchored rope ca. 1m above the sediment surface, this rope is then attached to a buoy floating on the water surface. Traps are generally located in the deepest part of the lake but more importantly away from inflow/outflow influences. Also, if possible, traps are placed below the photic zone to prevent algal growth around the cylinder aperture and restricting access to sedimenting materials. Each year the traps are retrieved and the cylinder contents emptied before redeploying at the same location. The dry weight of the recovered sediment typically ranges from 0.2g to 0.8g per cylinder depending on site. Additionally, a surface trap (at c.a. 1 m depth) has been deployed in conjunction with the deep water trap (c.a. 20 m depth) at Lochnagar to compare direct deposition inputs with resuspension from the lake littoral sediments.

More recently, in 1998, it was decided that a number of trap samples from each site should be sampled, processed and stored to specifically facilitate heavy metals analysis.

3.3.2 **Aquatic macrophytes and moss samples.**

During the annual AWMN sampling programme, some aquatic macrophytes and moss samples have been taken, mainly as an aid to taxonomic classification, but they also serve as a record of their environment at a particular time and could be analysed for heavy metals to give a spatial and temporal record of environmental concentrations. Collection of samples over the years has not been consistent but there are a number a archived samples which include;

- *Sphagnum auriculatum* taken from most lake sites annually from 1988-93 and bi-annually from 1993 to present.
- *Sphagnum auriculatum* taken each year from some stream sites where it occurs 1988-present.
- *Liverwort* spp. at some sites where there is coverage (generally where there is no sphagnum present) taken each year from 1988-present.

(Monteith, pers. comm.)

Unfortunately individual sample size of the aquatic macrophyte and moss archive is often small.

Sphagnum auriculatum has been used in moss bags to monitor atmospheric metal pollution (Vasconcelos and Tavares, 1998). However, although no record of using aquatic *Sphagnum* species could be found, other aquatic mosses have been used as biomonitors e.g. *Rhynchostegium riparioides* (Wehr and Whitton, 1983 and Mersch and Reichard, 1998) and *Fontinalis antipyretica Hedw*. (Say and Whitton, 1983; Yang, pers. comm.). Aquatic mosses could be used as a biomonitor of aqueous metals, as opposed to terrestrial species such as *Hylocomium* *splendens* which are routinely used for atmospheric biomonitoring for heavy metals (e.g. Berg *et al*, 1996).

3.3.3 **AWMN water samples**

Quarterly water samples are routinely taken from all AWMN sites (lakes and rivers). and an archive of acidified water samples from these sites is held at the Institute of Hydrology. The archived samples could be retrospectively analysed to provide a long-term record (1988-present) of surface water heavy metal concentrations at AWMN sites and would give indications of any temporal trends at sites. They would, also provide a good spatial record of heavy metal water concentrations trends in the UK, particularly on the west coast.

3.4 **Other sediment trap samples.**

In addition to sediment trap samples from the AWMN, there are also other lake sites in the UK which contain sediment traps from the ECRC, UCL. The sites are;

- Loch Laidon (Highland) - deployed since 1996
- Loch Enoch (Galloway) - - deployed since 1990.
- Loch Narroch (Galloway) - deployed since 1990.
- Round Loch of the Dungeon (Galloway) - deployed since 1991.

Traps at each of these additional sites have been sampled annually at a similar time to AWMN traps.

3.5 **AWMN terrestrial moss samples**

Terrestrial moss samples of the commonly used biomonitor species; *Hylocomium splendens* and *Pleurozium schreberi* have been taken from AWMN sites (where available) since 1998. All samples have been air-dried and archived at UCL.

3.6 **FLAME surface-sediment and moss samples.**

Surface sediment samples from 75 lake sites in the UK and Northern Ireland and 36 in Ireland were collected for analysis as part of the FLAME project during 1994 (Rose and Harlock, 1998 and Bowman and Harlock, 1998). In addition, moss samples (*Hylocomium splendens* and *Pleurozium schreberi*) were collected for analysis from each of the lake catchments (where available). A brief discussion of this work can be seen in 2.7. Data on heavy metals concentrations already exists for these sediment and moss samples and the material remains archived at UCL should further analysis be required. In addition, a full gravity sediment core (c.a. 20-40 cm) was taken at each site then dried and archived should retrospective analysis be needed. Further sampling in the future at some or all of the FLAME sites would provide a information on temporal changes in heavy metal concentrations.

3.7 **Assessment of heavy metal inputs to lake systems**

It has been stated previously in this section that lake sediment cores can be used to provide a record of past pollution inputs (e.g. Battarbee *et al*, 1995; Farmer *et al*, 1997 and Rippey, 1982) and that sediment traps are a useful method to employ in the collection of contemporary sedimenting particles (e.g. Hamilton-Taylor *et al*, 1984 and Koelmans, 1997). The uses of terrestrial mosses to provide information on recent atmospheric inputs of pollution (3-5 years) has also been discussed and is well documented in the literature (e.g. Markert *et al*, 1996b; Berg *et al*, 1996 and Rose *et al*, 1998). Surface sediments have also been used as a record of determining contemporary metal concentrations (e.g. Rose and Harlock, 1998 and Fott *et al*, 1998).

Lake systems provide a means by which deposition of heavy metal pollutants can be assessed and, mountain lake systems in particular, are of special interest to environmental studies because they are generally sensitive to changes in climate and to inputs of pollution (Skjelkvale and Wright, 1997). This can be achieved through analysis of surface waters, surface sediments, contemporary sedimenting particles and through analysis of dated sediment cores giving a temporal record of deposition. Remote lake sites, free from direct inputs, are uniquely suited for this purpose in that determinations of heavy metal concentrations above natural background levels can be considered as being atmospheric in origin.

By defining the whole lake catchment, input/output metal budgets can be determined and this is currently being undertaken at Lochnagar in northeast Scotland as part of a PhD project. Using this approach, a number of parameters must be measured, including catchment rainfall and lake hydrology data but most importantly, the concentrations of heavy metals in;

- Catchment soil profiles
- Lake sediment profiles
- Regularly sampled sediment trap material
- Phytoplankton samples
- Lake macrophyte samples
- Catchment terrestrial vegetation
- Lake input/output samples
- Bulk deposition samples

On a more simplistic level, heavy metal inputs to a lake system can be determined by sampling and analysing one or more of the following;

1. Bulk deposition
2. Catchment moss samples
3. Sediment trap samples
4. Surface sediment samples
5. Catchment soil samples and standing water samples

The above are ranked in order of their suitability in assessing atmospheric inputs, with (1) being the most suitable. Generally, (1)-(4) would all be suitable whereas number (5) is considered unsuitable for this type of work due to the variability in retention/release characteristics between the catchment soil and water. In terms of resolution, collection of bulk deposition offers high resolution with samples commonly taken on a weekly, fortnightly or monthly basis (Cawse *et al* (1994) and Baker (1997) collected monthly rainwater samples and bulked them into quarterly samples). Previously, limits of detection were so large, that large samples were needed followed by pre-concentration before analysis, in order that metal concentrations in natural waters could be determined. Now, however, with improvements in analytical methods smaller sample sizes are able to be used. For example, Neal *et al* (1996) switched from using ICP-OES to using ICP-MS from 1992 to analyse rainfall and surface waters because of increased sensitivity. This makes the analysis of ever smaller amounts of rainfall possible and consequently ever smaller time intervals. Trace metals in water samples are now routinely measured at the low $\mu g\ L^{-1}$ level (e.g. Neal *et al*, 1997b) and even down to $ng\ L^{-1}$ for metals such as mercury.

Metal concentrations in the fine-grained sediments of fluvial substrates can be more than 100 000 times higher than the dissolved concentrations of the same metal (Horowitz, 1991). Metals are readily taken up and stored on sediment surfaces, thus allowing smaller sample sizes to be analysed and yield meaningful results. Relatively small sample sizes are common in sediment trapping at rural upland areas where sedimentation rates are often very low. Sediment traps located in lakes will provide sufficient material to facilitate determination of heavy metal concentrations in the sedimenting material. The use of preservatives to preserve biological samples both prior to (Knauer *et al*, 1984) and after retrieval is not recommended as they can affect the integrity of heavy metals in the trap.

Lake surface sediments (e.g. Rose and Harlock, 1998) and stream sediments (e.g. Tarvainen *et al*, 1995 and Berlekamp *et al*, 1998) have been used to assess the levels of heavy metal contamination and have successfully been used to recognise spatial trends in concentrations. However, there is likely to be no temporal information on inputs because sediment accumulation rates will probably be unknown. In many ways, surface sediments can be likened to moss biomonitoring, as it is of more use in a spatial context than in a temporal one. Although the living material in commonly used moss species (e.g. *Hylocomium splendens*) are considered to represent 2-3 years of growth and therefore will give a measure of integrated (heavy metal) exposure over approximately 2-3 years (Berg *et al*, 1995). More positively, surface sediments and moss samples are relatively easy to sample and analyse and offer an inexpensive, albeit lower resolution, alternative to continuous deposition monitoring and sediment trapping methods.

3.8 **Potential of current monitoring locations and further locations in metals monitoring projects.**

It is recommended that lakes in the UK would provide suitable locations for the monitoring of atmospheric heavy metal deposition and this could be carried out at lake sites from;

I. Existing Acid Waters Monitoring (AWMN) sites (see Appendix 5)
II. Critical Loads Acidification and Metals (CLAM) sites
III. ECN sites (e.g. Llyn Llagi and Scoat Tarn)
IV. Areas of co-located monitoring (e.g. Wraymires, Styrrup and Chilton
V. Further locations selected to ensure UK-wide coverage.

The suitability of lake sites in monitoring atmospheric deposition of metals for a critical loads project has been discussed previously in this section. In addition, lake sites are suitable because of the large geographical network already set up (e.g. AWMN, CLAM and CLAG database) and sites could have co-located sediment traps and deposition collectors (collectors in place at CLAM sites). In areas of the country without suitable water bodies (e.g. sites with direct pollutant inputs, shallow, wind-stressed sites and sites of high disturbance/amenity use in the lake and/or catchment), such as areas in the midlands and south-east England, here deposition collectors could be sited alone.

AWMN and CLAM sites, which are already established sites, would be extremely important in a critical loads-related monitoring programme, they are located in areas of the UK which are geologically-sensitive to acidic inputs (see Patrick *et al*, 1991 for AWMN information) and because of this are concentrated in north Wales, the Lake District and upland Scotland. In order that widespread geographical coverage of the UK is achieved further sites need to be specified.

Currently, there is no unified approach to atmospheric heavy metals monitoring in the UK. The continuous deposition and aerosol monitoring of NETCEN (Cawse *et al* (1994) and Baker (1997)) is the most significant long-term rural study (26 years) and is only carried out at three sites in England. The data from the three North Sea network sites (see OSPARCOM 1996, 1997) has been collected for several years and feeds into a larger multi-disciplinary European project. In addition, the other major long-term network, the Multi-Element Survey (see McInnes, 1979 and 1992) is restricted to UK urban sites. There have been many short-term studies relating to atmospheric concentrations of heavy metals (e.g. Chester *et al*, 1993; Fowler *et al*, 1996; Yaaqub *et al*, 1991; Lee *et al*, 1994 and Lee *et al*, 1998) these studies, although useful in adding to available data, provide little in terms of information on atmospheric concentration trends. Furthermore, many studies on atmospheric metals are part of larger projects and it appears that information is often not widely distributed or published in peer-reviewed journals.

There is a need for a heavy metal atmospheric deposition monitoring programme which will provide nationwide coverage and provide data representative of deposition to upland areas. This aim can be achieved through the use of monitoring methods (deposition collectors and/or sediment traps) sited at current monitoring sites (provided that sites meet the criteria for a heavy metal monitoring programme) and at newly located rural sites free from large-scale environmental disturbances. To allow critical loads of heavy metals to be defined there must be determination of the lowest concentrations at which there is a discernible impact on ecosystems. In order to do this, heavy metal concentrations at sites which are relatively uncontaminated must be determined, not just at sites which are knowingly heavily polluted. Assessment of the sensitivity of specific organisms to inputs of heavy metals should be made in conjunction with compiling deposition data which will quantify these catchment inputs. A network as outlined above would fulfill the requirement necessary heavy metals data necessary for the UK in fulfilling the requirements of forthcoming EC directives.

Chapter 4 **Heavy metals legislation and the development of Critical Loads**

4.1 **EU Environmental Policy.**

4.1.1 **Heavy metals in the context of the Air Quality Framework Directive**

UK and European environmental policy has been introduced in section 1.9. Of particular interest to this study is the Heavy Metal Protocol signed at Aarhus, Denmark in June 1998, at which members of the UNECE addressed emissions of cadmium, lead and mercury, in addition to other heavy metal species. As the UK is a signatory of the UNECE and a member of the EU, the future direction of UK environmental policy and legislation must take into account the Heavy Metals Protocol and forthcoming Daughter Directives to the Air Quality Framework Directive (96/62/EC).

The four objectives of the Directive (EC, 1997a) are;

I. to define and establish objectives for ambient air pollution in the Community designed to avoid, prevent and reduce harmful effects on human health and the environment as a whole;
II. to assess ambient air quality in Member States on the basis of common methods and criteria;
III. to obtain adequate information on ambient air quality and ensure that it is made available to the public *inter alia* by means of alert thresholds;
IV. to maintain ambient air quality where it is good and improve in other cases.

The UK must comply with the above criteria and this is the objective of the National Air Quality Strategy (DETR, 1999) laid out by the British Government. National Air Quality Standards (NAQS) have been set for some common air pollutants (i.e. benzene, CO, NO_2, O_3 and SO_2). However, at present, lead is the only heavy metal to which a NAQS has been assigned (annual mean of 0.5 $\mu g\ m^{-3}$ by 2005) and this is a level adopted from the WHO guidelines on lead exposure related to public health effects. It is expected that forthcoming Daughter Directives will propose limits for other heavy metals including nickel, cadmium, arsenic and mercury and the UK National Air Quality Stategy will have to be updated accordingly.

4.1.2 **NAQS related to vegetation and ecosytems**

Until now, human health issues have been the main factor behind the implementation of NAQS and EU limit values. The World Health Organisation (WHO), however, has set guideline values for air pollutants on ecosystems and vegetation. At the moment, WHO has identified sulphur dioxide, nitrogen oxides and ozone as having significant effect on ecological systems below those known to have a direct impact on human health (DETR, 1999). With the development of critical limits for heavy metals (e.g. De Vries and Bakker, 1998 and De Vries *et al*, 1998) and increasing knowledge of the long-term harmful effects of heavy metals on ecosystems (e.g. Hutchinson and Symington, 1997), it is extremely likely that similar guideline values would be adopted for heavy metals.

The forthcoming EU Air Quality Daughter Directives will require “Definition and establishment of objectives for ambient air pollution in the Community designed to avoid, prevent and reduce harmful effects on (human health and) the environment as a whole”. The current understanding of the negative impacts of heavy metal pollution through continuing (albeit reduced) emissions and potential releases to the environment of already deposited metals make it imperative that the EU (and UK) react to assess the long-term effect of heavy metals on ecosystems.

4.2 **EU Environmental Legislation.**

It is a requirement of Article 4 of the EC Air Quality Framework Directive (96/62/EC) that;

- Limit values should be set and, attainment dates by which these should be met;
- temporary margins of tolerance should be set for the period between the Directive coming into force and the attainment date for the limit values;
- alert thresholds should be set, listing details to be supplied to the public if an alert threshold is exceeded.
- criteria and techniques should be set out.

(EC, 1997a)

It also notes that numerical concentrations included in the limit values and alert thresholds should be based on information from international scientific groups active in this field. At the moment, legislation in the EC (and Britain) relating to air is limited to the following pollutants, as set out in the National Air Quality Strategy;

- **Benzene** - objective of 5 ppb, measured as a running annual mean to be achieved by 2005

- **1,3-butadiene** - objective of 1 ppb, measured as a running annual mean to be achieved by 2005
- **Carbon monoxide** - 10 ppm, measured as a running 8-hour mean to be achieved by 2005.
- **Nitrogen dioxide** - 150 ppb, measured as a 1-hour mean and 21 ppb, measured as an annual mean.
- **Ozone** - 50 ppb, measured as the 97th percentile of daily 8-hour running means to be achieved by 2005.
- **Particles (PM_{10})** - 50 $\mu g/m^3$ as a running 24-hour mean measured as the 99th percentile of daily maximum running 24-hour means to be achieved by 2005.
- **Sulphur dioxide** - 100 ppb as a 15-minute mean measured as the 99.9th percentile in a calendar year to be achieved by 2005.

(DETR, 1999)

According to EC legislation (the EC Dangerous Substances Directive 73/464/EEC), relating to pollutant inputs to water within the Community, heavy metals such as mercury and cadmium are classified as List 1 substances with others such as zinc and copper classified as List 2 substances (EC, 1976). List 1 substances must eventually be eliminated as pollutants and List 2 substances are those which the aim is to reduce their potential to pollute. Both are considered as being of priority concern and measures should be taken to reduce their impact on the environment. Inputs of cadmium and mercury to water are already controlled by Daughter Directives, heavy metals such as zinc, copper, nickel, chromium, lead and arsenic are all classified as List 2 substances and are not covered by Daughter Directive legislation.

Despite this, legislation surrounding pollutant limit concentrations in air does not consider heavy metals other than **lead,** which has an objective of 0.5 $\mu g\ m^{-3}$, measured as an annual mean to be achieved by 2005. The EC is about to initiate work to develop proposals to set limit values for polycyclic-aromatic hydrocarbons (PAHs), **cadmium**, **arsenic**, **nickel** and **mercury** (DETR, 1999). It is hoped that this forthcoming legislation will also include provision for the protection of ecosystems and vegetation from the impacts of heavy metals in a similar way as has been proposed for sulphur dioxide and NOx compounds. However, before limit values can be defined there still needs to be much work done to assess heavy metal critical loads on terrestrial and aquatic ecosystems.

4.3 **Critical Loads.**

In the previous section it was stated that forthcoming European legislation is likely to see the setting of limit values for cadmium, arsenic, nickel and mercury, in addition to lead. Indeed, the

1994 Heavy Metals Protocol has led the way to setting controls on lead, cadmium and mercury emissions with the provision that other metals can be added at a later date, and this is likely with future EC daughter directives. Limit values and alert thresholds for cadmium, arsenic, nickel and mercury have already been laid down by the Community to be implemented by the 31st of December 1999 (SCAD, 1999). As it is one of the objectives of the Air Quality Framework Directive to "prevent or reduce harmful effects on.....the environment as a whole" in addition to "human health" (EC, 1997b), provision must be made to assess the negative effects of heavy metals on ecosystems. The critical loads of heavy metals in ecosystems must be determined before new EC legislation can be drawn up and implemented. A further impetus to the definition of critical loads lies in the fact that the EC Scientific Committee on Toxicity, ecotoxicology and the Environment (CSTEE) has proposed that water quality should be assessed in terms of the functioning and structure of ecological systems, rather than chemical contamination (EC, 1998). This will require an index of the potential effects of contaminants on specific indicator species to be made.

4.4 **Approaches to Critical Loads.**

The application of the critical loads concept has been successful in targeting emission controls of acidifying pollutants (esp. of SOx species). For acidity, the key variables that explain most of the variation in freshwater critical load relate to soil, geology and land-use within the catchment (Kernan *et al*, 1998). Definition of critical loads for trace metals in soils, however, can be considered as being a function of (1) biological uptake, (2) leaching by percolating water, (3) inputs of trace metals from bedrock weathering, and (4) the norms set to protect soil from metal pollution (Paces, 1998). The exceedance of the critical load is a difference between the calculated load and the measured input of the metals by atmospheric deposition (and in other cases, also inputs from agrochemicals and from industrial areas).

The development of critical loads for acidity are established (e.g. CLAG, 1995). However, assessing and setting critical loads for heavy metals is in the early stages of development. Critical loads for heavy metals require a different approach to that encountered for acidity and emphasis must be placed on the retention and release characteristics of metals within ecosystem compartments, in addition to input loads and natural geochemical levels. Indeed, the actual acidity at a site can affect the bioavailability of heavy metals because metals (e.g. Zn and Cd) are mobilized in an acidic environment (Vesely and Majer, 1996). Caution should also be taken when trying to define 'natural' baseline levels. Salminen and Tarvainen (1997) have found that in many areas of Finland, natural concentrations of heavy metals exceeded the guide, or limit values designated for contaminated soils. Furthermore, there is also evidence of pre-industrial lead contamination in lake sediments dating from Roman times (e.g. Jones, 1984) which imply that natural baseline concentrations, at some locations, do not necessarily date from immediately before the onset of industrialisation.

Much of the developmental work on critical loads for heavy metals has been initiated in the Netherlands. De Vries and Bakker (1998) and De Vries *et al* (1998) have presented different calculation methods to quantify the risk of inputs of several heavy metals in relation to critical limits, while focusing on the critical loads approach. Their approach consists of the following considerations, for terrestrial ecosystems;

- Selection of a suitable receptor organism;
- the assessment of a suitable critical limit which will provide information on the deposition level which will ultimately lead to a critical load in the ecosystem;
- creation of a model - either; (1) a steady state model or; (2) a simple dynamic approach.

(De Vries and Bakker, 1998)

for aquatic ecosystems;

- Selection of a suitable receptor organism;
- for surface waters, assessment of the critical load which equals the deposition level that will ultimately lead to critical metal concentrations in surface waters (dissolved or adsorbed onto suspended particles), in sediments or fish;
- derivation of effects-based critical limits to surface waters related to direct effects on aquatic organisms (e.g. algae, crustacea, fish) or indirect effects on fish or mussel eating birds;
- development of a surface water model consisting of a mass-balance equation which describes the input and output fluxes of heavy metals, combined with rate-limited and equilibrium equations, that describe processes in the catchment, with emphasis on the aquatic system involved.

(De Vries *et al*, 1998)

Figure 20 shows the general pathways of heavy metals within an aquatic ecosystem and is the biological equivalent of Figure 1 (1.7.2) which depicted the chemical and physical aspects of aquatic metal transfers. Three possible receptor classes are identified as being fish, aquatic organisms with the surface water compartment being central to all receptors. Effects-based critical limits would be based on species of fish, benthic and aquatic organisms with the available heavy metal concentration in surface water supplying heavy metals to these organisms. The figure is simplified and assumes that the waterbody is homogeneously mixed and that uptake is wholly from water (except for benthic organisms which are also supplied with metals from the sediment). The important pathways from compartment to receptor leading to primary ecotoxicological effects are those in bold. Other receptors and compartments indicated should not be overlooked as they are crucial in understanding secondary ecological effects and the supply of heavy metals to surface water.

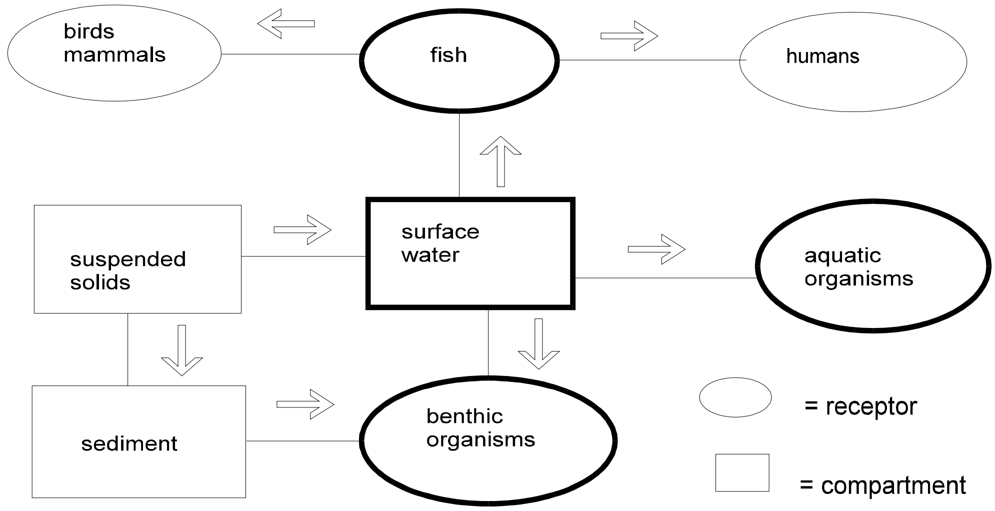


Figure 20 A simplified overview of pathways of heavy metals in aquatic ecosystems.
Receptors and compartments in bold are considered in deriving critical loads (after De Vries et al, 1998)

For terrestrial systems, there is a discrepancy between determining critical loads in soil using the steady-state model and the dynamic approach. Application of the steady-state model implies that the critical load increases with a decrease in metal accumulation and this calculates that lowest critical loads are seen in calcareous clay soils and highest for acid sandy soils, the reverse is true with the dynamic approach. An alternative approach to the steady-state model is also presented by De Vries and Bakker (1998), based on the use of critical dissolved metal concentrations.

The methods outline above by De Vries *et al* (1998) and De Vries and Bakker (1998) developed initially in the Netherlands have been proposed for use across Europe. However, for broader application across Europe they may need significant changes and for the UK in particular, the proposed methods will need to be adapted for application to upland areas where atmospheric deposition is dominant (DETR, 1999b)

There are three main sources of uncertainty in deriving critical loads:

1. Critical limits;
2. calculation methods (e.g. model selection and model implimentation);
3. input data (model inputs, parameters and initial state of variables) uncertainty due spatial variability and lack of knowledge (e.g. effects of additivity on toxicity).

(Kros *et al*, 1993)

In designing a critical loads programme the aim should be to address the sources of uncertainty in the input data (from emission inventories) in order that critical limits, and ultimately critical loads may be defined.

Even in remote areas such as the Scottish Cairngorm mountains, lakes are subject to heavy metal contamination (e.g. Battarbee *et al*, 1995). Heavy metals transported through the atmosphere will be the most common route of entry to remote environments (both to aquatic and terrestrial ecosystems), in order that these inputs are quantified there must be heavy metal deposition data available and this can be achieved through the use of atmospheric modelling programmes (e.g. EMEP, 1997) and preferably in conjunction with a network of monitoring sites to first identify, then consider spatial and catchment variables. Deposition monitoring in addition to receptor organism, soil and water data should be collated for inclusion into a heavy metal critical loads programme.

4.5 **The role of Critical Loads in UK and EU policy.**

The work of De Vries and Bakker (1998) and De Vries *et al* (1998) has been developed in accordance with the results and recommendations of the 'International Workshop on Critical Limits and Effects-based Approaches for Heavy Metals and POPs', held in Bad Harzburg, Germany, 1997 (UN ECE, 1998).

Future decisions affecting policy should reflect recommendations of critical loads findings, but it must be remembered that critical loads for metals are in the developmental stage and at present there are gaps in knowledge. For example, levels of mercury and cadmium in the environment are in some cases above current water quality criteria, whereas others such as lead and copper are below. On the basis of current understanding and data availability, the calculation of critical loads of cadmium and lead appear feasible but the methodology for mercury has to be further developed (Gregor, 1998)

Currently, European legislation relating to discharges to the aquatic environment (Framework Directive on Dangerous Substances in the aquatic environment 76/464/EEC) including the naming of priority List 1 and List 2 compounds of which future use and discharges to the water should be reduced/eliminated, is in advance of legislation surrounding the setting of limit values for heavy metal concentrations in the air. The Air Quality Framework Directive (96/62/EC) and subsequent Daughter Directives will eventually set limit/alert values for several heavy metals (including;

arsenic, nickel, cadmium and mercury) to reduce their impact on human health and on the environment as a whole (EC, 1997a).

