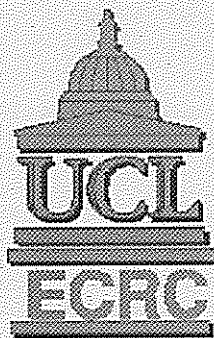


ISSN 1362-9301



**ENVIRONMENTAL CHANGE  
RESEARCH CENTRE**

**University College London**

**RESEARCH PAPERS**

**No. 9**

**Series Editor: S. Patrick**

**An Assessment of the Potential of the UK Acid Waters  
Monitoring Network to Monitor the Impact of  
Atmospheric Trace Metals and Persistent Organic  
Compounds on Freshwaters**

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A Report to the DoE, Air Quality Division

**February 1993**

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## EXECUTIVE SUMMARY

1. Despite low levels of atmospheric deposition trace metals and persistent organic compounds (POCs) can accumulate in aquatic flora and fauna to potentially toxic levels.
2. There is currently no comprehensive, long-term monitoring for atmospheric deposition of trace metals or POCs to freshwaters.
3. The national pattern of trace metal deposition to freshwaters in the United Kingdom appears to be similar to that of sulphur deposition. That of POCs is unclear due to the limited amount of data but may follow the same trends.
4. Because of these spatial distributions the Acid Waters Monitoring Network sites are generally well placed to monitor deposition of trace metals and POCs except in the south and east of England. Sites for monitoring national trends in deposition would need to be some distance from urban centres and this may preclude the use of some of the sites currently in the Network (e.g. Old Lodge, River Etherow). However, it may be impossible to locate suitable sites away from local influences in the high deposition areas of the Midlands/north-east England and as it is important to continue monitoring along the whole gradient of deposition, a "best available means" approach maybe required for site selection.
5. Due to the episodic nature of trace metal and POC deposition lake systems are likely to be better for monitoring purposes than streams although both could be used in different ways.
6. Due to the low levels of deposition, components of the ecosystem that accumulate trace metals and POCs (sediments, biota) will be better monitors than non-accumulating components such as waters.
7. Metal analyses on water samples are already undertaken as part of the AWMN. Full sediment profiles for Cu, Zn and Pb already exist for all lake sites and are repeated at 5-yearly intervals. Currently there are no analyses for POCs undertaken although PAH profiles exist for sediment cores taken from some AWMN lake sites during the Surface Water Acidification Project (SWAP).
8. Archived water samples, sediment trap material and macrophytes are stored and could be used for metal analyses. Data would then be available dating from the start of the Network in 1988. However, it is unlikely that there would be sufficient material for POC analyses.

## PRELIMINARY RECOMMENDATIONS.

### Metals

Little modification of the AWMN would be needed to effectively monitor the atmospheric deposition of trace metals to freshwaters across the United Kingdom. An extra three or four lake sites located in the south, east and in the high deposition area of central England, in addition to the present Network, would give good coverage of the metal deposition gradients. A few metals are currently analysed in the spot water samples and in the sediment cores taken every five years. Sub-samples of cores, sediment trap material, water samples and dried macrophytes have been stored and extra metals could be measured relatively easily. The use of aquatic macrophytes and especially bryophytes for monitoring trace metals is well documented and their use would be a simple and effective monitoring tool. In addition, the measurement of metals in fish tissue, invertebrates and diatoms could be easily undertaken and this would give a more comprehensive overview of metal contamination in the freshwater ecosystem.

### Persistent Organic Compounds

Some modification of the present AWMN would be needed to effectively monitor POCs in the aquatic ecosystem. A few extra lake sites (in the locations described above) in addition to the present Network would give a good coverage of the United Kingdom across the proposed deposition gradients. Such a network of sites would be enormously valuable, not only to monitor the atmospheric deposition of POCs, but also because there is a need to determine more effectively the pattern of deposition across the country. This is an area of research currently unfulfilled.

At present no POCs are analysed on a regular basis in the AWMN programme and it would probably make sense in the first instance to analyse for the few important compounds known to have good atmospheric pathways. Sampling strategies currently employed in the AWMN need change little as effective monitoring could be undertaken using lake sediment cores, sediment traps and possibly fish. The inclusion of macrophytes and invertebrates in the programme would give a more comprehensive picture of POCs in the freshwater ecosystem but are probably not necessary for monitoring purposes.

## 1. INTRODUCTION.

### 1.1. The United Kingdom Acid Waters Monitoring Network.

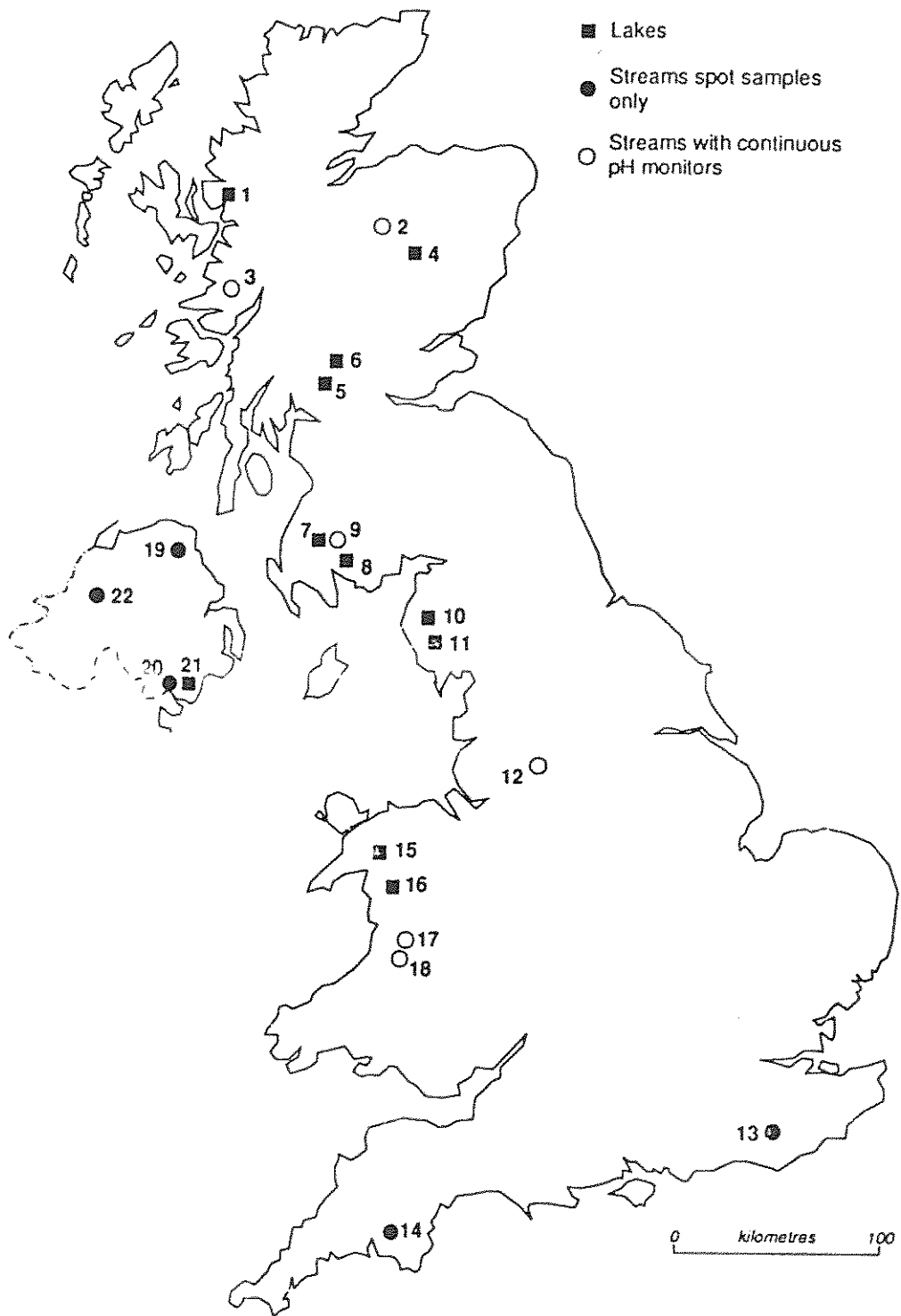
The United Kingdom Acid Waters Monitoring Network (AWMN) was established in April 1988 by the Department of the Environment following the recommendations of the United Kingdom Acid Waters Review Group (Watson, 1987). The objective of the Network is to provide a long-term high quality chemical and biological database, which in conjunction with the existing United Kingdom precipitation monitoring network will facilitate the assessment of trends in surface water acidity within the United Kingdom

The AWMN comprises 22 lake and stream sites throughout the United Kingdom (Figure 1, Table 1), which are considered sensitive to acidification. The sites cover a range of acidic atmospheric deposition from 3.8 - 25 kg S (wet deposited non-marine sulphate) ha<sup>-1</sup> yr<sup>-1</sup> (1988 data from Patrick *et al.* 1991). As the primary function of this network of sites is to assess the influence of changes in acidic depositions on water quality, the sites are generally some distance from major population centres and were chosen to minimise the effect of anthropogenic catchment-based impacts. However, as much evidence exists (e.g. Harriman & Morrison, 1982) to suggest that catchments with extensive conifer plantations respond to atmospheric depositions in a different manner to adjacent moorland catchments on a similar geology, a number of sites were selected with partly afforested catchments.

At all sites regular spot samples are taken for full laboratory analysis of an extensive suite of chemical determinands (see Patrick *et al.*, 1991 for listings and methods). At six stream sites pH, conductivity and stream flow are continuously monitored to obtain a better record of acidic episodes. In addition to water chemistry, epilithic diatoms, macroinvertebrates, macrophytes and fish are surveyed on an annual basis. The 11 lake sites have each had a full palaeoecological investigation conducted in the recent past. Each lake will be re-cored on a five yearly basis. In addition sediment traps are deployed at each site.

Following the completion of annual sampling in March 1993 an interpretative report assessing the first five years' data will be produced. This report is to be published in 1994.

Figure 1. Map showing the location of the Acid Waters Monitoring Network sites.



**Table 1. Key to location of the Acid Waters Monitoring Network sites**

Site	Site Altitude (m)	Catchment Area* (ha)	Rainfall (yr <sup>-1</sup> ) (1988)	Total S Deposition (kg yr <sup>-1</sup> ) (1988)	Planted Conifers (%)
1 Loch Coire nan Arr	125	897	2800	5.18	<1
2 Allt a'Mharcaidh	325	998	1200	3.83	0
3 Allt na Coire nan Con	10	790	2600	16.11	50
4 Lochnagar	785	92	1400	7.33	0
5 Loch Chon	100	1470	2500	11.55	49
6 Loch Tinker	420	112	2500	11.55	0
7 Round Loch of Glenhead	295	95	2700	21.73	0
8 Loch Grannoch	210	1287	2500	14.09	70
9 Dargall Lane	260	210	2500	14.36	0
10 Scoat Tarn	602	95	3300	24.63	0
11 Burnmoor Tarn	252	226	2100	16.14	0
12 River Etherow	280	1300	1600	16.80	0
13 Old Lodge	94	240	800	4.99	5
14 Narrator Brook	225	475	1800	6.35	10
15 Llyn Llgi	380	157	3000	11.75	0
16 Llyn Cwm Mynach	285	152	1800	6.37	51
17 Afon Hafren	355	358	2500	7.54	50
18 Afon Gwy	440	210	2500	7.54	0
19 Beagh's Burn	150	273	1400	11.40	0
20 Bencrom River	140	298	1700	12.51	0
21 Blue lough	340	42	1700	12.51	0
22 Coneyglen Burn	230	1414	1700	8.12	5



## **1.2. Assessing the potential of the Network to monitor other problems.**

Every year the AWMN produces a wealth of information, hundreds of samples are taken and many of these are archived. This facilitates the possibility of returning to these samples at a later date to analyse them for determinands not currently in the AWMN methodology. A continuous record will therefore be available back to 1988. This archive includes acidified water samples, dried sediment core and sediment trap material, dried macrophyte samples and epilithic diatom scrapes.

A study is being undertaken by ENSIS Ltd. for the Department of the Environment to assess how useful all this information, both contemporary and archived, might be when used to monitor other atmospherically-derived environmental problems in the United Kingdom. Problems that have been identified for consideration include: trace metals, persistent organic compounds, nitrogen deposition, and 'climate change'. For each of these topics suitable parameters and their deposition gradients across the country have to be identified so that it can be ascertained how effective the present network would be at effectively monitoring each problem. Where present site locations, measured determinands, sampling frequencies and sampling strategies are insufficient for effective monitoring, this study will also offer recommendations of how these might be changed to improve this situation. In addition, sampling strategies employed by other monitoring networks both in the United Kingdom and abroad will be assessed.

This report forms the first part of this study and assesses the potential of the AWMN to monitor the atmospheric deposition of trace metals and persistent organic compounds to freshwaters across the United Kingdom

## **1.3. Trace metals and persistent organic compounds.**

Some pollutants, in the amounts produced, do not have any direct effect on organisms but alter the physical and chemical environment such that the ability of the organism to survive may be altered (e.g. carbon dioxide leading to climate change). Other pollutants however, are directly toxic to organisms and the effect these have depends on the exposure and dose that the organism is subjected to. Trace metals and persistent organic compounds fall into this category, thus monitoring the atmospheric deposition of such substances is of interest. Additionally, in remote regions long-range atmospheric transport is often the main source of these compounds to the aquatic ecosystem (Oehme, 1991).

In some respects the behaviour of metals and persistent organic compounds in freshwaters is quite similar. Both are usually toxic at low concentrations but their availability (i.e. exposure and dose)

greatly depends on the physical characteristics of the freshwater environment. Both are readily complexed to humic compounds and this is a major route of transport of these substances to sediments. (The physical and chemical parameters effecting metal and persistent organic compound availability is discussed more fully in the relevant sections.)

The main difference between metals and persistent organics is that whereas the toxicity of the persistent organic compound depends specifically on the structure of the whole molecule, a metal is toxic in its own right and the potential for pollution does not disappear with a change of form. Metals are commonly measured as concentrations of the total metal but each occurs in a variety of forms of which only the biologically available species are likely to have any harmful effect. This is usually the aqueous ion  $M^{n+}$  (aq) (see 2.2). If conditions prevail that allow the remobilisation of the metal back into the aqueous ion then it will once again be available to an organism. In contrast, once the structure of a persistent organic compound has been disrupted, then although it may be remobilised, any change in molecular structure may considerably alter its chemical and physical properties.

## 2. TRACE METALS

### 2.1. Introduction.

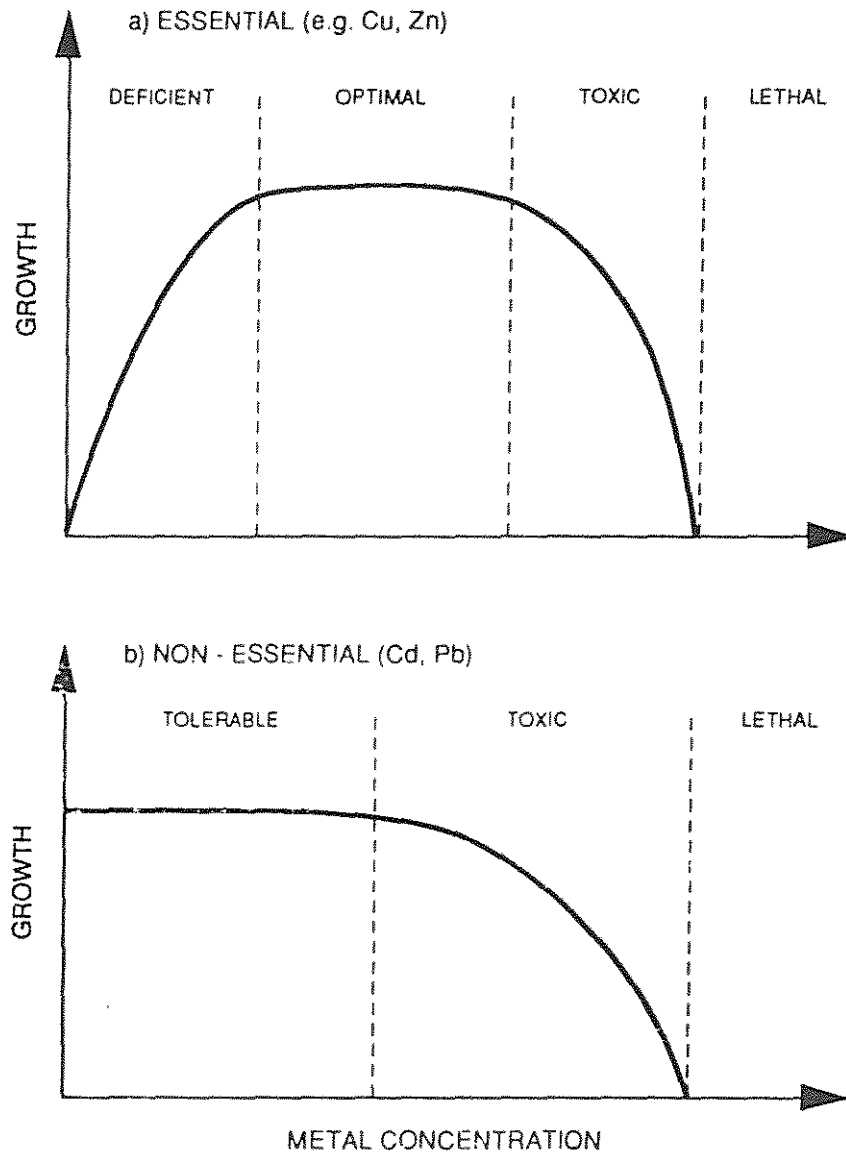
Many factors influence the availability and toxicity of metals to aquatic organisms. These include the form of the metal (soluble, particulate, ionic complex, inorganic, organic etc.), physical factors such as temperature, pH, light and dissolved oxygen which may influence both the physiology of the organism and the processes controlling the cycling of the metals in natural waters (processes such as precipitation, adsorption, complexation and methylation (Laxen, 1983)), the condition of the organism (age, size, stage in life history) as well as the behavioral response of the organism to the metal in question. These effects may then be further compounded by the presence of other metals or pollutants which may be deleterious to the condition of the organism.

Förstner & Wittmann (1979) classified metals into three toxicity categories using the criteria of solubility and abundance: (1) non-critical (e.g. Na, K, Ca), (2) toxic, but very insoluble or very rare (e.g. Ba, Os, Nb) and (3) very toxic and relatively accessible (e.g. Cd, Cu, Hg, Pb, Ni, Zn). This latter and most important group was then sub-divided into two by considering whether these elements are non-essential or essential to life, whereby a deficiency of the metal is also harmful to the organism (see Figure 2).

