LAKE SEDIMENT TOXICITY IN THE UK: THE ROLE OF TRACE METALS AND PERSISTENT ORGANIC POLLUTANTS

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SUMMARY

The aim of this project was to determine sediment toxicities to the sediment-dwelling chironomid *Chironomus riparius* and the free-swimming cladoceran *Daphnia magna* using empirical measurements from ten lakes distributed both geographically across the UK and across a predicted toxicity quotient gradient.

Homogenised sediments from each site were analysed for trace elements (Hg, Cd, Pb, Ni, Cu, Zn, As), spheroidal carbonaceous particles (SCPs), and a suite of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and organochlorine pesticides (α-HCH, γ-HCH, DDT and its derivatives DDE and DDD). These were compared with data from survival and growth tests on the two organisms exposed to the sediment samples in order to assess the role of these pollutants on toxicity.

The chemical and toxicological evidence from the lake sediments show that there is toxicity in some lakes due to trace metals and PAHs. Provisional toxicity quotients that may be used in risk assessment have also been derived. Toxicity was found to be likely when the mean toxicity quotient for trace metals and PAHs was greater than approximately 0.40 and when the sum of the quotients was greater than 0.80. Both values are provisional and a larger dataset is required to confirm them. The most important toxicants are likely to be Pb and As from within the trace elements and the PAHs chrysene, pyrene, fluoranthene, phenanthrene and benzo[a]pyrene.

The evaluation of toxicity test results for *Chironomus riparius* found evidence for toxicity in Agden Reservoir, Llyn Llagi, Loch Doilet and Scoat Tarn. Loch Doilet is an exception, as the sediment toxicity test shows evidence of toxicity, yet the concentration of the toxicants and the toxicity quotients are very low.

Two of the sites for which toxicity has been demonstrated are upland lakes removed from direct effects. The role of altitude in toxicity remains to be confirmed, but the remoteness of these sites suggests that sediment toxicity could be widespread across the UK. However, the central London site showed no toxicity and this may be due to rapid sediment accumulation rates diluting pollutant concentrations.

Upland lakes tend to have slow sediment accumulation rates and therefore, given the active burrowing depth of benthic invertebrates, it is likely that the sediments of these sites will remain toxic to these species for decades to come. This may be exacerbated, particularly at upland lakes, by the in-wash of previously deposited pollutants stored in catchment soils. This in-wash may be increased by the predicted effects of climate change.

CONTENTS

1. INTRODUCTION

This is a report of a pilot investigation into the scale of toxicity in UK lake sediments as a result of deposition of heavy metals and persistent organic pollutants from the atmosphere.

The UK is committed to the development of critical levels and loads for trace metals and persistent organic pollutants (POPs). This is driven by obligations under the Dangerous Substances Directive (and subsequently the Water Framework Directive), the Environmental Protection Act 1990 (the Red List), the UNECE protocols on Heavy Metals and Persistent Organic Pollutants and the agreed approaches on critical loads for heavy metals and POPs in freshwaters and soils resulting from the Bad Harzburg Workshop (UNECE, 1998). The UK is taking a major role in the development of critical levels and loads through, amongst other activities, projects in NERC's Environmental Diagnostics Programme.

Lake sediments have long been used as a natural archive of environmental change including the inputs of pollutants to lakes from both catchment and atmospheric sources. However, while there have been many investigations of toxicity in estuarine and marine sediments, there have been few in freshwaters and these almost completely on rivers, canals and harbours (MacDonald et al. 2000). Only Wiederholm & Dave (1989), Dave (1992a) and Dave (1992b) have shown, using laboratory toxicity tests with *Daphnia magna* and *Tubifex tubifex*, that there is toxicity in some Swedish lake sediments. Further, little work has been undertaken on the synergistic affect that multiple pollutants may have on organisms at ambient levels (i.e. reasonably low concentrations over long periods of time).

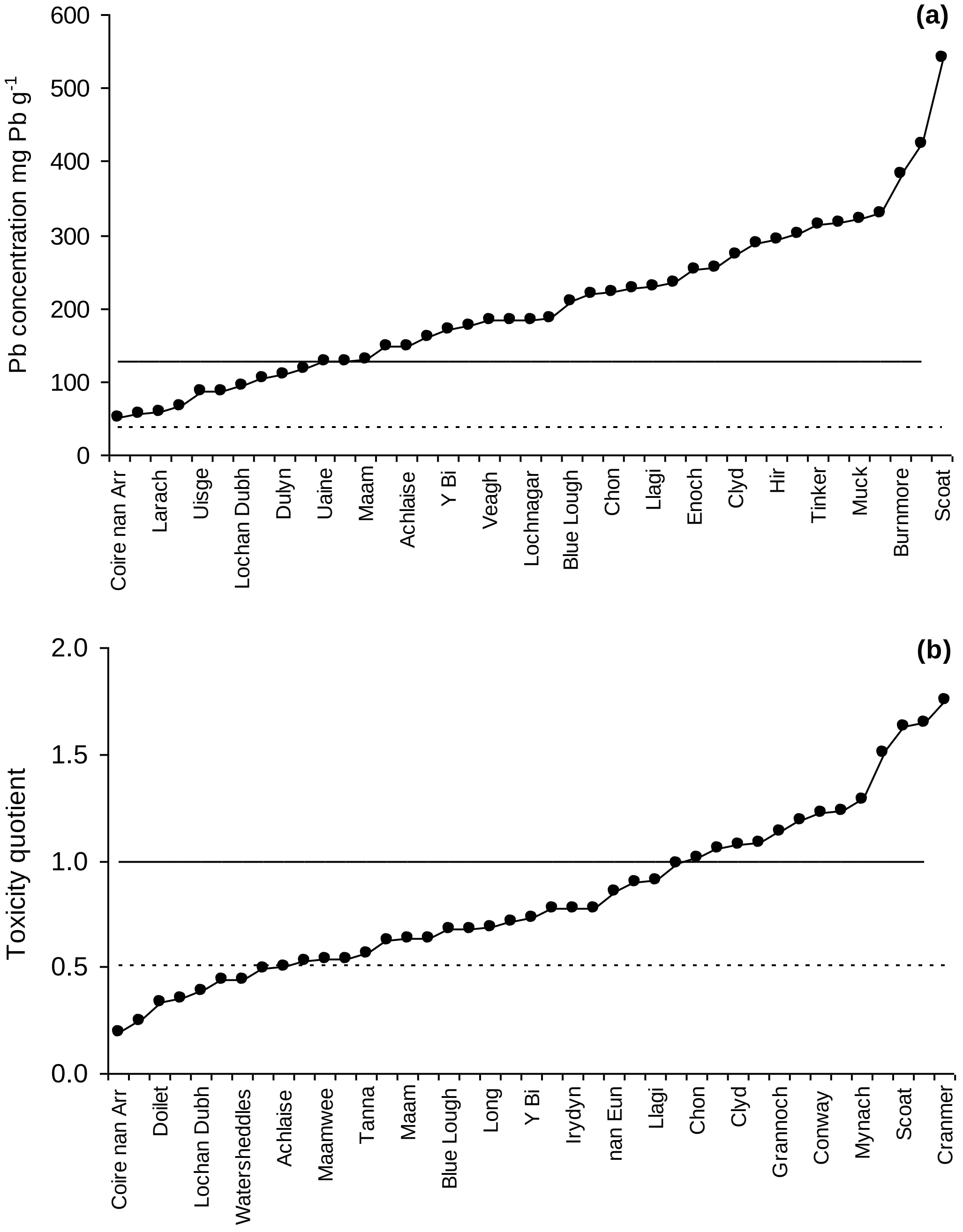
Nevertheless, chemical data can be used along with Sediment Quality Guidelines (SQGs) for freshwater sediments to investigate this topic. The SQGs of MacDonald et al. (2000) are the most soundly based, as they use a weight-of-evidence approach with a large database (Table 1), and together with heavy metal concentration data from 41 lake sediment cores in the UK and Ireland, taken during the 1980s, there is a *prima facie* case for sediment toxicity in many of the lakes due to Pb, Zn and, less importantly, Cu (Figure 1a). Using the toxicity quotient to estimate the combined toxicity of chemicals shows that there is likely to be toxicity in over half of these lake sediments (Figure 1b). Further, although considerable reductions in atmospheric deposition have occurred since these sediments were taken, lake acidification may enhance the toxicity of trace metals (Chapman et al. 1998).

This evidence suggests, but does not prove, that there is toxicity in many UK lake sediments due to heavy metals deposited from the atmosphere. Given that critical load models are being developed for heavy metals and POPs in freshwaters, direct proof of sediment toxicity and its ecological effects in lakes is needed in order to inform general policy development in the area.