The establishment of critical limits for heavy metals, based on the potential of heavy metal pollution to damage ecosystems is necessary in order that legislative limit values for air quality (below human health values) may be set. A network of monitoring sites will provide the means by which compliance with these limits may be assessed in the short term, in addition to providing the information required for initial critical load modelling. Clearly, future policy must take into consideration the potential of atmospheric trans-boundary pollution to come from countries outwith the European Community and impacting on rural areas of Europe, remote from direct pollutant inputs, and potentially leading to critical load exceedance. Continued atmospheric monitoring of heavy metals in the UK (and Europe) is therefore crucial in assessing metals deposition after future European Daughter Directive legislation has been implemented.

Chapter 5 **Climate change and the response of heavy metals**

5.1 **Possible climate change scenarios**

5.1.1 **Overview**

Increasing amounts of ‘Greenhouse gases’ in the atmosphere have led to concerns regarding the potential for global warming and climate change (e.g. Schnoor, 1996) and also to the possibilities of secondary environmental effects caused by climate change, such as the release of pollutants from environmental compartments (e.g. Stigliani, 1991).

Certainly, levels of gases (e.g. CO_2, CH_4, CFCs and NO_2) which are known to absorb long-wave radiation, and thus trap heat within the atmosphere, have increased, but what is not certain, is the extent to which climate will be affected by this occurrence. What is certain, however, is that global mean surface air temperatures have increased by between about 0.3 and 0.6 °C since the late 19th century (UNEP, 1995). The changes in the levels of Greenhouse gases and particles, when taken together are, however, projected to lead to regional and global changes in temperature, precipitation and other climate variables which will result in global changes in soil moisture, an increase in global mean sea level, and prospects for more severe extreme high-temperature events, floods and droughts in some places (UNEP, 1997). However, specific anthropogenic aerosols (microscopic airborne particles), such as sulphates, in the troposphere, resulting from combustion of fossil fuels and biomass burning have led to a negative direct forcing reflecting incoming radiation (Hulme and Jenkins, 1998) and effectively cooling the atmosphere. In addition, aerosols also promote cloud formation increasing the albedo effect to increase negative forcing. The extent to which global ‘cooling’ will ameliorate the effects of global warming are not fully known and has complicated modelling of future climate scenarios.

5.1.2 **General effects on ecosystems**

- Alteration of geographic location of ecological systems;
- species diversity;
- changes in climatic means (leading to the long term alteration of ecosystems) and extremes of climate (leading to the rapid degradation of ecosystems).

The above effects are based on the primary changes in climate. Secondary effects, such as the fires, pests, diseases and the potential for the increased mobilisation of pollutants will provide further stress to ecosystems under various climate change scenarios.

5.1.3 **Potential effect of climate change on Europe and the UK**

Ecosystems in northern Europe would show a marked response to climate change with projected movements of climate zones being faster than rates of species migration. High elevated ecosystems are particularly vulnerable because they have nowhere to migrate. Also, the diversity of freshwater species may increase in middle to high latitudes under global warming, the diversity in cool temperate and boreal regions, however, may show an initial decrease (UNEP, 1997). In terms of precipitation, under warming conditions, northern latitudes have experienced enhanced levels and southern latitudes reduced levels. The current uncertainties surrounding future precipitation levels are exacerbated by the effects of aerosols (UNEP, 1997). A warmer climate could also lead to reduced water quality, particularly if accompanied by reduced runoff.

In the UK, recent research into predicting climate change scenarios indicated that;

- Annual, winter and summer runoff will decrease in southern Britain, groundwater recharge will be reduced and water quality (characterised by nitrate concentrations and dissolved oxygen contents) will be reduced (Arnell, 1998).
- River flows will increase throughout the year, in northern Britain, particularly in the winter (Arnell, 1998).
- Largest actual changes in stream flow are predicted to occur during winter months, although largest percentage changes will occur in summer months (Roberts, 1998).
- Mean summer temperatures will increase by 0.7 °C, 1.4 °C and 2.1 °C by the years 2010, 2030, 2050, respectively. The change would occur uniformly throughout the UK maintaining the present north-south temperature gradient (Warrick and Barrow, 1991).
- For the winter season, a possible temperature change scenario suggests that there will be a south-west to north-east gradient. By 2050, temperatures in northern Scotland will have increased by 3.7 °C and in England and Wales, by 2.1 °C, effectively reducing the current temperature gradient (Warrick and Barrow, 1991).
- Rainfall in the UK increases over the year as a whole, with largest changes in winter. Summer rainfall decreases, except in the north. Results from an equilibrium experiment show that rainfall tends to be more intense but less frequent (Rowntree *et al*, 1993).
- Soil moisture decreases, except in winter (Rowntree *et al*, 1993) related to higher potential rates of evapotranspiration.

- Higher summer temperatures may lead to the temporary drying out of boggy areas, with subsequent very high levels of microbial activity which may mobilise large amounts of acids (Cresser *et al*, 1993).

More recently, Hulme and Jenkins (1998) have published UK climate change scenarios which show predicted changes until the year 2080, they include information on;

- Annual mean temperatures: by the 2080s, southeast England will be between 1.5 and 3.2 °C warmer than the 1961-90 average, but in Scotland only between 1.2 and 2.6 °C warmer;
- mean annual precipitation: by 2080s, between 0 and 10 per cent over England and Wales and between 5 and 20 per cent over Scotland. Winters and autumns become wetter over the whole UK with spring and summers getting drier in the south-east and wetter in the north-west;
- Potential evapotranspiration: increases in all seasons, by the greatest relative amount in autumn and by the smallest in spring. By the 2080s potential evapotranspiration over southern England is 10 to 20 per cent higher than at present.

5.2 **UK land use under a changing climate**

Changing UK temperature and rainfall regimes are predicted by Warrick and Barrow (1991) and Hulme and Jenkins (1998). Such changes in mean temperature and precipitation are expected to have an impact on the land use and vegetation pattern of the UK (Hulme *et al*, 1993). Furthermore, future UK government (and EU) policy unrelated to the direct concerns of environmental protection and climate change will affect land use. In the case of forestry, this will directly influence pollutant deposition patterns. Information given in (1) to (3) below only serves to provide some examples of climate change effects on land use and their subsequent effects on the chemical status of soil/sediment/water and is not exhaustive.

(1) Agriculture

Continued intensive agriculture in the UK coupled with predicted increases in winter rainfall, summer storm frequency and increases in the area of irrigated land will increase soil erosion rates (Boardman and Favis-Mortlock, 1993). Also, changing meteorological conditions combined with the further intensification of agriculture requiring increased inputs of fertiliser will lead to changes in water chemistry through catchment runoff processes. River water quality changes related to agriculture in northeast Scotland, brought about through climate change have been investigated using the river water quality model QUASAR (Quality Simulation Along Rivers) by Ferrier *et al* (1995) and it was found that there will be alterations in flow regimes, temperature and mineralisation rates. Overall leading to an increase in nitrogen entering river systems.

With future changing temperature and rainfall regimes throughout the UK, agricultural crop production, particularly cereals, will undergo radical shifts in locations (Hosell *et al*, 1996) and have consequential effects on soil and water quality, in addition to effects on ecosystems.

(2) Forestry

Under the Kyoto Protocol, a country may be able to reduce its obligations to cut carbon emissions by ‘sinking’ some carbon in trees (Mattoon, 1998). Increases in land under forestry will have an acidifying effect on catchment groundwater and surface water through the formation of acid exudates and leaf decomposition products (Alloway and Ayres, 1997). In addition, there may be an increase in peatland tree planting leading to drying of the peat resulting in the loss of their ability to act as carbon sinks. Peat will also be susceptible to erosion under the drying conditions and preserved organic matter will increasingly be mineralised. It is likely that in the UK areas which would be used for increasing forestry production would be those which are uneconomic for other uses (e.g. upland areas with poor soil cover), and often prone to acidification. The percentage of UK land cover under forestry is to be increased significantly in the future and this will affect soil conditions under plantations during planting, growth and eventual harvest. Increasing the area of forested land will also lead to changes in surface roughness changing pollutant deposition characteristics.

(3) Ecosystems

As there is likely to be large scale changes in land use under a changing climate this will have ‘knock-on’ effects on ecosystems. Simulation studies in a few case-study catchments have indicated that changes in river water temperatures and river flow regimes due to climate change would generally have little impact on water quality in Britain. However, changes in pollutant inputs to river systems, determined to a considerable extent by agricultural practices, would be more important (Jenkins *et al*, 1993). Nutrient levels in waters may be subject to change and there is potential for increased nitrate peaks following flushing after prolonged dry spells and higher mineralisation of organic nitrogen in the soil (Arnell and Duborg, 1995) Also, in rivers with high nutrient levels, an increase in algal blooms through global warming would lead to reduced dissolved oxygen levels in water. Forestry practices will also impact upon habitats, with increased afforestation leading to changes in water quality such as pH. In addition to the chemical response of climate change affecting habitats there is also the threat of physical disturbance leading to displacement of communities or even entire ecosystems as well as depleting the earth’s natural resources. Physical disturbances induced by changes in the usage of land space will be further exacerbated by increases in soil erosion (Boardman and Favis-Matlock, 1993) leading to deterioration of terrestrial and aquatic ecosystems.

5.3 **Effect on heavy metals in the environment**

Under possible climate change scenarios in the UK, suggested above, it is likely that there would be a significant remobilisation of heavy metals within the environment, Table 9 outlines the potential effects on heavy metals in the environment under various climate change scenarios.

Globally, there has been large-scale anthropogenic inputs of heavy metals to the environment (e.g. Pacyna, 1984) in addition to natural inputs (e.g. Nriagu, 1989). And although reducing since the early 1970s, anthropogenic emissions of heavy metals are still significant. Pacyna (1998) has given estimated total anthropogenic emissions of arsenic, cadmium, lead and zinc as being 2575 tonnes year^{-1}, 895 tonnes year^{-1}, 58090 tonnes year^{-1} and 32990 tonnes year^{-1}, respectively for the early 1990s.

Observed geographical, seasonal and vertical patterns of temperature change attributed to the human effect on climate are emerging from pattern-based studies (UNEP, 1995). Global temperature changes of this nature will affect the direction, duration and intensity of air mass movement worldwide, resulting in changes in the long-range transport and deposition of heavy metals after emission. Development of suitable atmospheric transport models must consider these potential future changes.

Past emissions to the environment have ultimately been bound up in various compartments such as soils and sediments. However, because soil (and sediments) have buffering systems that store and immobilise heavy metals, direct environmental effects of these cumulative inputs may not be observed immediately (Olendrzynski *et al*, 1996). The ability of soils and sediments to act as “chemical sinks” does not guarantee that the chemicals are stored forever. Factors influencing the storage capacity of soils and sediments and bioavailability of the stored chemical can change and indirectly cause sudden and often unexpected mobilisation of chemicals in the environment (Stigliani, 1988). This concept of “chemical time bombs” has been further developed in Stigliani (1991) and many of the proposals substantiate those already referred to in 5.1.3 including the mobilisation of heavy metals brought about by increased precipitation and temperature leading to changes in the chemical, physical and biological status of ecosystems. In view of the evidence that is available, under a changing climate, heavy metals could be released from soils and sediments and made biologically available.

Yang *et al* (1999) have suggested that 92% of anthropogenic mercury in the total catchment of the mountain lake, Lochnagar in northeast Scotland is stored within the sparse catchment soils. An increase in rainfall (and rainfall intensity) through climate change could lead to increased catchment soil erosion and subsequent re-release of mercury into the wider environment. The ability of soils and sediments to retain deposited pollutants is not finite. It would appear that even in remote areas such as Lochnagar that there has been an accumulation of anthropogenic pollutants since the beginning of industrialisation (see also Hamilton-Taylor, 1979) resulting in a large reservoir of heavy metals bound up in the ecosystem. Clearly, on a national and international scale this represents an enormous amount of stored pollution which could be potentially be re-mobilised through climate change.

Under the predicted climate change scenarios of Warrick and Barrow (1991), Rowntree *et al* (1993), and Arnell (1998), changes in precipitation and temperature would give rise to these effects over approximately the next 50 years. The sensitivity of lake in mountainous areas to climate change (and atmospheric pollution) mean that these systems are particularly useful in providing an early warning of more widespread changes (Skjelkvale *et al*, 1998). It is proposed that a monitoring programme of atmospheric heavy metals deposition in remote areas would provide, in conjunction with a critical loads approach, an insight into potential more widespread effects of heavy metal pollution under a changing climate.

5.3.1 **Mitigating factors**

Under predicted climate change scenarios, there are certain factors which will mitigate the effects of increased releases of heavy metals from reservoirs in the environment. Reductions in water table height through drought or land use changes has associated consequences for the release of many solutes. A reduced water table in constructed wetlands was shown to increase the rate of release of solutes (Freeman *et al*, 1993), including nitrate (1250%), sulphate (116%) and dissolved organic carbon (37%). In addition to adversely affecting water quality, the release of solutes such as DOC will increase the adsorption of metals. However, Schindler *et al* (1997) found decreases in DOC concentrations in boreal lakes of 15-20% following 20 years of drought, global warming and forest fires. This decrease was thought to be due to decreases in inputs from the catchment and upstream lakes in addition to increased lake removal. Although DOC release was shown to increase under simulated wetland drying by Freeman *et al* (1993), actual observation in the field by Schindler *et al* (1997) has shown a decrease in DOC concentrations primarily due to decreased stream flow. It is thought that long periods of drought followed by intense rainfall would however provide the ideal conditions to increase removal of DOC from catchment soils.

In addition, as plants uptake heavy metals from the soil through their roots, an increase in atmospheric CO_2 will allow an increased rate of plant growth which will uptake more metals. Indeed, some plants are extremely efficient at this; reeds are commonly used in constructed wetlands to remove metals from industrial runoff and urban wastewaters (e.g. Scholes *et al*, 1998). Other plants, such as species of brassicas have been shown to clean-up soils which are heavily contaminated with metals; Pb, Cr, Cu, Ni and Zn (Nanda-Kumar *et al*, 1995).

5.4 **Implications for Critical Loads of heavy metals**

It has been established that global climate change is occurring and that, potentially it will have many consequences for society. However, what is more uncertain is the magnitude of the changes and time scale of which they will take place. However, the potential of ‘chemical time bombs’ scenarios (Stigliani, 1991) may occur under these changing climatic conditions. Indeed, climatic-induced chemical effects have already been observed in the UK. Investigation of stream water quality over two years (1988-90) of exceptionally warm and arid conditions in an acidic catchment in the English midlands showed a four-fold increase in surface-water acidity (Wilby, 1994). Also, the simulated drying of peat from a riparian wetland in Wales had the effect of increasing the rate of release of many solutes including nitrate (1250%), sulphate (116%) and dissolved organic carbon (37%) (Wilby, 1994).

The potential of release of heavy metals through future climatic change must be considered in the defining of critical loads. It is quite possible that under predicted climate change scenarios various environmental compartments will be altered chemically, physically and biologically to an extent that the retention/release characteristics will differ from their present status. Essentially, climate change will affect critical loads for heavy metals. These future scenarios must, however, be countered with an immediate need to set critical limits that will aid the creation of future legislation surrounding emissions to the environment and protect ecosystems.

Potential Climate Change scenario	**Primary effect of change**	**Secondary effect of change**	**Possible effect on heavy metals (HMs) stored in the environment**
Increasing atmospheric concentration of CO_2	decrease in pH of precipitation	acidification of ground and standing waters	solubilisation of HMs
	increase in soil microbial activity	increased mineralisation of organic matter	release of bound HMs
		increased production of humic/fulvic acids	uptake of HMs
	increase in plant growth	increase in microbial nitrification (releasing H^+ ions)	solubilisation of HMs
			uptake of HMs
Changes in precipitation patterns	increase in precipitation	increase in leaching of base cations from soil (reduced acid-buffering capacity)	solubilisation of HMs
	increase in rainfall intensity	increased soil erosion and lake sediment disturbance	increased availability of HMs
	decrease in precipitation (in southern UK; summer)	longer periods of stable atmospheric conditions resulting in a accumulation of HMs	increased human-health risks and likelihood of high concentration 'flushes' with rainfall events.
	increase/decrease in soil moisture	increase/decrease in soil organic matter	changes in erosion rate and cation exchange capacity
		changes in soil redox potential (+/- Eh)	drying of soil - high redox leading to oxidation of insoluble sulphides releasing bound HMs wetting of soil - low redox leading to binding of HMs (Stigliani, 1991)
Increased temperature	increase in soil microbial activity	increased mineralisation of organic matter	release of bound HMs
Disruption of present ecosystems	physical, biological and chemical changes	e.g. pH, redox, erosion, species vulnerability	potential changes in HM uptake, retention and release characteristics

Table 9 Effects on heavy metals in the environment under various climate change scenarios for the UK.

Chapter 6 **Conclusions and recommendations for further work**

6.1 **Emissions**

- European anthropogenic emissions of heavy metals have been much reduced since the early 1970s. For example; Cadmium by 40%, lead by 39% and zinc by 32% (see
- Table 6 and Figure 9). Reductions have been brought about through more stringent controls on emissions introduced, most noticeably, by the EC and through advances in technological processes.
- Problem of continued high emissions from eastern Europe and developing countries coupled with long-range atmospheric transport of heavy metals. The best example of long-range transport of heavy metals is seen in sediments and ice cores from the Arctic. Metals produced in the industrial nations of the northern hemisphere are carried in the atmosphere on particles which are suspended in the cold Arctic air before being deposited. Remote areas of the Arctic have levels of heavy metals which could pose a risk to the environment and human health.
- The UK is a net exporter of atmospherically-transported heavy metals and the UK is the biggest single receiver of UK emissions.
- Uncertainty in the calculation of emission estimates still exists and, notably, errors are significant for lead, cadmium and mercury.
- Emissions from natural sources such as volcanoes, forest fires and seasalt are a significant source of atmospheric heavy metals (esp. for Cr, Cu, Hg and Se).

6.2 **UK deposition monitoring**

Currently, there are three main long-term multi-element heavy metal deposition networks in the UK;

- Rural Network - 3 sites (Wraymires, Cumbria; Styrrup, Nottinghamshire; Chilton, Oxfordshire). Operating since 1972.
- Multi-Element Network - 5 sites (London, Bridge Place and Brent; Leeds; Motherwell; Glasgow) plus one other in Central London). Operating since 1976.
- North Sea Network - 3 sites (High Muffles, Yorkshire; Banchory, Grampian; East Ruston, Norfolk). Operating since 1986

Other shorter term deposition monitoring programmes (e.g. the Reading/MAFF study and LIFE project) have also been carried out as part of larger multi-disciplinary projects or separate research studies (see 2.2.1/2.2.2). There are also studies which have concentrated on high resolution monitoring of aerosols and rainwater to identify specific emission sources and meteorological effects.

In addition, there have been a number of other studies which have looked at UK heavy metal concentrations in terrestrial mosses and surface waters trends.

- Decreasing trends in emissions have been identified most clearly in the UK's longest running heavy metal monitoring programme; the Rural Network. Concentrations in air at the three Rural Network sites have decreased by between 3% and 11% per year (see Figure 8) over the period 1972 and 1991 (see also Appendix 4).
- There has also been a general reduction in deposition to urban areas as identified in the multi-element network since 1976. Lead has shown the most consistent decreases with between 9 and 18% per year reduction of the thirteen year average concentration at the five sites. The largest decreases are seen post-1986/7 associated with the reduction of lead in petrol and with the introduction of unleaded fuels.
- Atmospheric transport and deposition regimes for heavy metals in the UK are influenced heavily by meteorological conditions. Atmospheric pressure, wind direction and rainfall are each of importance. Meteorological influences have been observed in correlated deposition data at two sites in eastern Scotland over a two year period. Deposition concentrations and trends cannot be assessed without reference to weather conditions and more work is needed to quantify these influences.
- Easterly air masses in the UK generally exhibit higher concentrations of heavy metals than westerly air flows. Stable high pressure systems also lead to a build-up of pollutant metals in the atmosphere which are 'flushed' out during subsequent rainfall events.
- Atmospheric deposition accounts for a large proportion of heavy metal inputs to lowland agricultural land in the UK, especially for mercury and lead. Attempts to model inputs of heavy metals to upland areas using lowland deposition data have proved unsuccessful due to altitudinal effects.
- Moss monitoring surveys of heavy metal deposition in the UK (e.g. the FLAME project in 1994 and the DETR-funded moss monitoring programme in 1996/7) have identified largest concentrations of deposition as being in the English midlands and in the north of England. And levels have been shown to be similar to those in other northern European countries.
- Modelling of heavy metal deposition is progressing and there is good agreement between models and measured deposition reported by several workers. However, the accuracy of models can be hindered by poor emissions data. Furthermore, there is some concern that the

large grid size (150 x 150 km) used by the EMEP HMET model can create over-estimates in metal transport between countries and that numerical approximations used may introduce additional errors.

The potential use, in critical loads development, of two datasets on UK atmospheric deposition of heavy metals (namely the survey in England and Wales carried out for MAFF at the University of Wales and the moss monitoring survey in England, Scotland and Wales carried out on behalf of the DETR by Imperial College London) will provide some of the necessary data but should compliment a dedicated network to serve the purposes of a critical loads programme. The three long-term UK networks have shown high quality deposition trends. The rural and North Sea networks provide high resolution data for rural areas but the number of sites are too few to enable accurate national deposition maps to be made and the multi-element network should be discounted for critical loads as it is urban based. However this data is of importance and is necessary to observe the effects of emissions reductions on air quality. It is also of relevance to critical loads, in that it shows these decreasing trends which should be considered in setting future critical loads.

6.3 **Methods of assessing heavy metal deposition**

In addition to active deposition monitoring as used in the main heavy metal monitoring networks in the UK there are other means by which deposition can be assessed:

- Sampling and analysis of standing waters (as carried out as part of the UK Environmental Change Network and the Welsh study at Plynlimon) offer high resolution data. Unfortunately with only between three and six years data in the ECN, long-term trends are difficult to identify with the associated ‘noise’. Indeed, clear trends have been difficult to observe in the longer Plynlimon study (1983-). Also, the use of surface waters as a means of determining atmospheric deposition concentrations is further complicated by the retention and interaction of soils and vegetation in the river/lake catchment.
- Terrestrial mosses (esp. *Hylocomium splendens* and *Pleurozium schreberi*) are widely used as biomonitors of atmospheric heavy metal pollution. The moss monitoring technique has been successfully applied in the UK, in the FLAME study and DETR 1996/7 moss survey. Mosses are now being routinely sampled at the AWMN sites where they occur.
- Sediment trap samples have also been used by various workers to monitor inputs of heavy metals to lake systems. Traps provide a means by which accurate time periods of deposition can be monitored relatively easily, even in remote locations. They have been successfully used to monitor changing diatom assemblages and carbonaceous particles at AWMN lake sites.

- Dated lake sediments have been widely used for the reconstruction of past heavy metal pollution. Upland and remote lakes offer the opportunity to study heavy metal pollution as it is entirely atmospheric in origin (after natural geochemical correction).
- Decreases in the concentrations of deposited heavy metals over a 20 year period at Wraymires, Cumbria (identified by the Rural Network) correspond with decreases in sediment-metal concentration at the nearby lake of Esthwaite Water.
- The remote, upland lake at Lochnagar in northeast Scotland is currently being used to study entire catchment input/output budgets of heavy metals from atmospheric sources.

Lake systems are extremely useful in the study of atmospheric depositions of heavy metals and are essential in developing methodologies for freshwater critical loads. Monitoring can be achieved through sampling and analysis of dated sediment profiles, sediment trap material, catchment terrestrial mosses and active deposition monitoring on site (if required). Remote sites which are only impacted by atmospherically-derived heavy metals will have their critical loads exceeded only by atmospheric deposits (unlike a lowland area which may also have point sources and local diffuse sources). It is crucial therefore that suitable monitoring at these locations is carried out to identify areas where there may be exceedence of critical loads in the future, currently the number of sites where there is monitoring of heavy metals in atmospheric deposition are too few to prepare deposition maps.

There are a number of lake sites in the UK already monitored as part of other projects which would be suitable for atmospheric heavy metal monitoring in upland areas. Sites currently monitored include those which constitute the Critical Loads Acidity and Metals (CLAM) project, the Environmental Change Network (ECN) [see Appendix 2] and the Acid Waters Monitoring Network (AWMN) [see Appendix 5]. Presently, at some (but not all) of these sites there is determination of surface water concentrations of heavy metals. Continuation of this surface water analysis would provide useful long-term information on trends but it would not be the most suitable means by which deposition itself could be monitored. It is recommended that surface water determinations of heavy metals in rural areas of the UK are enhanced by atmospheric deposition monitoring at these sites in order that catchment flux values can be ascertained.

6.4 **Critical loads and legislation**

Although emissions of heavy metals have reduced significantly over the past twenty years there is much debate over what constitutes a ‘safe’ level in terms of protection of human health and the environment as a whole. The development of critical loads for acidity has addressed the issue of acidifying pollution to answer the latter question and has actually driven environmental policy e.g.

The Oslo Protocol, 1994. It is hoped that a similar critical loads approach will do the same for heavy metals. Legislative controls on atmospheric emissions of cadmium, mercury and lead have been outlined in the Heavy Metals Protocol, signed at Aarhus, Denmark in 1998 and the EC proposes to further this by setting air quality standards (AQS) for arsenic, cadmium, mercury and nickel for inclusion into a forthcoming Air Quality Daughter Directive.

The definition of critical loads for heavy metals will be essential in “avoiding, preventing and reducing harmful effects on (human health and) the environment as a whole” as stated in the EC Air Quality Framework Directive (96/62/EC). In addition, critical load values provide guidance on the levels of atmospheric emission (and deposition) above which there will be a deterioration observed in ecosystems. There is, however, much work still to be done in defining such critical loads including;

- Provision of a unified critical loads methodology which is applicable at a national (and regional) level in upland and lowland areas across Europe.
- selection of suitable receptor organisms and setting of critical limits (e.g. in freshwater or terrestrial, ecosystem type and land-use).
- collection of suitable model input data and selection of a model.

6.5 **A changing climate**

The potential effects of a changing climate on the environmental fate of heavy metals are numerous and are outlined in chapter 5. There is a likelihood that in a generally warmer and wetter UK climate, that heavy metals retained (and unavailable) in the soil, vegetation and lake sediments currently, will be subject to being re-released and made available to the biota once more. Although there is no certainty surrounding the magnitude of any of the predicted climate change scenarios, what is certain that there will be some effect on heavy metal mobility and a critical loads programme should consider this. Modelling and mapping critical loads will need high quality monitoring of atmospheric deposition but it should also make provisions for future climate change effects.