Other classifications have relied on different criteria to assess toxicity. Jones (1964) used a 'solution pressure' concept which is based on the ease with which the metal, as a positively charged ion, passes into solution, or the ease with which the metal ions combine with other ions or compounds. This produced a tentative 'league table' of metal toxicity with Hg, Cu, Cd, Zn and Sn at the top (Hellowell, 1986). Kaiser (1980) related the toxicity of ions to the electron configurations of the outer orbitals, and used this to predict the toxicity of other ions under similar conditions.

Responses to different metals vary according to the groups of organisms involved. Winner *et al* (1980) suggested that there is a predictable graded response to metal pollution in a range of stream fauna and that a low continuous dose of one metal (Cu, Cr and Zn were tested) had similar effects to larger but fluctuating inputs of several metals.

**Figure 2.** Effect of increasing concentration of (a) essential and (b) non-essential metals on organism growth (after Förstner & Wittmann, 1979).



(after Förstner & Wittman 1979)

## 2.2. Toxic trace metals.

The group of metals classified 'very toxic and relatively accessible' by Förstner & Wittmann are considered more closely below.

### 2.2.1. Cadmium (Cd)

Cadmium, in the biologically available species  $\text{Cd}^{2+}$  (dissolved phase), is toxic to many organisms after exposure to low concentrations ( $<1 \mu\text{g Cd l}^{-1}$ ) although this may be over a period of months. Cd accumulates in the tissues of organisms and is thought to damage ion-regulating mechanisms rather than respiratory or nervous functions (Hellawell, 1986). It does not, however, appear to biomagnify along food chains (Mason, 1991; Wren & Stephenson, 1991). Although Cd may be lost from the tissues after exposure to a single dose, large amounts absorbed may be acquired rapidly, but lost slowly. Thus organisms may survive the initial exposure and die subsequently.

Several environmental factors influence the accumulation and toxicity of Cd to freshwater phytoplankton and invertebrates. Complexation by natural organic compounds such as humic acids and clay minerals such as kaolinite and montmorillonite bind Cd and therefore reduce its toxicity. Cd concentrations in lake water increase with decreasing pH (Wren & Stephenson, 1991) and phytoplankton and algae more readily accumulate Cd in lower pH waters (twice as much at pH 7 as at pH 8) and hence toxicity is increased (Wong, 1987). Cd toxicity to aquatic organisms and especially fish, was found to be higher in soft waters than in hard waters. This is also the case for phytoplankton and several species of algae, and is thought to be due to an antagonistic effect of calcium and magnesium (Hutchinson & Czyska, 1972). Cd toxicity to aquatic invertebrates may be increased by higher temperatures, more light and higher oxygen levels. These effects may be due to increased metabolic rates resulting in higher uptake of Cd from the environment (Wong, 1987).

Concentrations of Cd in the aquatic mosses *Fontinalis* spp. and *Sphagnum* spp. were found to be  $0.4 - 10 \mu\text{g g}^{-1}$  and  $0.5 - 5.6 \mu\text{g g}^{-1}$  respectively in a range of lakes representing different pH and metal concentrations (Miller *et al.*, 1983), although concentrations up to  $30 \mu\text{g g}^{-1}$  were found in mosses near smelters (Crowder, 1991). Some aquatic macrophyte species bioconcentrate Cd, with accumulation factors as high as 10,000 in *Myriophyllum* (Crowder, 1991). In *Isoetes*, *Juncus* and *Phragmites*, roots contain a higher concentration of Cd than shoots (Laxen, 1983). The main pathways of uptake are considered to be from the sediment and, for plants with floating leaves, from the atmosphere, but although macrophytes are good Cd accumulators they are relatively insensitive to the effects of high Cd concentrations and therefore they have potential to act as good monitoring species for Cd (Wong,

1987). In experimental studies of the effect of Cd on cultures of the diatom *Asterionella formosa* concentrations of 2 µg Cd l<sup>-1</sup> reduced the growth rate by an order of magnitude while populations exposed to more than 10 µg Cd l<sup>-1</sup> ceased growth in about one day (Conway, 1978).

Cd in aquatic systems accumulates more rapidly in sediments than in living organisms although bioconcentration factors of 2,000 - 4,000 have been recorded in some aquatic invertebrates (Wren & Stephenson, 1991). Some aquatic insects (stonefly, caddisfly) demonstrate a marked tolerance to Cd relative to other invertebrate species. Cd concentrations <10 µg l<sup>-1</sup> were lethal to mayfly and snail species in laboratory tests lasting 28 days whilst concentrations as high as 238 µg l<sup>-1</sup> had little or no effect on the survival of the caddisfly (*Hydropsyche betteni*) and stonefly (*Pterocercys dorsata*) (Clubb *et al.*, 1975). Insects transferred to clean water after exposure to Cd polluted waters lose Cd at a steady rate, a feature which may aid survival when organisms are exposed to intermittent doses of Cd pollution (Hellowell, 1986).

As Cd does not biomagnify along food chains, the concentrations in fish do not increase with increasing trophic level (Spry & Wiener, 1991) and furthermore, concentrations within a fish population do not typically increase with body size or age. However, accumulation of Cd by fish does increase with increasing exposure concentration in water (Murphy, *et al.*, 1978). Cd accumulates chiefly in the kidney, liver, gastrointestinal tract and gills, although the sites of accumulation may vary with route of uptake (Spry & Wiener, 1991).

### 2.2.2. Copper (Cu)

Cu toxicity is thought to be largely attributable to the Cu<sup>2+</sup> ion. Cu forms complexes with a wide range of substances commonly found in natural waters and is also readily adsorbed on to suspended solids. Factors which influence Cu availability and toxicity are water hardness (due to the formation of carbonate complexes), presence of organic matter, temperature, oxygen concentration and pH. For example, Cu<sup>2+</sup> in calcareous, organic-rich sediment at circumneutral pH is unlikely to be available at sufficient concentrations to be toxic (Flemming & Trevors, 1988).

Although Cu has been used extensively both as an algicide and to control the growth of macrophytes, bioaccumulation of Cu is slower than for other metals such as Mn and Zn (Radwan *et al.*, 1990). A study specifically on the alga *Chlamydomonas reinhardtii* showed that the algal surface had a high affinity for both Cu and Cd. The mechanism was found to be rapid adsorption of the metals followed by slow uptake into the inside of the cell (Xue *et al.*, 1988). Hart (1982) discussed the uptake of Cu

solubility and it is unlikely that acute toxicity will be observed under natural conditions (Hellawell, 1986). Therefore, Pb is most likely to cause sub-lethal effects (e.g. tissue contamination, changes in haematological parameters and spinal curvatures in fish (Hodson, 1976)). In addition, Pb forms highly toxic organo-lead compounds and these accumulate in fish. In the environment organo-lead compounds may be formed by microbial action, although they also have an atmospheric source from their use as 'anti-knock' additives in petrol.

Mechanisms for Pb uptake by macrophytes include the trapping of micron-sized particulates by mosses and an ion exchange mechanism in lichens (Crowder, 1991). Pb concentrations measured in aquatic bryophytes include 14,825  $\mu\text{g g}^{-1}$  in *Scapania undulata* and 10,800  $\mu\text{g g}^{-1}$  in *Fontinalis squarrosa*, at pH 6.3 - 7.2 (Ormerod *et al.*, 1987), 18 - 290  $\mu\text{g g}^{-1}$  in *Fontinalis spp.* and 32 - 430  $\mu\text{g g}^{-1}$  in *Sphagnum* at pH 4.4 - 6.4 (Miller *et al.*, 1983). Of the higher aquatic macrophytes, *Potamogeton* species have higher Pb concentrations than other genera, up to 118  $\mu\text{g g}^{-1}$  (Mason, 1991). Pb accumulations have been measured in different organs of many species and generally the below-ground parts have most Pb, again emphasising the importance of the sediment pathway for metal uptake.

Bioaccumulation of Pb in aquatic invertebrates is generally low and it has been found that Pb concentrations in some benthic invertebrates are so low that the level is due to sediment particles within the gut rather than accumulation of the metal in the body tissues. However, Nehring (1976) found Pb bioconcentration factors were >300 for stoneflies and >8000 for mayflies. Aquatic invertebrates display great interspecies variability in sensitivity to Pb toxicity, but toxicity is generally enhanced by low water hardness and alkalinity (Wren & Stephenson, 1991). The effect of lowered pH on Pb toxicity is also variable, but there is evidence to suggest that reduced pH increases Pb uptake by invertebrates (Wren & Stephenson, 1991). The grazing of diatom communities by some invertebrates is also considered to be an important pathway for Pb uptake (Everard & Denny, 1984).

The accumulation of Pb in fish, like Cd, typically increases with increasing exposure concentration in water. Pb accumulates chiefly in the bone, scales, gills, kidney and liver (Hodson *et al.*, 1982). Direct uptake across the gills as the free divalent ion ( $\text{Pb}^{2+}$ ) seems to be the primary route of uptake in fresh water fish (Spry & Wiener, 1991). With decreasing pH more Pb should exist as the readily assimilated  $\text{Pb}^{2+}$  and so in lower pH waters more Pb should be available to fish and hence toxicity should increase.

#### 2.2.4. Mercury (Hg)

Inorganic Hg is acutely toxic to fish at about  $1 \text{ mg Hg l}^{-1}$ , but it is the microbial conversion of inorganic Hg to highly toxic mono-methyl mercury (MeHg) which increases the potential toxicity of Hg pollution (Hellawell, 1986). MeHg is water soluble and has a high affinity for proteins, so readily accumulates in aquatic organisms (Lindqvist, 1991). Low water concentrations of Hg are concentrated in algae and other aquatic plants which are further biomagnified up the food chain. There is a marked increase in Hg concentration from plants and invertebrates to fish, especially carnivorous species (Mason, 1991). Due to the stability of Hg in body tissues, it is accumulated rapidly and eliminated only slowly.

Both bryophytes and lichens include bioaccumulator species with Hg tolerance, and species of *Sphagnum* have been recorded as having concentrations in the range  $680 - 1200 \mu\text{g Hg g}^{-1}$ . The mechanism of bioaccumulation in liverworts may involve the binding of Hg by sulphur compounds in cell walls (Crowder, 1991). Higher aquatic macrophytes contain Hg in lower concentrations, with reported values in the  $\text{ng g}^{-1}$  range for species of *Myriophyllum*, *Potamogeton*, *Nuphar*, and *Utricularia*. Toxic effects include discolouration and necrosis of floating leaves and death of roots. In culture, a toxic threshold of  $0.5 \mu\text{g ml}^{-1}$  was reported for *Myriophyllum* (Dolar *et al.*, 1971).

Typical concentrations of Hg in aquatic invertebrates from uncontaminated areas are generally less than  $1.0 \mu\text{g g}^{-1}$ , although tissue concentrations up to  $10 \mu\text{g g}^{-1}$  have been reported (Huckabee *et al.*, 1979). Bioconcentration factors of Hg range from 75 for water boatmen to 29,000 for damselfly nymphs. When grouped into community preference and trophic class, stream bottom dwellers have higher Hg concentrations than those in the water column and carnivores contain more Hg than herbivores and detritivores (Wren & Stephenson, 1991). The organic content of sediments has been shown to be important, such that Hg accumulation by benthic invertebrates was found to be low in sediments containing high levels of organic matter despite high Hg concentrations, and high in benthic invertebrates in sediments with low organic content. Water hardness and pH influence the rate of uptake and availability of Hg to aquatic biota and accumulation is greater in acidified waters, although whether lower pH increases the toxicity of Hg to invertebrates is unknown (Wren & Stephenson, 1991).

There have been many studies on the concentrations of Hg in fish and bioconcentration factors in excess of 400,000 have been recorded. As with invertebrates, open water species generally have lower amounts of Hg than bottom dwellers such as eels which spend much of their time in contact with



sediments. This emphasises the importance of sediments as a source of contamination (Mason, 1991). Fish take up Hg predominantly through their diet although they can also do so through their gills and 95 - 99% of the Hg is present as MeHg (Spry & Wiener, 1991). Wild populations can accumulate significant concentrations but it is unlikely that acutely toxic or lethal concentrations will be experienced in normal conditions (Spry & Wiener, 1991).

#### 2.2.5. Nickel (Ni)

The main environmental variable effecting Ni toxicity is water hardness and this is due to the formation of carbonate complexes. Like many metals, bioaccumulation of Ni is increased with a decrease in pH. The growth of several species of green alga was inhibited by concentrations as low as  $100 \mu\text{g Ni l}^{-1}$ , although some species of blue-green algae (e.g. *Anabaena cylindrica*) were unaffected by concentrations greater than  $600 \mu\text{g Ni l}^{-1}$  (Spencer & Green, 1981). It was suggested that extracellular products of the blue-green algae may form complexes with Ni as had been demonstrated for Cu. Dixit *et al.* (1991) used diatom assemblages to infer lake water Ni concentrations and found 7 species with Ni concentration optima  $\geq 100 \mu\text{g Ni l}^{-1}$  in their data-set. These were *Pinnularia hilseana* ( $694 \mu\text{g Ni l}^{-1}$ ), *Eunotia tenella* (243), *E. pectinalis* (144), *E. exigua* (132), *P. subcapitata* (122), *Achnanthes minutissima* (102) and *Synedra acus* (100).

In studies on the effects of trace metals on toxicity and the inhibition of photosynthesis to aquatic macrophytes, Brown & Rattigan (1979) found that Ni, unlike other trace metals, had little short term effect on photosynthesis, but was highly toxic to *Elodea* and *Lemna* after 4 weeks. Ni concentrations have been reported for several species of macrophyte in lakes of varying pH and this supports the hypothesis that more Ni is bioaccumulated in lower pH waters. In a survey of 259 Finnish headwater lakes, Ni concentrations in *Sparganium* sp. were  $1 - 3 \mu\text{g g}^{-1}$  at  $\text{pH} \leq 5.2$  and  $0.6 - 1.5 \mu\text{g g}^{-1}$  at  $\text{pH} \geq 5.9$ . For *Nuphar luteum*, Ni values were reported as  $0.7 - 2 \mu\text{g g}^{-1}$  at  $\text{pH} \leq 5.2$  and  $0.2 - 1 \mu\text{g g}^{-1}$  at  $\text{pH} \geq 5.9$  (Verta *et al.*, 1989b). Ni values have also been reported for *Potamogeton* sp. and fall in the range  $9 - 16 \mu\text{g g}^{-1}$  (Förstner & Wittmann, 1979).

The stonefly *Acroneuria lycorias* showed a high tolerance to Ni toxicity in soft water ( $44 \text{ mg l}^{-1} \text{ CaCO}_3$ ) with a 96 hr  $\text{LC}_{50}$  of  $33.5 \text{ mg Ni l}^{-1}$ , whilst the mayfly *Ephemerella subvaria* was more sensitive with a 95 hr  $\text{LC}_{50}$  of  $4 \text{ mg Ni l}^{-1}$  (Warnick & Bell, 1969). Water hardness and pH are also important for invertebrate bioaccumulation of Ni. The tubificid worm *Tubifex tubifex* has a Ni tolerance similar to that of the mayfly in soft water (a 48 hr  $\text{LC}_{50}$  of  $7.0 - 8.7 \text{ mg Ni l}^{-1}$  at  $34 \text{ mg l}^{-1} \text{ CaCO}_3$ ), but in hard water ( $260 \text{ mg l}^{-1} \text{ CaCO}_3$ ) this tolerance is increased to  $61.4 \text{ mg Ni l}^{-1}$  (Brkovic-

Popovic & Popovic, 1977). Ni concentrations in the Trichoptera larvae *Limnophilus* have been reported as 1.5 - 7.0  $\mu\text{g g}^{-1}$  at  $\text{pH} \leq 5.2$  and 0.8 - 4.0  $\mu\text{g g}^{-1}$  at  $\text{pH} \geq 5.9$ . For *Phryganea* larvae the Ni concentrations in these pH ranges are 0.4 - 1  $\mu\text{g g}^{-1}$  and 0.6 - 20  $\mu\text{g g}^{-1}$  respectively (Verta *et al.*, 1989a).

Bioaccumulation of Ni in fish is heavily influenced by water hardness, but even in soft water Ni is not very toxic. However, it appears to be the only trace metal which has a harmful effect on gill morphology (Hughes *et al.*, 1979). Mean concentrations of Ni in fish appear to be in the region of 1  $\mu\text{g g}^{-1}$  (Hellowell, 1986; Verta *et al.*, 1989a) and this mostly accumulates in the skeletal tissue (Radwan *et al.*, 1990).

#### 2.2.6. Zinc (Zn)

Zn is unusual in that it has low toxicity to people but high toxicity to fish, such that adequate standards for domestic water supply (maximum = 5  $\text{mg Zn l}^{-1}$ ) would be highly toxic to many fish species. The toxicity of Zn is influenced by many environmental factors including temperature, pH, dissolved oxygen, presence of organic matter and most importantly water hardness. The presence of suspended particulate matter (e.g. clay minerals, organic matter) is also important as it has been suggested that adsorption on to such particles and subsequent settling is one of the primary pathways of Zn to lake sediments (Nienke & Lee, 1982). Acidification of surface waters by acidic deposition indirectly causes increased concentrations of soluble Zn. This is because complexation of the aqueous ion ( $\text{Zn}^{2+}$ ) is limited due to low concentrations of dissolved and particulate complexing ligands present in such conditions (White & Driscoll, 1987).

In a study on the toxicity of Zn from mining wastes on the algae in a polluted stream, it was reported that changes in the species composition of the community were a more evident response to Zn pollution than the total number of species present (Say & Whitton, 1981). Diatom species associated with high concentrations of Zn included *Eunotia tenella* and *Pinnularia borealis*.

Aquatic bryophytes are tolerant of enhanced concentrations of Zn and consequently have been used as monitors of contamination (Say *et al.*, 1981). In particular high Zn concentrations have been reported for *Rhynchostegium riparoides* (a maximum reported concentration of 6,705  $\mu\text{g Zn g}^{-1}$ ), *Fontinalis squamosa*, *F. antipyretica* (5,430  $\mu\text{g Zn g}^{-1}$ ) and *Scapania undulata* (3,558  $\mu\text{g Zn g}^{-1}$ ) (Hellowell, 1986).