Table 1. *The concentration of heavy metals in uncontaminated lake sediment (Forstner, 1977) and the Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) of heavy metals and POPs in freshwater sediments (MacDonald et al. 2000). Biological effects are expected ≤5 % of the time when the concentration is less than the TEC and ≥95 % of the time above the PEC.*

		Uncontaminated	TEC	PEC
As	µg g^{-1}		9.79	33.0
Cd	µg g^{-1}	0.46	0.99	4.98
Cr	µg g^{-1}	82	43.4	111
Cu	µg g^{-1}	46	31.6	149
Pb	µg g^{-1}	31	35.8	128
Hg	µg g^{-1}	0.49	0.18	1.06
Ni	µg g^{-1}	103	22.7	48.6
Zn	µg g^{-1}	123	121	459
Fluorene	ng g^{-1}		77.4	536
Phenanthrene	ng g^{-1}		204	1170
Anthracene	ng g^{-1}		57.2	845
Fluoranthene	ng g^{-1}		423	2230
Pyrene	ng g^{-1}		195	1520
Benzo[a]anthracene	ng g^{-1}		108	1050
Chrysene	ng g^{-1}		166	1290
Benzo[a]pyrene	ng g^{-1}		150	1450
Dibenzo[a,h]anthracene	ng g^{-1}		33	
Total PAHs	ng g^{-1}		1610	22800
Total PCBs	ng g^{-1}		59.8	676
Sum DDD	ng g^{-1}		4.88	28.0
Sum DDE	ng g^{-1}		3.16	31.3
Sum DDT	ng g^{-1}		4.16	62.9
Total DDTs	ng g^{-1}		5.28	572
γ-HCH	ng g^{-1}		2.37	4.99

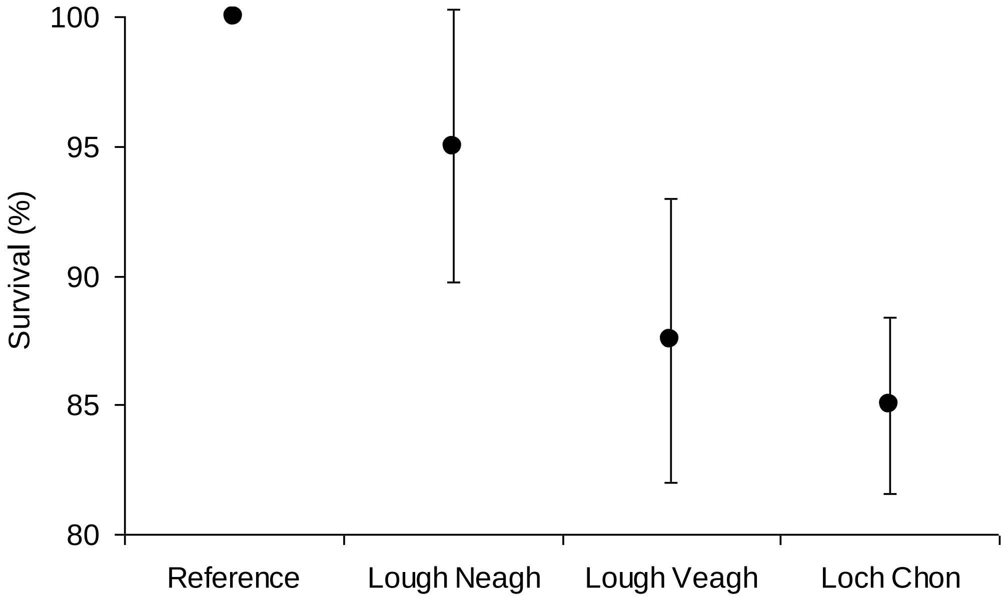
Figure 1. *Sediment toxicity due to heavy metals. (a) The mean Pb concentration in 0-5 cm of sediment and values of the Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) (MacDonald et al., 2000), illustrating that TEC (dotted line) was exceeded in all lakes and PEC (solid line) in 31. Similar data for Cu show that TEC was exceeded in 30 lakes, PEC in 0, and for Zn that TEC is exceeded in 33 lakes and PEC in 6. (b) The toxicity quotient for Pb, Cu and Zn in 0-5 cm of sediment. The quotient is the mean value of (concentration/PEL) for the three toxicants (Long et al., 1998) and toxicity is probable when the quotient is above 0.5 (dotted line) (MacDonald et al. 2000).*



A weight-of-evidence approach is the well-established methodology to investigate sediment toxicity, specifically the Sediment Quality Triad (SQT; Chapman *et al.* 1992). The SQT has the advantage of integrating effects (laboratory sediment toxicity tests and benthic community structure in the field) with the sedimentary concentration of toxicants and it makes no assumptions about toxicity. Taking a step-by-step approach suggests that the next stage is to investigate sediment toxicity using well-established assays.

Some preliminary work has been undertaken. The toxicity quotient for Pb, Zn and Cu (Figure 2) was used to choose three lakes with predicted low (Lough Neagh; quotient = 0.46), medium (Lough Veagh; 0.78) and high (Loch Chon; 1.01) sediment toxicity and the *Daphnia magna* 48-hour sediment toxicity test was completed using surface (0-5 cm) sediment from the lakes. The results are in agreement with the expected toxicities (Figure 2); survival was 95.0, 87.5 and 85.0 %, with toxicity quotients of 0.46, 0.78 and 1.10, respectively. However, while the *Daphnia magna* 48-hour sediment toxicity is very widely used, more appropriate sediment toxicity assays are desirable. Further, it is uncertain as to the reasons for the reduced toxicity observed in this preliminary study.

***Figure 2.** The survival of* Daphnia magna *in three lake sediments and a control during a 48-hour sediment toxicity test. Four replicates of each sample were completed. Error bars are standard errors.*



In effect, this pilot study is a rudimentary ecological risk assessment (Chapman & Mann 1999). The desk-based evaluation (Figure 1) is being supplemented by information on exposure and biological response to heavy metals and POPs, with some assessment of ecological relevance. It should be pointed out that biological variability is large and so large data sets of toxicant concentrations, toxicity test results and ecological effects are needed to provide statistical confidence to the findings (MacDonald et al., 2000; Field et al., 2002).

2. PROJECT AIMS

The predicted toxicities shown in Figure 1 are based on analyses undertaken almost 20 years ago since when there has been a significant decline in atmospheric deposition across the UK. However, this reduction may not have transferred to sediment dwelling organisms as 20 years additional sediment accumulation represents a depth down to which they may burrow, especially at upland sites. Further, given the possible synergistic effect of pollutants accumulated in the sediments there is a need to establish sediment toxicity using the SQT approach for a larger range of metals and for POPs.

The aim of this project is therefore to determine sediment toxicities to both the sediment-dwelling chironomid *Chironomus riparius* and the free-swimming cladoceran *Daphnia magna* using empirical measurements for 10 lakes distributed both geographically across the UK and across the predicted toxicity quotient gradient.

Homogenised sediments from each site was analysed for the following list of determinands:

- Trace elements: Hg, Cd, Pb, Ni, Cu, Zn, As;
- Polycyclic aromatic hydrocarbons (PAHs): acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j+k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[ah+ac]anthracene, benzo[ghi]perylene;
- Polychlorinated biphenyls (PCBs): 28, 52, 101, 118, 138, 153 and 180
- Polybrominated diphenyl ethers (PBDEs): 47, 99, 100, 153 and 154
- Organochlorine pesticides: α-HCH, γ-HCH (lindane), DDT and its derivatives DDE and DDD
- Spheroidal carbonaceous particles (SCPs): Unambiguous indicators of the high temperature combustion of fossil –fuels such as coal and oil.

These measurements will form the basis for calculation of toxicity quotients based on all pollutants for which Environmental Quality Standards (EQSs) are available. These will then be compared with data from survival and growth tests on the two organisms exposed to the same sediment samples in order to assess the role of these pollutants on toxicity to these freshwater invertebrates at ambient concentrations.

3. SITES

The locations for the sites selected for sampling are shown in Figure 3 and basic morphological information are given in Table 2. Sites were chosen to include examples from across the original contamination spectrum (Figure 1). However, because this original gradient was based on sites selected for acid deposition studies in the 1980s, and were therefore focused in the north and west of the UK, it was thought these might not include the full UK contamination gradient. Two further sites were therefore included, Agden Reservoir and Tooting Common Lake, which were expected to be more contaminated.

Table 2. *Site locations and basic morphology.*

Site	UK Grid reference	Altitude (m.a.s.l.)	Lake area (ha)	Maximum depth (m)
Loch Coire Fionnaraich	NG 945 498	235	10.0	14
Loch Doilet	NM 808 678	8	53.0	16.8
Burnmoor Tarn	NY 184 043	252	24.0	13
Lochnagar	NO 252 859	785	9.8	26
Tooting Common Lake	TQ 291 721	40	1.0	1.2
Llyn Cwm Mynach	SH 678 238	285	5.9	11
Scoat Tarn	NY 159 104	602	5.2	20
Llyn Llagi	SH 649 483	380	5.7	16.5
Loch Chon	NN 421 051	100	100.0	25
Agden Reservoir	SK 260 925	192	24.0	24

Loch Coire Fionnaraich is located above Loch Carron in the north-west of Scotland. It has an extensive catchment, resulting in a low water residence time, characterised by acid moorland species *Calluna, Molinia* and *Eriophorum.*

Loch Doilet is located to the north of Strontian in west Scotland. It has an afforested catchment and although found to be acidified in the Surface Water Acidification Project (SWAP) in the 1980s it was found to have little atmospheric trace metal contamination.

Lochnagar is a remote corrie loch located on a granitic massif above the Balmoral Forest. The catchment is precipitous with sparse moorland vegetation dominated by *Calluna* and *Vaccinium* and an extensive boulder field on the eastern side below which there are extensive areas of eroded peats.

Loch Chon is a large loch lying in the Trossachs region of central Scotland. Catchment soils consist of peaty gleys, peaty podsols and humus iron podsols. Much of the lower catchment is afforested whilst the upper reaches are characterised by *Calluna* and *Molinia* moorland.