6.6 **Report recommendations**

It would be unfeasible to only use monitoring data to prepare deposition maps on a UK or European scale, nor is it possible to create accurate models without the input of high quality deposition data. In addition, model input data must relate to the areas where deposition is to be modelled. It has been seen that data produced from a nationwide lowland monitoring programme is not suitable for application in upland areas. The approach should combine the creation of a nationwide (UK) deposition monitoring programme in upland and remote areas which would provide data for model building. The deposition network should;

- run for at least 5 years to allow for year to year variations in deposition patterns as a result meteorological conditions (not only emission decreases).
- relate emission decreases to decreases in observed deposition in a similar way to the UK Multi-Element Network and Rural Network. Again this requires long-term monitoring of more than 5 years.
- monitor atmospheric deposition at a number of sites throughout the country, selected to represent areas where it is thought there may be a risk of critical loads exceedence.
- specifically monitor at representative geographical areas to enable accurate deposition mapping of these areas to be achieved and to allow spatial differences in deposition to be considered.
- make use of existing long-term monitoring sites where there is already environmental data pertaining to that location (provided that consistency of data between sites can be achieved).
- objectively select sites (new and/or established) for the purposes of a critical loads programme where there is a strong likelihood of exceedence in upland and remote areas (e.g. those with thin soil cover of low base status prone to acidification)
- preferably consist of active monitoring of bulk deposition (+ dry deposition) and aerosol concentrations.
- utilise lake sites at which other means of assessing long-term deposition can be achieved i.e. through the use of dated sediment cores and sediment trap data.
- include the collection of terrestrial mosses species which can be used as biomonitors of atmospheric heavy metal pollution at network sites in support of active deposition monitoring.
- be able to separate long-range atmospherically deposited heavy metals from localised point sources by careful siting of deposition monitors and/or locations of sample points.
- focus on metals outlined in the Heavy Metals Protocol (Cd, Hg and Pb) and in proposals in the forthcoming EC AQ Daughter Directives (As, Cd, Hg and Ni) but also other heavy metals of concern, namely; Cu, Zn, Cr and V.
- consider long-term emission reductions and associated deposition reductions in future critical loads predictions.
- consider the potential effects of future climate change scenarios leading to the increased release and bioavailabilty of metals from environmental compartments.
- select data carefully for inclusion into maps of deposition to avoid anomalous values being included.

Data from lake sites (and specifically from uplands and remote sites) will contribute towards the development of freshwater critical loads for metals. These areas constitute a large proportion of northern England, Scotland and north Wales and may be particularly sensitive to the effects of atmospheric deposition of metals. Geology and soils in these areas are often of low base status and as such are prone to acidification leading to the solubilisation of metals into the often more toxic divalent M^{2+} form. Furthermore, deposition to these areas (often mountainous and forested) also differs from that of lowland and cannot be modelled using the same input data. The proposed use of data from a predominantly lowland heavy metal monitoring network in the development of critical loads methodology should be avoided if this were to be applied to upland areas. There is a need to collect high quality upland deposition data and deposition data from areas which have been neglected in past surveys. Also, as deposition patterns are strongly linked to weather systems it is fair to say that a short-term monitoring programme (e.g. of two to three years) may not be representative of actual long-term deposition concentrations and basing critical loads deposition maps on these data should be avoided. Protection of ecosystems are assisted by the use of critical loads data to produce maps of the areas which are sensitive to such deposition. In this way, sensitive areas can be targeted with a view to reducing deposition through future emission controls as required.

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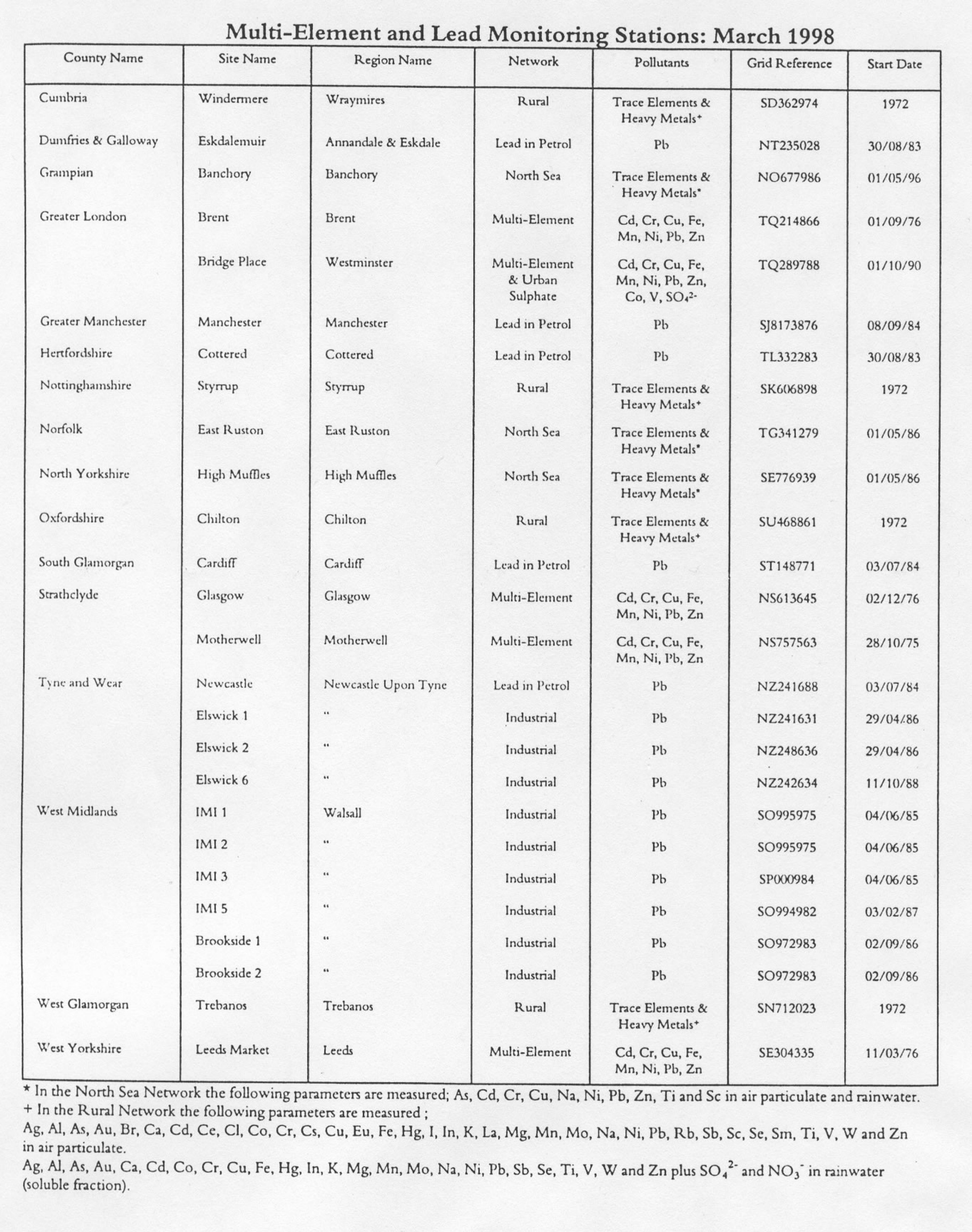
Appendices

Appendix 1 Information on UK Multi-Element and Lead Monitoring Stations: March 1998 (AEA, 1998)



Multi-Element and Lead Monitoring Stations: March 1998

County Name	Site Name	Region Name	Network	Pollutants	Grid Reference	Start Date
Cumbria	Windermere	Wraymires	Rural	Trace Elements & Heavy Metals+	SD362974	1972
Dumfries & Galloway	Eskdalemuir	Annandale & Eskdale	Lead in Petrol	Pb	NT235028	30/08/83
Grampian	Banchory	Banchory	North Sea	Trace Elements & Heavy Metals*	NO677986	01/05/96
Greater London	Brent	Brent	Multi-Element	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	TQ214866	01/09/76
	Bridge Place	Westminster	Multi-Element & Urban Sulphate	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Co, V, SO_4^{2-}	TQ289788	01/10/90
Greater Manchester	Manchester	Manchester	Lead in Petrol	Pb	SJ8173876	08/09/84
Hertfordshire	Cottered	Cottered	Lead in Petrol	Pb	TL332283	30/08/83
Nottinghamshire	Styrrup	Styrrup	Rural	Trace Elements & Heavy Metals+	SK606898	1972
Norfolk	East Ruston	East Ruston	North Sea	Trace Elements & Heavy Metals*	TG341279	01/05/86
North Yorkshire	High Muffles	High Muffles	North Sea	Trace Elements & Heavy Metals*	SE776939	01/05/86
Oxfordshire	Chilton	Chilton	Rural	Trace Elements & Heavy Metals+	SU468861	1972
South Glamorgan	Cardiff	Cardiff	Lead in Petrol	Pb	ST148771	03/07/84
Strathclyde	Glasgow	Glasgow	Multi-Element	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	NS613645	02/12/76
	Motherwell	Motherwell	Multi-Element	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	NS757563	28/10/75
Tyne and Wear	Newcastle	Newcastle Upon Tyne	Lead in Petrol	Pb	NZ241688	03/07/84
	Elswick 1	"	Industrial	Pb	NZ241631	29/04/86
	Elswick 2	"	Industrial	Pb	NZ248636	29/04/86
	Elswick 6	"	Industrial	Pb	NZ242634	11/10/88
West Midlands	IMI 1	Walsall	Industrial	Pb	SO995975	04/06/85
	IMI 2	"	Industrial	Pb	SO995975	04/06/85
	IMI 3	"	Industrial	Pb	SP000984	04/06/85
	IMI 5	"	Industrial	Pb	SO994982	03/02/87
	Brookside 1	"	Industrial	Pb	SO972983	02/09/86
	Brookside 2	"	Industrial	Pb	SO972983	02/09/86
West Glamorgan	Trebanos	Trebanos	Rural	Trace Elements & Heavy Metals+	SN712023	1972
West Yorkshire	Leeds Market	Leeds	Multi-Element	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	SE304335	11/03/76

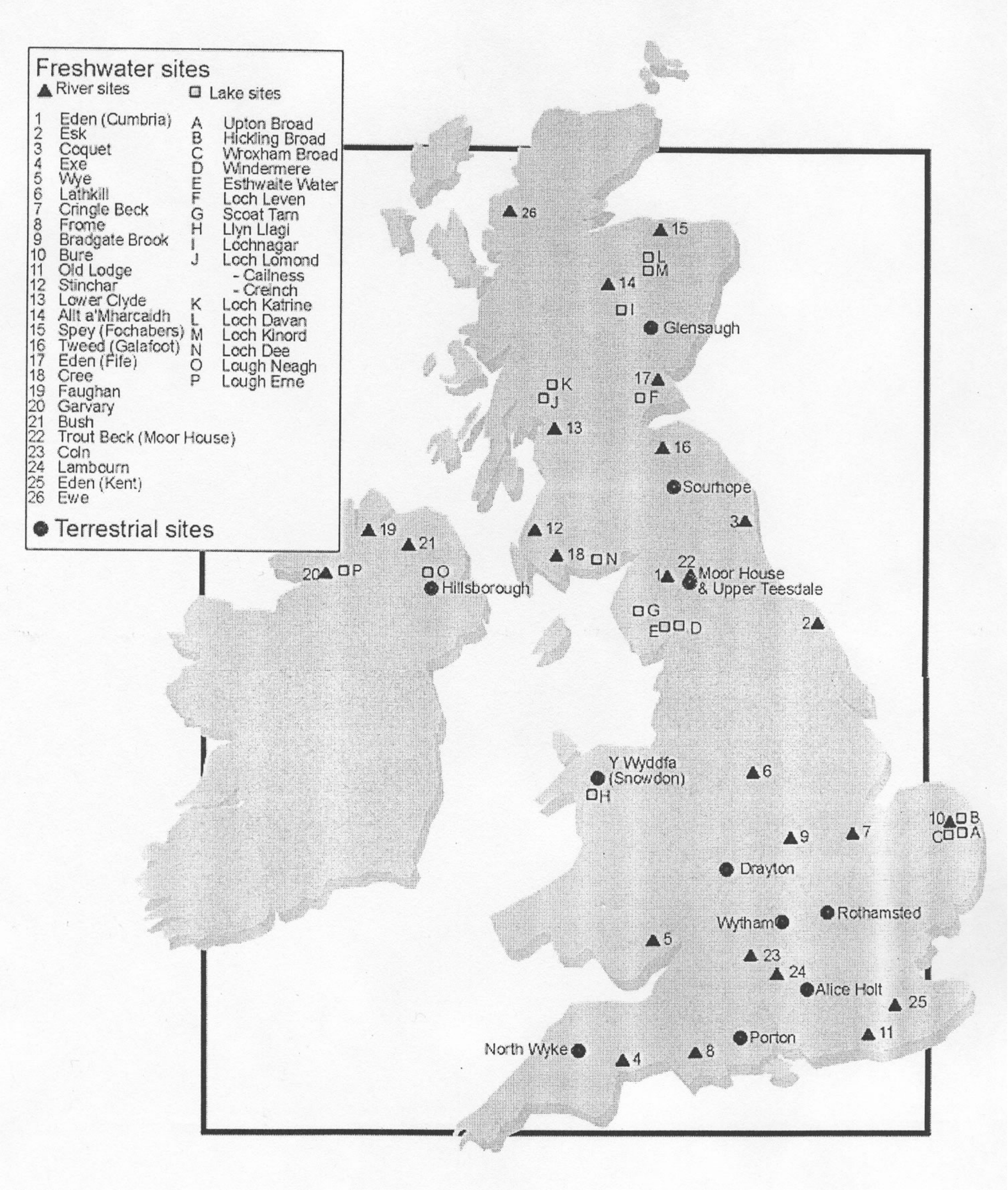
* In the North Sea Network the following parameters are measured; As, Cd, Cr, Cu, Na, Ni, Pb, Zn, Ti and Sc in air particulate and rainwater.

\+ In the Rural Network the following parameters are measured ;

Ag, Al, As, Au, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Hg, I, In, K, La, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Ti, V, W and Zn in air particulate.

Ag, Al, As, Au, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, W and Zn plus SO_4^{2-} and NO_3^- in rainwater (soluble fraction).

Appendix 2 Locations of UK Environmental Change Network (ECN) freshwater and terrestrial sites (after ECN, 1999)



Appendix 3 Locations of Ministry of Agriculture, Fisheries and Food (MAFF) heavy metal deposition monitoring sites in England and Wales with annual average total deposition of metals (after Alloway et al, 1998).

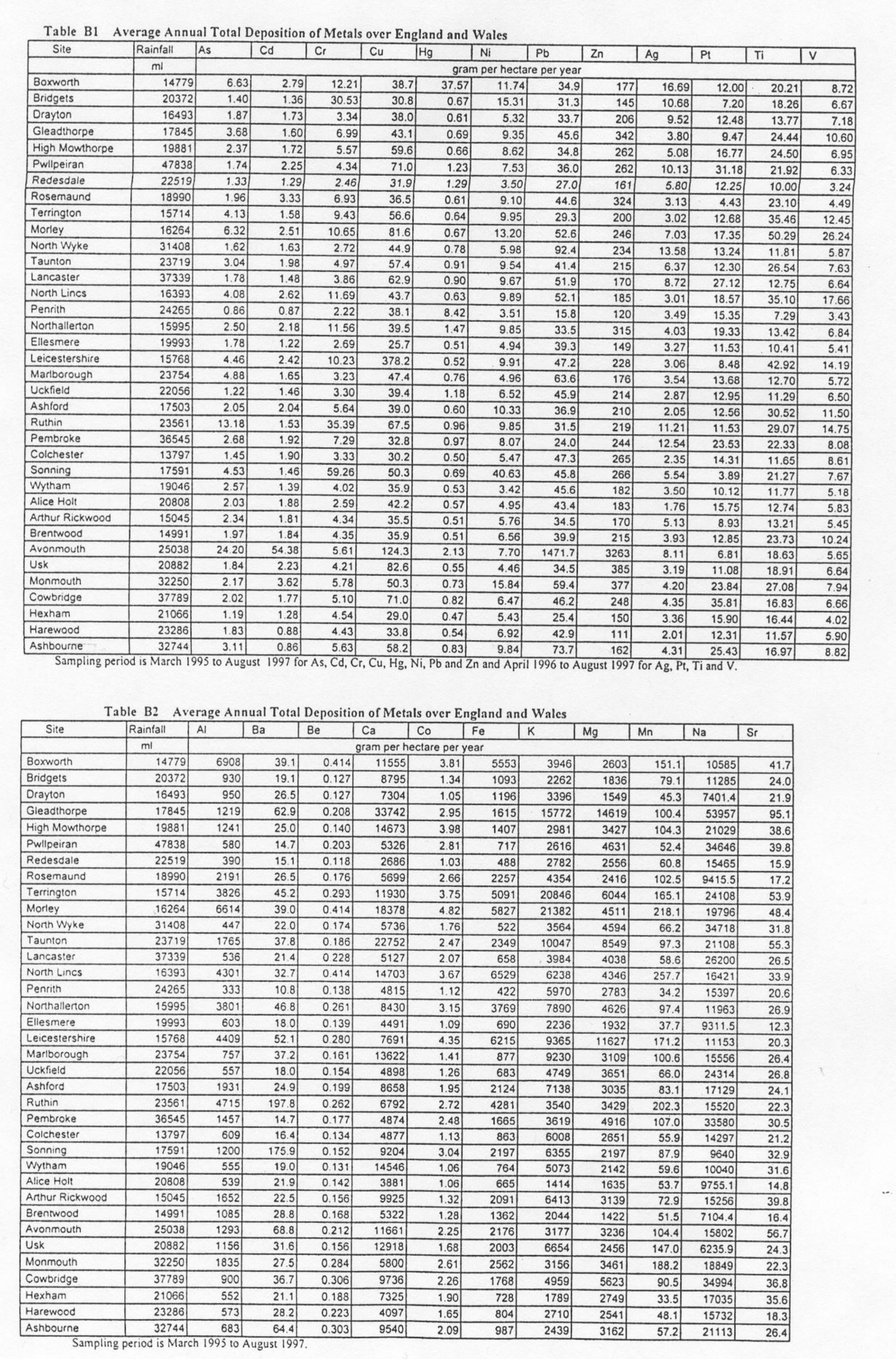


Table B1 Average Annual Total Deposition of Metals over England and Wales

Site	Rainfall	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Ag	Pt	Ti	V
	ml	gram per hectare per year											
Boxworth	14779	6.63	2.79	12.21	38.7	37.57	11.74	34.9	177	16.69	12.00	20.21	8.72
Bridgets	20372	1.40	1.36	30.53	30.8	0.67	15.31	31.3	145	10.68	7.20	18.26	6.67
Drayton	16493	1.87	1.73	3.34	38.0	0.61	5.32	33.7	206	9.52	12.48	13.77	7.18
Gleadthorpe	17845	3.68	1.60	6.99	43.1	0.69	9.35	45.6	342	3.80	9.47	24.44	10.60
High Mowthorpe	19881	2.37	1.72	5.57	59.6	0.66	8.62	34.8	262	5.08	16.77	24.50	6.95
Pwllpeiran	47838	1.74	2.25	4.34	71.0	1.23	7.53	36.0	262	10.13	31.18	21.92	6.33
Redesdale	*22519*	*1.33*	*1.29*	*2.46*	*31.9*	*1.29*	*3.50*	*27.0*	*161*	*5.80*	12.25	10.00	3.24
Rosemaund	18990	1.96	3.33	6.93	36.5	0.61	9.10	44.6	324	3.13	4.43	23.10	4.49
Terrington	15714	4.13	1.58	9.43	56.6	0.64	9.95	29.3	200	3.02	12.68	35.46	12.45
Morley	16264	6.32	2.51	10.65	81.6	0.67	13.20	52.6	246	7.03	17.35	50.29	26.24
North Wyke	31408	1.62	1.63	2.72	44.9	0.78	5.98	92.4	234	13.58	13.24	11.81	5.87
Taunton	23719	3.04	1.98	4.97	57.4	0.91	9.54	41.4	215	6.37	12.30	26.54	7.63
Lancaster	37339	1.78	1.48	3.86	62.9	0.90	9.67	51.9	170	8.72	27.12	12.75	6.64
North Lincs	16393	4.08	2.62	11.69	43.7	0.63	9.89	52.1	185	3.01	18.57	35.10	17.66
Penrith	24265	0.86	0.87	2.22	38.1	8.42	3.51	15.8	120	3.49	15.35	7.29	3.43
Northallerton	15995	2.50	2.18	11.56	39.5	1.47	9.85	33.5	315	4.03	19.33	13.42	6.84
Ellesmere	19993	1.78	1.22	2.69	25.7	0.51	4.94	39.3	149	3.27	11.53	10.41	5.41
Leicestershire	15768	4.46	2.42	10.23	378.2	0.52	9.91	47.2	228	3.06	8.48	42.92	14.19
Marlborough	23754	4.88	1.65	3.23	47.4	0.76	4.96	63.6	176	3.54	13.68	12.70	5.72
Uckfield	22056	1.22	1.46	3.30	39.4	1.18	6.52	45.9	214	2.87	12.95	11.29	6.50
Ashford	17503	2.05	2.04	5.64	39.0	0.60	10.33	36.9	210	2.05	12.56	30.52	11.50
Ruthin	23561	13.18	1.53	35.39	67.5	0.96	9.85	31.5	219	11.21	11.53	29.07	14.75
Pembroke	36545	2.68	1.92	7.29	32.8	0.97	8.07	24.0	244	12.54	23.53	22.33	8.08
Colchester	13797	1.45	1.90	3.33	30.2	0.50	5.47	47.3	265	2.35	14.31	11.65	8.61
Sonning	17591	4.53	1.46	59.26	50.3	0.69	40.63	45.8	266	5.54	3.89	21.27	7.67
Wytham	19046	2.57	1.39	4.02	35.9	0.53	3.42	45.6	182	3.50	10.12	11.77	5.18
Alice Holt	20808	2.03	1.88	2.59	42.2	0.57	4.95	43.4	183	1.76	15.75	12.74	5.83
Arthur Rickwood	15045	2.34	1.81	4.34	35.5	0.51	5.76	34.5	170	5.13	8.93	13.21	5.45
Brentwood	14991	1.97	1.84	4.35	35.9	0.51	6.56	39.9	215	3.93	12.85	23.73	10.24
Avonmouth	25038	24.20	54.38	5.61	124.3	2.13	7.70	1471.7	3263	8.11	6.81	18.63	5.65
Usk	20882	1.84	2.23	4.21	82.6	0.55	4.46	34.5	385	3.19	11.08	18.91	6.64
Monmouth	32250	2.17	3.62	5.78	50.3	0.73	15.84	59.4	377	4.20	23.84	27.08	7.94
Cowbridge	37789	2.02	1.77	5.10	71.0	0.82	6.47	46.2	248	4.35	35.81	16.83	6.66
Hexham	21066	1.19	1.28	4.54	29.0	0.47	5.43	25.4	150	3.36	15.90	16.44	4.02
Harewood	23286	1.83	0.88	4.43	33.8	0.54	6.92	42.9	111	2.01	12.31	11.57	5.90
Ashbourne	32744	3.11	0.86	5.63	58.2	0.83	9.84	73.7	162	4.31	25.43	16.97	8.82

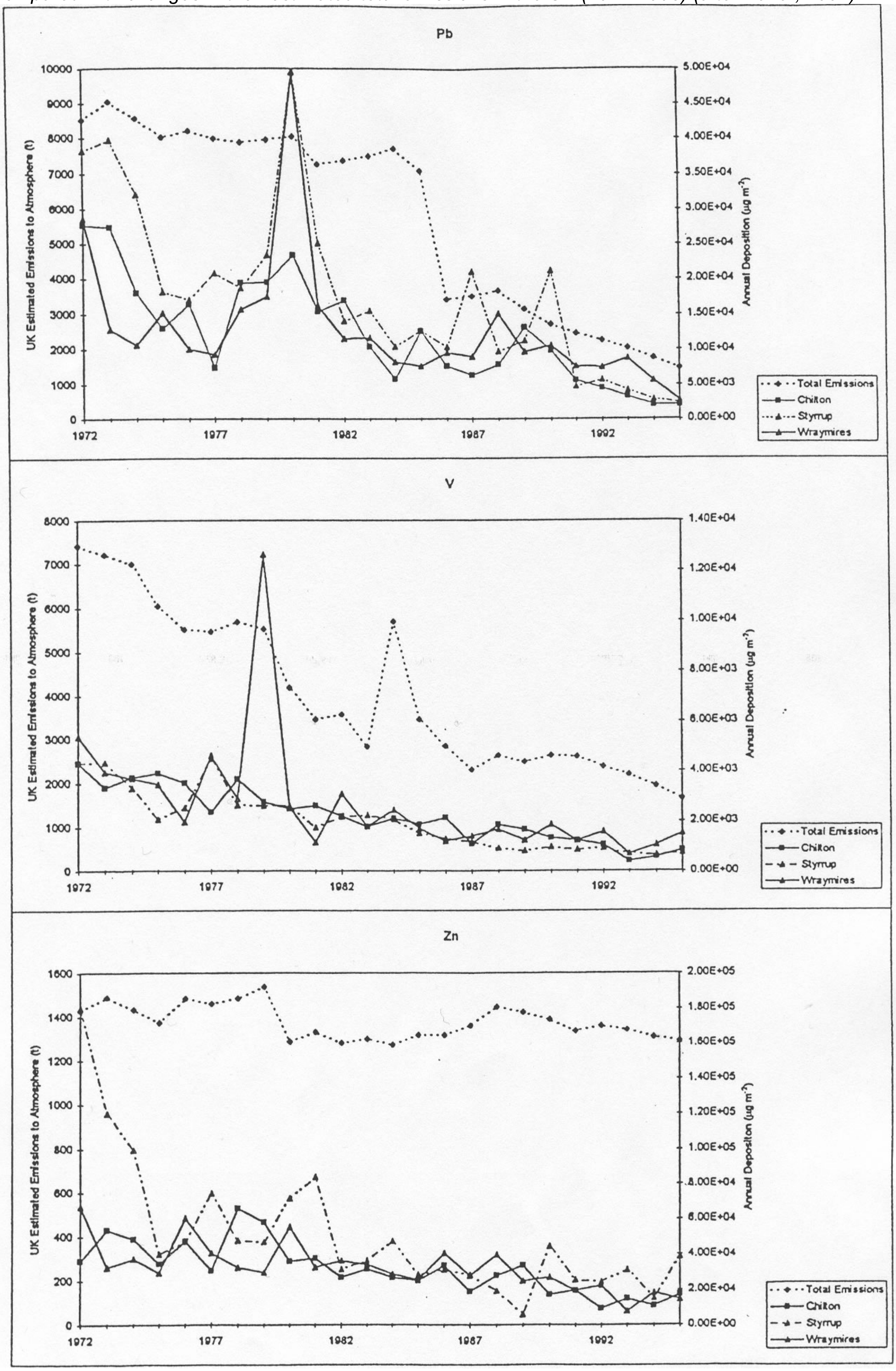
Sampling period is March 1995 to August 1997 for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn and April 1996 to August 1997 for Ag, Pt, Ti and V.