Zn is not as toxic to aquatic insects as some other trace metals and Warnick & Bell (1969) were unable to determine a 96 hr LC<sub>50</sub> for any species in hard water conditions as all survived. However longer tests (10 - 14 days) in soft waters (44 mg l<sup>-1</sup> CaCO<sub>3</sub>) did provide LC<sub>50</sub> values and showed that for the species tested, the mayfly *Ephemerella* was the most sensitive to Zn followed by the caddis *Hydropsyche* with the stonefly *Acroneuria* being the least sensitive. The oligochaete *Tubifex tubifex* appears to be more sensitive to Zn with an 48 hr LC<sub>50</sub> of 3.0 mg Zn l<sup>-1</sup> in soft waters (34 mg l<sup>-1</sup> CaCO<sub>3</sub>) and 60 mg Zn l<sup>-1</sup> in hard waters (260 mg l<sup>-1</sup> CaCO<sub>3</sub>) (Brkovic-Popovic & Popovic, 1977). Burrows & Whitton (1983) proposed that water and sediments were the main sources of contamination to benthic organisms, and it has been suggested that some animal cells actively absorb Zn. High bioaccumulation of Zn in plankton and benthic fauna does not, however, always correspond to high concentrations in fish (Radwan *et al.*, 1990).

There is an inverse linear correlation between the logarithms of water hardness and toxicity to salmonid fish, i.e. a ten-fold increase in hardness is accompanied by a tenfold increase in the LC<sub>50</sub> and it has been suggested that the presence of calcium ions provides some protection to fish exposed to Zn (Hellawell, 1986). Non-salmonids are generally more resistant to Zn poisoning, although variations in susceptibility do occur through the life history of some species. Zn has a higher bioaccumulation in the kidneys and skeletal tissue than in other organs and had the highest average concentration of all the trace metals in fish species analysed by Radwan *et al.* (1990).

#### 2.2.7. Other metals.

##### Chromium (Cr).

Cr has a wide range of oxidation states and it is the trivalent Cr<sup>3+</sup> ion and the hexavalent ion Cr<sup>6+</sup> that are most commonly found in nature. Fish are generally not sensitive to Cr but some invertebrates are relatively intolerant. Toxicity of Cr<sup>3+</sup> to two insects in soft water (44 mg l<sup>-1</sup> CaCO<sub>3</sub>) differs quite markedly. The 96 hr LC<sub>50</sub> for the mayfly *Ephemerella subvaria* was 2 mg Cr l<sup>-1</sup>, whilst that of the caddisfly *Hydropsyche betteni* was 64 mg Cr l<sup>-1</sup> (Warnick & Bell, 1969). Water hardness is important for Cr toxicity to invertebrates, the toxicity being much higher in soft waters than hard waters (Hellawell, 1986). Cr has been found to be moderately toxic to several algae and the growth of floating macrophytes including *Lemna* and *Spirodela* was inhibited by 10 ppm (Jana, 1988; Hellawell, 1986).

### **Cobalt (Co).**

The toxicity of Co is not well documented. Co does not appear to be very toxic to fish, but invertebrates are more sensitive. The 96 hr LC<sub>50</sub> of the mayfly larva *Ephemera* was found to be 16 mg Co l<sup>-1</sup> in soft water (44 mg l<sup>-1</sup> CaCO<sub>3</sub>) (Warnick & Bell, 1969).

### **Manganese (Mn).**

Mn does not appear to have much significance as a pollutant. It is rarely found at concentrations above 1 mg l<sup>-1</sup> and since tolerances of aquatic life range from 1.5 - 1000 mg Mn l<sup>-1</sup> it is not considered a problem in fresh waters (Train, 1979). Although some permanganates have been found to be lethal to fish at fairly low concentrations (several mg l<sup>-1</sup>), they readily oxidise organic matter and are therefore reduced and made non-toxic. In studies on the toxicity of trace metals to freshwater insects, Mn was found to be the least toxic (Hellawell, 1986).

### **Selenium (Se).**

The increasing presence of Se in the environment as a result of the burning of fossil-fuels makes it a potential pollutant. Se interacts with Hg, slows the rate of bioaccumulation of Hg in fish and other biota, and is an antidote to MeHg poisoning (Rudd *et al.*, 1980). Bioaccumulation in fish is highest in the spleen, heart, liver and kidney and, under natural conditions, concentrations of 10 µg Se l<sup>-1</sup> are potentially toxic (Lemly, 1982).

### **Tin (Sn).**

Little published data exist for Sn although its toxicity to fish and invertebrates appears to be low (Hellawell, 1986).

### **Vanadium (V).**

The combustion of fossil-fuels, especially oil, is a major source of V and although it is a fairly abundant element little seems to be known about its environmental significance. V is found in a wide range of ionic forms which do not complex with carbonates and bicarbonates as do most other trace metals. Consequently its toxic properties may be different to other metals and vary considerably depending on the ionic form the metal takes (Hellawell, 1986). Water hardness and pH appear to have little effect on the toxicity of V to fish, but it has been found that toxicity was highest at pH 7.7 and decreased with increasing water hardness. V is accumulated only slowly by fish and highest concentrations are found in the liver and kidney (Bell *et al.*, 1981).

## 2.3. Trends in metal deposition in the United Kingdom.

### 2.3.1. Sources of metals.

Metal-bearing airborne particulates are produced as a result of both natural and anthropogenic processes. The most important natural sources of metals are windblown dust, forest fires, volcanic particles, vegetation and sea salt sprays. Eroded soil particles account for 60 - 80% of Zn, Cu, and Pb emitted from natural sources (Nriagu, 1979) whilst plant exudates account for about 22% of the natural global emission of Zn (Nriagu & Davidson, 1980). Calculating enrichment factors of metals in airborne particulates relative to crustal abundances gives some indication as to the origin of metal contaminants. One such set of enrichment factors are shown in Table 2. Enrichment factors close to unity indicate crustal weathering as the atmospheric source for that particular metal e.g. Al, Co and to a lesser extent Cr and Ni. By contrast, the other metals, V, Cu, Zn, Hg, Cd, Pb and Se are enriched by up to four orders of magnitude, and these are likely to be of anthropogenic origin.

There are many anthropogenic sources of trace metals but the most important ones affecting the atmospheric environment are non-ferrous metal production, iron and steel production, wood combustion, refuse incineration, cement production, and for Pb emissions, gasoline combustion (Nriagu, 1979; Pacyna, 1984).

The combustion of fossil-fuels (coals, fuel oils, lignite) at high temperatures is also an important source of many metals. Klein & Russell (1973) showed that soils and plants in the vicinity of a coal-burning power plant were enriched in Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti and Zn, and lake sediments have also become metal-enriched as a response to an increase in fossil-fuel combustion on both a local (Galloway & Likens, 1979) and regional (Kemp *et al.*, 1978) basis. Coal especially is considered a major source of Hg emissions to the atmosphere (Joensuu, 1971; Billings and Matson, 1972), and the high V concentrations in heavy fuel oil are probably the main reason for the elevated V enrichment factors in Table 2.

**Table 2.** Enrichment of metals in atmospheric particles relative to the earth's crust (after Förstner & Wittmann, 1979).

Metal	Urban Air	North Atlantic Westerlies
Iron	* 1.0	1.1
Aluminium	0.5	* 1.0
Cobalt	2.0	3.5
Chromium	11	-
Nickel	12	-
Vanadium	42	13
Copper	83	84
Zinc	270	40
Mercury	1100	-
Cadmium	1900	300
Lead	2300	2300
Selenium	2500	16000

\* = Standard

Depending on the climatic conditions encountered by these particulates they can travel thousands of kilometres until they are deposited either as wet deposition (e.g. rainfall, snow) or as dry deposition. Sugden (1979) identified 3 levels of atmospheric pollution. (1) local, where sources and pathways are usually clearly defined, (2) regional, where pollutants occur up to several hundred miles from the source and the analysis of pathways becomes complicated due to a large number of potential sources, and, (3) global, where pollutants enter the stratosphere before circulation. Studies of the atmospheric transport of trace metals have shown that long range transport is of great importance (Fletcher, 1990), and so it is levels (2) and (3) that are of concern to a monitoring programme rather than local atmospheric influences (see Section 2.3.4.).

### 2.3.2. Background metal concentrations from lake sediment cores.

The measurable presence of metals in the freshwater ecosystem which are not commonly found in rock-forming minerals and which therefore have a very low crustal abundance may itself be evidence of contamination from an anthropogenic source. However, there are only a few such metals and it is

those which are both toxic and abundant that are the main concern as pollutants in freshwaters (Förstner & Wittmann, 1979). These metals (e.g. Cu, Zn, Pb) also occur as common minerals and consequently there is a need to determine natural or background concentrations of these metals at each site before the amount of contamination from anthropogenic sources can be assessed.

There are two reasons for an assessment of background concentrations. Firstly, it is important to determine temporal changes at the site in question to assess whether anthropogenic contamination has taken place and that the concentrations present in the ecosystem are not the result of natural processes. For example, Lough Neagh sediments were found to be high in Cr and Ni, and although there has been an anthropogenic enhancement in recent sediments, it was found from sediment core studies that the concentrations had always been high due to one third of the catchment being underlain by basic olivine-tholeiitic basalts, naturally high in these metals (Rippey *et al.*, 1982). Other examples are Blue Lough in Northern Ireland, Llyn Hir in Wales and Loch Tanna on Arran which were found to have high background lead concentrations due to their catchment geologies (Rippey, pers. comm.). Secondly, it is important that background concentrations are determined at each sample location to allow for spatial differences between sites. Differences in geology, proximity to the coast (sea salt inputs) and catchment vegetation can all alter background concentrations.

One way of determining pre-industrial concentrations of metals in the freshwater ecosystem and the subsequent increase in metal contamination due to anthropogenic sources is through the analysis of lake sediment cores and the production of dated metal profiles (e.g. Kemp *et al.*, 1978; Galloway & Likens, 1979; Rippey *et al.*, 1982; Thomas *et al.*, 1984; Battarbee *et al.*, 1988; Rippey, 1990; Johansson, 1991; etc.). It is important that sediment cores for metal analyses be dated (by annual varve counting, radiometric methods, etc.) so that sediment accumulation rates and fluxes of metals to the sediment can be calculated.

Metal flux measurements represent an absolute input over time (e.g.  $\text{mg m}^{-2} \text{yr}^{-1}$ ) and therefore they are preferable to metal concentrations (e.g.  $\mu\text{g g}^{-1}$ ) in sediment cores because they overcome differences in accumulation rate between one site and another. However, even with flux values, problems can occur. If the accumulation rate varies considerably within a sediment core, then the metal flux can reflect this variation rather than a real change in atmospheric deposition. There are two ways around this problem. Firstly, to select remote sites with small catchments where the dominant metal input to the site is atmospheric. In such cases changes in the metal profile should reflect changes in atmospheric deposition rather than changes in the accumulation rate or catchment sources from

agriculture or sewage. Secondly, pre-industrial deposition concentrations can be used to determine a background flux. This can then be subtracted from the total flux at all sampling intervals so that only the anthropogenic flux remains. These values can then be used to give a clearer indication of anthropogenic contamination through time at a given site (Fletcher, 1990). Where a lake has become acidified another problem can occur as some metals (e.g. Zn and Cd) become more mobile at lower pHs (White & Driscoll, 1987). Changes in the nature of these metals as a function of pH have implications for interpreting sediment geochemical profiles and these must be taken into account before any conclusions are reached.

Metal profiles already exist for some of the lakes in the AWMN, mostly from studies previously undertaken as part of the Surface Waters Acidification Project (SWAP) and by the Environmental Change Research Centre at University College London. The sites and metals involved are summarised in Table 3.

Sediment cores used in the ways described above to ascertain background concentrations of metals in freshwater systems, do not preclude the use of streams in monitoring for trace metal pollutants. However, stream systems must be monitored in different ways and these are discussed further in Section 2.4. In some instances it may be possible to use sources other than sediments to determine past levels of metals. For example, Lee & Tallis (1973) used dried samples of the moss *Hypnum cupressiforme* from museum and herbarium collections to compare metal levels from the mid-19th century with those of contemporary samples taken from the same locations.



**Table 3.** Metal profiles for lake sediment cores taken from Acid Waters Monitoring Network sites, before the Network was established.

Site	Date	Metal(s)	Reference
Lochnagar	1986	Pb, Zn	Battarbee <i>et al.</i> , 1988
Loch Chon	1987	Pb, Zn	Rippey, 1990
Loch Tinker	1985	Pb, Zn	Rippey, 1990
Round Loch of Glenhead	1984	Cu, Pb, Zn	Battarbee <i>et al.</i> , 1989
Scoat Tarn	1984	Cu, Pb, Zn	Haworth & Lishman, 1991
Llyn Llagi	1985	Pb, Zn	Battarbee <i>et al.</i> , 1989
Llyn Cwm Mynach	1985	Pb, Zn	Battarbee <i>et al.</i> , 1989

### 2.3.3. Determining spatial patterns of trace metal deposition.

There have been a range of studies to assess both temporal and spatial variations in metal deposition and these fall into two categories, direct sampling of the atmosphere and indirect sampling via lake sediment studies.

#### 2.3.3.1. Evidence from deposition collectors and air sampling.

Continuous sampling of air particulate, rainwater and dry deposition has been undertaken since 1972 at four rural sites in England & Wales by AEA Technology Harwell (formerly AERE Harwell) on behalf of the Department of the Environment (Cawse, 1987). 36 elements are routinely analysed (monthly sample changes) including all of those described in Section 2.2. except Sn, and the results for the first ten years of this study have been published. The four sites are at Chilton in Oxfordshire, Styrrup in Nottinghamshire, Trebanos, near Swansea in Glamorganshire and Wraymires, near Windermere in Lancashire. For all the trace metals mentioned in Section 2.2. the average annual elemental concentrations in air at these four sites showed the same pattern, i.e. Styrrup > Trebanos > Chilton > Wraymires. There were only two exceptions to this pattern, for Co and Ni where the order of Styrrup and Trebanos was reversed.

Five metals (Pb, Cd, Zn, Mn and Ni) in atmospheric aerosols were analysed daily over a one year period at a station in Hemsby, Norfolk (Yaaqub *et al.*, 1991). The Hemsby site is approximately 1 km from the east coast of Norfolk and consequently would be expected to have lower metal concentrations than all the sites in the Cawse study. This is found to be the case except in one instance, that of Mn

where the average air concentration for Hemsby is slightly higher than that of the Wraymires site.

The Comprehensive Atmospheric Monitoring Programme (CAMP), run by the Paris Commission as part of the Convention for the Prevention of Marine Pollution from Land-based Sources, monitors contaminants in precipitation at 4 coastal sites in Great Britain. Three are sited on the east coast of England and Scotland at Banchory near Aberdeen, Staxton Wold in Lincolnshire and East Ruston in Norfolk, and one at Lough Erne in north-west Ireland. This monitoring is part of a European Network to study pollution from land-based sources to the marine environment, principally the North Sea. The metals monitored on a monthly bulked sample basis are Cd, Hg, Cr, Cu, Ni, Pb and Zn. Comparing the annual mean concentrations to those sites already discussed, the East Ruston and Staxton Wold sites have similar metal concentrations to the Hemsby site, except that the Zn concentration at Staxton Wold is about twice as high. The Banchory site is by far the furthest north of all the sites so far discussed and has metal concentrations almost an order of magnitude lower than any other site.

These data suggest that within the United Kingdom there may be an area of high metal deposition over the Midlands, decreasing away from the region in all directions. This pattern is very similar to the map of sulphur deposition in the United Kingdom (Review Group on Acid Rain, 1987; 1990). Pacyna (1984) produced European emission maps for Cu, Cr, Mn, Cd and Zn. The highest emission areas in Great Britain were suggested to be in the Midlands/north-east area of England, except for Cd and Cu where two high areas were identified in the north-east and the south-west of England (Figure 3).

#### 2.3.3.2. Evidence from lake sediments.

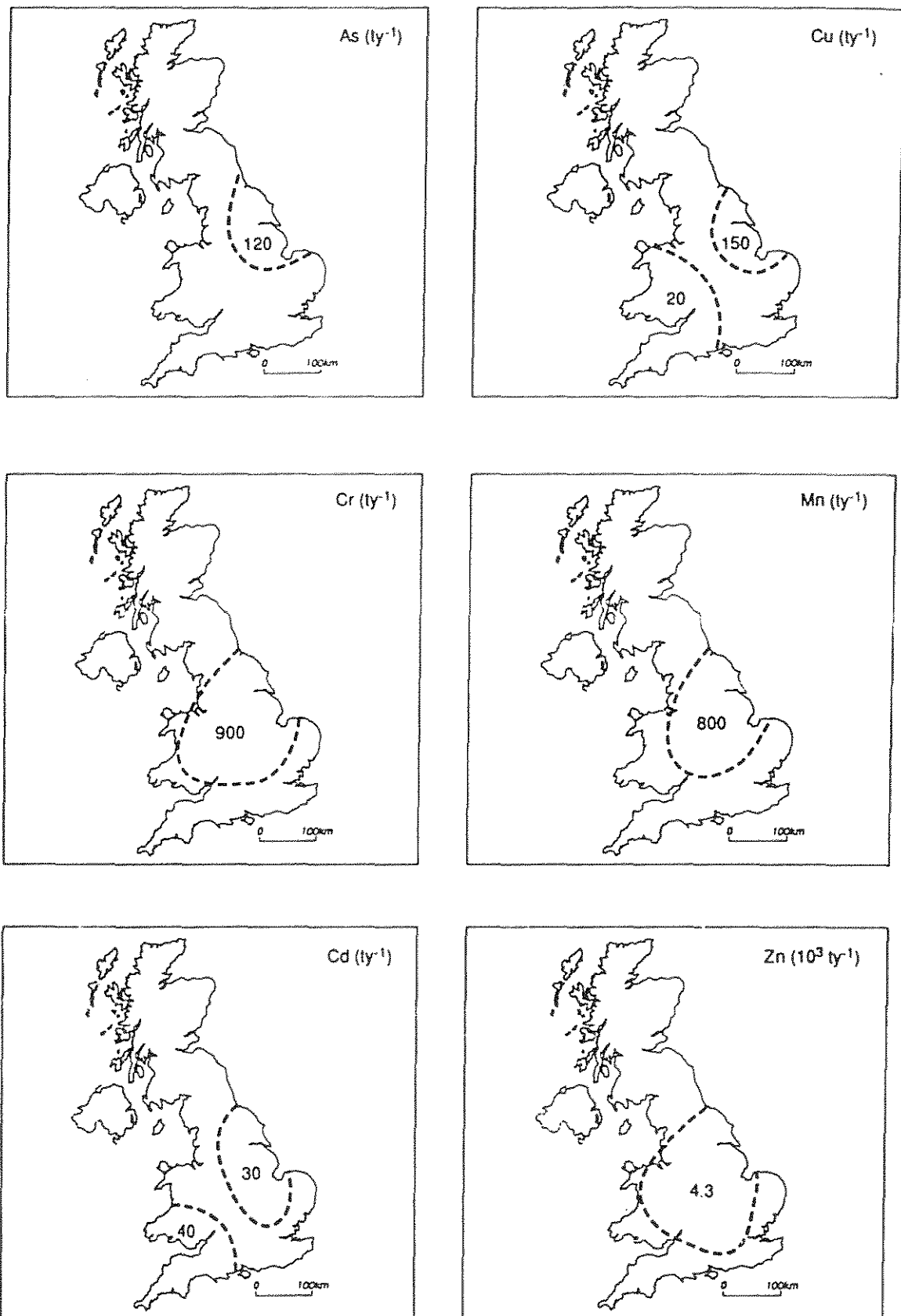
As with atmospheric monitoring, the lake sediment evidence for a trace metal deposition gradient must be pieced together from a variety of literature sources. With a few exceptions (e.g. Rippey *et al.*, (1982), Ochsenbein *et al.*, (1982), Farmer *et al.*, (1980)), most metal analyses published on United Kingdom lake sediments are restricted to Cu, Pb and Zn, and so only these metals can be used to try and determine a metal gradient. A summary of maximum and surface metal concentrations from lake sediment cores is given in Table 4.