Llyn Llagi occupies a north-facing corrie in the central area of the Snowdonia region of North Wales. Away from the bare rock of the steep back-wall the soils are mainly stagnopodsols and gleys interspersed with blanket peats, whilst the vegetation is characterised by acid moorland species *Calluna*, *Molinia* and *Eriophorum,* grazed at low intensity by sheep.

Llyn Cwm Mynach lies at the southern edge of the Rhinog Mountains in North Wales. Blanket peats dominate the north and east of the catchment while ranker soils characterise the south and west. The lower parts are afforested with conifers whilst the upper parts are dominated by *Calluna* and *Vaccinium* and utilised for rough grazing of sheep.

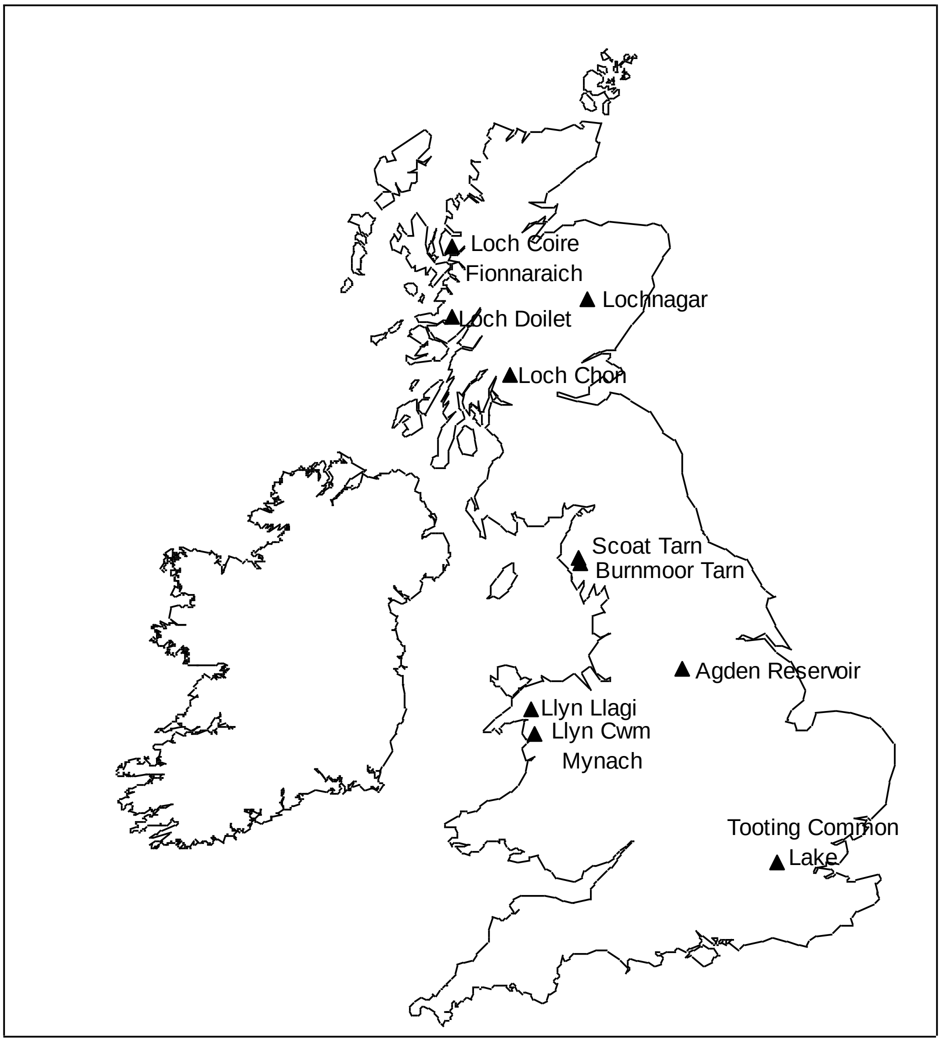
Scoat Tarn is a typical mountain corrie lake with a steep catchment of mainly rock and boulders on the eastern slopes while those of the north and south are less steep and covered with rough grass and *Sphagnum*. Soils are shallow, peaty rankers.

Burnmoor Tarn is the largest ‘tarn’ in the English Lake District. The catchment soils are characterised by podsols and shallow rankers whilst the vegetation is mainly rough grassland with *Pteridium*, *Calluna* and *Sphagnum*, utilised for rough grazing by sheep.

Agden Reservoir is located to the north-west of Sheffield below the Bradfield Moors and is utilised as a water supply for the city. It was formed in 1869 by the damming of Hobson Moss Dike a tributary of the River Loxley.

Tooting Common Lake is located in south London within parkland. It is a shallow, productive lake extensively stocked for local angling.

Figure 3. *Sampling site locations*



4. METHODS

4.1. Sediment coring and sub-sampling

Seven sediment cores were taken from the profundal area of each selected lake in November 2002 (Table 3) using a gravity corer fitted with a perspex tube of internal diameter of 74 mm. The 0 - 5 cm section of these cores is likely to be the most relevant to benthic invertebrates, (the 0-3 cm layer was used by Dave (1992a) and Long et al. (1998), and the 0-6 cm layer by Besser et al. (1996)), as they are active in this layer. The 0 – 5cm section of each core was extruded vertically in the field, amalgamated and homogenised in a hexane washed glass container. The core tube and all utensils in contact with the sediment were hexane washed, and kept contaminant-free until use by wrapping in hexane washed aluminium foil.

Approximately 100g of the homogenised wet sediment was transferred into hexane-washed amber jars. This sub-sample was freeze-dried before transfer for POPs analysis. A second sub-sample of c.10g wet sediment was stored in sealable plastic bags, freeze-dried, analysed for organic content (measured by loss-on-ignition at 550 °C), and for trace elements analysis. A third sample of c. 2g wet weight was also stored in sealable plastic bags and air-dried prior to the analysis of spheroidal carbonaceous particles (SCPs). The remainder of the amalgamated sediment was shipped to ABC Laboratories for toxicity tests. Unfortunately, the sample containers for Loch Doilet and Loch Coire Fionnaraich were damaged on arrival and the samples unusable. New samples were taken from Loch Doilet in January 2003 but ice conditions on Loch Coire Fionnaraich prevented new samples being taken from this site in time for toxicity measurements to be undertaken. All other analyses were, however, completed at all sites using the original samples.

4.2. Spheroidal carbonaceous particles (SCPs)

The procedure for extraction and enumeration of SCPs followed Rose (1994). Sequential attack using HNO_3, HF and HCl removed organic, siliceous, and carbonate fractions, respectively, resulting in a suspension of mainly carbonaceous material in distilled water. A known fraction of this suspension was then evaporated onto a coverslip and the number of SCPs counted at 400 times magnification under a light microscope. Sediment concentrations are calculated as ‘number of SCPs per gram dry mass of sediment’ or gDM^{-1}.

***Table 3**. Sampling dates, depths and periods covered by the 0-5cm homogenised sample (estimated from dated cores in previous studies except for Tooting Common)*

Site	Date	Depth (m)	Estimated period for 0 - 5cm sample
Loch Coire Fionnaraich	5.11.02	7.6	55 years
Loch Doilet	4.11.02	16.5	10 years
Burnmoor Tarn	20.11.02	10 - 10.5	12 years
Lochnagar	3.11.02	16.0	40 years
Tooting Common Lake	24.10.02	1.0	< 5 years
Llyn Cwm Mynach	14.10.02	6.6 - 7.6	90 years
Scoat Tarn	21.11.02	12.0	50 years
Llyn Llagi	15.10.02	12.5	20 years
Loch Chon	2.11.02	13.5 - 15.0	30 years
Agden Reservoir	16.10.02	24.0	8 years

4.3. Trace element analysis

Accurately weighed samples of approximately 0.2g freeze-dried sediment were heated at 100 °C on a hotplate with 8 ml Aristar HNO_3 for 1 hour. The solutions were transferred to 20 ml volumetric flasks and made up to volume using distilled deionised water. Duplicate certified standard reference materials (Buffalo River sediment SRM2704; Stream sediment GBW07305) and reagent blanks were digested and analysed with the samples. As was analysed using ICP-MS, Cd, Pb, Cu, Zn and Ni were analysed by AAS and Hg was analysed by cold vapour-AAS. Additional ‘geochemical’ elements, Si, Al, Ti, Ca, K, Fe, Mn, S, Zr, Rb, Sr, Y and Nb, were measured by XRF. These data are given in Appendix A.

***Table 4**. Measurement accuracy of standard reference materials. Pb, Zn, Cu, Cd and Ni are measured using SRM2704 whilst Hg and As were measured using GBW07305. Values in parentheses are standard deviations (n = 10). Hg in ng g^{-1}, other elements in $\mu g\ g^{-1}$.*

Element	Hg	As	Pb	Zn	Cu	Cd	Ni
Certified value	100	75	161	438	98.6	3.45	44.1
Measured value	93 (8.6)	68 (3.5)	158 (6)	318 (32)	84 (7)	3.72 (0.12)	37 (2.5)
Recovery	93%	91%	98%	73%	85%	108%	84%

4.4. Persistent organic pollutants

4.4.1. Determination of Organochlorine Pesticides

Accurately weighed aliquots of freeze-dried samples were spiked with 20 µg of d_{12} chrysene as an internal standard, prior to extraction with dichloromethane (3 x 30 ml) utilising sonication. The combined extracts were evaporated to ca. 1 ml. As a QA/QC measure, a blank and a matrix spike (equivalent to 0.5 mg kg^{-1}) were prepared and extracted following the same procedure. Sample extracts and QA samples were injected in the splitless mode onto a 30 m DB-5ms fused silica column directly coupled to the ion source of a Micromass AutoSpec Ultima mass spectrometer. The mass spectrometer was operated in the selected ion monitoring mode at 5,000 resolution (10% valley definition). GC conditions were: initial temperature 60 ˚C, held for one minute, then 10 ˚C/min to 280 ˚C, held for 5 minutes. Injection temperature 250 ˚C. Head pressure 12 psi.