Table B2 Average Annual Total Deposition of Metals over England and Wales

Site	Rainfall	Al	Ba	Be	Ca	Co	Fe	K	Mg	Mn	Na	Sr
	ml	gram per hectare per year										
Boxworth	14779	6908	39.1	0.414	11555	3.81	5553	3946	2603	151.1	10585	41.7
Bridgets	20372	930	19.1	0.127	8795	1.34	1093	2262	1836	79.1	11285	24.0
Drayton	16493	950	26.5	0.127	7304	1.05	1196	3396	1549	45.3	7401.4	21.9
Gleadthorpe	17845	1219	62.9	0.208	33742	2.95	1615	15772	14619	100.4	53957	95.1
High Mowthorpe	19881	1241	25.0	0.140	14673	3.98	1407	2981	3427	104.3	21029	38.6
Pwllpeiran	47838	580	14.7	0.203	5326	2.81	717	2616	4631	52.4	34646	39.8
Redesdale	22519	390	15.1	0.118	2686	1.03	488	2782	2556	60.8	15465	15.9
Rosemaund	18990	2191	26.5	0.176	5699	2.66	2257	4354	2416	102.5	9415.5	17.2
Terrington	15714	3826	45.2	0.293	11930	3.75	5091	20846	6044	165.1	24108	53.9
Morley	16264	6614	39.0	0.414	18378	4.82	5827	21382	4511	218.1	19796	48.4
North Wyke	31408	447	22.0	0.174	5736	1.76	522	3564	4594	66.2	34718	31.8
Taunton	23719	1765	37.8	0.186	22752	2.47	2349	10047	8549	97.3	21108	55.3
Lancaster	37339	536	21.4	0.228	5127	2.07	658	3984	4038	58.6	26200	26.5
North Lincs	16393	4301	32.7	0.414	14703	3.67	6529	6238	4346	257.7	16421	33.9
Penrith	24265	333	10.8	0.138	4815	1.12	422	5970	2783	34.2	15397	20.6
Northallerton	15995	3801	46.8	0.261	8430	3.15	3769	7890	4626	97.4	11963	26.9
Ellesmere	19993	603	18.0	0.139	4491	1.09	690	2236	1932	37.7	9311.5	12.3
Leicestershire	15768	4409	52.1	0.280	7691	4.35	6215	9365	11627	171.2	11153	20.3
Marlborough	23754	757	37.2	0.161	13622	1.41	877	9230	3109	100.6	15556	26.4
Uckfield	22056	557	18.0	0.154	4898	1.26	683	4749	3651	66.0	24314	26.8
Ashford	17503	1931	24.9	0.199	8658	1.95	2124	7138	3035	83.1	17129	24.1
Ruthin	23561	4715	197.8	0.262	6792	2.72	4281	3540	3429	202.3	15520	22.3
Pembroke	36545	1457	14.7	0.177	4874	2.48	1665	3619	4916	107.0	33580	30.5
Colchester	13797	609	16.4	0.134	4877	1.13	863	6008	2651	55.9	14297	21.2
Sonning	17591	1200	175.9	0.152	9204	3.04	2197	6355	2197	87.9	9640	32.9
Wytham	19046	555	19.0	0.131	14546	1.06	764	5073	2142	59.6	10040	31.6
Alice Holt	20808	539	21.9	0.142	3881	1.06	665	1414	1635	53.7	9755.1	14.8
Arthur Rickwood	15045	1652	22.5	0.156	9925	1.32	2091	6413	3139	72.9	15256	39.8
Brentwood	14991	1085	28.8	0.168	5322	1.28	1362	2044	1422	51.5	7104.4	16.4
Avonmouth	25038	1293	68.8	0.212	11661	2.25	2176	3177	3236	104.4	15802	56.7
Usk	20882	1156	31.6	0.156	12918	1.68	2003	6654	2456	147.0	6235.9	24.3
Monmouth	32250	1835	27.5	0.284	5800	2.61	2562	3156	3461	188.2	18849	22.3
Cowbridge	37789	900	36.7	0.306	9736	2.26	1768	4959	5623	90.5	34994	36.8
Hexham	21066	552	21.1	0.188	7325	1.90	728	1789	2749	33.5	17035	35.6
Harewood	23286	573	28.2	0.223	4097	1.65	804	2710	2541	48.1	15732	18.3
Ashbourne	32744	683	64.4	0.303	9540	2.09	987	2439	3162	57.2	21113	26.4

Sampling period is March 1995 to August 1997.

Appendix 4 Changes in the annual mean deposition of Pb, V and Zn at Chilton, Styrrup and Wraymires compared with changes in their estimated total emissions in the UK (1972-1995) (after Baker, 1997).

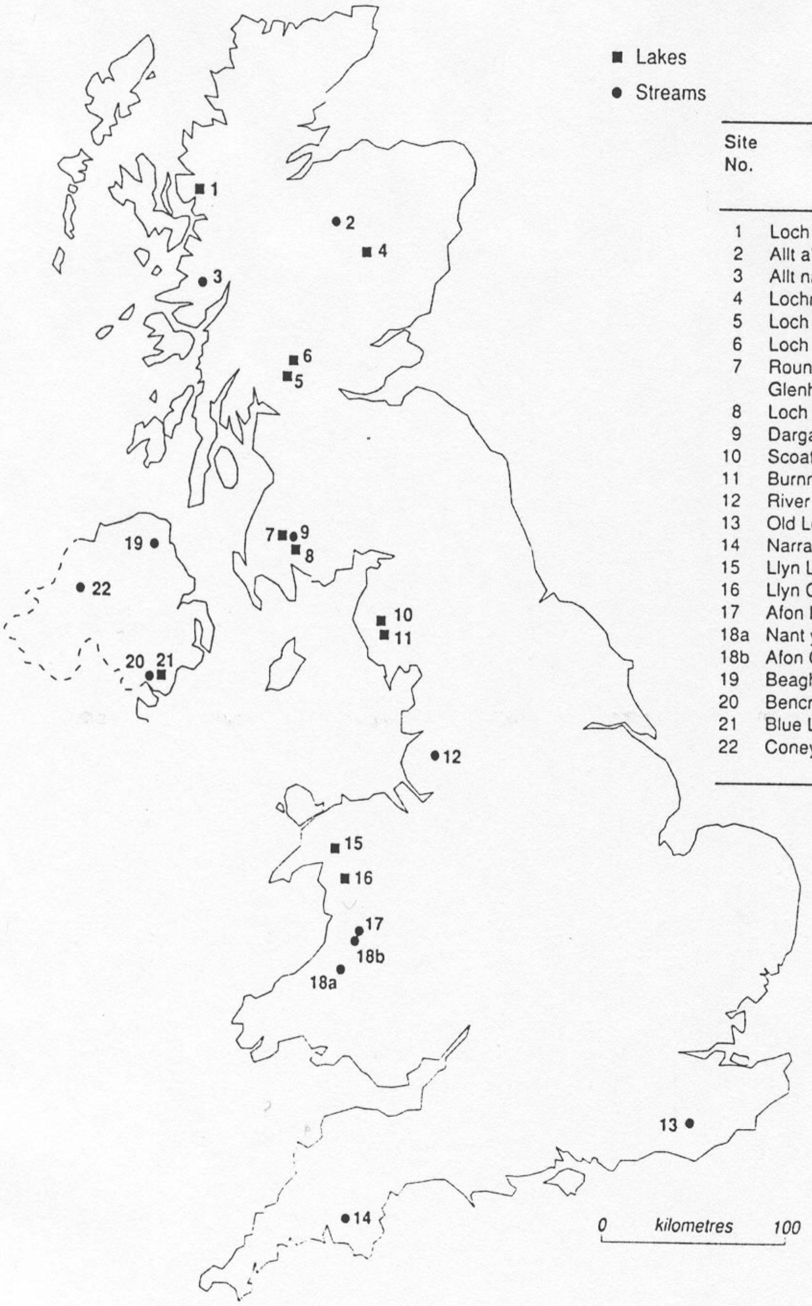


Appendix 5 Locations of UK Acid Waters Monitoring Network (AWMN) sites (after Patrick et al, 1981) with CLAM monitoring sites at Llyn Llagi (15), Scoat Tarn (10), River Etherow (12) and Lochnagar (4).

Location of Monitoring Network Sites

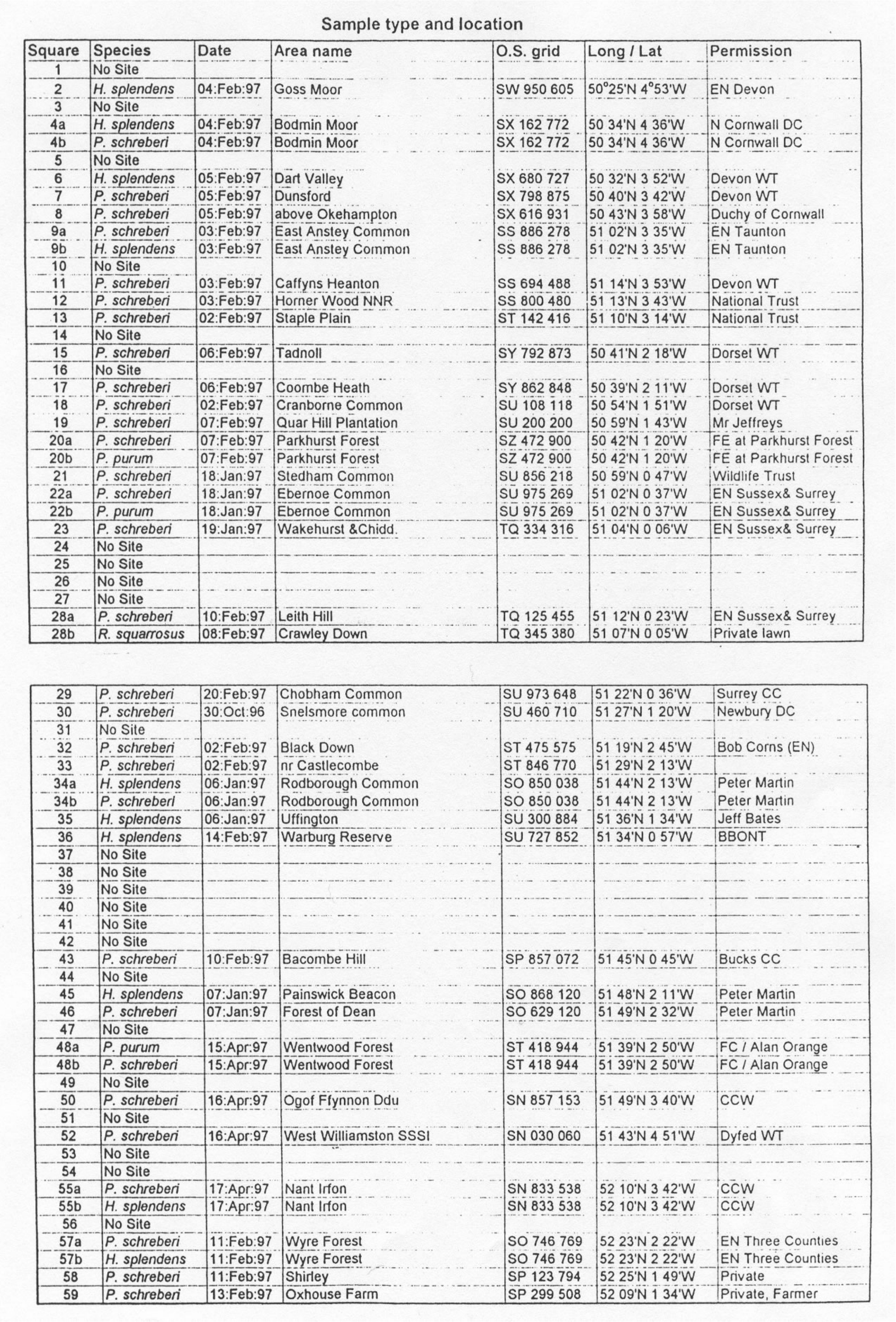
■ Lakes

● Streams



Site No.	Site name	Grid ref.	Catchment area (ha)	% mature planted conifers
1	Loch Coire nan Arr	NG 808422	897	<1%
2	Allt a' Mharcaidh	NH 881045	998	—
3	Allt na Coire nan Con	NM 793688	790	50
4	Lochnagar	NO 252859	92	—
5	Loch Chon	NN 421051	1470	52
6	Loch Tinker	NN 445068	112	—
7	Round Loch of Glenhead	NX 450804	95	—
8	Loch Grannoch	NX 542700	1287	70
9	Dargall Lane	NX 449786	210	—
10	Scoat Tarn	NY 159104	95	—
11	Burnmoor Tarn	NY 184043	226	—
12	River Etherow	SK 116996	1300	—
13	Old Lodge	TQ 456294	240	—
14	Narrator Brook	SX 568692	475	10
15	Llyn Llagi	SH 649483	157	—
16	Llyn Cwm Mynach	SH 678238	152	51
17	Afon Hafren	SN 844876	358	50
18a	Nant y Gronwen	SN 771556	77	—
18b	Afon Gwy	SN 824854	210	—
19	Beagh's Burn	D 173297	273	—
20	Bencrom River	J 304245	298	—
21	Blue Lough	J 327252	42	—
22	Coneyglen Burn	H 640885	1414	5

Appendix 6 Information on sample type, date of sampling and location of sampling for the UK heavy metal moss monitoring survey 1996/1997 (after Parry and Williams, 1998).



Sample type and location

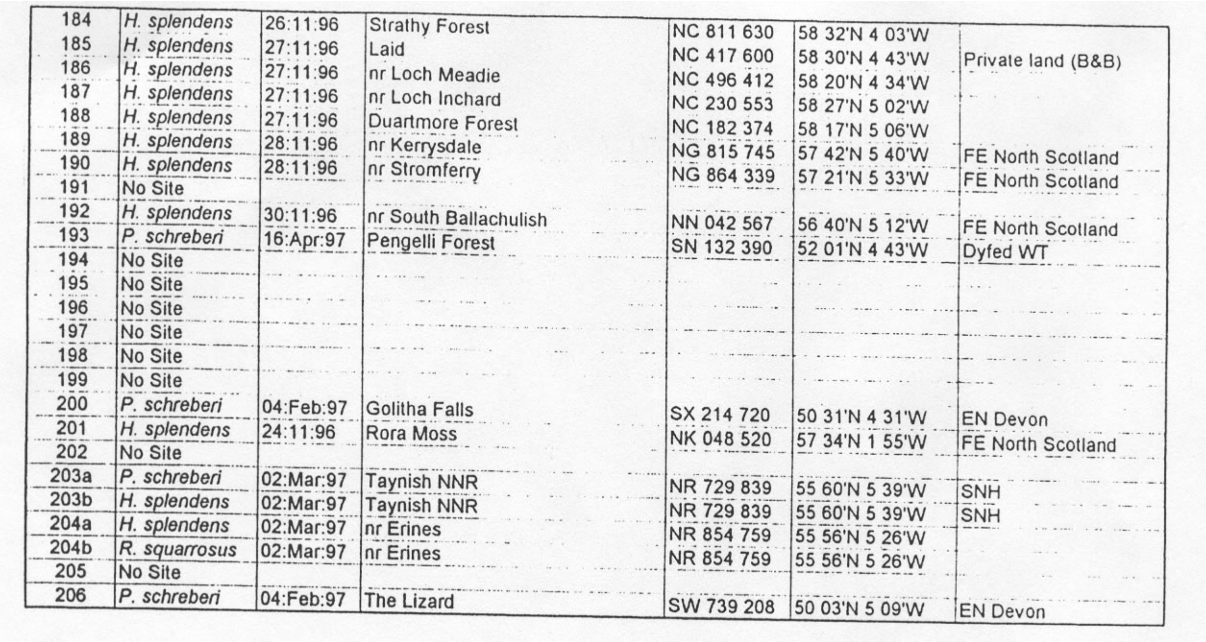
Square	Species	Date	Area name	O.S. grid	Long / Lat	Permission
1	No Site					
2	*H. splendens*	04:Feb:97	Goss Moor	SW 950 605	50°25'N 4°53'W	EN Devon
3	No Site					
4a	*H. splendens*	04:Feb:97	Bodmin Moor	SX 162 772	50 34'N 4 36'W	N Cornwall DC
4b	*P. schreberi*	04:Feb:97	Bodmin Moor	SX 162 772	50 34'N 4 36'W	N Cornwall DC
5	No Site					
6	*H. splendens*	05:Feb:97	Dart Valley	SX 680 727	50 32'N 3 52'W	Devon WT
7	*P. schreberi*	05:Feb:97	Dunsford	SX 798 875	50 40'N 3 42'W	Devon WT
8	*P. schreberi*	05:Feb:97	above Okehampton	SX 616 931	50 43'N 3 58'W	Duchy of Cornwall
9a	*P. schreberi*	03:Feb:97	East Anstey Common	SS 886 278	51 02'N 3 35'W	EN Taunton
9b	*H. splendens*	03:Feb:97	East Anstey Common	SS 886 278	51 02'N 3 35'W	EN Taunton
10	No Site					
11	*P. schreberi*	03:Feb:97	Caffyns Heanton	SS 694 488	51 14'N 3 53'W	Devon WT
12	*P. schreberi*	03:Feb:97	Horner Wood NNR	SS 800 480	51 13'N 3 43'W	National Trust
13	*P. schreberi*	02:Feb:97	Staple Plain	ST 142 416	51 10'N 3 14'W	National Trust
14	No Site					
15	*P. schreberi*	06:Feb:97	Tadnoll	SY 792 873	50 41'N 2 18'W	Dorset WT
16	No Site					
17	*P. schreberi*	06:Feb:97	Coombe Heath	SY 862 848	50 39'N 2 11'W	Dorset WT
18	*P. schreberi*	02:Feb:97	Cranborne Common	SU 108 118	50 54'N 1 51'W	Dorset WT
19	*P. schreberi*	07:Feb:97	Quar Hill Plantation	SU 200 200	50 59'N 1 43'W	Mr Jeffreys
20a	*P. schreberi*	07:Feb:97	Parkhurst Forest	SZ 472 900	50 42'N 1 20'W	FE at Parkhurst Forest
20b	*P. purum*	07:Feb:97	Parkhurst Forest	SZ 472 900	50 42'N 1 20'W	FE at Parkhurst Forest
21	*P. schreberi*	18:Jan:97	Stedham Common	SU 856 218	50 59'N 0 47'W	Wildlife Trust
22a	*P. schreberi*	18:Jan:97	Ebernoe Common	SU 975 269	51 02'N 0 37'W	EN Sussex& Surrey
22b	*P. purum*	18:Jan:97	Ebernoe Common	SU 975 269	51 02'N 0 37'W	EN Sussex& Surrey
23	*P. schreberi*	19:Jan:97	Wakehurst &Chidd.	TQ 334 316	51 04'N 0 06'W	EN Sussex& Surrey
24	No Site					
25	No Site					
26	No Site					
27	No Site					
28a	*P. schreberi*	10:Feb:97	Leith Hill	TQ 125 455	51 12'N 0 23'W	EN Sussex& Surrey
28b	*R. squarrosus*	08:Feb:97	Crawley Down	TQ 345 380	51 07'N 0 05'W	Private lawn
29	*P. schreberi*	20:Feb:97	Chobham Common	SU 973 648	51 22'N 0 36'W	Surrey CC
30	*P. schreberi*	30:Oct:96	Snelsmore common	SU 460 710	51 27'N 1 20'W	Newbury DC
31	No Site					
32	*P. schreberi*	02:Feb:97	Black Down	ST 475 575	51 19'N 2 45'W	Bob Corns (EN)
33	*P. schreberi*	02:Feb:97	nr Castlecombe	ST 846 770	51 29'N 2 13'W	
34a	*H. splendens*	06:Jan:97	Rodborough Common	SO 850 038	51 44'N 2 13'W	Peter Martin
34b	*P. schreberi*	06:Jan:97	Rodborough Common	SO 850 038	51 44'N 2 13'W	Peter Martin
35	*H. splendens*	06:Jan:97	Uffington	SU 300 884	51 36'N 1 34'W	Jeff Bates
36	*H. splendens*	14:Feb:97	Warburg Reserve	SU 727 852	51 34'N 0 57'W	BBONT
37	No Site					
38	No Site					
39	No Site					
40	No Site					
41	No Site					
42	No Site					
43	*P. schreberi*	10:Feb:97	Bacombe Hill	SP 857 072	51 45'N 0 45'W	Bucks CC
44	No Site					
45	*H. splendens*	07:Jan:97	Painswick Beacon	SO 868 120	51 48'N 2 11'W	Peter Martin
46	*P. schreberi*	07:Jan:97	Forest of Dean	SO 629 120	51 49'N 2 32'W	Peter Martin
47	No Site					
48a	*P. purum*	15:Apr:97	Wentwood Forest	ST 418 944	51 39'N 2 50'W	FC / Alan Orange
48b	*P. schreberi*	15:Apr:97	Wentwood Forest	ST 418 944	51 39'N 2 50'W	FC / Alan Orange
49	No Site					
50	*P. schreberi*	16:Apr:97	Ogof Ffynnon Ddu	SN 857 153	51 49'N 3 40'W	CCW
51	No Site					
52	*P. schreberi*	16:Apr:97	West Williamston SSSI	SN 030 060	51 43'N 4 51'W	Dyfed WT
53	No Site					
54	No Site					
55a	*P. schreberi*	17:Apr:97	Nant Irfon	SN 833 538	52 10'N 3 42'W	CCW
55b	*H. splendens*	17:Apr:97	Nant Irfon	SN 833 538	52 10'N 3 42'W	CCW
56	No Site					
57a	*P. schreberi*	11:Feb:97	Wyre Forest	SO 746 769	52 23'N 2 22'W	EN Three Counties
57b	*H. splendens*	11:Feb:97	Wyre Forest	SO 746 769	52 23'N 2 22'W	EN Three Counties
58	*P. schreberi*	11:Feb:97	Shirley	SP 123 794	52 25'N 1 49'W	Private
59	*P. schreberi*	13:Feb:97	Oxhouse Farm	SP 299 508	52 09'N 1 34'W	Private, Farmer

60	No Site					
61	No Site					
62	No Site					
63a	*P. schreberi*	27:Mar:97	Lakenheath	TL 757 828	52 25'N 0 35'E	Elveden Farm
63b	*P. purum*	27:Mar:97	Lakenheath	TL 757 828	52 25'N 0 35'E	Elveden Farm
64	No Site					
65	*P. schreberi*	27:Mar:97	New Buckenham Common	TM 090 906	52 28'N 1 05'E	Norfolk WT
66	*P. schreberi*	27:Mar:97	Brandon Park	TL 770 841	52 26'N 0 36'E	Suffolk CC
67	No Site					
68	No Site					
69	No Site					
70	*P. schreberi*	12:Feb:97	Tile Hill Wood	SP 282 792	52 25'N 1 35'W	Coventry NH Soc
71	*P. schreberi*	12:Feb:97	Sutton Park	SP 100 960	52 34'N 1 51'W	Sutton Park
72	*P. schreberi*	11:Feb:97	Mortimer Forest	SO 487 729	52 21'N 2 45'W	Ludlow FE
73	*P. schreberi*	17:Apr:97	Stapeley Hill	SO 310 990	52 35'N 3 01'W	EN West Midlands
74	No Site					
75	No Site					
76	*H. splendens*	17:Apr:97	Coed Crafnant	SH 619 289	52 51'N 4 04'W	N Wales WT
77	No Site					
78	*P. schreberi*	18:Apr:97	Cors Goch	SH 503 817	53 19'N 4 15'W	N Wales WT
79	*P. schreberi*	18:Apr:97	Aber Falls	SH 640 590	53 07'N 4 02'W	CCW
80	*P. schreberi*	18:Apr:97	Cors Bodgynydd	SH 767 597	53 07'N 3 51'W	N Wales WT
81	*H. splendens*	17:Apr:97	Cors Y Sarnau	SH 971 390	52 57'N 3 32'W	N Wales WT
82	No Site					
83	No Site					
84	No Site					
85	*P. schreberi*	12:Feb:97	nr A50 Bypass	SK 485 109	52 42'N 1 17'W	D Ballard, VC55
86	No Site					
87	No Site					
88	No Site					
89a	*P. schreberi*	26:Mar:97	Narborough Railway Line	TF 750 118	52 40'N 0 35'E	Norfolk WT
89b	*P. purum*	26:Mar:97	Narborough Railway Line	TF 750 118	52 40'N 0 35'E	Norfolk WT
90	No Site					
91	No Site					
92	*P. schreberi*	27:Apr:97	Kirkby Moor	TF 225 629	53 09'N 0 10'W	The Lincs. Trust

93	*P. schreberi*	27:Apr:97	Linwood Warren	TF 133 877	53 22'N 0 18'W	The Lincs. Trust
94	No Site					
95	*P. schreberi*	19:Apr:97	Stanton Edge	SK 250 630	53 10'N 1 37'W	Public access
96	No Site					
97	No Site					
98	No Site					
99	No Site					
100	No Site					
101	No Site					
102	*P. schreberi*	19:Apr:97	Abbey Brook	SK 170 920	53 26'N 1 45'W	Tom Blockeel
103	*P. schreberi*	27:Apr:97	Scotton Common	SK 870 985	53 29'N 0 41'W	The Lincs. Trust
104	No Site					
105	No Site					
106	No Site					
107	*P. schreberi*	09:Mar:97	Boltby	SE 490 890	54 18'N 1 15'W	FE N&E England
108	No Site					
109	*P. schreberi*	01:Mar:97	Forest of Bowland	SD 566 489	53 56'N 2 40'W	Public Access?
110	No Site					
111	No Square					
112	*P. schreberi*	08:Mar:97	Grizedale Forest	SD 331 938	54 20'N 3 02'W	FE N&E England
113a	*P. schreberi*	01:Mar:97	Gisburn Forest	SD 740 600	54 02'N 2 24'W	FE N&E England
113b	*R. squarrosus*	01:Mar:97	Gisburn Forest	SD 740 600	54 02'N 2 24'W	FE N&E England
114	*P. schreberi*	08:Mar:97	Agra, Witton Moors	SE 140 840	54 15'N 1 47'W	EN N&E Yorks
115a	*P. purum*	08:Mar:97	Bolton Moors	SE 022 958	54 21'N 1 58'W	EN N&E Yorks
115b	*H. splendens*	08:Mar:97	Bolton Moors	SE 022 958	54 21'N 1 58'W	EN N&E Yorks
116	*P. schreberi*	08:Mar:97	May Moss	SE 880960	53 35'N 1 52'W	EN N&E Yorks
117	No Site					
118	*P. schreberi*	07:Mar:97	nr Lealholm/Danby moor	NZ 752 096	54 29'N 0 50'W	EN N&E Yorks
119	No Site					
120	*P. schreberi*	07:Mar:97	Teesdale NNR	NY 830 320	54 41'N 2 16'W	EN N'land & Durham
121	*P. schreberi*	07:Mar:97	Asby Scar NNR	NY 650 100	54 29'N 2 32'W	EN Cumbria
122	*P. schreberi*	07:Mar:97	The Dodd	NY 340 360	54 43'N 3 01'W	FE N&E England
123a	*H. splendens*	07:Mar:97	Ennerdale Forest	NY 140 140	54 31'N 3 20'W	FE N&E England
123b	*P. schreberi*	07:Mar:97	Ennerdale Forest	NY 140 140	54 31'N 3 20'W	FE N&E England
124	*P. schreberi*	06:Mar:97	Smetmurthy Plantation	NY 160 320	54 41'N 3 18'W	FE N&E England