In general, the metal concentrations for lake sediments appear to follow the same pattern as that from the atmospheric monitoring (Section 2.3.3.1.). There are exceptions to this pattern, for example Loch Teanga in the Outer Hebrides has very high surface sediment metal concentrations when compared to other sites in the region. However, these high metal concentrations are mainly due to catchment inputs

and when removed from the total, the metal concentrations derived from atmospheric sources are found to be very low (Flower *et al.*, 1992b).

Sites in County Donegal, north-west Ireland also appear to have high metal concentrations. If the pattern described above is correct then these values are higher than expected, but it has been suggested that atmospheric pollutants travel preferentially westwards from the Midlands and north of England rather than to the north (Flower *et al.*, 1992a). This shows that there are effectively two gradients, a south to north gradient with metal concentrations decreasing rapidly northwards from the Midlands, and an east to west gradient where concentrations decrease more slowly. From the limited data available, metal concentrations south of the Midlands may have a gradient intermediate between these two.

Figure 3. Distribution of estimated metal emissions from anthropogenic sources (after Pacyna, 1984).



**Table 4.** A summary of maximum and surface trace metal concentrations in sediment cores from lakes in the United Kingdom with metal contamination.

Site	Zn ( $\mu\text{g g}^{-1}$ )		Cu ( $\mu\text{g g}^{-1}$ )		Pb ( $\mu\text{g g}^{-1}$ )		Reference
	Max.	Surface	Max.	Surface	Max.	Surface	
Lake Windermere	1180	-	140	-	589	-	Hamilton-Taylor, 1979
Loch Lomond	485	460	44	44	160	140	Farmer <i>et al.</i> , 1980
Blelham Tarn	590	500	79	-	250	180	Ochsenbein <i>et al.</i> , 1983
Rivington Reservoir	840	-	140	-	610	-	Hamilton-Taylor, 1983
Llangorse Lake	180	180	38	36	65	60	Jones, 1984
Loch Enoch	200	170	50	40	400	300	Battarbee <i>et al.</i> , 1985
Llyn Hir	500	300	90	90	350	300	Battarbee <i>et al.</i> , 1988
Llyn Gynon	450	250	30	30	200	200	Battarbee <i>et al.</i> , 1988
Llyn y Bi	500	500	25	25	200	200	Battarbee <i>et al.</i> , 1988
Llyn Dulyn	350	350	50	50	180	50	Battarbee <i>et al.</i> , 1988
Llyn Cwm Mynach	900	450	50	50	200	200	Battarbee <i>et al.</i> , 1988
Llyn Llagi	750	100	60	40	400	250	Battarbee <i>et al.</i> , 1988
Loch Urr	1000	1000	30	30	150	150	Battarbee <i>et al.</i> , 1988
Loch Tanna	180	150	40	40	180	150	Battarbee <i>et al.</i> , 1988
Loch Laidon	250	250	20	20	450	450	Battarbee <i>et al.</i> , 1988
Lochnagar	180	150	30	30	200	150	Battarbee <i>et al.</i> , 1988

Table 4 (cont).

Site	Zn ( $\mu\text{g g}^{-1}$ )		Cu ( $\mu\text{g g}^{-1}$ )		Pb ( $\mu\text{g g}^{-1}$ )		Reference
	Max.	Surface	Max.	Surface	Max.	Surface	
Round Loch of Glenhead	350	160	45	40	430	280	Battarbee <i>et al.</i> , 1989
Cranmer Pond	577	330	75	75	313	275	Beebee <i>et al.</i> , 1990
Lough Neagh	262	234	90	80	60	42	Fletcher, 1990
Low Tarn	100	100	40	28	320	175	Haworth & Lishman, 1991
Scoat Tarn	275	180	55	50	500	400	Haworth & Lishman, 1991
Merevale Lake	785	785	114.3	-	78	78	Foster <i>et al.</i> , 1991
Seeswood Pool	531	400	80	-	62	62	Foster <i>et al.</i> , 1991
Wyken Slough	1000	1000	490	-	476	476	Foster <i>et al.</i> , 1991
Swanswell Pool	1800	1800	292	-	311	311	Foster <i>et al.</i> , 1991
Loch Teanga	490	490	95	55	350	320	Flower <i>et al.</i> , 1992
Loch Coire nan Arr	262	262	12	12	53	53	Flower <i>et al.</i> , 1992
Loch Uisge	260	250	52	52	120	100	Flower <i>et al.</i> , 1992

#### 2.3.4. Site selection.

Having identified apparent metal deposition gradients across the United Kingdom, it may be possible to identify key areas where sites for the monitoring of atmospheric trace metal pollution should be located. As it is the countrywide deposition of trace metals that is of concern to a national monitoring programme, local influences must be excluded. Local sources only affect a limited number of water bodies, and their influence swamp any national deposition pattern. Consequently, sites must be chosen outside a region of local trace metal sources (e.g. industrial centres, major towns, etc.). A local point source has an influence within a radius of at least 20 km (Rippey, pers. comm.) and possibly up to 35 km (Nelson & Campbell, 1991), and so any sites chosen for monitoring the national deposition pattern should be outside this range.

#### 2.4. Methods of monitoring atmospheric trace metal inputs to freshwaters.

Trace metal concentrations in the freshwater ecosystem can be monitored from concentrations in waters, sediments or biota.

##### 2.4.1. Waters.

The sampling and analysis of trace metals in freshwaters is relatively simple but have two attendant problems. These are variability and detection limit.

Without the ability to continuously monitor trace metal concentrations, the spot sampling of streams has limited usefulness. Even converting stream concentrations to loads by using flow rate is not sufficient to reduce the variability of metals in these systems if they are only sampled monthly (as per the current AWMN protocol - see Patrick *et al.* 1991), and monitoring in this way would require many years data before any trend could be established. Lake waters are more stable and can be sampled less frequently than streams for this reason. However, even for lake waters it may be necessary to sample more frequently and may take many years to establish trends.

Another problem with the direct measurement of trace metals in freshwaters, especially remote sites away from point sources, is that of detection limit. The detection limits for the analytical methods currently used by the Acid Waters Monitoring Network for water samples are Cu - 20  $\mu\text{g l}^{-1}$ , Zn - 20  $\mu\text{g l}^{-1}$ , Fe - 15  $\mu\text{g g}^{-1}$  and Mn - 2  $\mu\text{g l}^{-1}$  measured by ICP/OES (Inductively Coupled Plasma/Optical Emission Spectroscopy). However, even these more common metals are often not present in sufficient concentrations to be above the limits of detection (Patrick *et al.*, 1991), and this problem would be more serious for the other metals considered in Section 2.2. To use metal concentrations in water

samples in isolation for monitoring may be misleading as low metal concentrations may still be toxic but also could simply mean that most of the metal has been complexed and incorporated into the sediment or biota.

#### 2.4.2. Sediments and sediment traps.

Lake sediments are good accumulators of trace metals because the organic fraction and clay minerals complex and adsorb them very effectively. Because of this efficient capture and sedimentation, concentrations are rarely below the limit of detection and consequently have even been used to measure atmospheric inputs of trace metals into lakes in the Canadian Arctic (Hermansen, 1991). Sediments also act as a major source of metals to benthic fauna and aquatic macrophytes rooted in the sediments.

If sediments are to be used to monitor atmospheric metal inputs, two techniques are available, sediment cores and sediment traps. As discussed in Section 2.3.2, lake sediment cores allow background concentrations of metals to be determined so that background fluxes can be removed from total fluxes to leave anthropogenic inputs. Such cores need to be reliably dated using, for example, radiometric techniques ( $^{210}\text{Pb}$  etc.). Re-coring of sites at regular periods and the use of fine sampling intervals within the core allow high resolution of the metal profile and an assessment of recent atmospheric inputs to be achieved. From Table 3 it can be seen that for metal profiles already exist for most of the lakes present within the AWMN. The five yearly re-coring programme is already in progress at all lake sites and so by the end of 1993 metal profiles will be available for all the lake sites.

Problems with the use of lake sediment cores were discussed in Section 2.3.2. Most of the lakes in the AWMN are small upland sites and the  $^{210}\text{Pb}$  dating available suggests that most have a constant sediment accumulation rate which negates the variable accumulation rate problem, although it would require consideration if new sites were to be added to the Network (see Section 2.5.1.). Catchment and atmospheric inputs can be distinguished by using the background flux approach discussed above.

The second way of using sediments to monitor trace metals is to use sediment traps. These take the form of an array of tubes sealed at one end and positioned in the water column a metre or two above the sediment by means of a buoy and anchor. These traps can be left in the lake for any period of time and can be readily removed, emptied and redeployed to continuously collect particulate material settling out of the water column to the sediment surface. The advantage of sediment traps is that as



the deployment and emptying dates are known, sediment over a known period is collected. Hence, no dating is necessary and the sampling interval can be adjusted to suit the needs of the particular monitoring programme. If the sampling interval is short, then this may result in only collecting small quantities of sediment. This is easily overcome by the deployment of more, or larger, sediment traps. The only potential problem with sediment traps is the possibility of contamination by resuspension of bottom sediments. This can be minimised by positioning the traps 1-2 m above the sediment surface. A sediment trapping programme is already in operation at all the lake sites in the AWMN.

This discussion has focused on the use of sediments in lakes. This is due to the limited amount of sediment accumulation taking place in streams. However, Mogollón *et al.* (1990) used river sediments to monitor for heavy metal pollutants from waste water drainage. Sediment concentrations of Fe, Mn, Cr, Co, Cu, Ni, Pb and Zn were analysed in the Tuy River, Venezuela between 1979 and 1986. It may also be possible to use sediment traps in streams to monitor for metals. The finest fractions of the sediment are likely to be best for this (Rippey, pers. comm.).

#### **2.4.3. Biota.**

The advantage of using bio-indicators to monitor for metals is that they supply an average metal concentration over a given time whereas a chemical measurement such as a water sample gives an instantaneous concentration which may or may not be representative of the biological availability of the metal to aquatic organisms (Celli, 1992). Suitable organisms for monitoring should be sedentary, abundant in a variety of environments and have a long life-span (Bonforte *et al.*, 1986).

##### **2.4.3.1. Diatoms**

The use of diatoms to indicate changes in environmental variables such as pH, nutrients and salinity is well documented (e.g. Battarbee, 1986, 1991; Dixit *et al.*, 1992). Diatoms are very sensitive to these variables and an assemblage will respond to even slight alterations to its environment. These floristic changes can be detected in the analysis of either living diatom communities, for example on rocks (epilithon) or plants (epiphyton), or fossil assemblages on the sediment surface or down a sediment core. In the case of fossil assemblages, environmental conditions can be reconstructed from the diatom record. It may be possible to use diatoms to monitor trace metals in two ways, by direct measurement of trace metal content and possibly by reconstruction from diatom assemblages where diatom tolerances to metals can be established.

Diatoms grow rapidly and accumulate trace metals. An artificial substrate placed in a lake or stream will become covered in diatom growth in a relatively short period of time. These can then be removed for analysis and an identical substrate replaced for the next sampling period. The diatom assemblage present should represent the average water quality over a period of weeks, but there may also be sufficient material to directly measure the metal content and this could be used as a monitoring tool. This technique was used to monitor trace metals in German rivers, where 30 x 30 cm glass plates were suspended in the water, parallel to the flow, for thirty days. After this period the growth was scraped off and analysed for trace metals (Pb, Cu, Zn, Cd and Hg) and organic compounds (e.g. PCB's) (Backhaus, 1991). Streams with high flow may actively remove growth from the substrate and so such samplers must be positioned with care.

Diatom assemblages have been used to infer concentrations of Ni, Al and Ca in Canadian lakes (Dixit *et al.*, 1991). However, it has been suggested that metal deposition is so closely related to acid deposition that the effects of metal concentration and pH on diatoms cannot be separated effectively. pH is so dominant that a metal reconstruction is only a poor pH reconstruction (Juggins pers. comm.). Further work is needed before diatoms could be used in this way. Preliminary research could be to establish which diatom species tolerate high concentrations by looking at metal gradients with constant pH.

#### 2.4.3.2. Macrophytes

Aquatic macrophytes and especially bryophytes have been used extensively to monitor trace metal pollutants for many years as part of individual studies (Whitton *et al.*, 1981; Caines *et al.*, 1985; Blake, 1992), and as part of national monitoring networks in, for example, Norway (Taugbol, 1990). The methods used are well established (e.g. Say *et al.*, 1981; Whitton *et al.*, 1981, 1982) and are now published in a Department of the Environment booklet prepared by the Standing Committee of Analysts in an attempt to standardise these procedures (Whitton *et al.*, 1991). These methods are discussed in detail in this booklet and will only be discussed briefly here.

A 'package' of ten aquatic plants common in many United Kingdom freshwaters in both lakes and streams is recommended. These are *Cladophora glomerata*, *Enteromorpha flexuosa*, *Lemanea fluviatilis*, *Nitella flexilis*, *Amblystegium riparium*, *Fontinalis antipyretica*, *Rhynchostegium riparoides*, *Scapania undulata*, *Elodea canadensis* and *Potamogeton pectinatus*. One or more of these plants are present in all the AWMN sites except for Round Loch of Glenhead and Llyn Cwm Mynach, but it may be possible to extend this 'package' to include species more common to upland waters. Of this

package of ten, *Scapania undulata* is probably the most useful as it is a widespread species and tolerant of high metal concentrations in waters (values of 7.0 mg Zn l<sup>-1</sup>, 0.028 mg Cd l<sup>-1</sup> and 1.74 mg Pb l<sup>-1</sup> have been recorded, but these may not be the tolerance limits (Whitton *et al.*, 1982)). It has been suggested that one reason why *Scapania* is so successful in waters with high metal concentrations, is that competition from other species is greatly reduced (Whitton *et al.*, 1982).

In places where these species do not exist, transplanting from clean sites using movable strata (such as boulders) and moss bags is a recognised procedure. Moss bags can be filled with several species, although *Fontinalis* and *Rhynchostegium* (Whitton *et al.*, 1991) and *Sphagnum* (Welsh & Denny, 1980; Denny, 1981) have been recommended. These can then be re-sampled after a suitable period and the metal accumulation established. Care must be taken in the use of transplanted species because of the risk that the species may spread and become a nuisance. This is particularly a problem where macrophyte distribution and long-term change is being studied (as at the AWMN sites).

One advantage with the use of macrophytes for trace metal monitoring is that field sampling and subsequent analysis are relatively simple. Usually the terminal 2 cm of the shoots are used as this length represents a compromise between one providing enough material for analysis and one reflecting growth over a period of weeks or months. (In the case of *Scapania undulata* this length is reduced to the terminal 1 cm). About 50 shoot tips then give sufficient dry material (25 - 50 mg (Say *et al.*, 1981)) for analysis. Only a very simple digestion of the material is necessary. Shoot tips were found to be the best indicators of current metal levels, older material being harder to clean as well as having accumulated metals over a long period. Only shoot tip concentrations (as opposed to whole plant concentrations) were found to have a good correlation with metal concentrations in the water (Whitton *et al.*, 1982). *Nuphar luteum* and *Sparganium* sp., species present in approximately half of the AWMN lake sites, have been used for trace metal monitoring in Finnish headwater lakes (Verta *et al.*, 1989b). Sampling of these plants involved collection of 10 whole young leaves for *N. luteum* and the top 10 cm of 50 - 100 leaves of *Sparganium*.

Aquatic macrophytes retain their trace metal content even after drying and careful storage (with the possible exception of Hg which is relatively volatile) and so it is possible to analyse plant material for metal content even after many years (Standing Committee of Analysts, 1987) and with some techniques, little pre-treatment (Satake *et al.*, 1981). Samples of each species from every site in the AWMN have been stored for each year of analysis, and although there are limited amounts of some of these species there is sufficient material to provide some metal concentrations for each year since

1988. Longer records may exist for some sites, for example, the River Etherow, as this was the subject of a more detailed study of the role of bryophytes (*Fontinalis* and *Rhynchostegium*) in monitoring trace metals such as Cr, Mn, Cu, Zn, Cd and Pb (Say *et al.*, 1981) some years before it was an AWMN site.

One problem with the use of bryophytes as monitors of metal pollution is that as pH decreases metal concentrations in the plant also decrease. This is because at low pH (higher H<sup>+</sup> concentration) H<sup>+</sup> ions replace metal ions in plant cells. Caines *et al.*, (1985) showed that metal loadings in bryophytes in an acidic stream in Scotland were strongly influenced by stream pH and suggested that below pH 5.5 metals could be released from the plant back into the water and become a 'source' of metal input into the stream. They also suggested that it may be possible that an acid episode could release sufficient trace metal from aquatic plants to exceed the lethal threshold for fish and other organisms.

#### 2.4.3.3. Invertebrates

Aquatic invertebrate species have many of the advantages for trace metal monitoring found in plants. They readily bioaccumulate metals enabling more dilute systems to be monitored and individual species are widespread across the United Kingdom. They have the advantage over some plant species, that larvae sampled at approximately the same time of the year will have been exposed to pollutants for roughly the same period of time. Consequently, the problem that occurs for macrophytes, of sampling only the most recent growth, does not occur for invertebrates and metal content will be reasonably comparable from year to year.

Hare & Campbell (1992) assessed the use of six aquatic insect taxa to monitor Cd, Cu and Zn over a 14 month period in a Canadian lake and found that there were considerable temporal fluctuations in concentrations of the metals in the insects, more so for Cd, a non-essential metal, than for Cu and Zn. They also indicated that it is still unknown (i) how metal burdens change as moulting and growth take place and (ii) what the rates of exchange of metals between insects and their environment are, and suggested that these questions must be addressed before aquatic insects could be effective biomonitors. Limiting temporal variability and using profundal sediment dwelling species gave the smallest fluctuations and this was recommended as the simplest way of using invertebrates for biomonitoring metal pollution.