Masses monitored were:	216.9145, 218.9116	HCHs
	235.0081, 237.0052	DDD & DDT
	315.9380, 317.9350	DDE
	240.1692	d_{12} chrysene internal standard
	Lock mass 281.051 from column bleed	

QA Data

Recoveries of all target analytes in the matrix spike fell in the range 90 to 110 %. In all samples, the percentage recovery of the d_{12} chrysene internal standard exceeded 70%. The limit of detection for all compounds was 0.1 µg kg^{-1}.

4.4.2. Determination of PCBs, PAHs and PBDEs

The extraction and purification methods employed was based on that of Ayris et al (1997), Lim et al (1999), and Wijesekera et al (2002). Briefly, accurately weighed 10 g aliquots of freeze-dried sediment were treated with known quantities of internal standards (PCBs 34, 62, 119, 131, and 173; deuterated PAH, and $^{13}C_{12}$-PBDEs) and soxhlet extracted for 16 h with dichloromethane in the presence of Cu powder (5 g, added to aid sulphur removal). After cooling, the crude extract was concentrated to ca. 40 ml; 10 ml was reserved for PAH analysis, while the remainder was used for the determination of PCBs and PBDEs.

The PCB and PBDE fraction was eluted through a 20 g florisil column with 200 ml of CH_2Cl_2. The eluate was reduced to 2 ml hexane in a Kuderna Danish apparatus, washed with 2 ml conc. H_2SO_4, before elution through a column of florisil and $AgNO_3$-impregnated alumina (2 g of each) with 100 ml CH_2Cl_2 to remove residual sulphur. The entire eluate was then concentrated to 50 µl nonane containing the recovery determination standards PCBs 29 and 129 ready for GC/MS analysis. The PAH fraction was eluted through a florisil column (2 g) with 30 ml CH_2Cl_2 and concentrated to a final extract volume of 200 µL to 2 ml CH_2Cl_2 containing p-terphenyl as a recovery determination standard. GC/MS analysis of all analytes was conducted on a Fisons' MD-800 instrument operated at unit mass resolution in EI selected ion monitoring mode, and fitted with a 60 m SGE BP-5 capillary column (0.2 mm x 0.25 µm). In all cases, 1 µl of the final sample extract was injected in splitless mode.

- For PCBs, the GC oven program was: 140 ^oC for 2 minutes, 5 ^oC/min to 200 ^oC, held for 2mins, 2 ^oC/min to 280 ^oC held for 5 minutes. Injector = 280 ^oC; Interface 250 ^oC; Source 200 ^oC. The following ions were monitored: 255.95, 257.95, 289.95, 291.95, 325.90, 327.90, 359.90, 361.90, 393.85, and 395.85.
- For PBDEs the GC oven program was 140^oC for 2 minutes, 5^oC/min till 200^oC and then 2^oC/min to 300^oC held for 5 minutes. Injector 280^oC; Interface 280^oC, Source 250^oC. The following ions were monitored: 485.8, 487.8, 403.8, 405.8, 481.7, 483.7, 497.8, 499.8, 415.8, 417.8, 493.7, 495.7
- For PAHs the GC oven program was 50 ^oC for 1min then 8 ^oC/min to 300 ^oC held for 40 minutes. Injector 300 ^oC; Interface 300 ^oC; Source 250 ^oC. The molecular ions for each target PAH, plus that of each deuterated internal standard, and the p-terphenyl recovery determination standard were monitored.

QA Data

Tables 5 and 6 give the results of the analysis of appropriate certified/standard reference materials in our laboratory for PCBs and PAH. Currently, no such reference materials exist for the determination of PBDEs in environmental matrices. However, the laboratory participated in the 2001-2002 BSEF/QUASIMEME inter-laboratory trial on brominated flame retardants. Our data for the freeze-dried sediment in this trial is given in Table 7 alongside the assigned values.

***Table 5**. Accuracy and Precision Data for PCBs*

Congener Number	CRM 392 Certified Concentration µg kg^{-1} (σ_{n-1})	CRM 392 Experimental Mean Concentration µg kg^{-1} (σ_{n-1})	NIST 1941a Certified Concentration µg kg^{-1} (σ_{n-1})	NIST 1941a Experimental Mean Concentration µg kg^{-1} (σ_{n-1})
28	100 (10)	98.4 (15.9)	-	-
52	70 (9)	80.6 (7.8)	6.89 (0.50)	7.4 (0.68)
101	134 (11)	142.3 (11.5)	10.1 (0.62)	11.5 (0.55)
118	97 (12)	104.6 (8.6)	9.38 (0.79)	8.9 (0.64)
138	-	-	13.07 (0.61)	11.7 (1.0)
153	288 (18)	262.6 (9.3)	17.31 (0.83)	16.6 (0.68)
180	313 (24)	310.4 (13.5)	6.06 (0.49)	5.8 (0.64)

CRM 392 = Sewage Sludge (6 replicates);

NIST 1941a = Marine Sediment (5 replicates)

Table 6. *Accuracy and Precision Data for PAH*

Compound	NIST1941a Certified	NIST1941a	Experimental
Acenaphthylene	37±14[a]	36.4±13	36
Acenaphthene	41±10[a]	39.1±11	28
Fluorene	97.3±8.6[a]	92.6±9	9.7
Phenanthrene	489±23	474.2±31	6.5
Anthracene	184±14	175±16	9.1
Fluoranthene	981±78	955.4±65	6.8
Pyrene	811±24	798.6±34	4.3
Benzo[*a*]anthracene	380±24	382.7±36	9.4
Chrysene	427±25[a]	433.5±32	7.4
Benzo[*k*]fluoranthene	361±18	366.2±24	6.6
Benzo[*b*]fluoranthene	740±110	725.3±107	15
Benzo[*a*]pyrene	628±52	631.4±60	9.5
Indeno[*1,2,3-cd*]pyrene	501±72	512.8±63	12
Benzo[*ghi*]perylene	525±67[a]	518.3±58	11
Dibenzo[*ah*]anthracene	73.9±9.7[a]	68.2±15	22

[a]Reference value only; NIST 1941a = Marine Sediment (8 replicates), except [c] (6 replicates).

Table 7. *Accuracy and Precision Data for PBDEs (mean of 3 replicate analyses)*

Congener Number	Assigned Value (Assigned Error) $\mu g\ kg^{-1}$	Experimental Mean (σ_{n-1}) $\mu g\ kg^{-1}$	Experimental precision (%)
47	8.93 (18.1%)	9.58 (0.42)	4.4
99	13.18 (16.29%)	13.50 (0.41)	3.0
100	2.65 (31.36%)	2.69 (0.15)	5.6
153	1.80 (40.25%)	2.16 (0.48)	22
154	1.64 (42.99%)	1.5 (0.25)	17

Data obtained from analysis of a freeze-dried sediment provided as part of 2001-2002.
BSEF/QUASIMEME inter-laboratory exercise on PBDE analysis

In summary, our data show satisfactory agreement with the certified/standard reference values. Detection limits were defined as either the lowest amount the instrument could detect, or in most cases, the average + 3 standard deviations of blank value obtained in the laboratory. Recoveries of internal standards for these samples were in the following ranges; PCBs: 32-100%, with an average of 68%; PBDEs: 22-93%, with an average of 54%; PAHs: 32-81%, with an average of 61%.

4.5. Toxicity

4.5.1. Sediment Samples

Ten sediment samples were received at ABC Laboratories in a single shipment received December

13, 2002. Two samples, Loch Coire Fionnaraich and Loch Doilet were damaged and unusable. The Loch Doilet sample was resampled in January but the Loch Coire Fionnaraich sample was unavailable for testing (see 4.1). Sediment samples were received in ~1.0-litre polypropylene containers. The first shipment was received at ~11.0°C and the second at 5.4°C. Sediment samples were logged in and then refrigerated at approximately 4ºC until use.

4.5.2. Test Organisms

Midge (*Chironomus riparius*)

Larval midges (Chironomus riparius) were obtained from ABC in-house cultures. Animals utilised for the studies were ~3 days post hatch.

Cladocerans (*Daphnia magna*)

Juvenile cladocerans (*Daphnia magna*) were obtained from ABC in-house cultures. Animals utilised for the study were five days old at study initiation.

4.5.3. Control Water and Sediment

The overlying water was laboratory freshwater prepared by blending well water with well water treated by reverse-osmosis to produce water with a hardness of 160 to 180 mg l^{-1} as $CaCO_3$. This water was utilised in both the *Chironomus riparius* and *Daphnia magna* tests.

The ABC control sediment was natural sediment collected from a small pond on the property of ABC Laboratories. The purpose of using control sediment is to show an appropriate response from the test organisms in regard to the endpoint in question for the particular study. This sediment is characterised as a sandy loam (74% sand, 20% silt, and 16% clay) with an organic carbon content of 0.2 to 0.7%. We have experienced excellent survival, growth, and reproduction in our controls and cultures with this sediment. This sediment has not been analysed for pesticides or elements.