125	*P. schreberi*	05:Mar:97	Town Wood	NX 854 582	54 54'N 3 47'W	FE South Scotland
126	No Site					
127	*P. schreberi*	05:Mar:97	Grey Mares Tail	NX 411 730	55 02'N 4 29'W	FE South Scotland
128	*H. splendens*	05:Mar:97	nr Blood Moss	NX 267 722	55 00'N 4 43'W	FE South Scotland
129a	*H. splendens*	05:Mar:97	Carsphairn Forest	NS 569 012	55 17'N 4 15'W	FE South Scotland
129b	*P. schreberi*	05:Mar:97	Carsphairn Forest	NS 569 012	55 17'N 4 15'W	FE South Scotland
130	No Site					
131	*H. splendens*	05:Mar:97	Ettrick Water	NT 180 070	55 21'N 3 18'W	SNH South East
132	*P. schreberi*	04:Mar:97	Kielder Forest	NY 660 911	55 13'N 2 32'W	FE N&E England
133	*H. splendens*	06:Mar:97	Williamston	NY 681 520	54 52'N 2 30'W	Newcastle Uni
134	*P. schreberi*	06:Mar:97	Rabbit Bank Wood	NZ 112 484	54 50'N 1 50'W	Durham WT
135	*P. schreberi*	06:Mar:97	Waldridge Fell	NZ 250 498	54 51'N 1 37'W	Durham CC
136	No Site					
137	*P. schreberi*	06:Mar:97	Gunnerton Crag	NY 915 750	55 04'N 2 08'W	Newcastle Uni
138	No Site					
139	No Site					
140	*P. schreberi*	04:Mar:97	Blackpool Moss	NT 517 289	55 33'N 2 46'W	SNH South East
141a	*P. schreberi*	04:Mar:97	Whim Bog and Wood	NT 200 530	55 46'N 3 16'W	SNH South East
141b	*H. splendens*	04:Mar:97	Whim Bog and Wood	NT 200 530	55 46'N 3 16'W	SNH South East
142	No Site					
143	No Site					
144	No Site					
145a	*P. schreberi*	02:Mar:97	Loch Lomond Reg Park	NS 349 989	56 09'N 4 40'W	SNH South West
145b	*R. squarrosus*	02:Mar:97	Loch Lomond Reg Park	NS 349 989	56 09'N 4 40'W	SNH South West
146a	*R. squarrosus*	02:Mar:97	nr Glenmavis	NS 759 681	55 53'N 3 59'W	Private (B&B)
146b	*R. squarrosus*	02:Mar:97	nr Glenmavis	NS 759 681	55 53'N 3 59'W	Private (B&B)
146c	*P. schreberi*	02:Mar:97	nr Glenmavis	NS 759 681	55 53'N 3 59'W	Private (B&B)
147	No Site					
148a	*H.splendens*	04:Mar:97	Wooded Area nr Dunbar Common	NT 639 690	55 55'N 2 35'W	
148b	*P. purum*	04:Mar:97	Wooded Area nr Dunbar Common	NT 639 690	55 55'N 2 35'W	
148c	*R. squarrosus*	04:Mar:97	Wooded Area nr Dunbar Common	NT 639 690	55 55'N 2 35'W	
149	*H. splendens*	04:Mar:97	Dowlaw Dean	NT 860 700	55 55'N 2 13'W	SNH South East
150	No Site					
151	*P. schreberi*	03:Mar:97	Pitmedden Forest	NO 210 140	56 19'N 3 17'W	
152	No Site					

153	No Site					
154a	*P. schreberi*	30:11:96	Fearnoch Forest (South)	NM 963 283	56 24'N 5 18'W	FE North Scotland
154b	*H. splendens*	30:11:96	Fearnoch Forest (South)	NM 963 283	56 24'N 5 18'W	FE North Scotland
155	*H. splendens*	30:11:96	Fearnoch Forest (North)	NM 959 315	56 26'N 5 19'W	FE North Scotland
156	*H. splendens*	30:11:96	Glen Orchy	NN 232 333	56 28'N 4 52'W	SNH South East
157a	*P. schreberi*	03:Mar:97	Rannoch Moor	NN 284 424	56 33'N 4 48'W	SNH South East
157b	*H. splendens*	03:Mar:97	Rannoch Moor	NN 284 424	56 33'N 4 48'W	SNH South East
158	No Site					
159	No Site					
160a	*H. splendens*	03:Mar:97	Fetteresso Forest	NO 769 870	56 58'N 2 23'W	FE North Scotland
160b	*R. squarrosus*	03:Mar:97	Fetteresso Forest	NO 769 870	56 58'N 2 23'W	FE North Scotland
161	No Site					
162	*H. splendens*	29:11:96	The Queens Forest	NH 968 100	57 10'N 3 42'W	FE North Scotland
163	*P. schreberi*	29:11:96	Inshriach Forest	NH 830 020	57 06'N 3 56'W	FE North Scotland
164	*H. splendens*	29:11:96	nr Loch Oich	NH 321 004	57 04'N 4 46'W	
165	*H. splendens*	29:11:96	nr Fort William	NN 105 761	56 50'N 5 06'W	
166	*H. splendens*	28:11:96	Inverinate Forest	NG 978 253	57 16'N 5 21'W	FE North Scotland
167	*H. splendens*	29:11:96	Boblainy Forest	NH 491 382	57 25'N 4 31'W	FE North Scotland
168	*H. splendens*	29:11:96	nr Meall Mor	NH 728 352	57 23'N 4 07'W	FE North Scotland
169	No Site					
170a	*H. splendens*	24:11:96	Corrennie Forest	NJ 639 100	57 11'N 2 36'W	FE North Scotland
170b	*P. purum*	24:11:96	Corrennie Forest	NJ 639 100	57 11'N 2 36'W	FE North Scotland
171	*H. splendens*	25:11:96	E Bennachie Forest	NJ 681 202	57 16'N 2 32'W	FE North Scotland
172	*H. splendens*	24:11:96	Delgaty Forest	NJ 757 482	57 31'N 2 24'W	FE North Scotland
173	*H. splendens*	24:11:96	The Bin Forest	NJ 514 461	57 30'N 2 49'W	FE North Scotland
174	*H. splendens*	25:11:96	Culbin	NH 970 610	57 38'N 3 44'W	FE North Scotland
175	*H. splendens*	25:11:96	Culloden Forest	NH 759 470	57 30'N 4 04'W	FE North Scotland
176	*H. splendens*	25:11:96	Blackmuir Wood	NH 485 573	57 35'N 4 32'W	SNH North West
177	*H. splendens*	28:11:96	Strathconon Forest	NH 238 474	57 29'N 4 56'W	FE North Scotland
178	*H. splendens*	27:11:96	Dundonnell Forest	NH 108 812	57 47'N 5 11'W	FE North Scotland
179	*H. splendens*	27:11:96	nr Cnoc Chaornaidh	NC 306 079	58 02'N 4 52'W	
180	*H. splendens*	26:11:96	Morangie Forest	NH 740 803	57 48'N 4 07'W	
181	*H. splendens*	26:11:96	Woodcock Hill	NC 874 466	58 24'N 3 56'W	
182	*H. splendens*	26:11:96	Rumster Forest Walks	ND 208 380	58 19'N 3 21'W	
183	*H. splendens*	26:11:96	Dunnet	ND 213 716	58 38'N 3 21'W	



184	*H. splendens*	26:11:96	Strathy Forest	NC 811 630	58 32'N 4 03'W	
185	*H. splendens*	27:11:96	Laid	NC 417 600	58 30'N 4 43'W	Private land (B&B)
186	*H. splendens*	27:11:96	nr Loch Meadie	NC 496 412	58 20'N 4 34'W	
187	*H. splendens*	27:11:96	nr Loch Inchard	NC 230 553	58 27'N 5 02'W	
188	*H. splendens*	27:11:96	Duartmore Forest	NC 182 374	58 17'N 5 06'W	
189	*H. splendens*	28:11:96	nr Kerrysdale	NG 815 745	57 42'N 5 40'W	FE North Scotland
190	*H. splendens*	28:11:96	nr Stromferry	NG 864 339	57 21'N 5 33'W	FE North Scotland
191	No Site					
192	*H. splendens*	30:11:96	nr South Ballachulish	NN 042 567	56 40'N 5 12'W	FE North Scotland
193	*P. schreberi*	16:Apr:97	Pengelli Forest	SN 132 390	52 01'N 4 43'W	Dyfed WT
194	No Site					
195	No Site					
196	No Site					
197	No Site					
198	No Site					
199	No Site					
200	*P. schreberi*	04:Feb:97	Golitha Falls	SX 214 720	50 31'N 4 31'W	EN Devon
201	*H. splendens*	24:11:96	Rora Moss	NK 048 520	57 34'N 1 55'W	FE North Scotland
202	No Site					
203a	*P. schreberi*	02:Mar:97	Taynish NNR	NR 729 839	55 60'N 5 39'W	SNH
203b	*H. splendens*	02:Mar:97	Taynish NNR	NR 729 839	55 60'N 5 39'W	SNH
204a	*H. splendens*	02:Mar:97	nr Erines	NR 854 759	55 56'N 5 26'W	
204b	*R. squarrosus*	02:Mar:97	nr Erines	NR 854 759	55 56'N 5 26'W	
205	No Site					
206	*P. schreberi*	04:Feb:97	The Lizard	SW 739 208	50 03'N 5 09'W	EN Devon

Task 3.2: Metal deposition and cycling at Lochnagar

N. Rose and H. Yang.

3.2. Metal deposition and cycling at Lochnagar

Neil Rose and Handong Yang.

Introduction

Over the last decade Lochnagar has become an important part of both national and international monitoring networks and research programmes. The loch experiences some of the harshest conditions in the UK and because of its altitude and underlying geology it is particularly sensitive to atmospherically deposited pollutants. Further, prevailing south-westerly winds carry pollutants to the site from the main industrial centres of the UK.

Trace metal analyses were first undertaken at the site in 1986 when a palaeoecological investigation was undertaken by the ECRC as part of a Department of the Environment (Air Quality) funded study into the causes of surface water acidification in the UK. In 1988, Lochnagar was selected as one of the sites in the newly established Acid Waters Monitoring Network (AWMN) and chemical and biological data from the site have since contributed to both national (Environmental Change Network) and international (UNECE International Co-operative Programme for Assessment and Monitoring of Acidification of Rivers and Lakes) monitoring networks. Furthermore, the loch has been one of the flag-ship sites in the EU funded European mountain lakes research programmes AL:PE and AL:PE II (1991 – 1996), MOLAR (1997 – 1999) and more recently EMERGE (2000 – 2003).

The monitoring of trace metals at Lochnagar became more intensive in 1996, when sampling for the EU MOLAR project and a linked PhD study by Handong Yang (Yang, 2000) at the ECRC, began. The combined aims of these studies was to try and link depositional fluxes of metals at Lochnagar to the lake sediment record in such a way that historical deposition could more accurately and quantitatively be determined. Further, sampling of many ecological compartments including not only atmospheric deposition and lake waters, but also lake sediments, suspended sediments, catchment soils, various terrestrial plant and aquatic macrophyte species, epilithic diatoms and zooplankton were undertaken and analysed for a range of metals in order that a mass balance for the lake system could be obtained. This study also showed, for the first time, the major input of metals from the catchment of an upland lake site, thought to be as a result of increased catchment erosion. Finally, the level of deposition at which atmospheric fluxes recorded in the sediment first exceed the background metal flux could be determined thus providing a sediment-based ‘critical load’ and atmospheric flux equivalent. This could then be compared to contemporary deposition and the critical load ‘exceedance’ calculated.

The aim of this part of the Critical Load of Acidity and Metals (CLAM) project was to continue this sampling programme in order to provide:

- Data on inter- and intra-annual variability in deposition of metals at a remote site
- An assessment of the role that catchment and lake biota and sediment trapping can play in the monitoring of metal deposition and / or lake water metal concentrations with a view to future monitoring at a larger number of sites.
- An indication of any temporal trends that might become apparent
- Further evidence for the role of catchment release in lake metal inputs

- Data on Hg, sparse within the UK, in the various ecological compartments at an upland lake site

Sampling programme

Physical parameters

Essential information on meteorological and lake temperature parameters were monitored automatically at Lochnagar throughout the CLAM sampling period by means of an Automatic Weather Station (AWS) located near the loch shore and by a thermistor chain located in the deepest area of the loch basin. The meteorological parameters measured were air temperature, air pressure, wind speed and direction, relative humidity and rainfall. Net radiation and solarimeter sensors were added in August 2000 as part of the EU EMERGE project. Readings of air temperature, air pressure and relative humidity were taken every 30 minutes, whilst wind speed and direction were recorded as 30 minute averages. Rainfall was recorded daily. Measurements were taken throughout the period except for May 5th - August 23rd 2000 following an AWS logger power failure. These measurements are ongoing.

Bulk deposition and lake water

NILU (Norwegian Institute of Air Research) -type bulk deposition collectors (P.no. 9713, RS1; NILU, 2001) were deployed at the site in late summer 1996 as part of the EU MOLAR project. Over the period of the CLAM project, samples were collected fortnightly. Samples were acidified to 1% Aristar HNO_3 and analysed for a suite of trace elements by inductively coupled plasma – mass spectrometry (ICP-MS).

A separate collector was installed for mercury (Hg) deposition sampling in September 1997. This was an IVL (Institutet för Vatten-och Luftvårdsforskning – Swedish Environmental Research Institute) –type sampler (Lindqvist et al., 1991; Jensen and Iverfeldt, 1994). 5ml concentrated Aristar HCl was placed in the sample collection bottle before fitting to the collector in order that the collected samples were immediately acidified. Samples were collected monthly and sent to the Norwegian Institute of Air Research (NILU) for analysis by cold vapour – atomic fluorescence spectroscopy (CV-AFS).

Lake water samples were collected by submerging a rigorously acid leached 250 ml Teflon bottle approximately 20 cm beneath the surface of the water near the outflow where the lake water is well mixed. The bottles were completely filled and the lids tightened by gloved hands underwater. The bottles were then double bagged. Samples were taken fortnightly for trace metal analyses and monthly for Hg. Sample treatment was the same as for the deposition samples.

Initially, deposition and lake water samples were filtered prior to analysis, and it was not until analysis of the first significant batch of samples that this was perceived as a problem due to the possibility of leaching from the filters. From May 1999 onwards, samples were no longer filtered and a step-change can be observed in the data at this point (see results). We believe that the data post-May 1999 are reliable and accurate and represent a good dataset. It should be noted that this does not affect the Hg data as these samples were collected and analysed separately throughout. The Hg data therefore cover the full sampling period.

Sediment trapping

Sediment trapping at Lochnagar began in 1991 as part of the AWMN programme. The sediment traps, deployed c.1m above the sediment-water interface, are a simple tube design with a diameter of 5 cm and an aspect ratio (length to diameter) of 7:1. Three traps are deployed together in a triangular array and are emptied annually in late summer. From 1998, an additional array of three traps was deployed at c. 2m below the water surface in order to obtain information on the relative roles of catchment input and direct deposition. All trap samples were air dried up to 1999 making them unsuitable for Hg analysis. In 2000, samples were freeze-dried and hence Hg information is available for that year.

Terrestrial and aquatic plants

Samples of the main terrestrial plant species were collected annually in late summer. These included mosses, *Pleurozium schreberi* and *Hylocomium splendens*; grasses and rushes, *Nardus stricta* and *Juncus sp.*; and ericaceous species *Calluna vulgaris, Vaccinium myrtillus* and *Vaccinium vitis-idaea.* Leaf and shoot samples for each species were collected at various locations around the catchment and then combined to form a single sample. Plastic gloves were worn during collection and the samples stored in re-sealable plastic bags. The sampled vegetation was rinsed with deionised water and stored cool until freeze-dried prior to analysis.

Aquatic plants were collected using an Ekman grab operated from an inflatable boat, again during late summer. This grab sampling technique cannot guarantee collection of species especially as many do not grow extensively in the loch. For this reason sampling of all selected species was not always possible in each year. The species collected were as follows: liverworts, *Nardia compressa* and *Scapania undulata*; aquatic mosses, *Fontinalis antipyretica* and *Sphagnum auriculatum.*, and the aquatic macrophyte, *Isoetes lacustris.* Once sampled by the Ekman grab, the entire aquatic growth (whole plant excluding root) was collected, washed, freeze-dried and treated as for the terrestrial species.

Epilithic diatoms

Artificial substrates were deployed in the littoral areas of the loch in the spring of each year and retrieved in late summer. Diatom growth was then removed and placed into a 30ml Sterilin tube where it was stored cool until freeze-drying. The amount of diatom growth on the substrates was never very extensive in Lochnagar and the amount collected, when freeze-dried, represented only a very small mass of material. On occasion, there was only sufficient for a single digestion (Hg requires a separate digestion procedure from the other trace elements) and in these instances the digestion for trace elements other than Hg was chosen. This was because it allowed the generation of data for more elements.

Zooplankton

Zooplankton samples were collected annually in late summer by using horizontal and vertical hauls of a 200 μm mesh net from an inflatable boat in the deepwater area of the loch. The zooplankton were stored in a polyethylene bottle. The sample was then filtered using a Whatman GF/A filter paper and washed using deionised water. This sample was then freeze-dried prior to analysis.

Analytical procedures

All bottles and glassware used in sample collection and analysis were rigorously cleaned prior to sample collection. This procedure involved soaking in 5% Decon® 90 solution for 24 hrs, multiple rinses with deionised distilled water, soaking in 1M HCl for another 24 hrs followed by extensive rinsing in deionised distilled water. All cleaned bottles and glassware were double bagged after drying. Further procedures to avoid sample contamination followed Fitzgerald and Watras (1989) and Watras et al. (1995).

Trace metal analyses

Hg in precipitation and lake water samples were measured by cold vapour atomic fluorescence spectrometry (CV-AFS) at the Norwegian Institute for Air Research (NILU). The detection limit for the method is 0.3 ng/L and analytical uncertainties lie within ±20% of the measured level. The other trace metals were measured by inductively coupled plasma mass spectrometry (ICP-MS). A standard sample for trace elements in natural waters, Standard Reference Material® 1640, was used for monitoring precipitation and lake water analysis.

In order to measure trace metals in sediment trap and biological material, samples (c. 0.2 g) were extracted using 8 ml concentrated Aristar HNO_3 at 100°C for 1 hour in rigorously acid leached 50 ml Teflon beakers. For Hg measurements, after digestion, the supernates were carefully transferred in polyethylene tubes. The residue in the beakers were then washed with deionized distilled water and the supernates transferred into the same tubes. Hg concentrations were measured by cold vapour atomic absorption spectrometry (CV-AAS) following reduction of Hg in the digested sample to its elemental state by $SnCl_2$ (Engstrom and Swain, 1997). For the other metals, after digestion, samples were made up to 20 ml with deionized distilled water, filtered through Whatman GF/A filter paper and stored in polyethylene tubes prior to analysis. Measurements were then undertaken by ICP-MS. For Zn, ICP-MS measurements were not reliable due to poor calibration and high detection limits. Therefore, Zn data were confirmed using flame atomic adsorption spectroscopy (flame-AAS) where the detection limit is <1 μg/l. Detection limits for the elements analysed by ICP-MS are shown in Table 3.1.

During digestion and measurement, standard reference material (Buffalo River sediment 2704) and sample blanks were analysed every twenty samples. The standard solution was measured every five samples to monitor measurement stability. Measured mean concentrations of Hg were 93 ng g^{-1} in Buffalo River sediment (n = 12; relative standard deviation (RSD) = 8.6 ng g^{-1}; certified value = 100 ng g^{-1}). The coefficient of variation and precision was < 5% for Pb, Cd and <15% for Zn, Cu, Ni.

Table 3.1. ICP-MS Detection limits.

V (μg/l)	Cr (μg/l)	Ni (μg/l)	Cu (μg/l)	As (μg/l)	Cd (μg/l)	Pb (μg/l)
0.001	0.012	0.054	0.015	0.007	0.004	0.002

Results

Automatic Weather Station

The mean daily wind speed, air temperature, relative humidity, air pressure and the daily rainfall for 1997, 1998 1999 and 2000 for Lochnagar are shown in Figures 3.1, 3.2, 3.3 and 3.4 respectively. The only loss of data occurred in summer of 2000 following a power failure in the data logger. This was restored in August. However, the fault was caused by an electrical short in the barometer, which was removed for repair. Therefore, no further air pressure readings were possible for 2000 after May (e.g. Figure 3.4). The barometer will be re-installed in early 2001.

The Figures and the annual means, maxima and minima given in Table 3.2 show that for the three full years of data 1997 – 1999 the meteorology at Lochnagar is remarkably consistent.2000 data are not included in Table 3.2 due to the gap in the dataset.

Table 3.2. Annual means, maxima and minima for meteorological variables at Lochnagar 1997 – 1999.

		1997	1998	1999
Wind speed (m/s)	Mean	3.51	3.77	3.86
	Maximum	13.6	16.6	14.7
	Minimum	0	0	0
Air temperature (°C)	Mean	5.06	4.14	4.42
	Maximum	22.29	20.81	20.87
	Minimum	-9.39	-9.44	-7.75
Relative Humidity (%)	Mean	80.6	82.3	85.4
	Maximum	100.86	105.6	115.3
	Minimum	6.5	10.2	-
Air Pressure (Pa)	Mean	919.5	917.2	916.7
	Maximum	946.6	945.3	950.4
	Minimum	866.6	864.0	862.7
Rainfall (mm)	Sum	1992.6	1665.4	1551.6

Lake thermistors

Figure 3.5 shows the lake water temperature data at 1.5m depth for the period July 1997 - July 2000. Similar data are available from thermistors at 2.5 m, 3.5 m, 4.5 m, 6.0 m, 7.0 m, 9.0 m, 11.0 m and 16.0 m depths. These measurements are ongoing. As might be expected water temperatures show close correlations with air temperature with the correlation decreasing with depth. Periods of stratification occur throughout the year especially in periods of elevated air temperatures and low wind speeds and these are broken down by periods of high winds. During the winter and particularly during periods of ice-cover, temperature stratification is reversed such that surface waters are cooler than deeper waters. These air and water temperature data are currently being used by Prof. Roy Thompson at University of Edinburgh to reconstruct historical air and water temperature and ice cover periods for Lochnagar as part of the EU project EMERGE. Annual mean temperatures for the site back to 1781 have already been reconstructed by Prof. Thompson and suggest an increasing temperature trend.

Bulk deposition and lake water samples

Concentrations of Hg (ng /l) in bulk deposition and lake water are shown in Figure 3.6. Concentrations of V, Cr, Cu, Ni, Cd, As, Pb and Zn (μg/l) for bulk deposition and lake water are shown in Figures 3.7 and 3.8 respectively. Recent Zn data remain to be confirmed. Comparisons between the depositional and lake water data for 1999 and 2000 data are presented in Figure 3.9. Gaps appear in the Hg deposition data due to freezing of the sampler in winter. The data between May and August 1999 were lost due to contamination of the preserving acid. Unfortunately, due to the delay between sending the samples to NILU and receiving the data several months' data were lost. However, once identified, the problem was quickly rectified.

Lake water Hg data appear to be reasonably stable over the period whilst deposition values are more variable. Linear trendlines superimposed on the data suggest an increase in both lake water and bulk deposition concentrations over time with a steeper slope for deposition than for lake water. However, a longer dataset is required to confirm these. Converting these data to annual means (lake water) and depositional fluxes (ng /cm^2/yr – bulk deposition) (Figure 3.11) suggests little trend in lake water and an increase in depositional flux of Hg over the study period. Again this must be treated with caution. At present, these sampling programmes are continuing and it is hoped that a longer dataset will be generated to provide more confidence in any observed trends.

Figure 3.6 also shows that lake water and deposition concentrations show similar intra-annual temporal trends. Furthermore, with a single exception, concentrations of Hg in bulk deposition are always higher than their equivalent lake water concentration suggesting that Hg in deposition is being retained in the catchment. This may be caused by Hg binding to organic matter in the catchment soils. Yang (2000) estimated that more than 90% of anthropogenic Hg deposited from the atmosphere over post-industrial time is stored within the catchment soils of Lochnagar suggesting an enormous reservoir of the element. The catchment is already a major source of Hg to the lake and the recent increase in catchment peat erosion at the site is reflected in the sediment record where Hg fluxes have levelled off in recent years rather than mirroring the decline shown by national emission figures. This has implications for the input of Hg from the catchment to the lake given possible future climate change scenarios, which may increase the rate of soil erosion in upland areas. It may be that Hg inputs to Lochnagar do not decline, and may even increase as a result, despite continued emission reductions. Restoration to low Hg sediment levels may therefore be delayed for decades. Increased inputs of metals from the catchment is supported by the sediment trap data (see below).

Trends in the bulk deposition and lake water data for the other metals (Figures 3.7 and 3.8) are dominated by the step change in May 1999 as a result of the move from filtered to non-filtered samples. This appears to have less effect on Pb data. It should be stated that the data prior to the change to non-filtering were also reliable measurements as confirmed by analyses of standard reference materials and up until the analysis of the last filtered batch there was no reason to doubt the values. However, the presence of high blank analyses and a subsequent test study revealed the possibility of metal inputs from filters to the samples and the procedure was immediately stopped. The remainder of the discussion will focus on the non-filtered data.

The non-filtered data for both lake water and bulk deposition show a decline from 1999 to 2000 for all metals except Pb in lake water. This latter result may also be due to increased catchment inputs. Indeed, the data prior to the step change also show a decline from 1997 to 1998 in most cases suggesting a probable continuous decline over the study period. This decline is further indicated by the increased numbers of 'below detection limit' values in 2000 compared to 1999, despite the low levels for the limit of detection shown in Table 3.1. Conversion of the deposition concentration data (Figure 3.7) to annual deposition flux data (3.11 – 3.16) also show the decline in deposition between the two latter years. Here, for values below the limit of detection, a figure of half the detection limit concentration (Table 3.1) was used in the calculation of flux values.

There is obviously a value in continuing to monitor lake water and bulk deposition directly, especially for Hg where there were no values below the limit of detection for the CV-AAS technique. However, continued deposition reductions may result in considerably more metal concentration measurements below detection limit and hence there is a major advantage in supporting this approach with measurements of biota where metals bioaccumulate to measurable levels and, in particular, sediment traps where the binding of metals to organic matter also raises concentrations to easily detectable levels.

Figure 3.9 shows a comparison between the bulk deposition and lake water concentrations for V, Cr, Ni, Cu, Pb, Cd and As for the 1999 – 2000 period. Of these trace elements, only V shows a similar pattern to that of Hg, i.e. deposition values almost always greater than lake water values. Cu is the only other element that shows deposition concentrations greater than lake water concentrations for more than 50% of the samples. Interestingly, Figure 3.9 shows that for the winter period November 1999 - February 2000, the outflow concentrations are always higher than deposition concentrations, for every element except Hg. This is not due to rainfall diluting the deposition concentrations as conversion to fluxes (Figure 3.10) shows that fluxes and concentrations follow each other very closely over this period. The reason is currently unclear, although wind direction data show that a northerly direction is more common in winter and hence deposition of metals might be reduced with respect to other times of the year when the prevailing winds are from the south and south-west. Longer-term monitoring and more detailed analysis of deposition data with meteorological variables will enable these hypotheses to be tested further.

Biological and sediment trap data

Mercury (Hg)

Hg data for the terrestrial and catchment plant species, epilithic diatoms and zooplankton are shown in Figure 3.11 along with lake water annual means and Hg deposition fluxes, for the years 1997 – 2000. As mentioned above the lake water appears to show little trend over the period, whilst the deposition flux appears to show a significant increase in 2000. Further monitoring is required to determine whether this is simply an anomalously high year.

Of the terrestrial plant species, the mosses *Pleurozium schreberi* and *Hylocomium splendens* show very stable levels year to year and also show comparable concentrations between the two species which, from a Hg monitoring perspective, is encouraging. Although there are missing years of data, due to lack of material, *Nardus stricta, Calluna vulgaris* and *Juncus sp.* all appear to show declining trends whilst *Vaccinium myrtilus* shows little pattern over the period. Of the aquatic species all except *Fontinalis antipyretica* show a decline over the sampling period. Lack of sample precluded analysis of epilithic diatoms for Hg in the years 1999 and 2000 as there was only sufficient for a single metals digestion. Diatom sampling is therefore unlikely to be a useful tool for metals monitoring in the future, unless greater quantities of sample can easily be obtained. Conversely, zooplankton show high concentrations of Hg and this may be due to bioaccumulation from the lower trophic level. Zooplankton patterns show good agreement with lake water trends although this is not observed for any other metal. Sediment trap data for Hg are limited to 2000 as the samples were not dried in a suitable way for retrospective analysis. Mean concentrations are 161.3 ng/g suggesting that this could be a useful monitoring tool (cf. other metals below) for Hg.