There are other disadvantages with the use of invertebrates. Only the metal concentration of the same species can be compared between sites and so the problem arises of finding sufficient individuals of the right species to enable comparisons to take place. This number depends upon the species

concerned, and in the Finnish monitoring of metals in headwater lakes (Verta *et al.*, 1989b), the numbers recommended were 20 - 50 individuals for Trichoptera species (*Limnophilus* sp. and *Phryganea* sp.) and 1 - 5 individuals for dragonfly larvae (Odonata) and water beetles (Coleoptera). Another disadvantage of invertebrates is movement. Not only do some species have special mechanisms for dealing with metals, such as avoidance behaviour (Abel & Green, 1981), but in streams in periods of high flow invertebrates may be dislodged and travel downstream a considerable distance. Subsequent sampling of invertebrates may not be representative of metals affecting that section of the stream.

It may be possible to use invertebrates for monitoring in two ways. Firstly, by finding sufficient numbers of the individual species and measuring the metal content directly. It is unlikely that any individual species would occur in all sites in enough abundance to be used for metal monitoring in isolation and so this could perhaps be best done by using a 'package' of invertebrate species in the same way as has been used in macrophyte work (Whitton *et al.*, 1991). This 'package' would include species from different tolerance ranges, e.g. tubificid worms and chironomidae in areas of high metal pollution, Trichoptera species (caddis flies) at moderate levels and Ephemeroptera (mayflies) in waters with mild metal pollution (Winner *et al.*, 1980). Such a package covers a wide range of waters in the United Kingdom and these groups are common in the present AWMN sites.

The second possibility for monitoring with invertebrates would be to employ a 'trapping technique' using a standard substrate and analysing the invertebrate population present after a known period of time. It has been suggested that the composition of species in a community is a more evident response to metal pollution than the total number of species present (Hellawell, 1986) and so it may be possible to relate species diversity and abundance back to metal concentrations. However, as with diatoms it may be difficult to separate the effect of the metals from that of decreased pH (Nelson & Campbell, 1991).

#### 2.4.3.4. Fish

Although some metals such as Cd and Pb do not biomagnify along food chains, fish species, being amongst the largest freshwater fauna will have high concentrations of metals in their body tissues. This has obvious advantages for monitoring purposes as few fish need be sampled to provide sufficient material for metal analysis. Fish are also relatively easy to age and so samples from the same age class can be selected (usually 2+ or 3+ years) and this makes metal concentrations within a species and between sites fairly comparable.

Fish are usually collected by netting in lake sites and by electrofishing streams (or the outflow streams of lakes). Nets are generally set in lake sites in the evening and retrieved the following day. This means that sites must be visited two days in succession and for remote sites this can be very time consuming. However, the AWMN sites are already electrofished annually to assess stocks and it would take little extra time to collect fish of the correct species and age class for subsequent metal analysis.

From Section 2.2 it was seen that different metals tend to accumulate in different organs (Cu in liver, Zn in skeletal tissue etc.), but the composition of metals in organs can change through time and generally it is muscle tissue, gill tissue and occasionally the livers that are used for metal analysis. Lipids could also be sampled from the same fish for analysis of persistent organics (see Section 3). Digestion of fish material is also relatively simple using nitric acid and hydrogen peroxide (Verta *et al.*, 1989a) and metals are then determined using the same techniques as for waters and sediments (e.g. AAS or ICP/OES).

#### 2.4.4. Inputs to catchments.

Direct sampling of inputs to catchments would help to fully assess metal budgets within the freshwater ecosystem. This could be undertaken on different levels of sophistication from a bulk deposition collector sampled monthly up to semi-automatic weather stations incorporating wet and dry deposition samplers. Weather stations require a great deal of time, effort and money to set up and run and for metal monitoring only would seem rather extravagant and unnecessary. However, if collectors or stations were set up to look at other problems where they were more fundamental to the sampling strategy (e.g. climate change), then it would be a simple matter to sub-sample and analyse for metal content.

There are simpler and easier techniques available to monitor deposition of metals in particulate form. For example, tape peels on microscope slides exposed to the atmosphere for a set period can be taken from the sampling site and after coating put directly into an electron dispersive spectrometer (EDS) for immediate metal analysis without any pre-treatment. This can also be done using leaves from trees within a catchment, either deciduous for a seasonal pattern or coniferous needles for deposition covering several years. These also can be placed directly into the EDS for analysis after freeze-drying (Watt, pers. comm.).

## 2.5. Modification of the AWMN to monitor trace metal deposition.

### 2.5.1. Sites.

Section 2.3.3. discussed trace metal gradients across the United Kingdom and showed that there is evidence to suggest a region of high metal deposition in the north of England and the Midlands with concentrations decreasing away from this region. This suggests that an effective strategy for monitoring trace metal deposition might be to look at two series of sites, one series running north - south, and the other east - west. Lake sites appear to be the most suitable for monitoring metals as these systems are more stable than streams and through the use of sediment cores, allow historical and pre-contamination concentrations to be determined.

With these points in mind it is possible to look at a map of the AWMN (Figure 1) and see whether appropriate areas are covered by existing sites. For the north - south transect, the AWMN does well with a series of lake sites running down the western side of the country, although there are no lake sites further south than north Wales, and hence no further south than the high deposition zone. Because the sites are predominantly in the west, the east-west transect is less well covered with the Old Lodge stream site in the south-east being the sole site in the eastern half of England. Old Lodge is also on the borderline of being within 20-35 km of a major town (see Section 2.3.4.) and this criterion also excludes the River Etherow site. The River Etherow site should still be included in any metal monitoring however, as there is a great deal of data already in existence about metals there.

To effectively monitor for atmospheric deposition of trace metals 3 or 4 more lake sites should be chosen. (1) in the area of high deposition maybe in the north Midlands, (2) in East Anglia for the east-west transect, (3) in the south-east for both transects and to give another site for comparison with the stream site at Old Lodge and possibly (4) in the south west, again for both transects and to give a lake site in this region where at present there is only the stream site at Narrator Brook.

To monitor the impact of trace metal deposition on freshwater ecosystems in more detail, the effects of other environmental variables on metal availability and toxicity could be assessed by using a series of waterbodies that are subjected to the same metal deposition. Section 2.2. described the importance of pH and water hardness to the availability and toxicity of the various metals, and metal toxicity is more likely to occur in clearer waters (low dissolved organic carbon, DOC) as less complexing of the metal by organic compounds takes place (Nienke & Lee, 1982). Lakes with the same metal depositions but with a range of pH, or water hardness, or DOC concentration could be identified and the influence of each parameter on the metals within the freshwater / sediment / biota studied in isolation.

### 2.5.2. Parameters.

At present, only Cu, Zn, Fe and Mn are analysed in spot water samples (monthly for streams and quarterly for lakes). These are done using an ICP/OES at the Institute of Hydrology in Wallingford. It would therefore be a relatively simple and easy task to include more metals in this suite of analyses. No extra sample volume than is already being taken would be necessary, and if the rarer metals are found to be present in concentrations above the detection limits of the method it may be worthwhile analysing lake waters on a monthly basis.

Sediment metal profiles already exist for many of the lake sites, but for only a few metals (see Table 2.). As part of the AWMN re-coring programme, all the lake sites are cored every five years and sediment chemistry is one of the sets of analyses performed on the cores. Consequently, when the first set of coring and analyses are complete there will be full profiles for every lake site for Cu, Ni, Pb and Zn. These profiles will then be updated every five years. As with the waters, it is a relatively simple task to add extra metals to these analyses. The metals discussed in detail in Section 2.2. are probably the most important and so this would only mean the addition of Cd, Hg and possibly Cr to these analyses.

No metals are at present being analysed in sediment trap material or any of the biological samples. However, digestion of these materials into a suitable form for analysis is fairly quick and these could then be analysed in the same way as the water samples above.

### 2.5.3. Sampling.

It appears that sediments (cores and traps), macrophytes and fish are likely to be the most important components in monitoring for trace metals and this agrees with other reported findings (Wehr *et al.*, 1981). Water samples would also be useful if metal concentrations are above detection limits. The use of invertebrates and diatoms (either by direct measurement or population studies) would enhance this work although effective monitoring of metals could be done without them.

With the possible exception of more frequent water samples, little extra sampling would be necessary to monitor for metals, as all the components described above are already sampled annually. The collection of the necessary plant, invertebrate and fish samples would require little extra time and effort.



#### 2.5.4. Stored samples and data.

In addition to the metal analyses already undertaken on a regular basis (water samples, sediment cores) there is a large amount of stored material from the first five years of AWMN sampling. These include:

- acidified sub-samples from every spot water sample
- dried sub-samples from all core and sediment trap material
- dried samples of macrophytes from each site.

This archive of material could be used to 'back date' metal monitoring to the start of the AWMN sampling programme in 1988.

#### 2.6. Other networks and sampling strategies.

##### 2.6.1. United Kingdom.

A great deal of work has been done on trace metal concentrations in the freshwaters of the United Kingdom but little organised monitoring for atmospheric inputs. The literature shows studies on the chemistry of metals in freshwaters as well as the availability and toxicity of individual or groups of metals on the freshwater biota. Some of these studies have involved some monitoring using either a group of species at a single site (e.g. Say *et al.*, 1981) or a single species at a small group of sites (e.g. Whitton *et al.*, 1982) but these studies have generally lasted only a year or two.

There are also many studies involving metal profiles in sediment cores (e.g. Rippey *et al.* 1982; Haworth & Lishman, 1991), but these are often only concerned with a few sites and have not involved looking at trends spatially as well as temporally. The nearest to a network of sites is the analysis of a series of sediment cores across the United Kingdom for Pb and Zn as part of a wider study on atmospheric deposition (Battarbee *et al.*, 1988). Similarly, the Surface Water Acidification Project (SWAP), also involved the analysis of Pb and Zn in sediment cores taken in the United Kingdom, Norway and Sweden (Rippey, 1990). However, these projects involved the analysis of only one core from each site and so cannot be considered monitoring programmes.

##### The National Rivers Authority.

The National Rivers Authority (NRA) are involved in a number of water quality monitoring activities to fulfil both national and international obligations imposed by UK and European legislation. Existing monitoring programmes vary widely between regions and it is recognised within the NRA that a nationally consistent strategy is needed (NRA, 1992). The statutory requirements concerning trace

metal monitoring in fresh waters are outlined below although these deal primarily with direct discharges into water bodies rather than atmospheric inputs.

EC Directive 78/659/EEC sets out requirements for the "quality of fresh waters needing protection or improvement in order to support fish life". The Directive sets out the determinands to be measured and minimum sampling frequencies. Stretches of water were initially nominated by the former Regional Water Authorities and have been designated by Government for both salmonid and cyprinid (e.g. carp, tench) fisheries. The trace metal determinands are total Zn and dissolved Cu and permitted values vary according to water hardness. These are monitored monthly although total Zn need not be measured unless there is a known discharge and Article 702 of the Directive allows competent authorities to reduce the frequency of monitoring where it is recorded that the quality of the waters is appreciably better than the values set.

The Surface Water (Dangerous Substances)(Classification) Regulations 1989 (SI 1989/2286) cover the legislation for List I and List II substances. The metals included on List I are the same as the EC 'Black list' and the DoE 'Red List' i.e. Hg, Cd and their compounds. However, the persistent organic compounds differ (see Section 3.5.1.). The "Direction to the National Rivers Authority under section 146 of the Water Act 1989 and relating to Council Directives on discharges of dangerous substances" from the DoE requires the NRA to carry out monitoring of List I discharges. List I substances are monitored in waters receiving discharges from processes which have been identified to DoE. These include industrial plants as well as sewage treatment works and sewers. Water samples are analysed monthly.

In addition to monitoring waters in the vicinity of discharges, more general monitoring of background levels of List I substances in the aquatic environment is undertaken. The extent of National Network monitoring is left largely to the discretion of the NRA, although this monitoring is required to reflect the ubiquity of the substance and is concentrated in waters where substances are thought most likely to be detected in significant concentrations in relation to quality standards. There is also the requirement that the NRA should monitor all List I substances at the tidal limits of all significant rivers. These general requirements should be met by sampling at the existing network of sites known as the Harmonised Monitoring Scheme (see below). For some List I substances (including Hg and Cd) there is a requirement that levels in sediment and/or molluscs and/or fish flesh should not increase with time. The minimum frequency of this sampling is once a year and the samples are taken from identified sites at the same time each year.

List II substances include the metals: Pb, Cr, Zn, Cu, Ni, V and Fe (iron). There are no strict rules for the monitoring of these substances and the extent and sampling frequency is left to the NRA's judgement. However, the monitoring programme is required to show that quality objectives are being consistently achieved. The minimum sampling frequency is monthly.

The Harmonised Monitoring Scheme (HMS) was set up in 1974 by DoE to provide a network of sites at which river quality data could be collected and analysed in a nationally consistent manner. It enables estimates to be made of the loadings being carried to estuaries (here it links in with the Paris Commission's work on land-based inputs to the North Sea) and also allows long term trends in river quality to be assessed. There are over 250 sites in the HMS situated at, or just above, the tidal limit or in the case of major tributaries at, or just above, the confluence. The list of determinands measured at each site is extensive and covers 80 different parameters. These include the following trace metals: Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, Se, V, Zn, Sb, Ba, Be, Co, Mo, Te (tellurium), Tl (thallium), Sn, Ti, U and Ag. Average and instantaneous flows are measured to calculate loadings. Although the objectives of the HMS were to harmonise regional monitoring practises, different Regional Water Authorities selected different determinand suites, different frequencies and reported at varying intervals. Major differences still exist amongst NRA Regions (NRA, 1992).

In the final declaration of the Third North Sea Conference it was agreed that discharges of all substances that are persistent, toxic and liable to bioaccumulate should be reduced to levels that are not harmful to man or nature before the year 2000. These substances included all the existing List I and Red List substances, except PCBs, as well as dioxins and most of the List II metals. This list is known as the Priority Hazardous Substances List or the 'Extended Red List'. The NRA is required to carry out the necessary monitoring, except for dioxins, to enable Government to report on the progress in reducing inputs. As for the Paris Commission monitoring 12 samples are taken every year and these are generally from HMS sites.

#### The Natural Environment Research Council, Environmental Change Network (ECN)

The Environmental Change Network (ECN) was launched by the Natural Environment Research Council (NERC) in January 1992. At present there are 7 sites all of which are part of the NRA's Harmonised Monitoring Scheme:

- 1) Cringle Brook at Thunder Bridge
- 2) River Coquet at Tyelaw Burn
- 3) River Eden at Temple Sowerby

- 4) River Lathkill at Alport
- 5) River Exe at Thorveton
- 6) River Esk at Ruswarp
- 7) River Wye at Redbrook

These are all lowland sites and it is hoped that upland sites (e.g. AWMN sites) may also be included in the future. Surveys for invertebrates, macrophytes and fish are undertaken at all the sites and water samples taken monthly. These are analysed for a suite of determinands including total concentrations of the following trace metals: Cu, Ag, Zn, Cd, Sn, Pb, V, Cr, Mn and Ni.

#### The Institute of Freshwater Ecology.

Over the years, the Institute of Freshwater Ecology (IFE) and its predecessor the Freshwater Biological Association have undertaken a large number of studies on all aspects of the freshwater ecosystem. Some of these have involved the regular monitoring of waterbodies, especially in the Lake District, for long periods of time. e.g. 'The Lakes Tour', a sampling programme which has been running for over 20 years where water chemistry for all the lakes in the Lake District has been measured every few years. Routine determinands for this monitoring do not include trace metals but metal analyses have been performed on samples taken on this programme where this has been part of other projects.

There has been no specific long term monitoring of trace metals in the aquatic ecosystem by the IFE, but metal analyses have been undertaken at some sites over a number of years for different projects and so to a certain extent long term metals data do exist for waters, sediments and biota in certain regions.

#### The Institute of Hydrology.

The Institute of Hydrology (IH) monitor trace metals in waters at three stream sites in Wales, the Afon Hore, Afon Hafren and Afon Gwy (Afon Hafren and Afon Gwy are AWMN sites). Samples are taken weekly and analysed for a full suite of elements using ICP/MS including the following: Mn, Cu, Fe, Co, Zn, Al, Be, Ni, Pb, Cr, Ba, Y and Sr. 'Sub-trace' elements such as Cs and Au are analysed less frequently. IH also measured trace metals on a weekly basis for 9 years at their Plynlimon site in Wales. This included measuring metals in rainfall, throughfall and run-off in the catchment area.

#### The British Geological Survey (BGS)

The British Geological Survey are in the process of producing maps of a number of trace metals in waters using ICP/MS. This work is to determine metal distribution in groundwaters and water samples are taken on a 1 km<sup>2</sup> basis. Springs are sampled preferentially if present within the square, but if not then streams at base flow are sampled, and if these are not present, a standing water body is sampled. So far, maps of Northern Ireland, Galloway and north Wales have been produced.

#### The Scottish Office Agriculture and Fisheries Department (SOAFD).

The Scottish Office Agriculture and Fisheries Department (SOAFD - formerly DAFS) monitored metals (Pb, Zn, Cu, Mn and Al) in lochs in many areas of Scotland (Galloway, Dunnett Head, Trossachs, Scourie, Rannoch, Glencoe and Forsinard) between 1978 and 1981. (Harriman, pers. comm.) The same metals were measured in Brown trout in 1975-76 at the following sites: Loch Mhuchraidh, Loch Ordie, River Solway, Loch an Duin, Loch Broom, Loch Pattach, Loch Watten, River Don and Crag Lough. Over the same period, the same metals were measured in sea-trout in the following rivers: Spey, Dee, Findhorn, Tweed, Solway, North Esk, Tay, Laxford, Achiltibuie and Dovne. This monitoring is no longer in operation.

#### Others.

The Scottish River Purification Boards undertake some metal analyses, but these are mostly on larger rivers. This metal monitoring is directly concerned with metal inputs into these rivers from industrial and domestic effluents and hence are not suitable for monitoring atmospheric inputs of metals to these systems.

The Water Research Centre (WRC) undertake no long term monitoring of trace metals. There have been short studies, covering a period of about a year where rain gauge samples were analysed for metals but these are no longer in progress.

The Warren Spring Laboratory run the United Kingdom Acid Rain Monitoring Network for the DoE. This includes 32 sites covering the United Kingdom, 5 primary sites where measurements are taken daily and 27 secondary sites where measurements are taken weekly. Precipitation samples are analysed for a range of parameters, but these do not include trace metals.

At present in the United Kingdom there is no long term national monitoring of trace metal deposition from the atmosphere to freshwaters. The only monitoring currently taking place is through air sampling

and the direct analysis of metals in deposition. There are two networks in the United Kingdom both running four sampling stations and these have already been discussed in Section 2.3.3.1.