4.5.4. Test Procedures

General

The test procedures for of the 10-day chironomid and 7-day cladoceran toxicity tests were based upon procedures described in “Standard Test Methods for Measuring the Toxicity of Sediment-Associated Contaminants with Freshwater Invertebrates” Annexes A1 and A2 (American Society for Testing and Materials, 2000) and “Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants with Freshwater Invertebrates” (US EPA, 2000).

Chironomus riparius

Testing began on January 24th and ended on February 10th 2003. The ABC control was replicated eight times and site sediment samples for all screening toxicity tests were replicated five times with 10 organisms per replicate chamber. The test chambers were approximately 0.5 litre glass jars containing approximately 100 ml of sediment. The overlying water was renewed using an automated system that provided approximately two volume additions per day. Each test chamber was fitted with a screened collar to allow water to drain from the chamber while retaining the test organisms. The animals were fed ~1 ml of a prepared invertebrate food daily. Beginning on day 9 all site samples and the control were observed for the number of adults emerged from the sediment. The number of live and dead animals in each test chamber was enumerated at test termination (Day 17) by sieving the sediment through a No. 35 (500 µm) sieve. Animals were considered dead if they did not respond to a gentle physical stimulus. The criterion for test acceptability was mean survival in the controls of ≥70 percent.

Cladocerans

Testing began on February 5th and ended on February 12th 2003. Tests were conducted in 50 ml beakers each containing ~20 ml of overlying water and 5 ml of test sediment. Each control and site sample was replicated 10 times (replicates 1 - 10). One *Daphnia magna* juvenile (~5 days old) was added to each of 10 replicate beakers per control and site samples. All beakers were monitored daily for survival of *Daphnia* and for production of young. Overlying water in each replicate was renewed daily. Solutions were renewed daily by removing the adult and temporarily placing it in a 50 ml beaker with fresh water and food. The remaining old solution was then removed along with any young present. Care was taken not to disturb the sediment in the bottom of the beaker. Old solutions were removed with a large bore glass pipette or a 60 ml syringe fitted with a piece of screen. New solution volumes of ~20 ml and food were added to beakers and the adult daphnid returned to the beaker. Each replicate beaker with a live adult received approximately 0.3-0.5 ml of a mixture of live algae (*Selenastrum* sp. and *Ankistrodesmus* sp.) and *Daphnia* feeding supplement daily in new solutions prior to the transfer of adults to new solutions. The criterion for test acceptability was mean survival of ≥80% in the control(s), an average of 20 or more young per surviving female in the control solutions, and production of at least three broods in 60% of the surviving control organisms.

4.5.5. Environmental Monitoring

The monitoring routine for the environmental conditions during the tests is summarised in Tables 8 and 9. The test chambers were maintained in a temperature-controlled water bath adjusted to maintain a sediment temperature of 23 ± 1ºC for chironomids and 25 ± 1ºC for cladocerans each under a 16 hour light: 8 hour dark photoperiod. Water bath and environmental chamber temperatures were monitored continuously using a Multi-Scan data logging system. Overlying water temperature and DO were measured using a WTW OXI 330 dissolved oxygen meter. A Denver Instruments pH meter was used to measure pH. Light intensity was measured using a Li-Cor Model LI-189 light meter equipped with a photometric sensor. Conductivity was measured with an Orion model 140 salinity/conductivity meter. Total ammonia, hardness, and alkalinity were conducted using a colorimetric method by HACH Company, Loveland, Colorado (HACH, 1997).

4.5.6. Reference Testing

Reference tests were conducted for both species tested. An acute 96-hour test with *Chironomus riparius* was conducted using potassium chloride. Test levels were 0.0 (control), 630, 1,250, 2,500, 5,000, and 10,000 mg l^{-1}. An acute 48-hour test with *Daphnia magna* was conducted using potassium chloride. Test levels were 0.0 (control), 125, 250, 500, 1,000, and 2,000 mg l^{-1}.

4.5.7. Statistical Analyses

Statistical significance for animal survival was determined by hypothesis testing. ABC Laboratories utilised specially written SAS or Excel based ToxCalc (1994) programs to calculate statistically significant differences from controls at the $p = 0.05$ level. Generally, the statistical approach was as follows. Analyses of each end-point between samples was evaluated by first analysing the data for normality and homogeneity of variance with Shapiro-Wilk's Test and either Bartlett's, Hartley's, or Lavene’s Test, respectively, before comparison of means. If the data were normally distributed and the variance was homogeneous, then analysis of variances (ANOVA) was utilised for the reproduction data along with Dunnett's procedure for comparing the means. Survival data were analysed using Fisher’s Exact test. If the assumptions of normality or homogeneity of variance were not met, transformations of the survival data were employed to allow the use of parametric procedures. If transformations (e.g., arc sine-square root transformation) of the survival data still did not meet assumptions of normality and homogeneity, then a non-parametric test was used to analyse these data.

Table 8. Chironomus riparius *study. Routine environmental conditions and frequency of measurement*

Environmental Condition	Frequency of Measurement	Measurement Location
Temperature	Continuously	Water Bath
Overlying Water Temperature	Daily during the first 10 days Three times per week thereafter	One Replicate of each Control & Site Samples
Dissolved Oxygen	Daily during the first 10 days	All Control & Site Samples
Overlying Water pH	Initiation and Termination	Composite Samples
Conductivity	Initiation and Termination	Composite Samples
Total Ammonia	Initiation and Termination	Composite Samples
Alkalinity	Initiation and Termination	Composite Samples
Hardness	Initiation and Termination	Composite Samples

Table 9. *Cladoceran study. Routine environmental conditions and frequency of measurement*

Environmental Condition	Frequency of Measurement	Measurement Location
Temperature	Continuously	Water Bath
Overlying Water Temperature	Daily New and Old Solutions	Extra Replicate For Water
Dissolved Oxygen	Daily New and Old Solutions	Extra Replicate For Water
Overlying Water pH	Daily New and Old Solutions	Extra Replicate For Water
Conductivity	Daily Old Solutions	Extra Replicate For Water
Total Ammonia	Daily Old Solutions	Extra Replicate For Water
Alkalinity	Daily Old Solutions	Extra Replicate For Water
Hardness	Daily Old Solutions	Extra Replicate For Water

5. RESULTS

5.1. Trace elements and SCPs

Trace element, SCP and organic content as loss-on-ignition (LOI) data are given in Table 10. As expected the north Scotland sites, Loch Coire Fionnaraich and Loch Doilet, show the lowest concentrations for all determinands except for Hg, Cu (higher than Burnmoor Tarn) and Ni (higher than all but Llagi, Chon and Agden) for Loch Doilet and As (higher than Tooting Common and Llagi) for Loch Coire Fionnaraich. Unexpectedly, Tooting Common Lake is not one of the more contaminated sites for these determinands. This may be due to the high sediment accumulation rate at the site (Table 3) effectively diluting the contaminant concentration. Table 3 shows that the period covered by the 0 – 5cm sample of Tooting Common Lake is estimated to be < 5 years whereas that of, for example, Scoat Tarn and Loch Coire Fionnaraich is estimated to be 50 – 55 years and that of Llyn Cwm Mynach, c. 90 years and this will be a significant factor in contaminant concentration and hence invertebrate exposure.

***Table 10**. SCP, trace element and LOI data.*

Site	SCP conc.	Hg	Pb	Cu	Ni	Zn	Cd	As	Loss-on-ignition
	(gDM^{-1})	(ng/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(%)
Loch Coire Fionnaraich	900	104	20	9.5	4.3	10.6	< 0.15	10.8	15.4
Loch Doilet	1840	188	41	21.7	27.5	67	0.34	3.08	27.6
Burnmoor Tarn	2465	126	60	17.1	9.2	178	3.41	39.3	31.6
Lochnagar	6154	206	236	22.7	4.4	74.2	1.07	34.7	31.4
Tooting Common Lake	6891	266	100	28.9	17.8	99	0.8	5.28	12.3
Llyn Cwm Mynach	9255	339	175	36.2	20.4	246	5.4	59.2	33.5
Scoat Tarn	11526	266	398	29.5	8.81	72.7	1.45	110.7	25.3
Llyn Llagi	13850	322	298	46.6	35.3	193	0.34	3.08	27.2
Loch Chon	14619	216	162	58.7	40.9	197	1.88	30.5	23.9
Agden Reservoir	15107	260	234	44.2	44.6	193	3.08	58.5	33.2

As the concentrations are low for all determinands in Tooting Common Lake, the correlations between determinands for the ten sites are good and, except for Ni / As positive. Many correlations are significant at the p=0.05 level especially, as shown in Table 11, where SCPs (indicators of deposition from industrial fossil-fuel combustion sources) are included. This suggests a primarily atmospheric source of these trace elements to the sites.