Lead (Pb)

Pb data for biota and sediment traps are shown in Figure 3.12. As with Hg, lake water and deposition flux data show opposite trends for the two available years, deposition decreasing markedly, whilst lake water increases. The step-change affecting water analyses was not so marked for Pb (Figures 3.7 & 3.8) as for other metals and, this being the case, a decline for both deposition and lake water is observed when the whole sampling period is considered.

Although there are missing values it could be argued that all terrestrial plant species show declines in Pb over the period 1997 – 2000. Of all the metals recent declines in Pb emission are probably the largest and so it might be expected that if any decline would be observed then it would be for Pb. Aquatic plants, epilithic diatoms and zooplankton do not show any decline however, and may even show the opposite trend with *Fontinalis antipyretica,* epilithic diatoms and zooplankton all showing a marked increase in Pb concentration over 1998 – 2000. Again, this is a short time span over which to try and determine trends and further monitoring is required for confirmation.

The reason for the opposite trends between deposition (deposition flux, terrestrial plants) and lake (water, aquatic flora and fauna) Pb concentrations may be explained by looking at the trends in the sediment traps over the period 1993 – 2000 (also Figure 3.12). For the deep water traps, an increase in Pb concentration is observed over the period and certainly from 1995 onwards. In the surface water traps a large increase is seen, but only in the 2000 sample. Data for these surface traps are only available over 1998 – 2000. An increase in deep water sediment trap Pb over a period of 6-7 years could be caused by three possibilities. First, an increase in Pb deposition, second, an increase in mineral Pb weathered from the catchment, and third, an increase in Pb as a result of catchment inputs either as a result of increased erosion or possibly as a result of increased leaching from the soils. Pb deposition, as already discussed, is known to have decreased significantly in recent years, and the data from deposition collectors and catchment plants here and deposition collectors across the UK suggest that this trend is readily observed. Trends in sediment trap Ti show no increase over the same period, effectively ruling out increased mineral weathering as a source and so we are left with catchment inputs. As mentioned above soil erosion at the site is known to have increased, whereas pH in deposition and lake water has increased since the mid-1990s (AWMN data) suggesting that leaching from the catchment may not have increased over the period. It seems likely that the increased metal input to the loch is due to increased soil erosion at the site. This is repeated for the other metals except possibly Zn (see below).

Nickel (Ni)

Ni data for biota and sediment traps are shown in Figure 3.13. For Ni, both deposition flux and lake concentrations decline over 1999 – 2000 and Ni concentration trends in all terrestrial plant species except *Juncus sp.* and possibly *Vaccinium myrtilus* show agreement with this. As with Pb, however, all aquatic plant species appear to show increases in concentration between 1997 – 1999 although several show values below the limit of detection in the 2000 sample. Epilithic diatoms decline over the period whilst data for zooplankton show no real trend.

Sediment trap data show increases in concentrations over the full period available, i.e 1993 – 2000 for deep water traps and 1998 – 2000 for shallow traps, suggesting a similar cause to that discussed for Pb. This would explain the decline in Ni for terrestrial species whilst trends in lake water species, where present, show an increase.

Cadmium (Cd)
Cd data for biota and sediment traps are shown in Figure 3.14 and show similar patterns to the Ni data. For Cd, deposition flux and lake water concentrations decline 1999 – 2000 and this is reflected in most of the terrestrial plant species. However, for Cd, the 2000 sample appears to be have a higher value and it is currently uncertain whether this is a single anomalous year. As with Hg, the terrestrial mosses *Hylocomium splendens* and *Pleurozium schreberi* show similar trends and concentrations for the three years 1997 – 1999. In 2000, however, this relationship breaks down; whilst *Hylocomium splendens* shows a significant increase in Cd concentration, in *Pleurozium schreberi* it falls to below the limit of detection.

Zooplankton and aquatic plant species, except *Fontinalis antipyretica*, show an increase in Cd concentration over the sampling period, whilst epilithic diatoms show little trend. Both deep water and shallow sediment traps show increases over the periods 1991 – 2000 and 1998 – 2000 respectively and again this may be due to an increase in catchment sources. The reason for the exceptionally high 2000 Cd concentrations for *Hylocomium splendens, Calluna vulgaris, Vaccinium vitis-idaea, Juncus sp.*and *Sphagnum auriculatum* is currently unclear.

Copper (Cu)
Cu data for biota and sediment traps are shown in Figure 3.15. As for other metals, deposition flux and lake water concentration both decline 1999 – 2000. However, for Cu, this is not reflected in the terrestrial plant data, where little trend is observed, although *Vaccinium vitis-idaea* may show an increase in concentration over the sampling period. An increase in concentration would also appear to be observed for aquatic plant species (except *Scapania undulata*), epilithic diatoms and zooplankton.

Again, both deep and shallow water sediment traps show an increase over the available period, although the 1993 deep water trap shows the highest Cu concentration.

Zinc (Zn)
Zn data for biota and sediment traps are shown in Figure 3.16 although Zn measurements for 2000 remain to be confirmed. Of the available data, terrestrial plant species, except *Nardus stricta*, show declines in concentration whilst the aquatic plants show no trend (*Isoetes lacustris)* or an increase in Zn concentration (the rest). Epilithic diatoms also appear to show a slight increase, whilst zooplankton show a decline. Further interpretation requires the 2000 data, and confirmation of any trends an even longer dataset.

For Zn, the sediment trap data are slightly ambiguous. The deep water traps show a high concentration in 1993 (cf. Cu) but otherwise show an increase to 1998, followed by a decline. The shallow traps, with data available only for 1999 and 2000 (2000 data for traps measured by XRF and hence available) also show this recent decline in sediment trap Zn.

Discussion

One of the aims of this part of the CLAM study was to assess the role that catchment and lake biota and sediment trapping can play in the monitoring of metal deposition and / or lake water metal concentrations with a view to employing the most successful techniques at a larger number of sites. In particular, this was directed towards Hg as there are few data available for the UK and even less for upland freshwater sites.

As regards the trends that the biota and traps needed to identify to successfully fulfil this role, with the exception of Hg, annual deposition fluxes and mean annual lake water concentrations appear to show a decline over the period of available data. For Hg, this trend would also be apparent except for elevated levels in the 2000 data. However, as discussed above, for the lake water species, this may not be a simple matter of looking for a similar decline in the concentrations of the biota or trapped sediment, as this may well be complicated by increased inputs from the catchment.

With this in mind, it might be expected that terrestrial species would provide the best means for monitoring atmospheric deposition, whilst aquatic species might identify the enhanced levels of input due to additional catchment sources. In general, the terrestrial plant species do show a decline in concentrations over the study period. The least successful species in this regard were *Nardus stricta* and *Juncus sp.* categorised as ‘grasses and rushes’ and hence these might safely be omitted from any future monitoring strategy. A further criterion for comparative monitoring at other sites must be ubiquity of species and here the ericaceous species and terrestrial mosses are good, except perhaps at extensively afforested sites.

Terrestrial mosses, and in particular *Hylocomium splendens* and *Pleurozium schreberi*, have been used widely in Europe to monitor metals and the data here suggest that they provide reasonable agreement both with trends in directly monitored atmospheric deposition and, perhaps equally importantly, each other. Again, there are exceptions, with Ni and Zn data being less comparable between the two species. The aquatic plants, for many of the metals, showed little trend or concentration increases over the period of the study and hence do not provide reliable biomonitoring of metal deposition. However, as discussed above there could be other factors that have influenced metal concentrations in these species and it may be that these species should be used to monitor the trends of metals within the lake rather than in deposition. It has already been seen that catchment sources of metals at sites like Lochnagar are considerable and, therefore, in order to adequately assess the levels of metals available to aquatic fauna it may be that a ‘within-lake’ monitoring tool is the most appropriate. Such a tool could either be the biota itself (aquatic plants, zooplankton) or a sediment trapping approach. Again, for inter-site comparisons, ubiquity is important and whereas species may vary from site to site, installation of sediment traps can be undertaken at any site, upland or lowland.

In summary, all approaches to monitoring have advantages and disadvantages, but a selected combination may provide the data required to interpret metal inputs, pathways, and availability to aquatic biota. In order to measure metal deposition and water concentrations, direct measurements obviously have advantages. There are no interpretations to be made and time resolution can be high. However, high resolution involves many site visits, and water analyses, especially at remote sites, can be affected by analytical detection limits. A large number of ‘below detection limit’ values are of little use, especially when temporal or spatial patterns are required. Biota measurements, as discussed above, have advantages that metal concentrations are higher and hence detection limit problems are not frequently encountered. However, there may be some doubt over whether the selected terrestrial or aquatic species are truly reflecting the deposition or lake water metal concentration, respectively, and also over the accumulation period covered by the tissue sampled. Furthermore, terrestrial samples may have been contaminated prior to sampling, whilst for aquatic species, the exact role of atmospheric versus catchment inputs are unknown. Finally, as mentioned above, in order to obtain a good spatial comparison, the species need to be present at all sampling sites.

Sediment traps offer some of the advantages of both direct measurements and biota sampling. Concentrations in traps are higher and hence detection limit problems are not encountered. The precise accumulation period is known and can be made as long or short as required (as long as sufficient material is collected for analysis – a potential problem at upland sites). Trap size can be modified to obtain more material for shorter periods. There are also no problems over the period of metal accumulation in the sample, and finally they can be installed at any site and hence samples can be obtained from any site type. If sediment traps have a problem, it is a practical one. Retrieval and redeployment requires a boat, whereas direct sampling or terrestrial plant sampling simply require bottles, bags and gloves. Sediment traps, being artificial, can also attract unwanted attention, and as they have to be left, often for long periods of time, they can be removed, often with the best of intentions, and the sample is then lost. This has certainly happened at the AWMN sites although over recent years recovery rates have been very good at these upland sites. Lowland, more accessible areas would pose more of a problem.

In conclusion, direct sampling of waters and deposition, supplemented by sampling of key terrestrial and aquatic species and sediment traps, provide a breadth of data and allow as full an interpretation of metal inputs and pathways to be obtained as possible.

Conclusions

1. Hg data suggest that atmospheric deposition has increased over the last three years. A longer dataset is needed to follow, and confirm, this trend

2. Hg deposition concentrations are greater than their equivalent lake water concentrations. This suggests that Hg is bound and stored in catchment soils. This is supported by other studies and implies that there is a massive store of Hg and other trace metals in the catchment soils which could be released if soil erosion were to continue to increase as a result of, for example, future climate change.

3. Other metals show a decline in deposition, and all except Pb show a decline in lake water concentrations.

4. V and Cu, like Hg, show deposition concentrations greater than lake water concentrations most of the time. However, all metals have higher concentrations in lake water than deposition during the winter period November 1999 – February

2000. The reason for this is currently unclear, but may be due to wind directions from a more northerly (less polluted) direction during the winter.

5. Most terrestrial plant species followed similar decreasing trends to those of atmospheric deposition, suggesting possibilities as a monitoring tool. *Hylocomium splendens* and *Pleurozium schreberi*, widely and inter-changeably used in monitoring programmes, generally showed good agreement with atmospheric trends and with each other.

6. Reeds and grasses (*Nardus stricta* and *Juncus sp*.) showed poor agreement with atmospheric deposition trends.

7. Aquatic plants showed less agreement with depositional trends and generally showed no trend or an increase over the period. This may be due to increased inputs from the catchment.

8. Epilithic diatoms on artificial substrates showed limited usefulness primarily due to the low amounts of material produced. They may be more useful at more productive sites.

9. Sediment traps show very good potential for monitoring lake metal trends and suggest catchment inputs may be very important.

10. Some trends have been observed, but longer periods are required. Monitoring needs to be undertaken at other upland sites to confirm Lochnagar results. This is particularly important in NW Scotland, which could act as a reference site for contemporary deposition.

11. Ongoing and extended spatial monitoring is particularly important for Hg, as there are so few UK data.

Recommendations for further research

Monitoring

The Lochnagar dataset with the range of metals information available for a number of ecological compartments within the loch and its catchment is probably unique within the UK. However, although some trends would appear to have been identified, the dataset is too short to determine their significance. Long-term monitoring is recommended at the site. Direct monitoring of lake waters and deposition should be continued. However, it is suggested that the full range of terrestrial and catchment plants collected and analysed for this study is probably neither necessary nor desirable. A sub-set of the more ubiquitous species should be continued. Sediment trapping should be continued and the frequency of sampling could be increased from the current annual programme to quarterly to obtain more data on seasonal inputs. The metals Hg, Pb, Cd, Ni, Cu and Zn should be measured.

Further, given the lack of data for UK upland sites, especially with respect to Hg, more sites should be included in this monitoring programme. Initially, the 10 other AWMN lake sites, with the wealth of background and long-term data already available, should be included.

Catchment inputs

The results of the work at Lochnagar, both within CLAM and as part of the study reported in Yang (2000), suggest that the catchment is a major source of lake metals. This may become more the case in the future, if emissions continue to decrease and soil erosion continues to increase, the latter possibly exacerbated by future climate change.

However, as there is so little metals data for upland freshwaters within the UK it is currently unclear whether this is the normal situation, in which case many sensitive ecosystems may be under threat, or a unique one. Mass balance studies at a small number of selected sites within the UK (again utilising AWMN sites) should be undertaken in order to ascertain whether this is the case. Sampling would involve sediment and soil analyses, and regular sampling of deposition and lake water in order to construct a mass balance for each site and assess the relative inputs from atmosphere and catchment.

Further spatial and temporal data

One obvious conclusion to be drawn from any detailed metals study undertaken in the UK is the lack of any comparable data. There is a need to determine spatial and temporal patterns within the UK in order that reference conditions (pre-industrial levels, clean contemporary areas) can be identified. Only in this way can the gap between current levels in freshwaters across the country and desired future levels be determined. This is of particular importance for Hg, as the lack of data is most extreme for this important metal.

Acknowledgements

We thank Jo Porter and members of the ECRC for sampling at Lochnagar, Spiros Pergantis (University College London) and John Boyle (University of Liverpool) for help with the metals analyses and the DETR for funding.

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Figure 3.1. Mean daily meteorology for Lochnagar in 1997

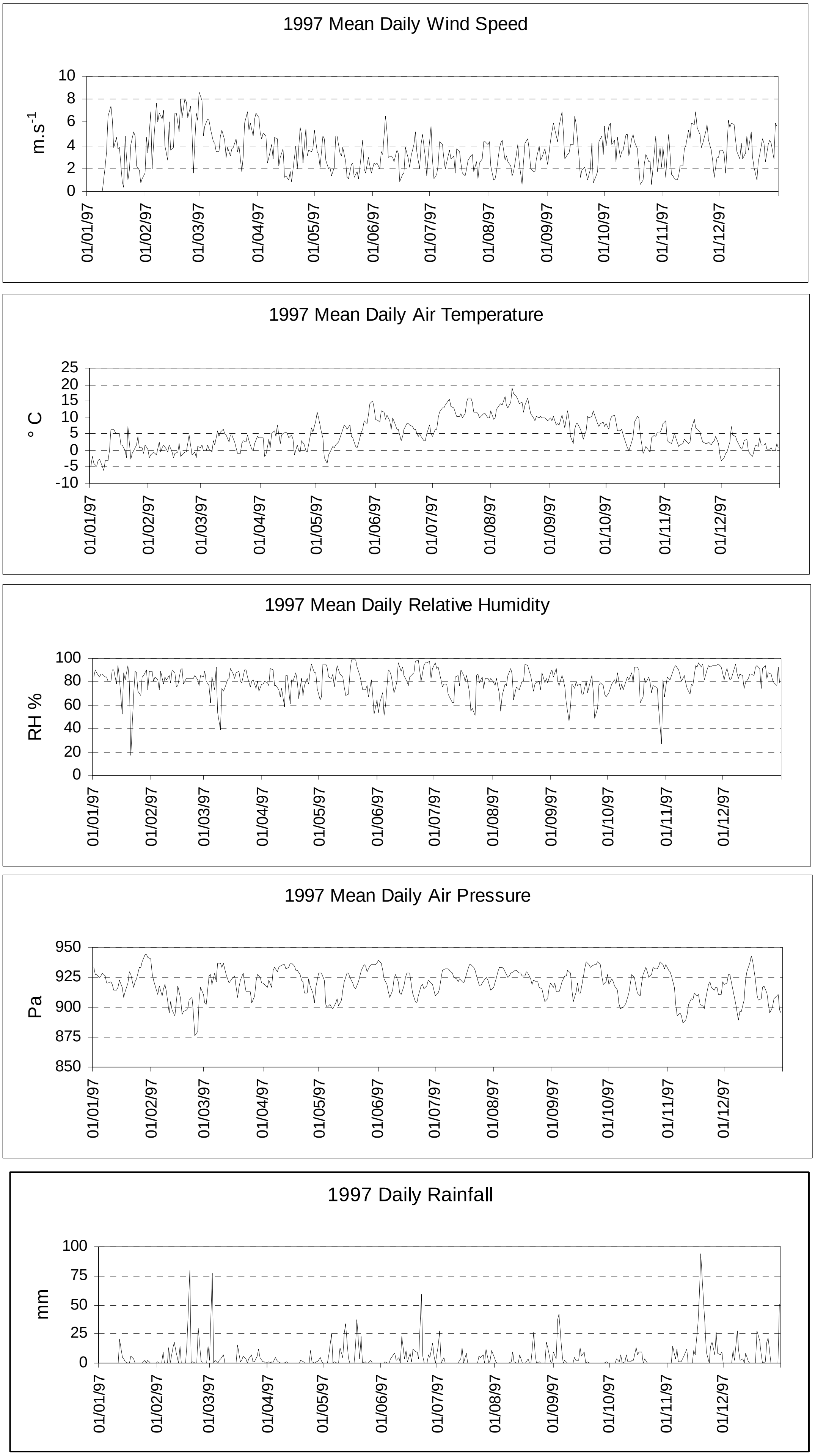
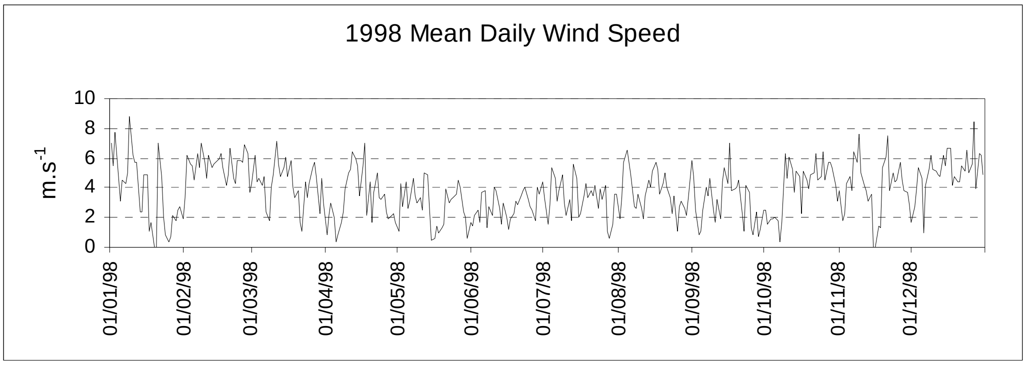
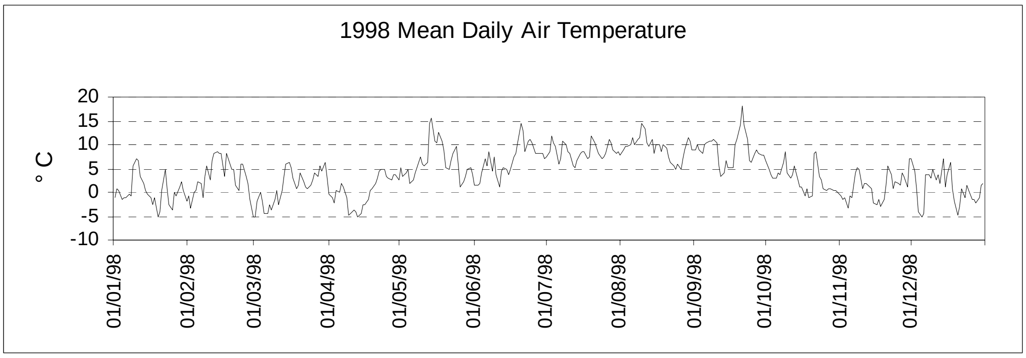
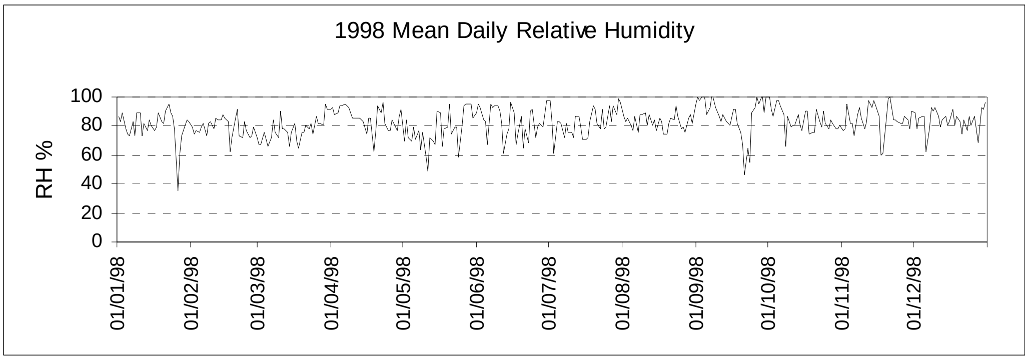
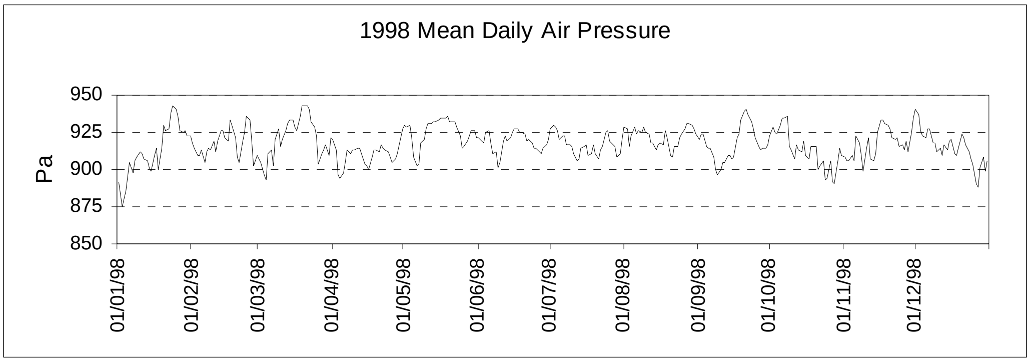


Figure 3.2. Mean daily meteorology for Lochnagar in 1998









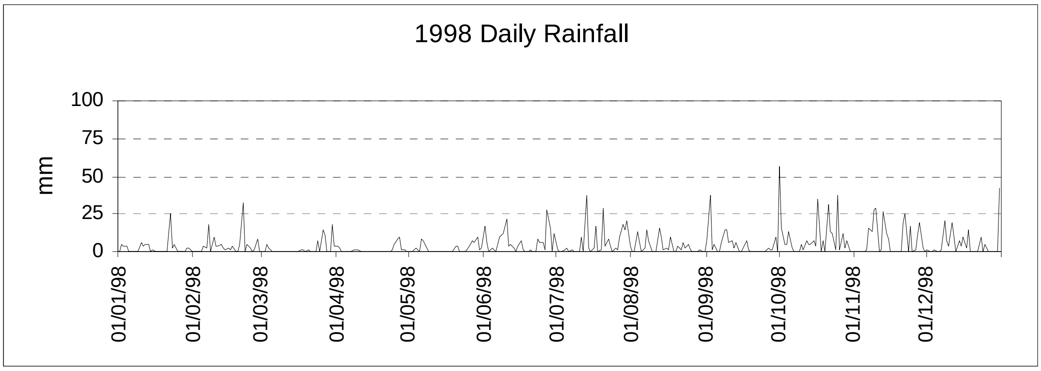


Figure 3.3. Mean daily meteorology for Lochnagar in 1999.