### **2.6.2. International**

The Global Environment Monitoring System (GEMS) collates data from a global network of 300 lakes, rivers and groundwater sites of which 12 are in the United Kingdom. These are some of the major freshwater systems in the country: River Thames, River Avon, River Exe, River Trent, River Dee, River Leven, River Mersey, River Tweed, River Carron, Lough Neagh, Rutland Water Reservoir and Tunstall Reservoir. The rivers are sampled fortnightly and the lakes bi-monthly and the trace metals analysed are Cr, Mn, Fe, Ni, Cu, Zn, Cd, Hg and Pb. Apart from Mn and Fe these are the same metals recommended in Section 2.5.2. These systems are so large and their catchments so extensive that little of the metal input would be atmospherically derived. GEMS is sponsored by the United Nations Environment Programme (UNEP), the World Health Organisation (WHO), the United Nations Educational, Scientific and Cultural Organisation (UNESCO) and the World Meteorological Organisation (WMO) and as such this monitoring is more concerned with total concentrations of pollutants rather than specific origins.

Since 1991, the chemical and biological data from six AWMN lake sites have also been contributed to the GEMS network. These sites are: Lochnagar, Loch Coire nan Arr, Llyn Llagi, Blue Lough, Scoat Tarn and Round Loch of Glenhead. These are the same data from the same sites as are included in the UNECE Integrated Co-Operative Programme (ICP) for Waters (run by NIVA in Norway) as all data from the IMP are made available to GEMS.

In addition, data from two AWMN stream sites, the Allt a' Mharcaidh and the Afon Hafren are contributed to the ICP on Integrated Monitoring. Within the United Kingdom this is co-ordinated by Dr Alan Jenkins at the Institute of Hydrology.

### **2.7. Conclusions.**

Little modification of the present United Kingdom Acid Waters Monitoring Network would be needed to effectively monitor the atmospheric deposition of trace metals to freshwaters across the country. An extra 3 or 4 lake sites in addition to the present Network would give good coverage of the major metal deposition gradients. A few metals are currently analysed in the spot water samples and in the sediment cores taken every five years. Sub-samples of cores, sediment trap material, water samples and dried macrophytes have been stored and extra metals could be measured relatively easily.

The use of aquatic macrophytes and especially bryophytes for monitoring trace metals is well documented and their use would be a simple and effective monitoring tool. In addition, the measurement of metals in fish tissue, invertebrates and diatoms could be easily undertaken and this would give a more comprehensive overview of metal contamination in the freshwater ecosystem.

### 3. PERSISTENT ORGANIC COMPOUNDS.

#### 3.1. Introduction.

There are similarities between the ways in which trace metals and persistent organic compounds (POCs) behave in the freshwater ecosystem. Both are deposited from the atmosphere in trace quantities and it is their affinity to complexation, especially to organic matter, that leads to the bioaccumulation of potentially toxic levels in freshwater biota. For this reason many of the ideas discussed in this section relating to organic compounds will already have been dealt with more fully in Section 2 on trace metals.

Differences between the two groups of pollutants occur when quantities are considered. Whereas trace metals in the aquatic environment are measured in terms of  $\text{mg l}^{-1}$  and  $\mu\text{g l}^{-1}$ , for POCs the equivalent measurements are  $\text{ng l}^{-1}$  and  $\text{pg l}^{-1}$ , are six orders of magnitude less. However, many groups of organic compounds are far more toxic than trace metals and thus only need be present in these much reduced quantities to have damaging effects on biota.

The EEC 'Black list' includes only two metals (Hg and Cd) and their compounds whilst the remaining six substances on the list are groups of toxic organic compounds and their derivatives. These substances were selected mainly for their toxicity, persistence or bioaccumulation and are listed in Table 5. All the metals apart from Hg and Cd mentioned in Section 2 are present on the EEC 'Grey list', described as 'less dangerous than those of the 'Black List' and the impact of which may be local'. Similarly, the Department of the Environment has a 'Red list' identifying a number of dangerous substances with the aim to control the input of these substances to the aquatic environment. These substances, listed in Table 6, are also known as 'Prescribed substances under SI 1156' and come under the control of Her Majesty's Inspectorate of Pollution (HMIP).

Another difference is that some metals (e.g. Cu, Zn) are essential to life and deficiency can be harmful to organisms. On the other hand, of the groups of organic compounds considered here, none are essential to life, all are pollutants and all are potentially toxic to a greater or lesser degree.

In terms of assessment and monitoring of POCs in the aquatic environment all groups of compounds can be treated in a similar way. However, some of the more common (and therefore potentially more ecologically damaging) classes are discussed in more detail below.



**Table 5.** Organic substances included in the EC 'Black list'.

- Organohalogen compounds and substances which may form such compounds in the aquatic environment.
- Organophosphorus compounds
- Organotin compounds
- Substances, the carcinogenic activity of which is exhibited in or by the aquatic environment.
- Persistent mineral oils and hydrocarbons
- Persistent synthetic substances

**Table 6.** Organic substances included on the Department of the Environment's 'Red List'.

- $\gamma$ -Hexachlorocyclohexane ( $\gamma$ -HCH, Lindane,  $\gamma$ -BHC)
- DDT
- Pentachlorophenol (PCP)
- Hexachlorobenzene
- Hexachlorobutadiene
- Aldrin
- Dieldrin
- Endrin
- Carbon tetrachloride
- Polychlorinated biphenyls (PCBs)
- Dichlorvos
- Dichloroethane
- Trichlorobenzene
- Atrazine
- Simazine
- Tributyltin
- Triphenyltin
- Trifluralin
- Fenitrothion
- Azinphos-methyl
- Malathion
- Endosulfan

Although organotins are on the EEC 'Black list' and the DoE 'Red list' and can have chronic toxic effects at aqueous concentrations of a few  $\text{ng l}^{-1}$  (Fent *et al.*, 1991), they will not be dealt with here as the main sources of these compounds affecting the aquatic environment are from industrial wastewaters and sludges, landfill leaching and antifouling paint on boats (Fent & Hunn, 1991). None of these sources are atmospheric.

### 3.1.1. Polycyclic Aromatic Hydrocarbons (PAHs).

PAHs are composed of two or more fused aromatic (benzene) rings. Two aromatic rings are said to be fused when a pair of carbon atoms are shared and the resulting structure is a molecule with all carbon and hydrogen atoms lying in a single plane. The simplest structure is that of naphthalene ( $\text{C}_{10}\text{H}_8$ ) where only two rings are fused and this is the PAH of lowest molecular weight (see Figure 4a). The PAH of most concern are the large number of compounds that fall in the molecular weight range from naphthalene to coronene ( $\text{C}_{24}\text{H}_{12}$ ) (Figure 4f) as these are most mobile in the environment. Physical and chemical characteristics vary in a more or less regular fashion with molecular weight, for example, resistance to oxidation or reduction decreases with increase in molecular weight and aqueous solubility decreases virtually logarithmically with increasing molecular weight (Neff, 1979). Consequently, PAHs of differing molecular weight vary substantially in their behaviour in the environment and their effects on biological systems. However, two molecular weight classes can be distinguished on the basis of physical, chemical and biological properties. These are the 2-3 ring low weight compounds (e.g. naphthalene, fluorene, phenanthrene) and the 4-7 ring high weight compounds (e.g. chrysene, benzo[a]pyrene, coronene) (see Figure 4).

The presence of PAHs in waters, sediments and organisms has been recognised for 25 years. With the development of sensitive, high resolution techniques for the analysis of PAHs in environmental samples, it has become apparent that complex mixtures of PAHs, including carcinogenic forms such as benzo[a]pyrene are nearly ubiquitous pollutants of aquatic ecosystems.

PAHs have low aqueous solubilities and this reflects their nonpolar, hydrophobic nature. The water phase is energetically unfavourable for such pollutants (Jaffé, 1991) and so PAHs entering waters from the atmosphere are readily adsorbed to organic and inorganic matter to become incorporated in sediments and biota. Other routes of removal of PAHs from waters, such as volatilisation, photo-oxidation, chemical oxidation and metabolism result in concentrations of PAHs in waters being the lowest in the aquatic ecosystem. Removal pathways such as these depend on various physical, chemical and biological parameters of the compound (chemical stability, resistance to biodegradation,

lipophilicity, solubility) and the characteristics of the particular aquatic environment, such as temperature, pH, oxygen content, dissolved organic matter, types of biota etc. (Jaffé, 1991).

The characteristics of PAHs which makes the water phase energetically unfavourable also makes sediments energetically highly favourable and PAHs tend to be greatly enriched in the inorganic and organic suspended particulate fraction in the water column (Neff, 1979). These particulates gradually settle out and the adsorbed PAHs, once deposited, are less available for photochemical or biological oxidation. Sedimentary PAHs are therefore stable, persistent and, especially where the sediment is anoxic, can potentially remain adsorbed for even 'geological' time periods. This allows PAHs in the sediments to accumulate to high concentrations, usually over 1000 times higher than the overlying water and the subsequent PAH assemblage can serve as a guide to the rates of input to the aquatic environment (Neff, 1979). PAHs in sediments show good geographical resolution, but the composition of the sedimentary assemblage may be different from that of the PAH source due to differential partitioning between the water and sediment phases (Dunn & Stich, 1976).

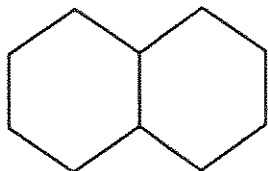
Lipid/water partition coefficients favour the rapid transfer of PAHs from the aqueous phase into a biotic phase, for example, biological membranes and lipid stores in organisms (Neely *et al.*, 1974). Release of PAHs from tissues of contaminated organisms may be passive (i.e. an equilibrium distribution exists between the aqueous and lipid phases) or active, whereby PAHs are transformed into polar, water soluble metabolites which are easily removed.

PAHs interact with cells to cause toxic responses in two ways. Firstly, by binding reversibly to lipophilic sites in the cell and interfering with cellular processes, and secondly, they can bind covalently to cellular structures causing long-term damage. PAHs have been shown to increase the permeability of plant cells to water by binding to the plasma membrane. PAHs also disrupt chloroplasts, interfering with the light reactions of photosynthesis, those in the C<sub>8</sub> - C<sub>14</sub> range being most toxic. PAH induced cancer-like growths and developmental anomalies have also been reported in several aquatic plants (Neff, 1979). Inhibition of photosynthetic activity has been reported for many species of algae (e.g. *Chorella vulgaris*, *Chlamydomonas angulosa*, *Fragilaria* sp.) after short exposures to relatively high concentrations (20 ppm for 2 hours) (Kauss & Hutchinson, 1975), but at lower concentrations, (e.g. 10 - 20 µg l<sup>-1</sup>), several PAHs have been reported to stimulate growth in both algae and higher plants (Graf & Nowak, 1966).

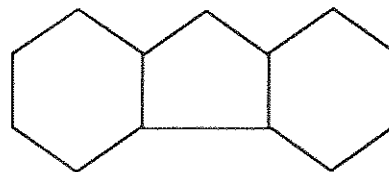
**Figure 4. Examples of Polycyclic Aromatic Hydrocarbons (PAHs)**

Polycyclic Aromatic Hydrocarbons (PAH)

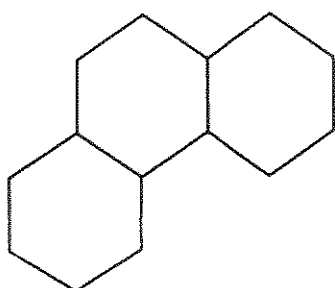
a) Naphthalene



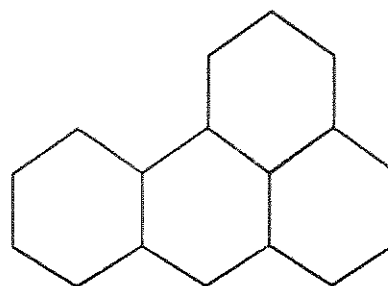
b) Fluorene



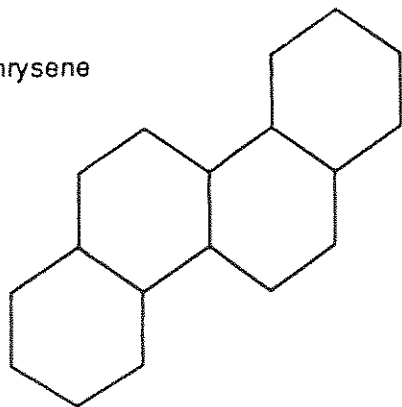
c) Phenanthrene



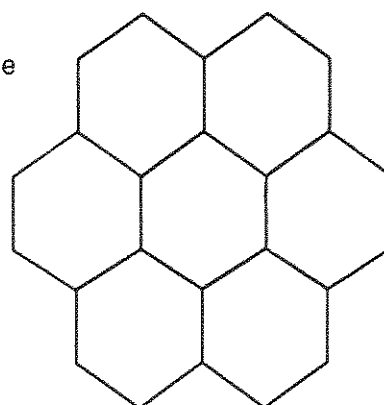
d) Benzo [a] pyrene



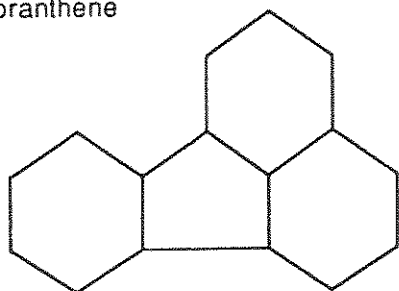
e) Chrysene



f) Coronene



g) Fluoranthene



PAHs are acutely toxic to aquatic animals at concentrations above 0.2 ppm, although deleterious sub-lethal responses have been observed in the 5 - 100 ppb range. Although aquatic fauna are able to accumulate PAHs from water, food and sediments, sediment adsorbed PAHs have only limited availability and benthic animals rarely contain higher levels of PAH than the sediments in which they live. In general, acute toxicity of PAHs to a particular species increases with increasing molecular weight, except at high molecular weights where toxicity is low due to very low solubilities. Many studies (e.g. Environmental Protection Agency, 1970; Anderson *et al.*, 1974) have been undertaken on the toxicity of different PAHs on both marine and freshwater species and in all but a few cases the concentrations that are acutely toxic to aquatic animals are several orders of magnitude higher than the most heavily polluted marine and fresh waters. In general however, crustaceans are the most sensitive to PAHs, polychaete worms intermediate in sensitivity and fish the most resistant. Studies have shown that carcinogenic PAHs can produce cancer-like growths in some aquatic invertebrates and vertebrates, but there are no reports of this taking place with PAHs at environmentally realistic levels. The incidence of these growths in tissues of natural populations of freshwater invertebrates and fish is increasing, although no carcinogenic PAH has been unequivocally identified as the cause in any natural population of aquatic organisms (Neff, 1979). As noted above, aquatic animals have the ability to metabolise PAHs and excrete the more soluble products. Even species lacking these abilities are able to release accumulated PAHs rapidly when returned to a PAH-free environment. Consequently, food-chain biomagnification occurs only to a very limited extent, if at all.

### 3.1.2. Organochlorine compounds.

Organochlorine compounds are a large class of chemicals including industrial organics (e.g. PCBs), agricultural organics (DDT, HCH, aldrin) and by-products of anthropogenic activities (PCDDs, PCDFs). They are important environmental contaminants due to their high stability and persistence, high bioaccumulation and biomagnification potential and high toxicity. Organochlorine compounds are now ubiquitous in the global ecosystem and have been detected even in remote regions such as the Arctic and Antarctic (e.g. Oehme, 1991). There are no proven natural sources of these substances and consequently there is no natural background level in the environment and any level represents environmental contamination. Two classes are discussed in more detail below, although many of the characteristics discussed, for example, low water solubility, high lipophilicity and high bioaccumulation factors apply to all organochlorine compounds.

### 3.1.2.1. Polychlorinated Biphenyls (PCBs)

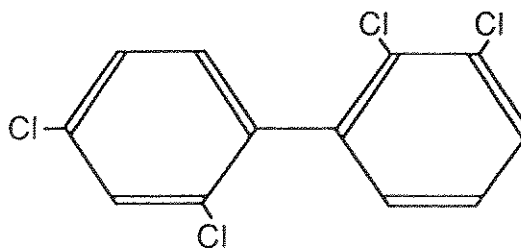
PCBs are a group of chlorinated hydrocarbons manufactured by the controlled chlorination of the biphenyl molecule. Chlorine replaces hydrogen at two or more sites (Figure 5) so that more than 200 compounds are possible. The stability of PCBs is unique. They are resistant to acid-base reactions, hydrolysis, chemical oxidation, photodegradation, thermal changes and most chemical agents and it is these characteristics that make them industrially desirable. However, they are also the characteristics which make them persistent in the environment (Sonzogni & Swain, 1984) and difficult to metabolise by biological systems. Although water solubility is low (and decreases with increasing chlorination), PCBs are extremely soluble in oils and fats, and this coupled with high persistence and low metabolism means that they tend to bioaccumulate in the food chain. PCB concentration often increases by several orders of magnitude at each trophic level and accumulation factors of 50,000 are widely reported for fish (Mayer *et al.*, 1977). Nebeker *et al.* (1974) reported bioaccumulation factors of over 270,000 in a species of fathead minnow.

Like PAHs, PCBs are readily adsorbed onto organic and inorganic matter suspended in the water column. This results in significant partitioning between the water and sediment phases. Studies in Canada (summarised in Strachan, 1988) show PCB concentrations in river waters to be in the range 0.2 - 0.4 ng l<sup>-1</sup> (0.0002 - 0.0004 µg l<sup>-1</sup>), in suspended sediments 0.9 - 1.5 ng l<sup>-1</sup>, and in bottom sediments about 0.01 µg g<sup>-1</sup>. Values for fish in these waters were also in the region of 0.01 - 0.07 µg g<sup>-1</sup>.

Sanders *et al.* (1992) show the results of analyses for PCBs and DDT (and its metabolites) for a dated sediment core taken from Esthwaite Water in the Lake District. The maximum flux of PCBs was 3.26 ng cm<sup>-2</sup> yr<sup>-1</sup> at 10 - 12 cm depth (1963) followed by a general decrease to the surface. PCBs were detected in sediment layers corresponding to dates prior to 1954 when PCB production in the UK first started and it is suggested that this may be due to long-range transport from across the Atlantic and from Europe. However, PCBs were also detected prior to 1929, before industrial synthesis began and this is thought to be possibly due to combustion processes and/or biogenic production. Problems with dating may also have occurred due to sediment amalgamation from different cores. DDT and its metabolites (DDD, DDE) followed similar trends with a peak in concentration at 1958 followed by a decrease to the surface of the sediment core.