Table 11. *Correlation coefficients for trace element and SCP data. (Shaded values are significant at the p = 0.05 level)*

	SCP	*Hg*	*Pb*	*Cu*	*Ni*	*Zn*	*Cd*	*As*
SCP	1.00							
Hg	0.71	1.00						
Pb	0.74	0.65	1.00					
Cu	0.92	0.64	0.48	1.00				
Ni	0.70	0.44	0.15	0.84	1.00			
Zn	0.61	0.57	0.22	0.71	0.61	1.00		
Cd	0.23	0.32	0.07	0.23	0.12	0.74	1.00	
As	0.38	0.26	0.65	0.11	-0.15	0.16	0.50	1.00

5.2. Persistent organic pollutants

5.2.1. Organochlorine pesticides

Sediment concentration data for the organochlorine pesticides α-HCH, γ-HCH (lindane), DDT and its derivatives DDE and DDD are given in Table 12. Although the detection limits for these pesticides are low, almost all concentrations are below them. Neither of the HCH compounds are present in any sample. Similarly, DDT is not present in any sample although DDD and DDE are in a few. This is consistent with the banned status of DDT and the fact that DDD and DDE, as the stable degradation products, would be expected to predominate. Detectable levels of these are only observed at Loch Chon, Lochnagar, Scoat Tarn and Llyn Cwm Mynach.

Table 12. *Concentrations (μg kg^{-1} dry weight) of organochlorine pesticides in the sediment samples*

	α - HCH	γ - HCH (lindane)	DDE	DDD	DDT
Agden Reservoir	<0.1	<0.1	<0.1	<0.1	<0.1
Burnmoor Tarn	<0.1	<0.1	<0.1	<0.1	<0.1
Loch Chon	<0.1	<0.1	0.20	0.20	<0.1
Loch Doilet	<0.1	<0.1	<0.1	<0.1	<0.1
Loch Corrie Fionnaraich	<0.1	<0.1	<0.1	<0.1	<0.1
Llyn Llagi	<0.1	<0.1	<0.1	<0.1	<0.1
Llyn Cwm Mynach	<0.1	<0.1	0.10	<0.1	<0.1
Lochnagar	<0.1	<0.1	0.20	0.20	<0.1
Scoat Tarn	<0.1	<0.1	0.20	0.10	<0.1
Tooting Common Lake	<0.1	<0.1	<0.1	<0.1	<0.1

5.2.2. PCBs

Sediment concentrations of PCBs 28, 52, 101, 118, 138, 153 and 180 are given in Table 13. For all congeners except PCB 180, the highest concentrations are found at Tooting Common Lake, considerably so for PCB 28 – 118. Lochnagar has the highest concentration of PCB 180 and is also one of the more contaminated sites for PCB 118 – 153, as are Llyn Llagi and Scoat Tarn. Interestingly, Lochnagar, Llyn Llagi and Scoat Tarn are the three highest altitude sites in the dataset suggesting that this could be due to selective trapping of heavier PCBs at cooler, higher altitudes. The lowest concentrations for all congeners are found at Loch Coire Fionnaraich, Loch Doilet and Burnmoor Tarn. Concentrations for Loch Coire Fionnaraich are similar to those reported for recent sediments at a nearby site (Loch Coire nan Arr; Rose & Rippey, 2002) whilst reported concentrations for the uppermost sediments for a core (1988) from Esthwaite Water (Sanders et al., 1992) are significantly higher than any of our data for PCB 28 and 180 and at the upper end of our dataset for PCB 138 and 153.

Table 13. *Concentrations (µg kg^{-1} dry weight) of PCBs in the sediment sample. For each compound the highest concentration is shaded.*

	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180
Agden Reservoir	0.48	0.32	0.47	1.51	0.71	0.63	0.37
Burnmoor Tarn	<0.2	<0.2	<0.2	0.34	0.17	<0.1	<0.2
Loch Chon	0.29	0.26	0.41	1.67	0.92	0.75	0.51
Loch Doilet	<0.2	0.30	<0.2	0.54	0.28	0.25	<0.2
Loch Coire Fionnaraich	<0.2	<0.2	<0.2	0.35	0.25	0.22	<0.2
Llyn Llagi	0.44	0.32	0.62	1.93	1.15	1.01	0.62
Llyn Cwm Mynach	0.38	0.32	0.49	1.44	0.72	0.67	0.31
Lochnagar	0.30	0.31	0.55	2.19	1.37	1.01	0.81
Scoat Tarn	0.39	0.34	0.49	1.97	1.10	0.92	0.71
Tooting Common Lake	0.86	0.68	1.17	4.19	1.46	1.26	0.59

5.2.3. PBDEs

Sediment concentrations of PBDEs 47, 99, 100, 153 and 154 are shown in Table 14. In contrast to the PCB data where Tooting Common was one of the most contaminated sites, all PBDEs at this site are below the limit of detection. Similarly, Loch Coire Fionnaraich, Loch Doilet, Burnmoor Tarn (the three least contaminated sites from the PCB data) and Llyn Cwm Mynach also show concentrations below the limit of detection for all PBDEs. Agden Reservoir, Lochnagar and Loch Chon show the highest concentrations and in general the pattern within the PBDEs are as expected i.e. PBDE 99 > 47 >> 100, 153, and 154. Comparable data for UK sediments are rare, especially for lakes. Allchin et al. (1999) provide some PBDE data for UK river sediments although these are mainly from sites known to be contaminated by industrial sources. As expected, our results are at the low end of these data, and show similar concentrations for PBDEs 47 and 99 at Allchin et al.'s reference site on the River Tweed.

Table 14. *Concentrations (µg kg^{-1} dry weight) of PBDEs in the sediment samples. For each compound the highest concentration is shaded.*

	PBDE 47	PBDE 99	PBDE 100	PBDE 153	PBDE 154
Agden Reservoir	1.23	2.41	0.24	0.72	<0.2
Burnmoor Tarn	<0.4	<0.4	<0.2	<0.3	<0.2
Loch Chon	0.72	1.36	<0.2	0.36	<0.2
Loch Doilet	<0.4	<0.4	<0.2	<0.3	<0.2
Loch Coire Fionnaraich	<0.4	<0.4	<0.2	<0.3	<0.2
Llyn Llagi	<0.4	0.57	<0.2	<0.3	<0.2
Llyn Cwm Mynach	<0.4	<0.4	<0.2	<0.3	<0.2
Lochnagar	0.85	1.97	0.24	0.50	0.20
Scoat Tarn	<0.4	0.66	<0.2	<0.3	<0.2
Tooting Common Lake	<0.4	<0.4	<0.2	<0.3	<0.2

5.2.4. PAHs

Sediment concentrations for a range of PAH compounds are shown in Table 15. In general, molecular weight, boiling point and heat of vaporisation of the PAHs increase from left to right. Lowest concentrations for all compounds are found at Loch Coire Fionnaraich whilst low concentrations for most compounds are also found at Loch Doilet and Burnmoor Tarn. The exceptions are dibenzo[ah+ac]anthracene at Burnmoor Tarn and Loch Doilet and benzo[ghi] perylene at Loch Doilet where the sites appear to be relatively more contaminated with respect to other PAHs. These two PAH compounds have the greatest molecular weight of those measured.

For most PAHs, Agden Reservoir and Tooting Common Lake, the two sites closest to urban centres, have by far the highest concentrations. This is especially the case for benzo[j+k]fluoranthene and benzo[a]pyrene where concentrations in Agden Reservoir are 3 and 8 times higher than the next highest concentration (at Lochnagar and Llyn Llagi) respectively, despite Agden's reasonably rapid sediment accumulation rate (see Table 3). However, for the PAHs of greatest molecular weight neither Agden nor Tooting Common Lake have the highest concentrations and instead Llyn Llagi and Lochnagar appear to be the most contaminated. This seems to follow a similar altitudinal pattern to the PCBs whereby the compounds of greatest molecular weight show elevated concentrations at the higher sites.

In general, our data for Loch Coire Fionnaraich show similar concentrations to those reported for Loch Coire nan Arr (Rose & Rippey, 2002) whilst data reported for sediment cores taken from Lake District sites (Windermere, Esthwaite Water, Priest Pot) (Cranwell & Koul, 1989; Sanders et al., 1993) show concentrations significantly higher than those found in our samples. Exceptions are for phenanthrene where concentrations for Llyn Cwm Mynach were of a similar order to those reported for the Lake District, and for benzo[b]fluoranthene and benzo[a]pyrene where concentrations for Agden Reservoir are higher than for the reported Lake District sites except for Esthwaite Water (Sanders et al., 1993).