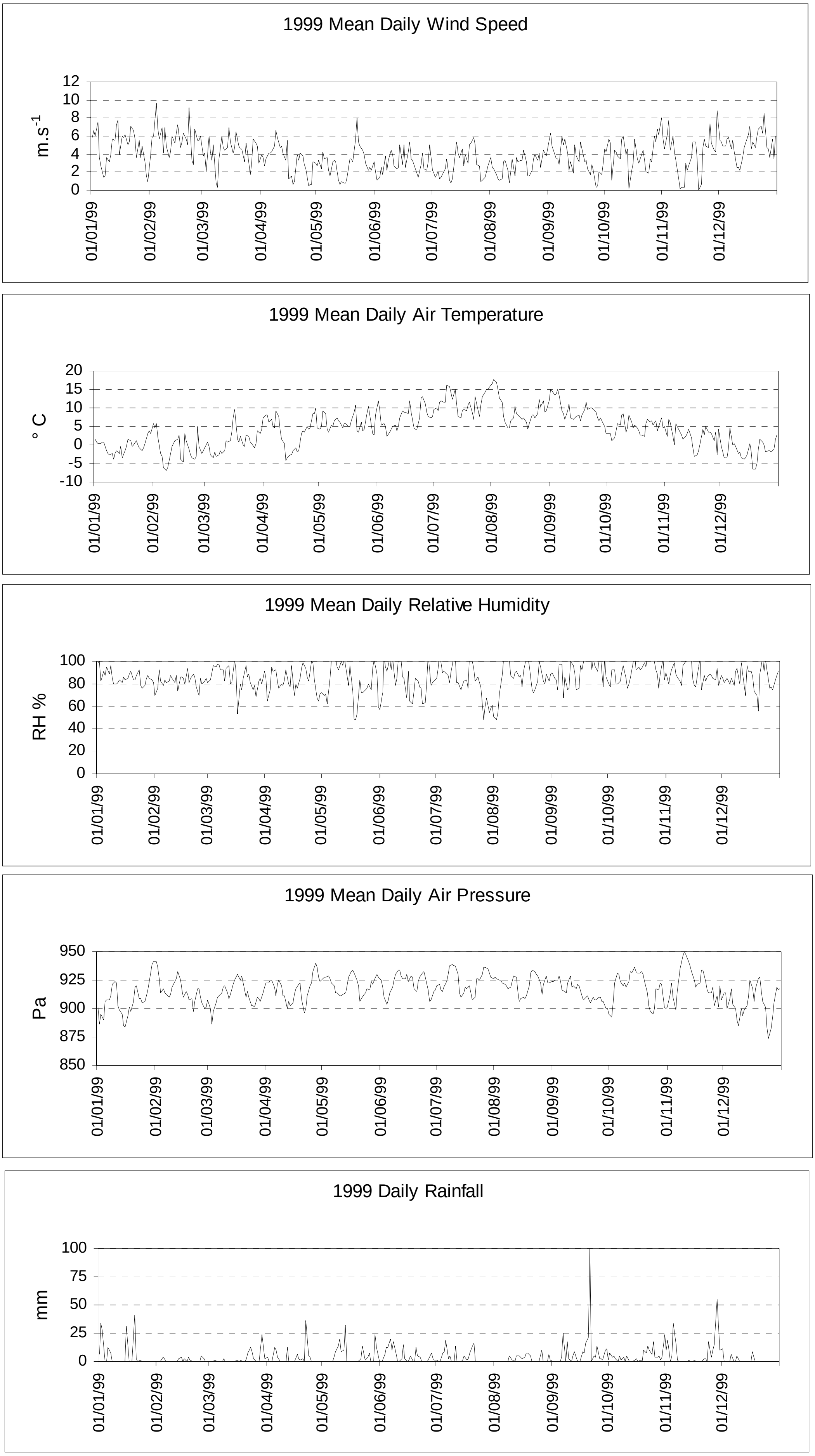
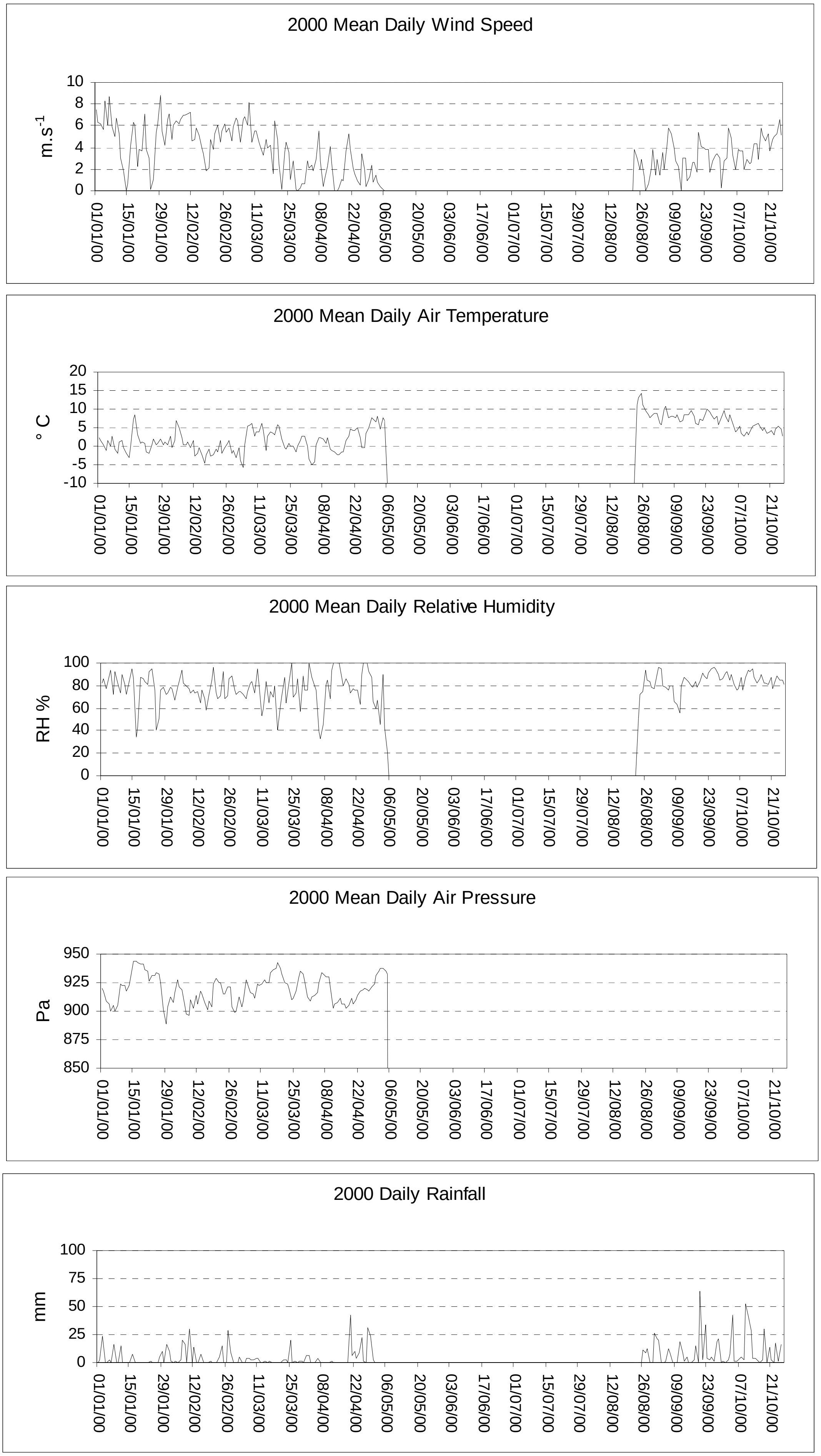


Figure 3.4. Mean daily meteorology for Lochnagar in 2000.



2000 Mean Daily Wind Speed

2000 Mean Daily Air Temperature

2000 Mean Daily Relative Humidity

2000 Mean Daily Air Pressure

2000 Daily Rainfall

Figure 3.5. Mean daily surface temperature (1.5m) for Lochnagar. July 1997 – August 2000.

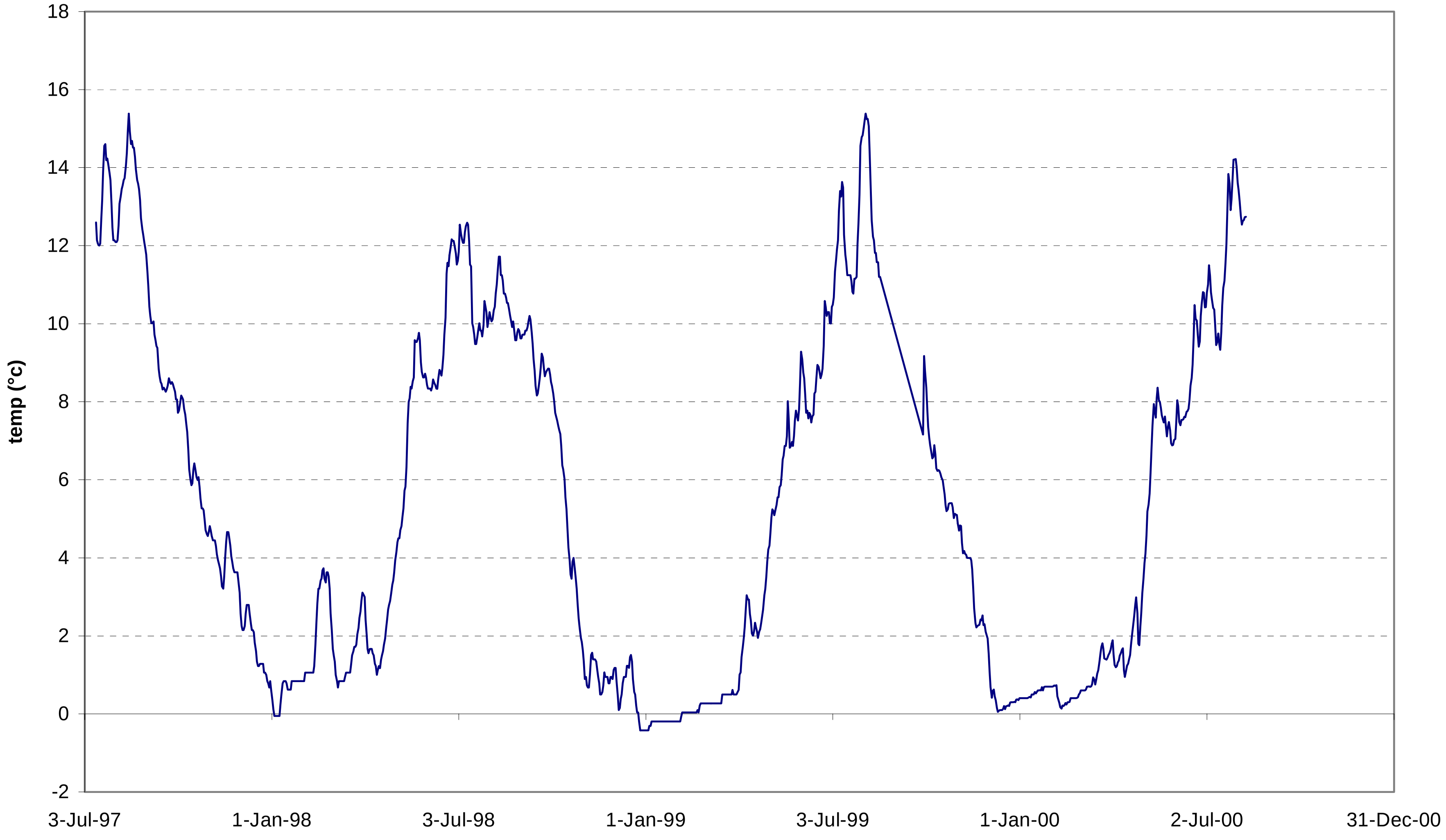


Figure 3.6. Hg concentrations for Lochnagar bulk deposition and lake outflow 1996 - 2000

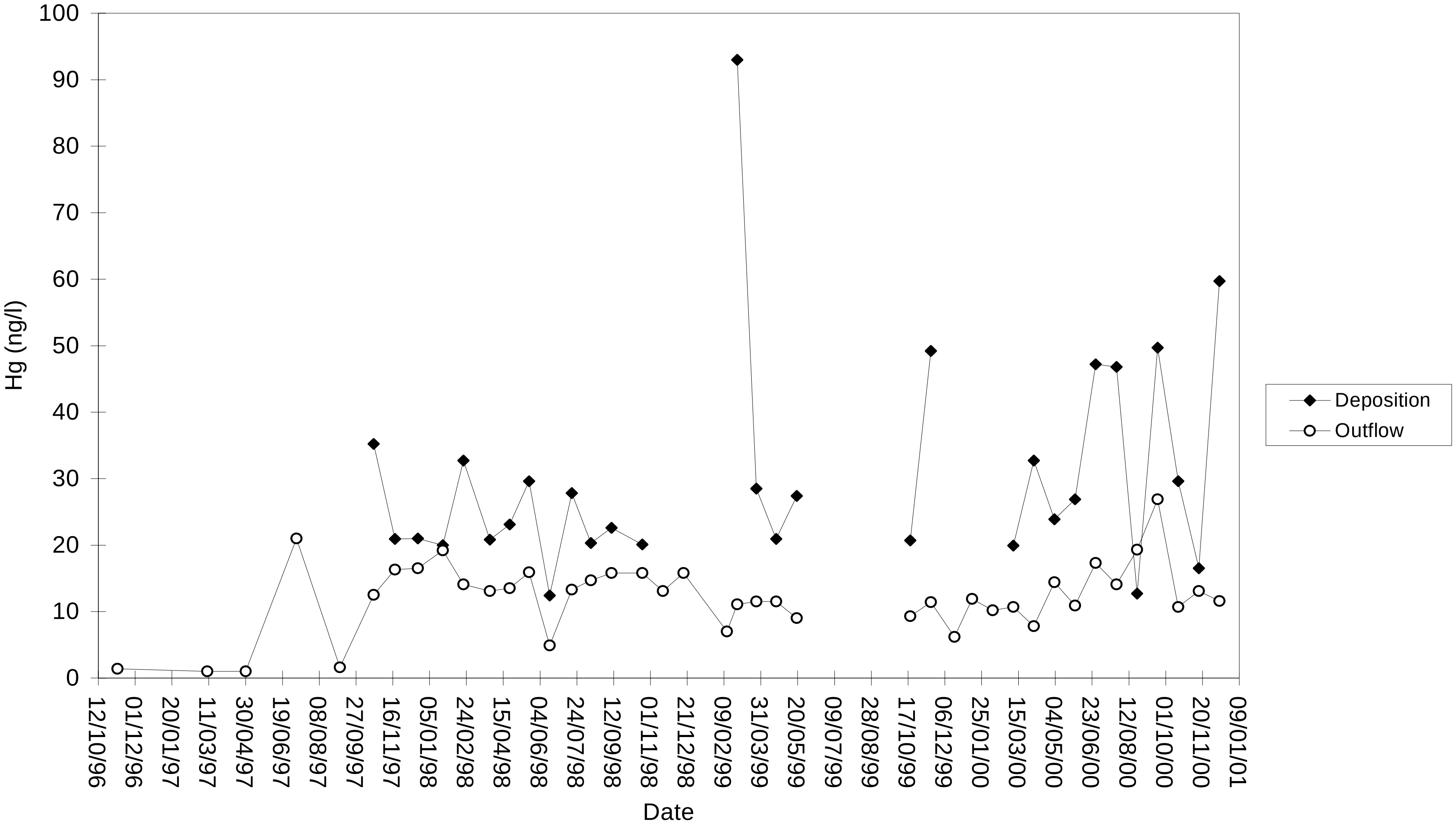
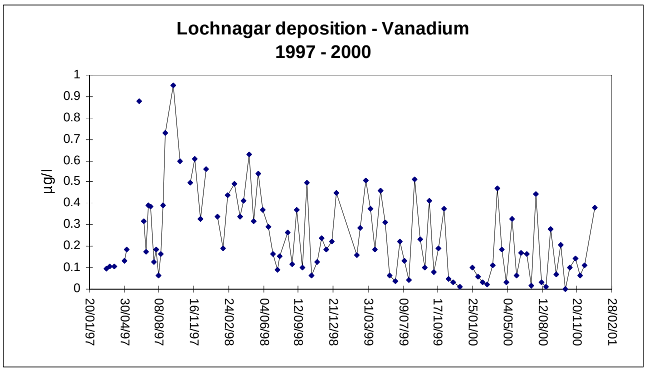
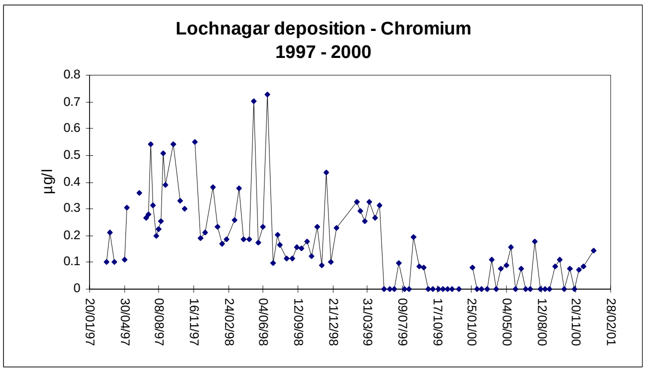
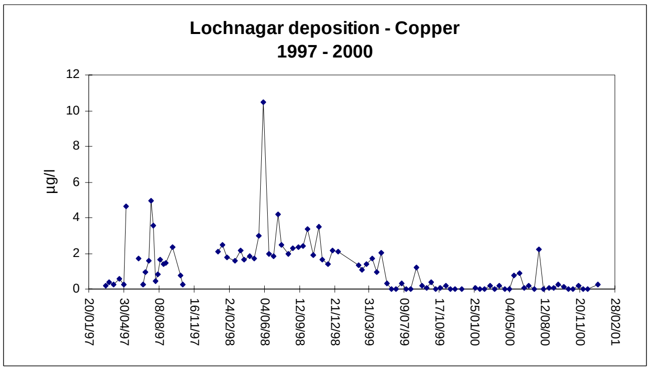
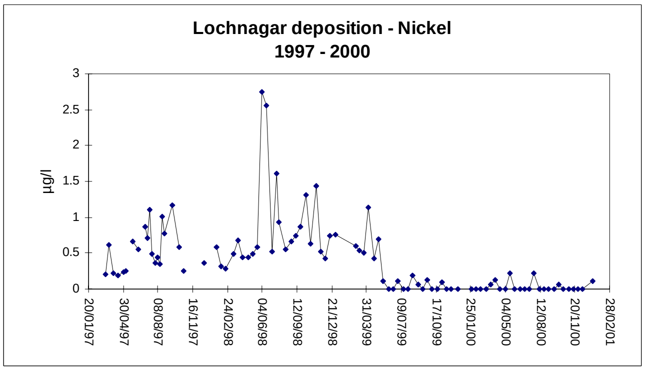


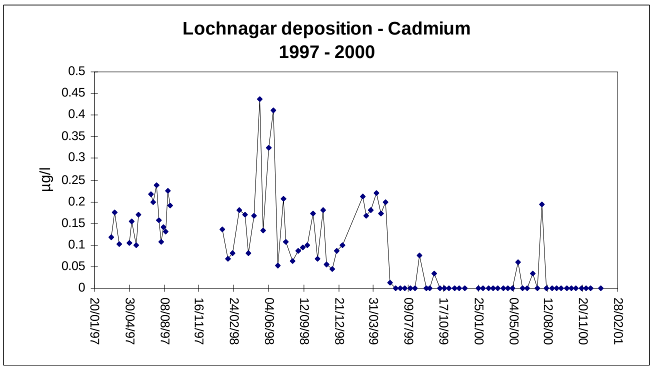
Figure 3.7. Trace element concentrations in bulk deposition for Lochnagar

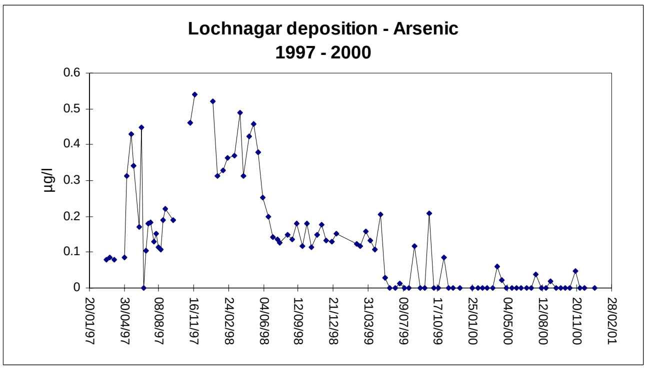


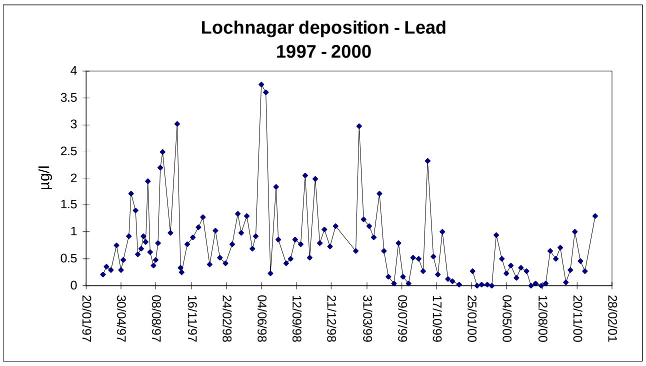












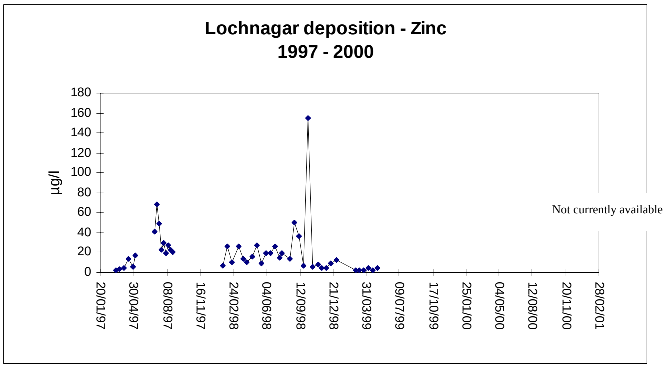


Figure 3.8. Trace element concentrations in lake water for Lochnagar

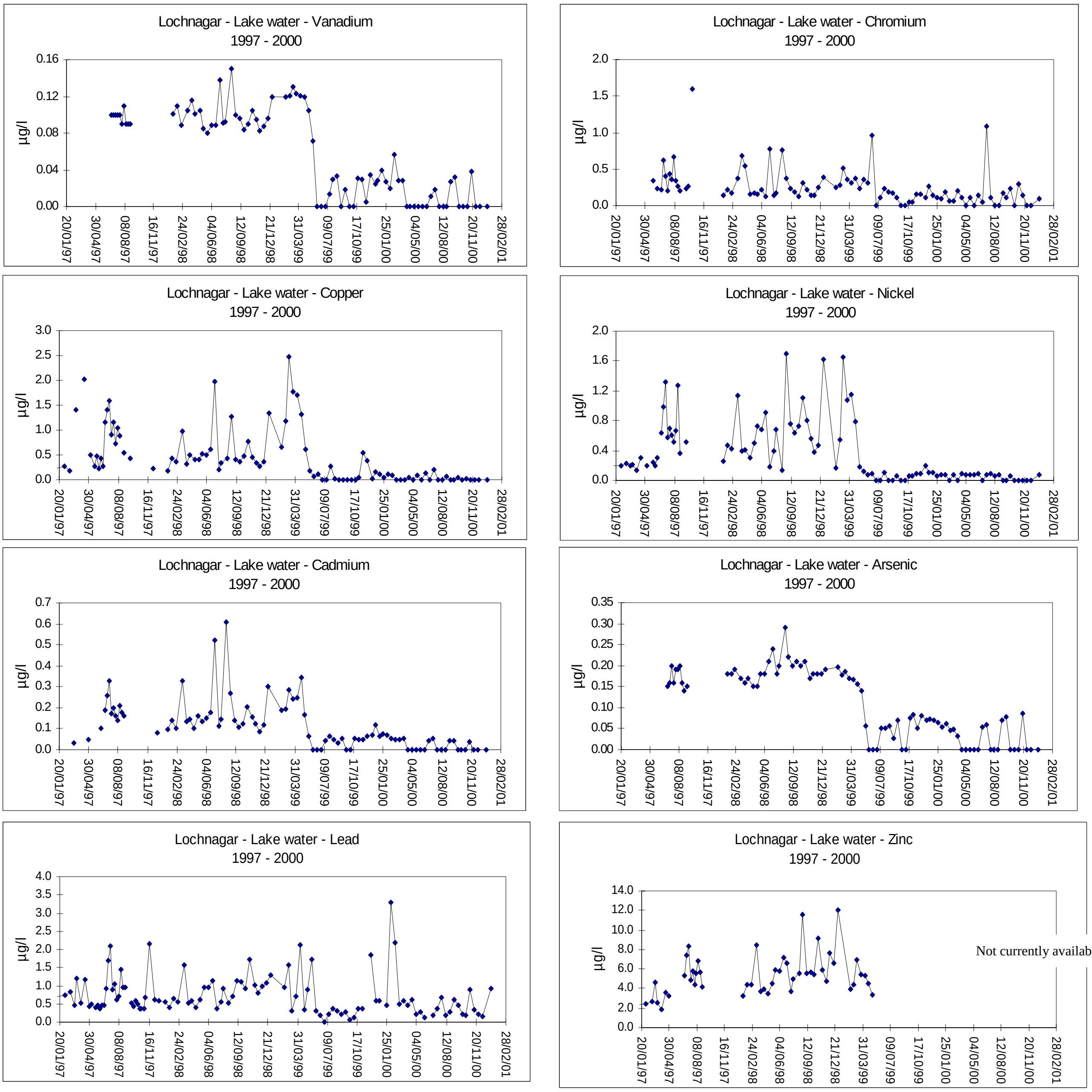


Figure 3.9. Comparison between deposition and lake water concentrations

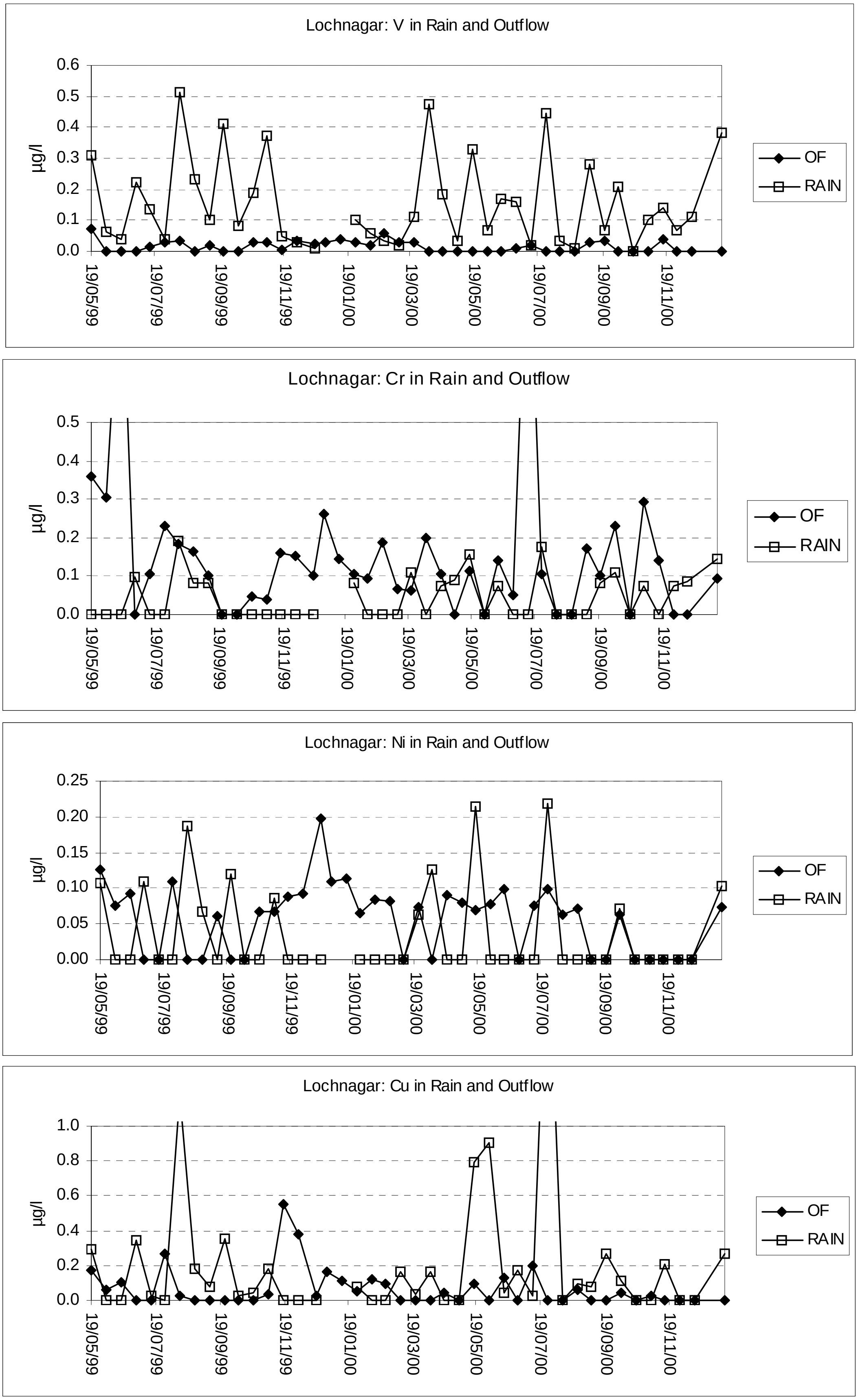
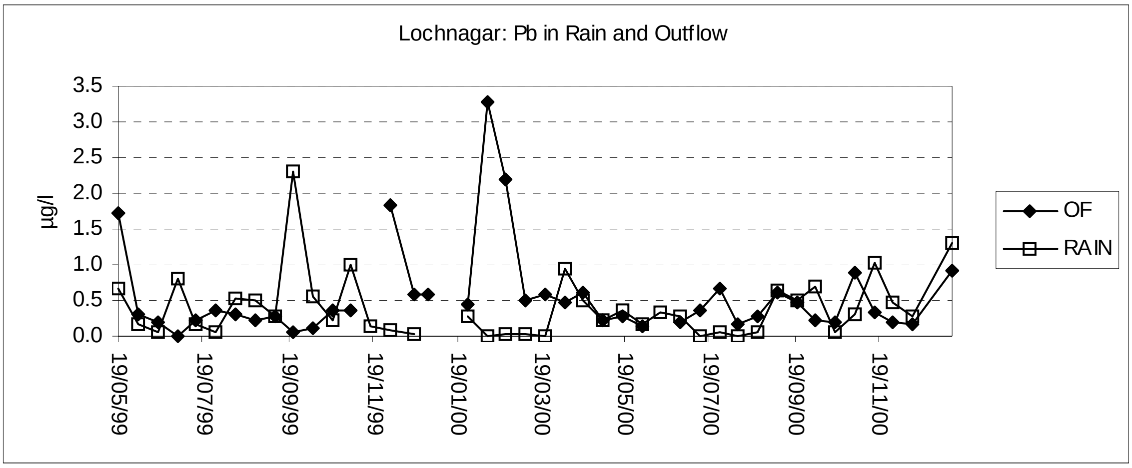
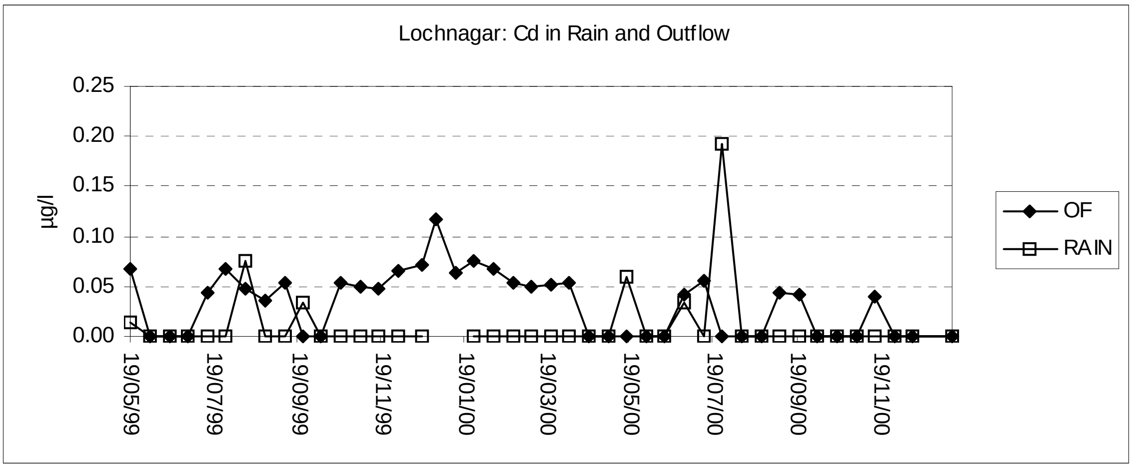