**Figure 5. Polychlorinated biphenyls (PCBs)**

Polychlorinated Biphenyls  
e.g. 2,2',3,4' - Tetrachlorobiphenyl



There is little literature on the effect of PCBs on aquatic plants and early studies seemed to imply that they were not particularly sensitive except at very high concentrations. For example, algal growth was inhibited at PCB concentrations of 10 - 100  $\mu\text{g l}^{-1}$  (Christensen & Zielski, 1980). However, in one freshwater study in Lake Huron, it was demonstrated that a concentration of 5  $\text{ng l}^{-1}$  of hexachlorobiphenyl inhibited photosynthesis in a natural phytoplankton community (McNaught *et al.*, 1984). It is thought that inhibition of photosynthesis is the most sensitive plant response to PCBs (Conner, 1981). Higher levels of PCBs (1 - 5  $\mu\text{g l}^{-1}$ ) have been shown to effect chlorophyll-a and cell biomass in phytoplankton and diatoms, inhibit algal growth and effect long-term species composition (Strachan, 1988).

Aquatic invertebrates are more sensitive to PCBs than fish. Being lower in the food chain than fish, bioaccumulation factors tend to be lower, e.g. 3,800 for *Daphnia magna*, 750 for *Pteronarcys dorsata* (Mayer *et al.*, 1977), although values of up to 108,000 have been recorded for *Gammarus pseudolimnaeus*. Exposures to 0.1  $\mu\text{g l}^{-1}$  PCB for two weeks resulted in death of midge larvae and pupae, impairment of reproductive ability in *Daphnia*, and the inability to metamorphose in mosquito larvae (Nebeker & Puglisi, 1974).

There have been many studies on the acute toxicity (i.e. 96 hr LC<sub>50</sub> tests) of PCBs on fish, but these values are generally many orders of magnitude higher than would be found in environmental conditions. Longer tests e.g. 30 day LC<sub>50</sub>, have values in the region of 3 - 5 µg l<sup>-1</sup>. Sub-lethal effects occur at much lower concentrations (0.1 - 0.5 µg l<sup>-1</sup>) over longer time periods and effect growth, backbone development and reproduction. Increased mortality was reported in lake trout at levels of 0.05 µg l<sup>-1</sup> over a period of 50 days (Seelye & Mac, 1981) and it is long exposure at lower PCB concentrations which is a more environmentally realistic situation. PCB levels of 12 - 70 ng g<sup>-1</sup> have been reported in the tissues of Canadian river fish (Strachan, 1988).

### 3.1.2.2. Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs).

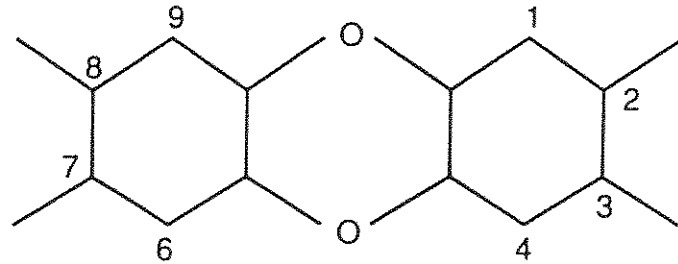
Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are often grouped together under the general term 'dioxins'. This can cause confusion as there are structural differences between the two groups (Figure 6) and so they are best separated. PCDD/Fs, like PCBs, are compounds composed of two linked aromatic rings which are polychlorinated. The differences between these three groups of compounds arise from the way that the two rings are linked. In PCBs the two rings are linked by a carbon - carbon bond (see Figure 5), in PCDDs they are linked by two oxygen atoms (see Figure 6a) and in PCDF's the link is made by a carbon - carbon bond and a single oxygen atom (Figure 6b). There are 210 PCDD/Fs but generally it is the seventeen 2,3,7,8-chlorine substituted compounds which are of most interest due to their toxicity and carcinogenic potential (DoE, 1989). The most toxic PCDD/F is 2,3,7,8-TCDD which is given a toxic equivalent (TEQ) of 1.0. The toxicity of other PCDD/Fs can then be compared with this. PCDD/Fs are not produced commercially and are the unwanted by-products of chemical production (i.e. PCBs and herbicides) and combustion processes (e.g. incineration plants, domestic fires, vehicle exhausts) (DoE, 1989; Harrad *et al.*, 1991).

Like the other classes of POC already discussed, PCDD/Fs are highly lipophilic and have very low water solubilities, (for example, 2,3,7,8-TCDD has a solubility in the range 8 - 19 ng l<sup>-1</sup>) (Fletcher & McKay, in press) and this decreases with increasing chlorine content (DoE, 1989). In the aquatic environment solubility is effected by temperature and the presence of dissolved organic matter. A high degree of water/sediment and water/biota partitioning therefore takes place and upon entering the aquatic environment PCDD/Fs are readily adsorbed onto organic particulates suspended in the water column. Associations of PCDD/Fs with inorganic particulate material itself maybe relatively unimportant, but clay minerals coated with organic matter are potentially important sites for adsorption (Hart, 1982). No figures exist for concentrations of PCDD/Fs in natural waters where there has been no specific contamination as the values are below the limits of detection.

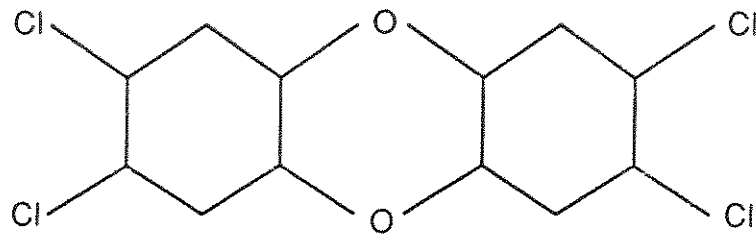


Figure 6. Structure of (a) PCDDs and (b) PCDFs.

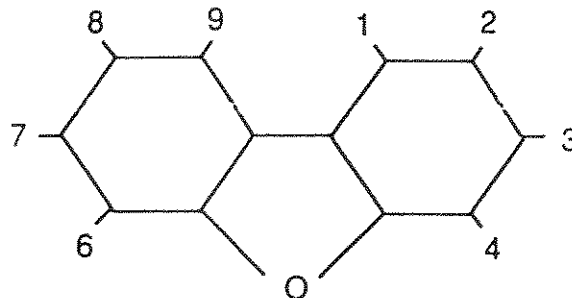
a) Polychlorinated dibenzo - p - dioxin (PCDD)



e.g. 2,3,7,8 - Tetrachlorinated dibenzo - p - dioxin (2,3,7,8 - TCDD)



b) Polychlorinated dibenzofuran (PCDF)



Due to the affinity of PCDD/Fs to particulate organics suspended in the water column, the settling of these particles is important to the fate of PCDD/Fs and also to the introduction of these compounds into the aquatic food chain. Particulate-associated PCDD/Fs may be ingested, taken up through the gills or desorbed and taken up in dissolved form (Broman *et al.*, 1989). Once deposited, remobilisation of sediment-associated PCDD/Fs can take place due to physical processes such as water turbulence and the release of gas bubbles and biological processes such as bioturbation. However, once incorporated into the sediment PCDD/Fs are stable and relatively immobile (Czuczwa & Hites, 1984) and this is an important consideration in sediment core studies.

Reported concentrations of PCDD/Fs in freshwater sediments vary considerably from 4.5 ppt (parts per trillion  $\equiv$   $\mu\text{g g}^{-1}$ ) which was considered to be a baseline value (Reed *et al.*, 1990), to 40 ppb (parts per billion  $\equiv$   $\text{ng g}^{-1}$ ) in the Saginaw River, Lake Huron (Czuczwa & Hites, 1984). There has been no published work on PCDD/Fs in the freshwater sediments of the United Kingdom, although work is being undertaken at four sites in Galloway, Northern Ireland and southern England by AEA Environment & Energy (Harwell) on behalf of the DoE (Air Quality). The results of this work are currently not available.

Little has been reported on PCDD/Fs in freshwater plants and invertebrates. Crunkilton *et al.* (1987) reported a 2,3,7,8-TCDD concentration of  $12 \mu\text{g g}^{-1}$  for a 'composite of benthic macroinvertebrates' including stream dwelling insects, crustaceans and annelids in the Spring River, Missouri.

There is however, a large literature on PCDD/Fs and fish, although a lot of this work has been laboratory based. Fish studies from natural waters are difficult to compare as different sampling procedures have been followed, notably the use of whole fish or fillets (more important for human impact work) or the assessment of fish lipid content. Fish PCDD/F content is greatly effected by sediment concentrations and it has been suggested that in steady state conditions the concentrations of PCDD/F in fish fat could be predicted from known sediment concentrations (van der Weiden *et al.*, 1989). In pollution studies in natural waters, fish have generally been used in association with other media, for example sediments (e.g. Stalling *et al.*, 1983), or in combination with sediments and invertebrates (Crunkilton *et al.*, 1987). Reported PCDD/F concentrations in river fish (fillet or whole fish) range between 4 -  $120 \mu\text{g g}^{-1}$ .

## 3.2. Sources and gradients of POCs.

### 3.2.1. Sources.

Most POCs that are of environmental concern in the freshwater ecosystem are not produced naturally. All organochlorines are either produced commercially (PCBs, insecticides such as DDT, HCH etc.) or are unwanted products of combustion and chemical production (PCDD/Fs).

PAHs are an exception and can be produced in three ways. (1) high temperature pyrolysis of organic materials, (2) low to moderate diagenesis of sedimentary organic material to form fossil-fuels, and (3) biosynthesis by microbes and plants. Heit *et al.* (1988), suggested that high efficiency fossil-fuel fired power stations are minor sources of PAHs compared with coal related residential heating and industrial combustion. Non-technological sources such as uncontrolled combustion in forest fires, volcanic activities and agricultural burning are also thought to contribute significantly (1 - 20% total PAH) to global annual emissions (Björseth *et al.*, 1979).

POCs enter the atmosphere either from direct emission or from wind-blown agricultural sprays. These substances can be carried thousands of kilometres before deposition. Non-atmospheric sources include sewage, agricultural run-off and industrial discharges.

### 3.2.2. Spatial patterns of POC deposition in the United Kingdom.

With trace metals it is possible to establish approximate metal deposition gradients across the United Kingdom from lake sediment and atmospheric sampling data (Sections 2.3.3.1 & 2.3.3.2). These data give a relatively incomplete picture as there are areas of the country where such data are not available. However, it does enable a high deposition region to be identified in the Midlands/north England area with deposition decreasing away from it. The situation for POCs is even less well established. There are so few reference points on the potential deposition map that it is impossible to draw any firm conclusions.

As part of the Paris Commission's Comprehensive Atmospheric Monitoring Programme (CAMP) (see Section 2.3.3.1.) aerosol, gas and precipitation samples are analysed for certain organic compounds (HCH, PCBs, insecticides etc. see Section 3.5 for the full list), at three of the four British sites. These are the sites on the east coast at East Ruston, Staxton Wold and Banchory. From the results for 1989 (CAMP, 1990), there appears to be no particular spatial pattern in concentrations of POC and it is not justifiable to identify patterns from so few data points.

The same is true with lake sediment data. Rippey (1990), discussed PAH concentration profiles for some Scottish lochs as part of the Surface Waters Acidification Project (SWAP). These were Loch Tinker and Loch Chon from the Trossachs, Round Loch of Glenhead in Galloway, Loch Doilet and Lochan Dubh from north-west Scotland and Lochan Uaine from the Cairngorms. Round Loch of Glenhead, Loch Tinker and Loch Chon are Acid Waters Monitoring Network (AWMN) sites. Benzo[a]pyrene concentrations for high acid deposition sites in Scotland (Loch Chon and Loch Tinker) were shown to be intermediate to high acid deposition sites in Scandinavia (Lilla Öresjön in southern Sweden and Verevatn in southern Norway), and low acid deposition sites in north-west Scotland. These results are concentrations rather than fluxes and so cannot be compared too closely, but the correlation between acid deposition and PAH deposition is notable.

Few other data exist for POCs in United Kingdom freshwaters and sediments. The GEMS programme reports some POC analyses (see section 3.5), but these are mostly on the waters of major river systems and so cannot be compared with the data from small upland sites.

As PAH concentration profiles in lake sediments show good agreement with known historical and spatial distribution of acid deposition, it might be expected that this trend would continue over the rest of the United Kingdom. If this were the case then PAH deposition gradients would follow the same patterns as those of sulphur and, by inference, trace metals. The major sources of PAHs are similar to those of acid deposition and trace metals, but this is not the case for all POC substances and it should not be concluded that all groups of organic compounds follow this same distribution pattern. There are virtually no data on the distribution of other POC classes in freshwaters and so alternative distributions for these are difficult to assess. The best way to monitor POCs in freshwaters might therefore be to study a series of sites on north-south and east-west transects, similar to those discussed in Section 2. This would cover the proposed gradients for PAHs and would also include all parts of the United Kingdom should subsequent work find that other POC classes do not follow this distribution pattern.

### 3.2.3. Local effects

As discussed in Section 2.3.4., local sources of pollutants can swamp the national deposition pattern, but they usually only affect a limited number of water bodies. These sources can be extremely localised, for example agricultural run-off effecting a single water body or a small atmospheric source affecting a few localised lakes and streams.

Heit (1985) suggested that PAH inputs from local sources decline in concentration very rapidly with distance from the source. The effect of a coal-fired power station was only seen in lake sediments within 24 km of the source and beyond this point concentrations once again reflected a region-wide pattern of deposition. Windsor & Hites (1979) suggested a similar rapid decrease but over a larger area. They found that total PAH concentration in marine sediments decreased by three orders of magnitude to a background concentration within 90 km of a major urban centre, in this case, Boston, U.S.A.. McVeety & Hites (1988) reported that lake sediment results agreed with these findings.

It appears that it may be necessary to ensure that monitoring sites are further from major urban centres than from individual sources. However, more localised effects such as agricultural sprays and run-off may have a more dramatic effect on POC concentrations and these impacts should be assessed very carefully before sites are included in a POC monitoring programme.

### 3.3. Methods of monitoring atmospheric POC inputs to freshwaters.

#### 3.3.1. Potential problems.

There are three main potential problems with monitoring POCs in the aquatic environment. Firstly, inputs are often episodic. This is a problem for all atmospheric pollutants which are present only in trace quantities. Changes in meteorological conditions on a daily or even hourly basis, alter inputs to freshwater bodies. For example, in a study on PAHs in the River Derwent, Evans *et al.*, (1990) found an association between storm events and PAH peaks in river sediments. Consequently a sampling programme which includes a degree of 'time averaging' rather than a more detailed one which gives a series of 'snap-shot' values would be the preferable approach for monitoring. The second potential problem is one of very low levels of POCs, especially in the more remote areas of the United Kingdom. Even though detection limits are as low as parts per trillion ( $\text{pg g}^{-1}$ ), there may still be problems in detecting certain classes of POCs in non-accumulating phases such as natural waters. This can be overcome by relying more on accumulating phases such as sediments and biota. Finally, the effects of agriculture must be seriously considered. This problem will be particularly acute at the less remote monitoring sites and in the south where new sites may have to be selected for effective geographical coverage of the country. It may be possible to overcome this problem by careful site selection.

### 3.3.2. Waters.

Except in very polluted areas, POC concentrations in waters will be very low and it is therefore unlikely that this would prove to be a very effective way of monitoring. Lewis (1975) gave total PAH values for two large rivers, the Trent and the Severn, to be 25 - 3790 ng l<sup>-1</sup> and 20 - 266 ng l<sup>-1</sup> respectively. Concentrations for upland sites are likely to be very much lower. However, were it possible to use waters directly, lakes would be more useful than streams due to the episodic nature of POC depositions. In order to use lake water in this way large quantities would be needed for analysis making it impractical to take the samples away from the site. It would be necessary to use a POC adsorption column through which a large known quantity of water could be passed at the site. The column alone could then be taken away for subsequent analysis.

Brown water sites (high dissolved organic carbon - DOC) could also be used for POC monitoring. POCs are so strongly bound to DOC that analytical methods tend to underestimate POC concentrations at sites where there is high DOC (Gjessing & Berglund, 1981). Even so, because the POC can bind to DOC, water POC concentrations are higher than in clear water sites where the POC binds to particulate matter and rapidly precipitates out of the water column. At present, there are no brown water sites in the AWMN and it would be useful to include one or two near to comparable clear water sites to assess the potential of brown waters for monitoring POCs. DOC concentrations can also vary both seasonally, and annually, due to hydrological and climatological factors. POC measurements would therefore need standardising at such sites.

### 3.3.3. Sediments and sediment traps

As waters have such low concentrations of POCs, a better way to monitor their atmospheric deposition is to use phases of the ecosystem that accumulate POCs. Due to the hydrophobic nature of these pollutants and their affinity for natural organic material, accumulators are either sediments or aquatic biota.

As discussed in Section 2.4.2., lake sediments are an effective way of monitoring pollutants and also enable the study of the historical perspective of pollutant deposition. The value of sediment cores for the analysis and monitoring of POCs has been reported for PAHs (Hites *et al.*, 1977; Furlong *et al.*, 1987; Rippey, 1990), PCBs (Eisenreich, 1987) and PCDD/Fs (Fletcher & McKay., in press). However, unlike the metal record, for most POC classes there is no natural background as there are no natural sources. Where natural sources exist, for example with PAHs, sediment core analysis allows the extent of natural production to be determined and the subsequent anthropogenic atmospheric impact. Due to

the strong binding of POCs to particulate matter, they are very stable once sedimentation has taken place. Consequently, apart from movement of the particles themselves (by, for example, bioturbation) there is no mobility in the sediment of POC and the integrity of the record is very good, better than that of the trace metal sediment record.

Because of the affinity of POCs to particulate matter, there is no problem obtaining sufficient material for the analysis of POCs in sediments. 1-2 g of dried material is sufficient even at very low concentrations, although for higher resolution studies (i.e. finer core slices) it may be necessary to amalgamate cores. Three of the AWMN sites (Round Loch of Glenhead, Loch Chon and Loch Tinker) already have PAH profiles from sediment cores taken in 1986 (Rippey, 1990). These profiles showed a decrease in PAH concentration over the last 10 - 30 years. This trend agrees with other reported PAH profiles (Heit *et al.*, 1981; Furlong *et al.*, 1987; Wickstrom & Tolonen, 1987). All the AWMN sites are re-cored every five years as part of the monitoring programme.

Sediment traps, as discussed in Section 2.4.2., can be used to monitor pollutant fluxes as the dates of deployment and emptying are known. Consequently, sediments can be collected and pollutants monitored at fine time intervals (i.e. months or years) without the need for expensive radiometric dating. Sediment traps have been reported as being effective in POC monitoring, for example PAHs (McVeety & Hites, 1988), PAHs and PCBs (Baker *et al.*, 1991) and PCDD/Fs (Broman *et al.*, 1989). It may be necessary to deploy more or larger traps than are currently used in the AWMN to collect sufficient material for POC analysis, although Baker *et al.*, (1991) used as little as 0.05 - 2.5 g of dried material. There may be some contamination in traps from resuspension of recent sediments during storm events, but other mixing problems such as bioturbation are removed. Loss of POCs by volatilisation and degradation whilst in the traps is generally not a problem especially for larger POC compounds as strong adsorption causes high stability once the POCs are bound to particulates (Rippey, pers comm.).