Table 15. *Concentrations (µg kg^{-1} dry weight) of PAHs in the sediment samples. For each compound the highest concentration is shaded.*

	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benzo[a]anthracene	Chrysene	Benzo[b]fluoranthene	Benzo[j+k]fluoranthene	Benzo[a]pyrene	Indeno[1,2,3-cd]pyrene	Dibenzo[ah+ac]anthracene	Benzo[ghi]perylene
Agden Reservoir	29.0	29.6	42.8	354.4	75.1	1212.9	1047.8	451.4	730.1	1713.5	1705.7	1731.1	141.5	54.7	157.5
Burnmoor Tarn	1.9	4.0	2.5	22.3	2.2	35.4	29.8	11.3	38.6	31.4	16.4	7.1	33.6	85.8	24.3
Loch Chon	8.2	6.0	12.1	263.6	33.3	324.1	225.9	112.9	323.1	240.9	173.9	76.3	199.8	62.9	178.3
Loch Doilet	1.0	1.3	1.9	16.3	1.8	33.5	26.7	11.7	43.4	43.8	27.4	11.8	52.6	49.4	47.2
Loch Coire Fionnaraich	1.3	<1	1.6	12.3	1.2	17.6	13.0	4.9	23.0	15.2	6.1	3.1	35.1	8.4	31.5
Llyn Llagi	19.8	23.9	34.9	327.9	67.2	764.3	611.2	236.8	593.3	494.1	386.8	206.0	404.4	136.0	388.4
Llyn Cwm Mynach	12.9	14.5	21.8	465.7	62.6	544.6	320.7	130.7	396.1	432.5	364.6	120.3	217.0	67.8	188.9
Lochnagar	13.9	6.9	14.6	196.5	39.2	440.5	255.8	107.1	559.9	1156.1	584.2	150.8	298.8	72.4	293.1
Scoat Tarn	19.0	25.9	28.8	315.7	50.7	446.0	295.2	132.0	309.4	113.4	68.7	34.7	83.6	29.2	76.2
Tooting Common	110.0	23.4	33.1	331.6	101.1	870.0	655.2	278.4	408.5	103.6	109.4	93.7	74.3	31.2	78.5

The sums of the PCB and PAH data are given in Table 16 and show that the highest PCB contamination is found in Tooting Common Lake whilst the highest PAH contamination is in Agden Reservoir. Both are considerably higher than any other site for these summed variables. Lowest concentrations for both ΣPCB and ΣPAH are found in Burnmoor Tarn, Loch Coire Fionnaraich and Loch Doilet which have been shown to be the least contaminated for almost all measured determinands.

Table 16. *ΣPCB and ΣPAH data for the sediment samples.*

	Sum PCB	Sum PAH
Burnmoor Tarn	0.96	346.74
Loch Coire Fionnaraich	1.22	174.56
Loch Doilet	1.67	369.67
Llyn Cwm Mynach	4.33	3360.43
Agden Reservoir	4.49	9477.04
Loch Chon	4.81	2241.27
Scoat Tarn	5.92	2028.47
Llyn Llagi	6.09	4694.92
Lochnagar	6.54	4189.58
Tooting Common Lake	10.21	3301.99

5.3. Toxicity tests

5.3.1. Chironomid test results

Initially this study was to be conducted as a 10-day survival and growth test. However, midge began to emerge in the control and in the Scoat Tarn sample on Day 9. Animals that pupate cannot be measured for growth so the study was continued as a survival and emergence test. The study was continued until four days after the last control animal had emerged. The control reached 100% emergence on Day 12. All remaining replicates were terminated on Day 17 and observed for any remaining chironomids. Early emergence can be explained primarily by the elevated temperatures during culture and testing.

Survival

Day 17 biological observations are presented in Table 17. Survival percentages of chironomids for all replicate test chambers are presented in Table 18. Survival numbers include those animals that emerged prior to termination on Day 17. Mean survival ranged from 58% in Llyn Llagi to 100% in Tooting Common Lake. Survival in the ABC control was 100%. Using Fishers Exact test, survival of Agden Reservoir (88%), Loch Doilet (64%), Llyn Llagi (58%), and Scoat Tarn (88%) were significantly reduced as compared to the ABC control. The ABC control met the test acceptability criterion for survival.

***Table 17**. Chironomus riparius: Biological Observations. Day 17 Termination*

	Number of Organisms					Treatment Percent Survival
	1	2	3	4	5	
ABC Control (1 - 5)	10 E	10 E	10 E	10 E	10 E	100
ABC Control (6 - 8)	10 E	10 E	10 E			
Agden Reservoir	9 E 1 NF	8 E 2 NF	10 E	10 E	7 E 3 NF	88
Burnmoor Tarn	9 E 1 NF	10 E	7 E 2 PN 1 NF	10 E	8 E 1 PN 1 NF	94
Llyn Cwm Mynach	10 E	10 E	9 E 1 PN	7 E 3 NF	10 E	94
Llyn Llagi	10 E	1 E 9 NF	1 E 9 NF	7 E 3 NF	10 E	58
Loch Chon	9 E 1 NF	10 E	10 E	8 E 2 NF	9 E 1 LN	94
Loch Doilet	10 E	4 E 2 LS 4 NF	9 E 1 PS	2 E 8 NF	3 E 1 PS 6 NF	64
Lochnagar	8 E 2 NF	10 E	9 E 1 NF	10 E	9 E 1 NF	92
Scoat Tarn	10 E	9 E 1 NF	5 E 5 NF	10 E	10 E	88
Tooting Common Lake	10 E	10 E	9 E 1 LS	10 E	6 E 1 PS 3 LS	100

Key: E = Emerged, L = Larvae, P = Pupae, N = Normal, S = Small, NF = Not Found

Emergence

Emergence percentages of chironomids for all replicate test chambers are presented in Tables 19 to 29. Emergence on Day 12 ranged from 16% in Burnmoor Tarn to 78% in Tooting Common Lake. Total emergence to Day 17 (termination) ranged from 56% in Loch Doilet to 92% in Lochnagar. Emergence in the ABC control was 100% on Day 12. All site samples were significantly reduced for the number emerged as compared to the control for Day 12 and for Day 17. All lake sediments showed delayed emergence as compared to the control. However, only lake samples from Llyn Llagi and Loch Doilet appear to have any ecological significance as all other samples exhibited greater than 88% emergence by Day 17. Llyn Llagi was 58% and Loch Doilet 56% emerged at Day 17. The ABC control met the test acceptability criterion of greater than 50% for emergence.

Table 18. Chironomus riparius*: Replicate Percent Survival*

	Midge: Replicate Percent survival [a]					
	1	2	3	4	5	Treatment
ABC Control (1-5)	100	100	100	100	100	100
ABC Control (6 - 8)	100	100	100			
Agden Reservoir	90	80	100	100	70	88 [b]
Burnmoor Tarn	90	100	90	100	90	94
Llyn Cwm Mynach	100	100	100	70	100	94
Llyn Llagi	100	10	10	70	100	58 [b]
Loch Chon	90	100	100	80	100	94
Loch Doilet	100	60	100	20	40	64 [b]
Lochnagar	80	100	90	100	90	92
Scoat Tarn	100	90	50	100	100	88 [b]
Tooting Common Lake	100	100	100	100	100	100

[a] Includes emergence and larvae / pupae present at termination.
[b] Statistically significant reduction as compared to the ABC Control.

Chironomus riparius environmental monitoring results

Water bath temperature was maintained between 22.2 and 24.3 °C as recorded continuously with the multi-scan data recording system. Mean system temperature was 23.8 °C as indicated from the multi-scan graph. Overlying water temperatures were maintained between 21.8 and 23.9 °C as recorded in each replicate sample. Overlying dissolved oxygen ranged from 3.5 to 9.6 mg l^{-1} during the test. Water quality ranges are presented in Table 30. All water quality parameters were within acceptable limits for maintenance of healthy *Chironomus riparius* populations. Temperature was outside the 23 ± 1 °C limits. This excursion did not impact the health and survival of the animals. It may have, however, impacted the rate at which the animals emerged by decreasing the time to emergence.

Table 19. Chironomus riparius- *Daily emergence: ABC Control*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	5	3	1	1	--	--	--	--	--	10
2	5	2	1	2	--	--	--	--	--	10
3	7	3	--	--	--	--	--	--	--	10
4	6	4	--	--	--	--	--	--	--	10
5	5	3	1	1	--	--	--	--	--	10
6	4	5	1	--	--	--	--	--	--	10
7	7	3	--	--	--	--	--	--	--	10
8	4	5	1	--	--	--	--	--	--	10
Total	43	28	5	4	--	--	--	--	--	80
Running Total	43	71	76	80	--	--	--	--	--	--
Daily % Emergence	54	35	6	5	--	--	--	--	--	--
Overall % Emergence	54	89	95	100	--	--	--	--	--	100

Table 20. Chironomus riparius - *Daily emergence: Agden Reservoir*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	--	1	1	1	0	2	1	3	0	9
2	--	1	2	1	1	1	2	0	0	8
3	--	1	1	3	4	0	1	--	--	10
4	--	3	2	1	2	1	1	--	--	10
5	--	1	2	1	1	1	0	1	0	7
Total	--	7	8	7	8	5	5	4	0	44
Running Total	--	7	15	22	30	35	40	44	44	44
Daily % Emergence	--	14	16	14	16	10	10	8	0	--
Overall % Emergence		14	30	44	60	70	80	88	88	88

Table 21. Chironomus riparius - *Daily emergence: Burnmoor Tarn*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	1	1	1	3	2	0	1	0	9
2	0	1	0	1	3	3	0	1	1	10
3	0	0	1	0	1	1	1	1	2	7
4	0	0	1	0	1	1	2	4	1	10
5	0	1	0	0	0	1	0	4	2	8
Total	0	3	3	2	8	8	3	11	6	44
Running Total	0	3	6	8	16	24	27	38	44	44
Daily % Emergence	0	6	6	4	16	16	6	22	12	--
Overall % Emergence	0	6	12	16	32	48	54	76	88	88

Table 22. Chironomus riparius – *Daily emergence: Llyn Cwm Mynach*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	1	0	0	2	1	1	4	1	10
2	0	2	2	2	2	0	1	1	--	10
3	0	0	0	0	2	1	1	3	2	9
4	0	0	2	0	2	1	1	1	0	7
5	0	0	1	1	2	3	2	1	--	10
Total	0	3	5	3	10	6	6	10	2	46
Running Total	0	3	8	11	21	27	33	43	45	46
Daily % Emergence	0	6	10	6	20	12	12	20	4	--
Overall % Emergence	0	6	16	22	42	54	66	86	90	92