Figure 3.9 (cont)





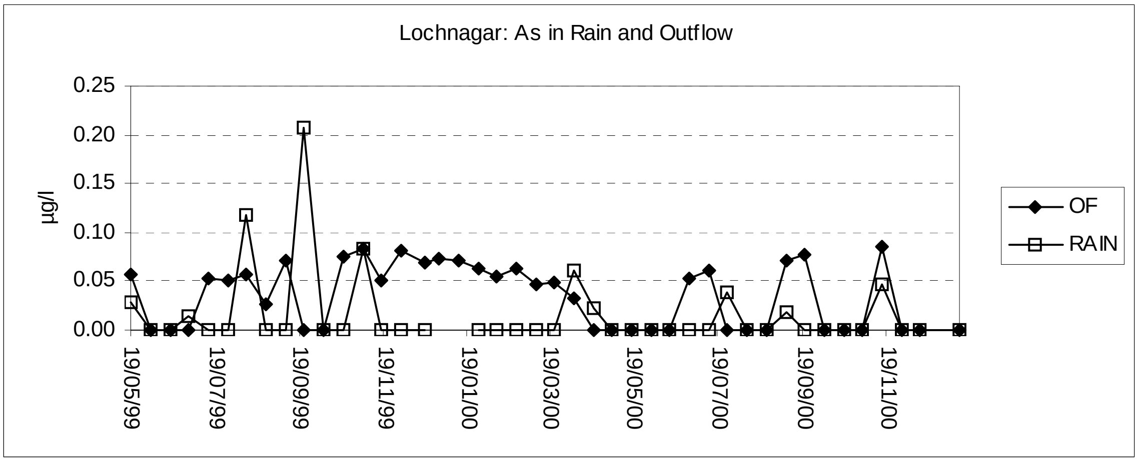


Figure 3.10. Trace element concentrations and fluxes for Lochnagar

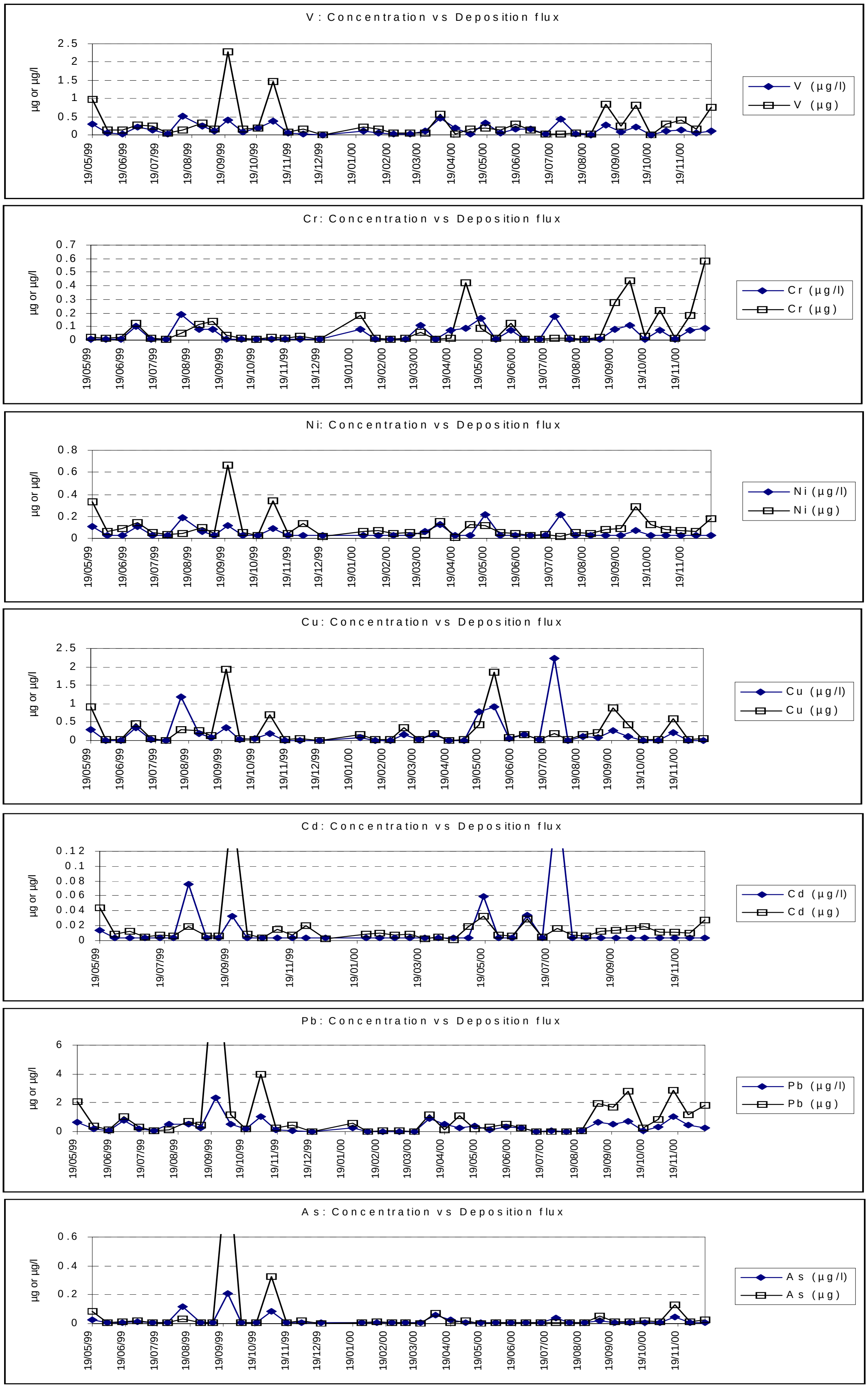


Figure 3.11. Hg concentrations in Lochnagar deposition, water, biota and sediment traps

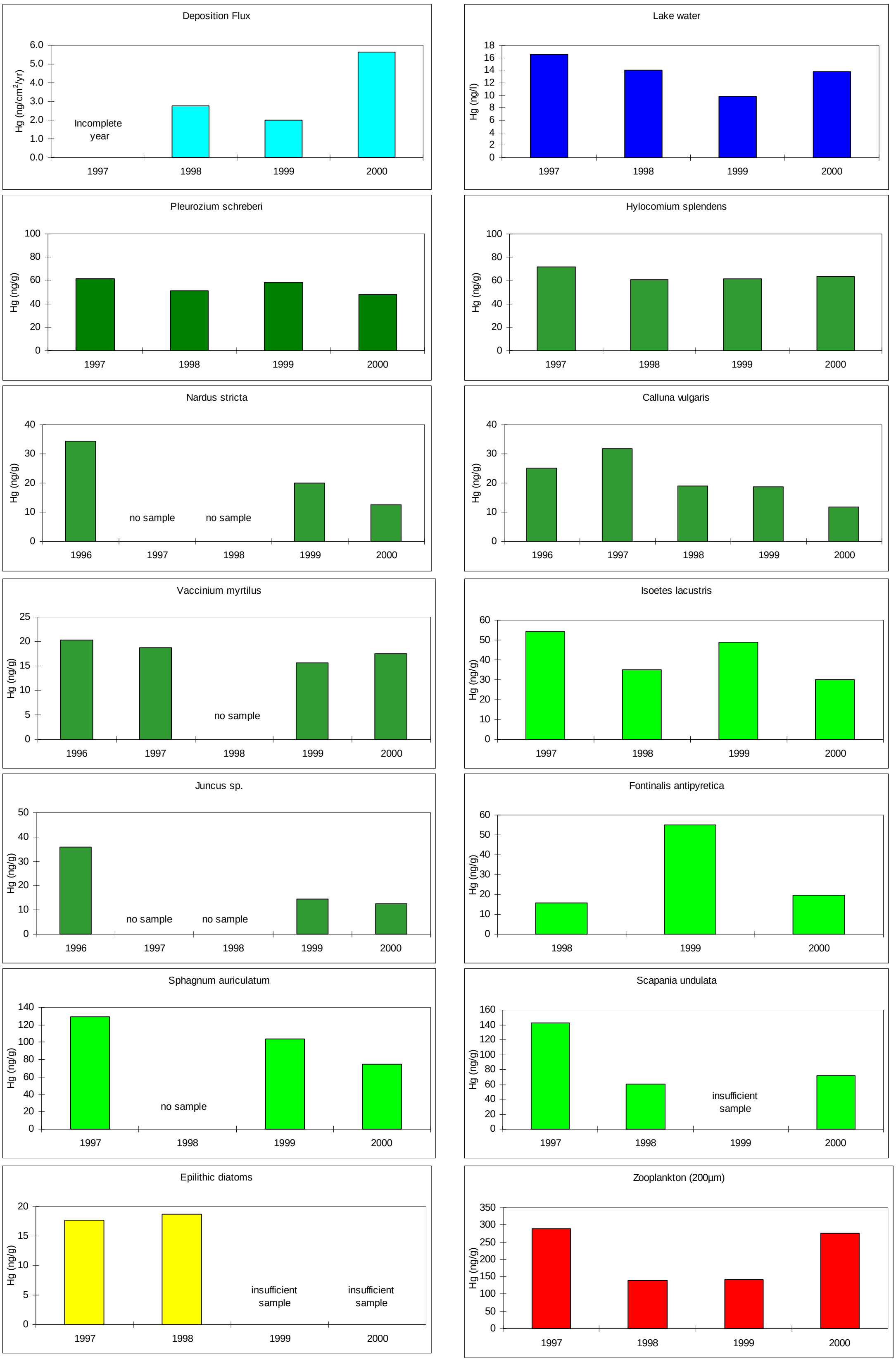


Figure 3.12. Pb concentrations in Lochnagar deposition, water, biota and sediment traps.

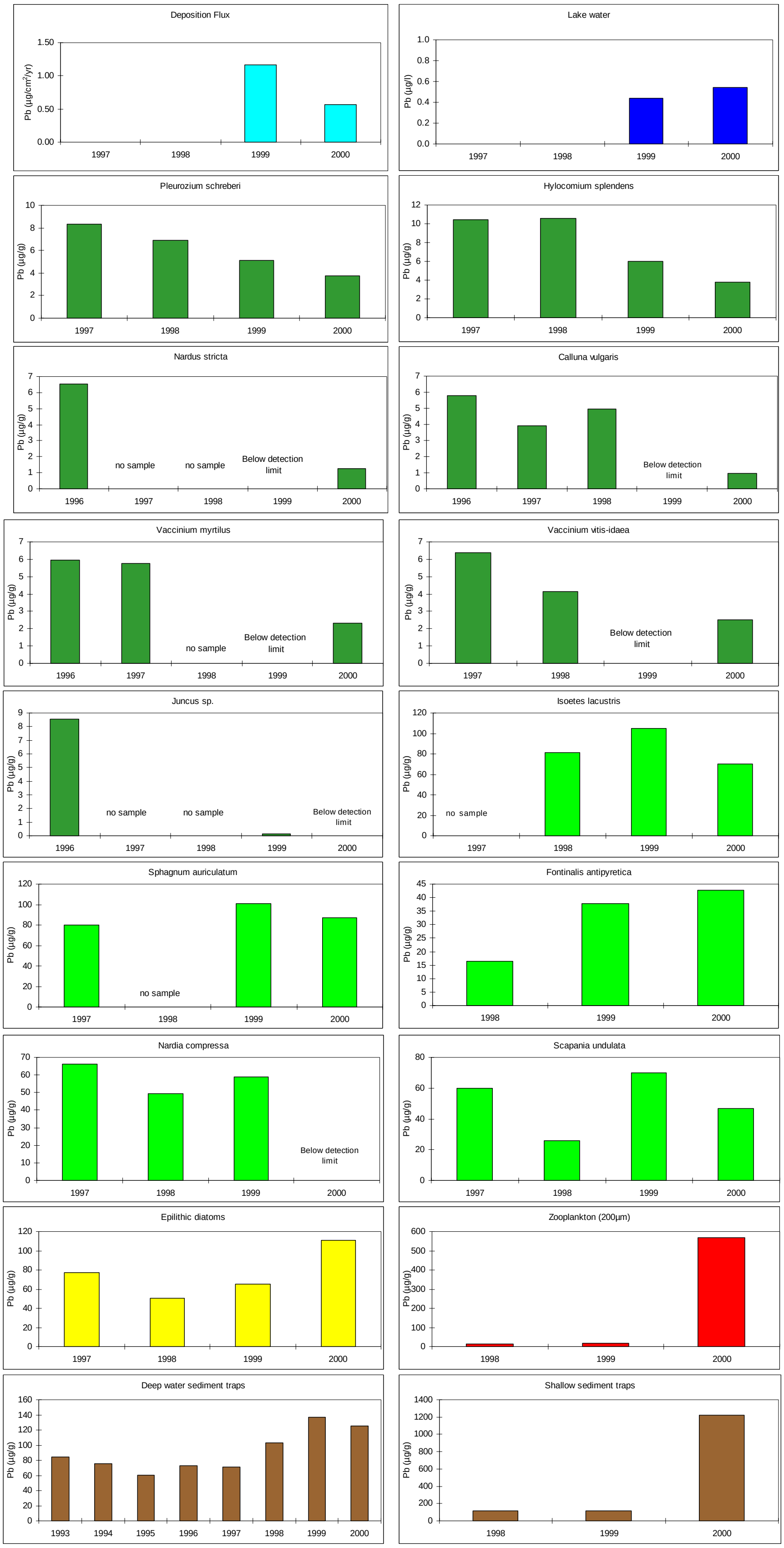
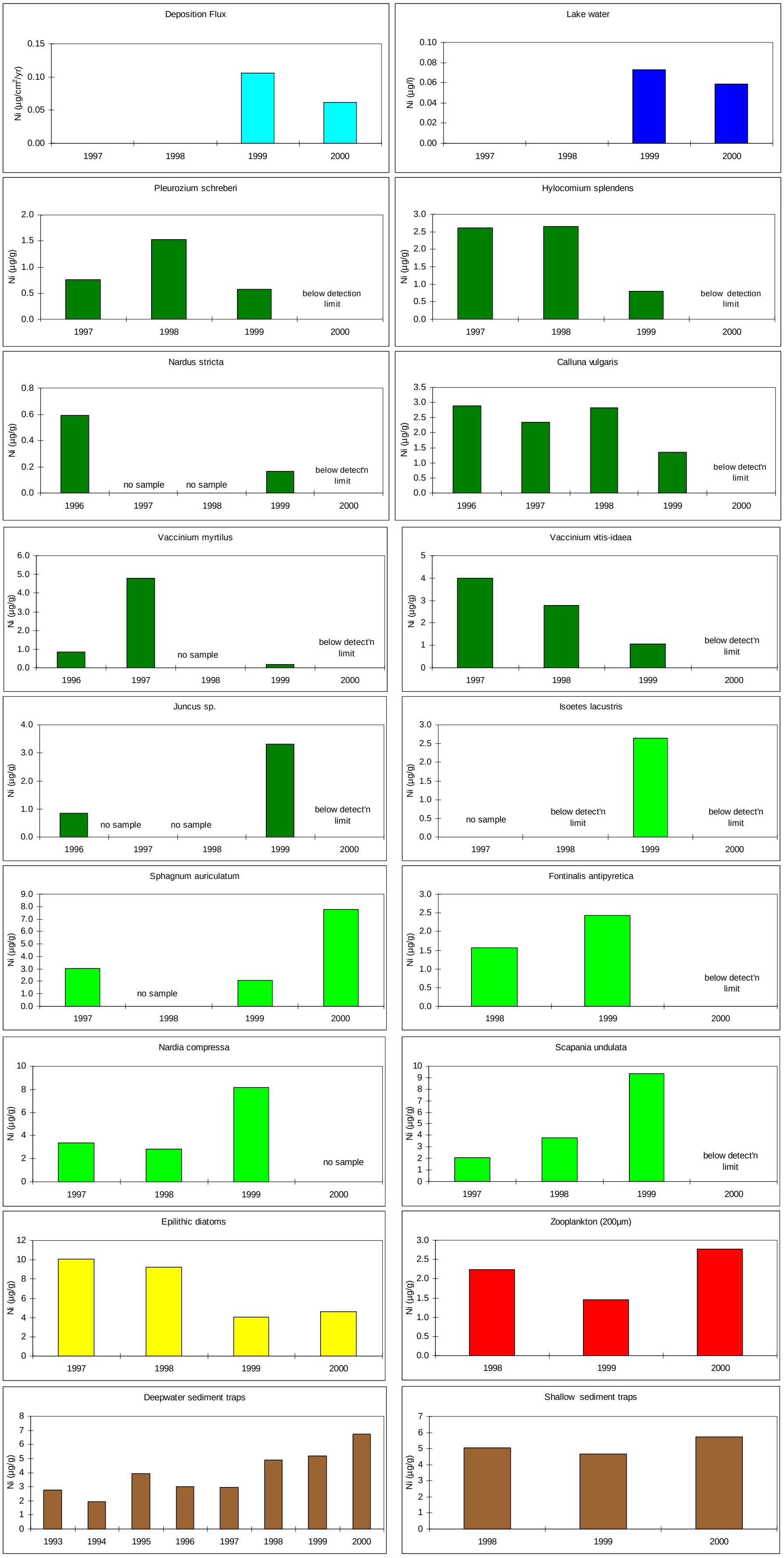


Figure 3.13. Ni concentrations in Lochnagar deposition, water, biota and sediment traps



Deposition Flux

Lake water

Pleurozium schreberi

Hylocomium splendens

Nardus stricta

Calluna vulgaris

Vaccinium myrtilus

Vaccinium vitis-idaea

Juncus sp.

Isoetes lacustris

Sphagnum auriculatum

Fontinalis antipyretica

Nardia compressa

Scapania undulata

Epilithic diatoms

Zooplankton (200µm)

Deepwater sediment traps

Shallow sediment traps

Figure 3.14. Cd concentrations in Lochnagar deposition, water, biota and sediment traps.

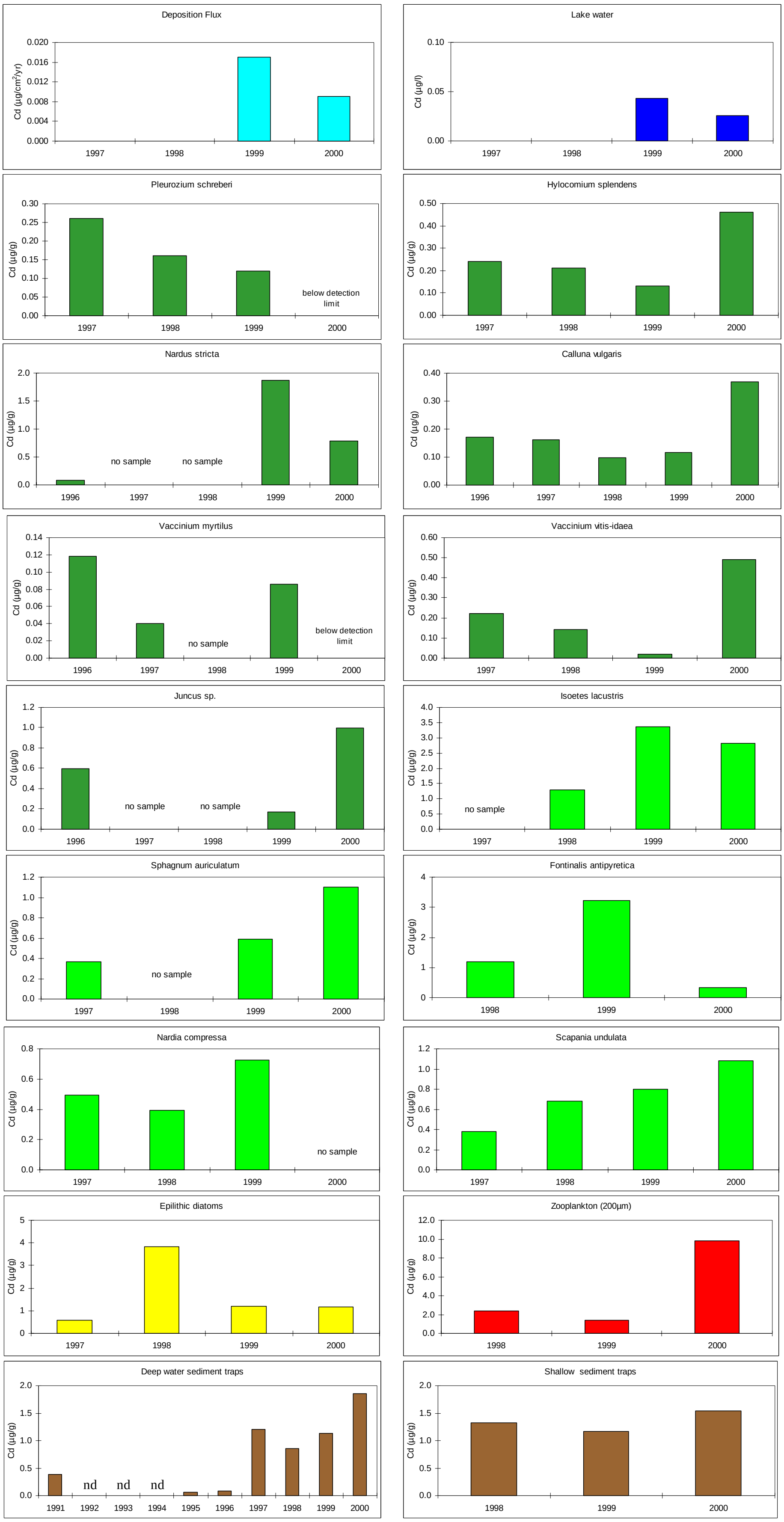


Figure 3.15 Cu concentrations in Lochnagar deposition, water, biota and sediment traps.

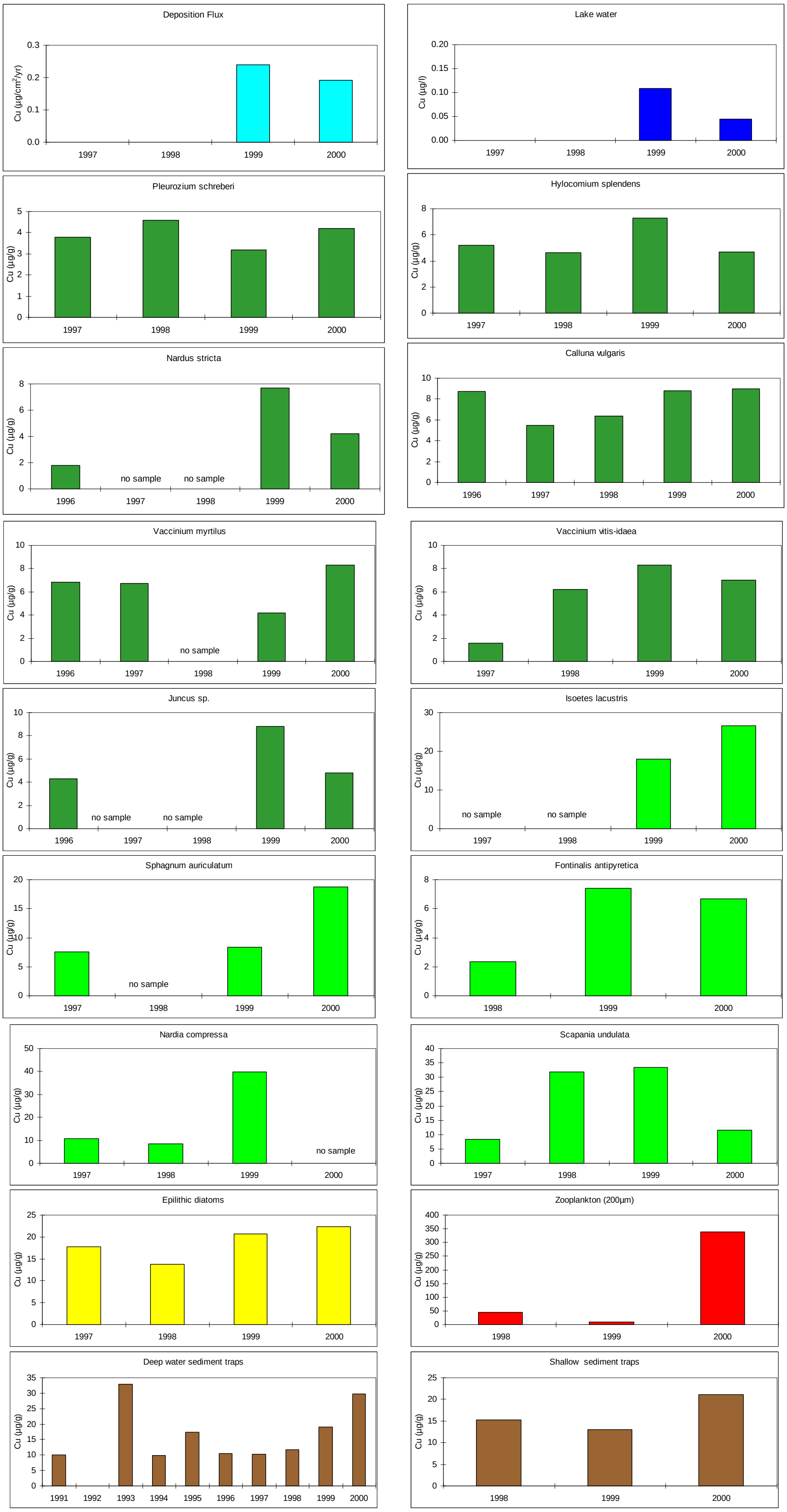


Figure 3.16 Zn concentrations in Lochnagar deposition, water, biota and sediment traps.