Stream sediments are not usually used to monitor pollutants in the ways described above because of the obvious deposition problems. However, they have been used to a certain degree to monitor PAHs in rivers inasmuch as they are the foundation of the food chain for burrowing aquatic organisms (Evans *et al.*, 1990). The sampling strategy of sediments in this study was to sample the top 10 cm of the River Derwent sediments as this is the depth commonly utilised by these organisms. It was shown that PAH concentrations in river sediments increased after storm events, but it is unlikely that such a sampling approach would be suitable for a long term POC monitoring programme.

#### 3.3.4. Biota.

Apart from fish there are very few studies on POCs in freshwater biota. This is probably due to very low concentrations and the subsequent sampling difficulties. For instance, with trace metals it is sufficient to sample 50 shoot tips of *Scapania undulata* or 20 - 50 individuals of Trichoptera species for analysis (Section 2.4.3). POCs are generally present in the environment at concentrations more than a thousand times less than trace metals and consequently many more samples would need to be taken.

In Section 2.4.3.2 the use of moss bags was discussed for monitoring trace metals in freshwaters (e.g. Whitton *et al.*, 1991). Wegener *et al.*, (1992) have applied a similar technique for monitoring PAHs in the atmosphere. 20 g of moss (*Sphagnum* spp.) was packed into spherical bags and exposed for 30 days. The PAHs were then extracted and analysed. This technique could be readily applied to the monitoring of PAHs and other POC species in freshwaters. However, the same caveat, that species may be introduced to sites, or relative abundances altered, where macrophyte monitoring takes place still applies.

Without further work on the levels available of different classes of POCs in diatoms, macrophytes and invertebrates, it is difficult to ascertain which, if any of these classes would be suitable for monitoring POCs. The problems outlined above would appear to make it impractical to use macrophytes and invertebrates except in 'one off' studies as so much material would need to be removed at each site. Little is known of the diatom response to POCs, but it is likely that in natural waters the level of POCs would be so low that diatom assemblages would be reflecting other environmental variables rather than POC concentration. The alternative (as discussed in Section 2.4.3.1.) is to use diatoms as a natural biofilm and to measure POC levels directly. However, once again there is the problem of obtaining sufficient quantities of material. It seems probable, therefore, that fish represent the only biotic component in which it is practical to measure and monitor POCs, where 20 g dry weight is sufficient for analysis of trace organics such as 2,3,7,8-TCDD (Kuehl *et al.*, 1989). Where large amounts of material are required, the removal of sufficient biotic material for annual POC analysis may affect the year to year distribution of species and this should be considered carefully before embarking on any sampling strategy.

Organochlorines have also been measured in other aquatic fauna e.g. the eggs of two river passerines, the Grey Wagtail (*Motacilla cinerea*) and the Eurasian Dipper (*Cinclus cinclus*,) (Ormerod & Tyler, 1992) and the European Otter (*Lutra lutra*) (Mason & O'Sullivan, 1992). These are discussed in more detail in Section 3.5.1.



Sampling considerations aside, the advantages and disadvantages of each class of aquatic biota to monitor POC are the same as discussed in Section 2.4.3.

### 3.3.5. Semi-permeable membrane devices (SPMDs).

Lebo *et al.* (1992) have developed the use of semipermeable membrane devices (SPMDs) for passive monitoring of PAHs in aquatic environments. The SPMDs are polymeric membranes enclosing lipids thus mimicking the bioconcentration process of aquatic animals. These membranes were deployed in galvanised conduit shrouds which gave protection but allowed water to move over the membranes. It is interesting to note that the two main problems encountered in using the SPMD method are the same as those encountered during the sediment trapping programme in the AWMN, algal growth on the sampling device and human interference and vandalism. The SPMDs were deployed in two streams, a control site and an urban site and collected after 21 days for analysis. Although this study concentrated on PAHs any other lipophilic compound will be concentrated in a similar way and could be monitored. Lebo *et al.* stress that so far this work is only preliminary and suggest that close inter-site comparisons could only be made where temperature and algal growth are similar. Research is continuing to overcome these problems, but it seems that the technique could easily be adapted to sites where POC concentrations are lower than in urban streams (e.g. AWMN sites).

### 3.3.6. Measurement of inputs.

As discussed in Section 2.4.4. direct sampling of inputs to catchments using bulk deposition collectors would supplement other studies in pollutant monitoring. However, as with trace metals the implementation of such a programme for POC monitoring alone is probably not necessary, but it would be a simple matter to add a deposition collector for POCs were a programme initiated and the extra data produced might prove very valuable. Volatilisation of lighter compounds may result in loss from bulk collectors although monthly bulk deposition samples are already analysed as part of the CAMP programme (see Section 3.5) and there appears to be little difficulty in analysing for POCs on the quantities collected. Murray & Andren (1992) evaluated the efficiency of a precipitation collector for PCB analysis and found the recovery to be very good (99 - 104%).

Another technique to monitor POC inputs is the use of pine needles. The waxy outer surfaces of the needles accumulate lipophilic organic pollutants from the atmosphere and POCs identified on plant surfaces include DDT, HCH, PCBs and PCDD/Fs (Safe *et al.*, 1992; Jensen *et al.*, 1992). Eight AWMN sites have some degree of afforestation in their catchments (from <1% at Loch Coire nan Arr to 70% at Loch Grannoch (Patrick *et al.*, 1991)) where this monitoring could take place.

### 3.4. Modification of the AWMN to monitor persistent organics.

#### 3.4.1. Sites.

If POC deposition follows the same patterns as that of trace metals (see Section 3.2.2.) then sites in the same areas as those discussed in Section 2.5.1. would be needed for efficient monitoring of POCs. This would give good coverage of both north-south and east-west gradients. Even though it is not known that this is the case, should it be found that POC deposition patterns differed significantly, such a distribution of sites would cover all areas of the country . At present there is no widespread monitoring of POCs in the United Kingdom and until such work is undertaken the true deposition patterns will remain unknown. Consequently, a north-south and east-west site distribution is probably the most applicable given current knowledge.

As with trace metals, lake sites are preferable to streams and so 3 or 4 additional lake sites should be selected to fill gaps in the coverage. This is more important for POCs than for trace metals as more of the existing sites must be excluded. It was seen in Section 3.2.3. that POC emissions from large urban centres require a greater distance to decrease to regional levels than do individual sources. The distance of 90 km cited by Windsor & Hites (1979) is probably a maximum for the United Kingdom but sites such as Old Lodge (too near London), River Etherow (Manchester), Loch Chon and Loch Tinker (Glasgow) should probably be excluded from a POC monitoring network. Further work would be needed to ascertain whether Blue Lough (Belfast), Scoat and Burnmoor Tam (Manchester/Preston) were locally affected.

To complete north-south and east-west distributions the four sites already selected in Section 2 for trace metals would be needed. These would be lake sites in the south-east, south-west, East Anglia and in the high deposition area of the Midlands/north England. Whether it would be possible to select undisturbed lake sites in these areas suitably remote from major urban centres is doubtful and it may be that a 'best available means' approach should be taken for site selection.

Brown water sites could also be selected adjacent to clear water sites. These are not strictly necessary to POC monitoring but would provide a way to study the monitoring potential of high DOC (and therefore high POC adsorbing) waters. They would also supply a comparison of the effectiveness of monitoring at the two types of site.

### 3.4.2. Parameters.

At present no POC analyses are done in the AWMN, although PAH profiles in sediment cores are extant for 3 sites, Round Loch of Glenhead, Loch Chon and Loch Tinker (Rippey, 1990).

A small number of important POCs have especially good atmospheric pathways and consequently are good indicators of the regional deposition picture rather than 'local' effects. These include  $\alpha$ - and  $\gamma$ - hexachlorocyclohexane ( $\alpha$ -HCH and  $\gamma$ -HCH), hexachlorobenzene (HCB) and fluoranthene (Figure 4g) (Rippey, pers. comm.). In view of this, it might be best to start off a POC monitoring programme looking at these indicator compounds before diversifying into other POC species.

### 3.4.3. Sampling.

It appears that sediments (cores and traps) and fish are likely to be the most important components in POC monitoring. If these are the only components included then there need be little change in the present sampling programme. An extra sediment trap might need to be deployed at each lake site and an extra core or two taken during the five yearly re-coring to obtain sufficient material for the analyses but there would be few other alterations.

The inclusion of water analysis into the programme depends on the feasibility of using adsorption columns at the site as it would be impractical to sample the quantities of water required (up to 20 litres) and take them back to the laboratory at monthly intervals. There would appear to be little need for the use of macrophytes, invertebrates and water analysis as the use of sediments and fish alone should be sufficient for effective POC monitoring.

## 3.5. Other networks.

### 3.5.1. United Kingdom.

#### The National Rivers Authority.

The various monitoring activities of the NRA have been described in Section 2.6.1. The details will not be repeated here and only the persistent organic compounds analysed for each requirement are listed.

Freshwater Fisheries (78/659/EEC) - Phenolic compounds and petroleum hydrocarbons. These are only measured where they are discharged to waters where fish are taken for human consumption.

List I substances - Aldrin, Dieldrin, Endrin, Isodrin, Carbon tetrachloride, Chloroform, DDT (all isomers), para-para DDT, Hexachlorobenzene, Hexachlorobutadiene, Hexachlorocyclohexane (all isomers), Pentachlorophenol and its compounds, 1,2 Dichloroethane, Trichloroethane, Pentachloroethane, Trichlorobenzene.

List II substances - Tributyltin, Triphenyltin.

Harmonised Monitoring Scheme - Phenol, Benzo (g,h,i) perylene, Fluoranthene, Indeno (1,2,3-c,d) pyrene, 11,12-Benzofluoranthene, 3,4-Benzofluoranthene, 3,4-Benzpyrene, Aldrin,  $\gamma$  - Hexachlorocyclohexane, Heptachlor, para-para DDE, Dieldrin, para-para DDT, Total organic tin, Persistent oils and hydrocarbons, PCBs, Chlorinated phenols, para-para TDE, PAHs, Endrin.

Paris Commission Inputs - PCBs,  $\gamma$  - Hexachlorocyclohexane.

Third North Sea Conference Declaration - (The extended 'Red List') - Aldrin, Dieldrin, Endrin, Hexachlorocyclohexane, DDT, Pentachlorophenol, Hexachlorobenzene, Hexachlorobutadiene, Carbon tetrachloride, Chloroform, Trifluralin, Endosulfan, Simazine, Atrazine, Tributyltin compounds, Triphenyltin compounds, Azinphos-ethyl, Azinphos-methyl, Fenitrothion, Fenithion, Malathion, Parathion, Parathion-methyl, Dichlorvos, Trichloroethylene, Tetrachloroethylene, Trichlorobenzene, 1,2-Dichloroethane, Trichloroethane.

#### The Institute of Freshwater Ecology.

As with trace metals no specific monitoring of POCs in freshwaters is undertaken at IFE, but POC analyses are performed as part of other projects. A recent study by IFE for DoE has focused on particular groups of pesticides in rivers, and methods were developed to analyse for these compounds in river waters and sediments from a number of sites in England and Wales. Chosen compounds included the pyrethroids (e.g. permethrin, deltamethrin), the triazines (e.g. simazine, atrazine) and organochlorine compounds such as  $\alpha$ -BHC, lindane, heptachlor, dieldrin. DDT, DDE, TDE and endrin (IFE, 1992).

#### The Institute of Hydrology (IH).

The Institute of Hydrology analyse for pesticides and herbicides at two stream sites, Rosemaunde Experimental Husbandry Farm near Hereford and Witham in Oxfordshire an ECN terrestrial site. Analyses performed depends on what applications have been made to the catchment.

### The British Geological Survey (BGS).

The British Geological Survey analyse for POC in groundwaters, principally in areas of chalk geology, although this is not a monitoring programme as such.

### Others.

The Water Research Centre (WRC) undertake no long term monitoring of persistent organic compounds. There have been short studies, covering a period of about a year where rain gauge samples were analysed for POCs but these are no longer in progress.

The Warren Spring Laboratory does not analyse for POC as part of their monitoring programmes.

Little work has been done on the distribution of atmospherically derived POCs in the aquatic environment and no monitoring networks exist in the United Kingdom. The nearest to a study on the distribution of a class of POCs in different sites through time was the PAH analyses performed on lake sediment cores for the Surface Water Acidification Project (SWAP) sites reported in Rippey (1990).

In the United Kingdom even studies following POCs at individual sites are rare, for example Evans *et al.*, (1990) sampled surface sediments from 11 locations on the River Derwent for PAH on a monthly basis between June 1987 and May 1988, but this is hardly 'long-term' monitoring.

Ormerod & Tyler (1992) measured a range of POCs (DDE, TDE, DDT, PCBs, HEOD and HCB) and mercury in the unhatched eggs of two species of river passerines, the Grey Wagtail (*Motacilla cinera*) and the Eurasian Dipper (*Cinclus cinclus*) at three sites in Wales, eastern Scotland and south-western Ireland in 1988 and 1990. They suggested that both the diet and the non-migratory nature of the Dipper (occupying linear territories of 0.3 - 2 km and seldom dispersing more than 10 - 20 km from their birthplace) gives this species good potential for the monitoring of contamination in upland rivers. However, this form of monitoring relies on the presence of deserted or addled eggs to enable sampling to take place. Similarly, Mason & O'Sullivan (1992) measured pesticide residues and PCBs in the livers and muscle tissue of the European Otter (*Lutra lutra*) in Ireland between 1984 and 1990. This relies on the availability of otter carcasses and so would probably not be suitable for monitoring purposes.

Atmospheric monitoring is more extensive. The Paris Commission's Comprehensive Atmospheric Monitoring Programme (CAMP) has three sites on east coast (see Section 2.3.3.1.) to monitor

atmospheric inputs into the North Sea. Bulk deposition is analysed monthly for a range of organic compounds including total HCH's,  $\alpha$ -HCH,  $\gamma$ -HCH, PCBs, DDE, TDE, DDT, Aldrin, Dieldrin, Endrin, Heptachlor, Atrazine, Simazine and Propazine.

Jones *et al.*, (1992) used archived plant foliage to monitor levels of PAHs and PCBs at Rothamsted between 1965 and 1989. Their results suggested that air concentrations of lower chlorinated PCBs in rural England have decreased up to a factor of 50 between 1965-69 and 1985-89. High molecular weight PCBs and PAHs have also decreased in concentration, but not to such a great extent.

### 3.5.2. International.

The Global Environment Monitoring System (GEMS) reports from global network of 300 lakes, rivers and groundwater sites of which 12 are major freshwater systems in the United Kingdom (see Section 2.6.2.). The rivers are sampled fortnightly and the lakes bi-monthly and analysed for a range of compounds: Aldrin,  $\alpha$ -BHC, BHC, total DDT, Dieldrin, Endrin, o,p-DDD, o,p-DDE, o,p-DDT, p,p-DDD, p,p-DDD Olefin, p,p-DDE, p,p-DDT, and PCBs. These systems are so large that little of the POC input would be atmospherically derived. As noted in Section 2.6.2.1 the data from six AWMN sites are now contributed to the GEMS programme, but the FOC determinands outlined above are not currently measured.

The Concerted Action "Organic micropollutants in the Aquatic Environment" (Cost Project 641) (Commission of the European Communities, 1991) has been implemented since 1984 as an extension of earlier research undertaken between 1972 and 1983 on the analysis of organic micropollutants in water. The aims of this project were to provide a scientific basis for the implementation of policies on human health and the environment and to coordinate national research activities. One of the areas of research was "focused on the identification of input routes for organic micropollutants into the aquatic environment, to study their transport, distribution, transformation and possible accumulation in biota". This work was mainly involved with groundwaters and has not yet been collated.

### 3.6. Conclusions

In Europe the concern regarding the public health and ecological impacts from atmospheric toxic emissions is increasing. The first international atmospheric toxics (organic compounds and metals) policy action in Europe was concluded in March 1990 at the North Sea Conference III in which ten European countries agreed to reduce the emission of 17 atmospheric toxic substances by 50% before 2000 AD based on 1985 emission levels (DoE, 1991). The Government's White Paper "This Common

Inheritance - The Second Year Report" was published in 1992 and sets out Britain's environmental strategy for the 1990s, the action to date and commitments to further action. One of these commitments is to phase out the use of PCBs by 1999. Jones *et al.* (1992) suggest that atmospheric levels of PAHs and PCBs as recorded in archived foliage have been declining since the 1960s. The impacts of these substances on the freshwater environment and the temporal trends of atmospheric input to aquatic ecosystems across the United Kingdom are less well known.

A little modification of the present AWMN would be needed to effectively monitor POCs in the aquatic ecosystem. A few extra lake sites in addition to the present Network would give a good coverage of the United Kingdom across the proposed deposition gradients. Such a network of sites would be enormously valuable, not only to monitor the atmospheric deposition of POCs, but also because there is a need to determine more effectively the pattern of deposition across the country. This is an area of research currently unfulfilled.

At present no POCs are analysed on a regular basis in the AWMN programme and it would probably make sense in the first instance to analyse for the few important compounds known to have good atmospheric pathways (see Section 3.4.2.). Sampling strategies currently employed in the AWMN need change little as effective monitoring could be undertaken using lake sediment cores, sediment traps and possibly fish. The inclusion of macrophytes and invertebrates in the programme would give a more comprehensive picture of POCs in the freshwater ecosystem but are probably not necessary for monitoring purposes.

### **Acknowledgements**

The author wishes to thank Brian Rippey (University of Ulster), Tony Shiels (DoE Water Quality), Stan Sadowski (Paris Commission), Peter Cawse, Cath Fletcher, Keith Playford (AEA Technology, Harwell), John Seager, Paul Barrowclough (NRA), Mike Gardiner (WRc), Glen Campbell (Warren Spring), Ron Harriman (SOAFD) and Alan Jenkins (IH) for supplying information on the work at their respective institutions.

Rick Battarbee, Brian Rippey, Ron Harriman, Cath Fletcher, John Boyle, Mark Macklin, Tim Allott, Steve Juggins, Simon Patrick and Don Monteith read and commented upon some or all of this paper.

Diagrams were prepared by Tim Aspden and Louise Saunders in the Geography Department at UCL.

This work was funded by the Department of the Environment (Air Quality) under contract number PECD 7/12/02.



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## RESEARCH PAPERS

### 1981-1991: Palaeoecology Research Unit

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