Table 23. Chironomus riparius – *Daily emergence: Llyn Llagi*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	1	0	2	1	4	1	0	1	10
2	0	1	0	0	0	0	0	0	0	1
3	0	1	0	0	0	0	0	0	0	1
4	0	0	1	0	0	1	3	0	2	7
5	0	1	2	0	1	0	5	1	--	10
Total	0	4	3	2	2	5	9	1	3	29
Running Total	0	4	7	9	11	16	25	26	29	29
Daily % Emergence	0	8	6	4	4	10	18	2	6	--
Overall % Emergence	0	8	14	18	22	32	50	52	58	58

Table 24. Chironomus riparius- *Daily emergence: Loch Chon*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	0	2	3	3	1	0	0	0	9
2	0	2	3	2	2	1	--	--	--	10
3	0	1	3	1	1	3	1	--	--	10
4	0	1	3	2	1	1	0	0	0	8
5	0	1	3	2	2	1	0	0	0	9
Total	0	5	14	10	9	7	1	0	0	46
Running Total	0	5	19	29	38	45	46	46	46	46
Daily % Emergence	0	10	28	20	18	14	2	0	0	--
Overall % Emergence	0	10	38	58	76	90	92	92	92	92

Table 25. Chironomus riparius - *Daily emergence: Loch Doilet*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	3	2	2	1	2	--	--	--	10
2	0	0	1	1	0	2	0	0	0	4
3	0	1	0	0	2	5	1	0	0	9
4	0	1	0	1	0	0	0	0	0	2
5	0	1	0	1	1	0	0	0	0	3
Total	0	6	3	5	4	9	1	0	0	28
Running Total	0	6	9	14	18	27	28	28	28	28
Daily % Emergence	0	12	6	10	8	18	2	0	0	--
Overall % Emergence	0	12	18	28	36	54	56	56	56	56

Table 26. Chironomus riparius - *Daily emergence: Lochnagar*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	2	1	1	1	3	0	0	0	8
2	0	0	1	1	1	4	1	1	1	10
3	0	1	0	1	5	1	1	0	0	9
4	0	0	4	2	0	2	2	--	--	10
5	0	1	1	1	0	3	2	1	0	9
Total	0	4	7	6	7	13	6	2	1	46
Running Total	0	4	11	17	24	37	43	45	46	46
Daily % Emergence	0	8	14	12	14	26	12	4	2	--
Overall % Emergence	0	8	22	34	48	74	86	90	92	92

Table 27. Chironomus riparius – *Daily emergence: Scoat Tarn*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	1	1	1	5	1	1	--	--	10
2	0	1	3	4	1	0	0	0	0	9
3	0	1	2	1	1	0	0	0	0	5
4	0	2	1	2	2	2	1	--	--	10
5	1	1	1	5	0	1	1	--	--	10
Total	1	6	8	13	9	4	3	0	0	45
Running Total	1	7	15	28	37	41	44	44	44	44
Daily % Emergence	2	12	16	26	18	8	6	0	0	--
Overall % Emergence	2	14	30	56	74	82	88	88	88	88

Table 28. Chironomus riparius - *Daily emergence: Tooting Common Lake*

Replicate	Day Number									
	9	10	11	12	13	14	15	16	17	Total
1	0	7	3	--	--	--	--	--	--	10
2	0	5	2	1	0	2	--	--	--	10
3	0	4	0	2	2	1	0	0	0	9
4	0	7	1	2	--	--	--	--	--	10
5	0	3	0	2	1	0	0	0	0	6
Total	0	26	6	7	3	3	0	0	0	45
Running Total	0	26	32	39	42	45	45	45	45	45
Daily % Emergence	0	52	12	14	6	6	0	0	0	--
Overall % Emergence	0	52	64	78	84	90	90	90	90	90

Table 29. Chironomus riparius - *Emergence Days 12 and 17*

	Day 12 Emergence							Day 17 Emergence	
	Replicates Number Emerged					Sample Total	% Emergence	Sample Total	% Emergence
	1	2	3	4	5				
ABC Control (1-5)	10	10	10	10	10	80	100	80	100
ABC Control (6-8)	10	10	10						
Agden Reservoir	3	4	5	6	4	22	44	44	88
Burnmoor Tarn	3	2	1	1	1	8	16	44	88
Llyn Cwm Mynach	1	6	0	2	2	11	22	46	92
Llyn Llagi	3	1	1	1	3	9	18	28	56
Loch Chon	5	7	5	6	6	29	58	46	92
Loch Doilet	7	2	1	2	2	14	28	28	56
Lochnagar	4	2	2	6	3	17	34	46	92
Scoat Tarn	3	8	4	5	8	28	56	44	88
Tooting Common Lake	10	8	6	10	5	39	78	45	90

Table 30. Chironomus riparius*: Overlying water quality ranges*

	Temperature (°C)	Dissolved Oxygen (mg l^{-1})
ABC Control	21.8 – 23.9	4.2 – 8.3
Agden Reservoir	22.0 – 23.7	5.3 – 8.8
Burnmoor Tarn	21.9 – 23.7	5.7 – 9.6
Llyn Cwm Mynach	22.2 – 23.7	5.8 – 9.2
Llyn Llagi	22.3 – 23.7	5.4 – 9.3
Loch Chon	22.5 – 23.8	6.2 – 9.0
Loch Doilet	22.2 – 23.8	4.8 – 9.3
Lochnagar	22.2 – 23.9	5.4 – 8.9
Scoat Tarn	22.1 – 23.9	5.2 – 9.1
Tooting Common Lake	21.8 – 23.9	3.5 – 8.0

5.3.2. Cladoceran test results

Survival

Replicate percent survival is presented in Table 31. Survival ranged from 80% in Llyn Llagi to 100% in all other lake sediment samples. Survival in the control was 100%. There was no significant reduction in survival for any of the lake sediment samples as compared to the control.

Reproduction

Mean reproduction ranged from 36 neonates in the lake sediment sample from Llyn Llagi to 68 in the sample from Tooting Common Lake (Table 32). Mean reproduction in the control was 67 neonates. Reproduction was significantly reduced in lake sediment sample Llyn Llagi as compared to the control.

Cladoceran environmental monitoring results

Water bath temperature was maintained between 31 and 25.7 °C as recorded continuously with the multi-scan data recording system. The low reading was due to the probe being removed from the water for a short time. Overlying water temperatures were maintained between 24.0 and 25.3 °C as recorded in each replicate sample. Overlying dissolved oxygen concentration ranged from 5.2 to 8.6 mg l^{-1} during the test. Overlying pH ranged from 7.48 to 8.60 during the test. Water quality ranges can be found in Table 33. All water quality parameters were within acceptable limits for maintenance of healthy *Daphnia magna* populations.

***Table 31**. Survival of* Daphnia magna *during a 7-day static renewal exposure to lake sediments.*

	Replicate Percent Survival										
	1	2	3	4	5	6	7	8	9	10	Treatment
ABC Control	100	100	100	100	100	100	100	100	100	100	100
Agden Reservoir	100	100	100	100	100	100	100	100	100	100	100
Burnmoor Tarn	100	100	100	100	100	100	100	100	100	100	100
Llyn Cwm Mynach	100	100	100	100	100	100	100	100	100	100	100
Llyn Llagi	100	0	100	100	100	0	100	100	100	100	80
Loch Chon	100	100	100	100	100	100	100	100	100	100	100
Loch Doilet	100	100	100	100	100	100	100	100	100	100	100
Lochnagar	100	100	100	100	100	100	100	100	100	100	100
Scoat Tarn	100	100	100	100	100	100	100	100	100	100	100
Tooting Common	100	100	100	100	100	100	100	100	100	100	100

Table 32. *Total young production per adult* Daphnia magna *during a 7-day static renewal exposure to lake sediment*

	Number of Young/Adult											
	1	2	3	4	5	6	7	8	9	10	Treatment Total	Treatment Mean [a]
ABC Control	61	49	72	58	58	68	62	67	56	65	616	61.6
Agden Reservoir	58	66	55	61	58	57	72	56	57	70	610	61.0
Burnmoor Tarn	64	68	66	65	63	74	68	64	56	60	648	64.8
Llyn Cwm Mynach	43	61	63	65	73	70	72	68	66	57	638	63.8
Llyn Llagi	47	9	45	44	44	6	46	33	45	38	357	35.7 [b]
Loch Chon	62	62	65	61	59	68	64	68	56	69	634	63.4
Loch Doilet	59	45	53	50	58	61	56	60	64	54	560	56.0
Lochnagar	53	46	55	59	60	55	55	55	61	73	572	57.2
Scoat Tarn	64	57	53	62	59	59	60	52	68	57	591	59.1
Tooting Common	64	60	70	66	70	67	57	69	80	75	678	67.8

[a] Based on all ten replicates not number surviving.

[b] Statistically significant reduction in reproduction as compared to the control (α=0.05).

Table 33. *Ranges for water quality measurements during a 7-day static renewal exposure of* Daphnia magna *to lake sediments*

	Temperature (°C)	Dissolved Oxygen (mg l^{-1})	pH
ABC Control	24.0 – 24.8	6.1 – 7.9	8.18 – 8.60
Agden Reservoir	24.0 – 24.6	6.1 – 8.1	7.48 – 8.02
Burnmoor Tarn	24.0 – 24.7	6.4 – 8.6	7.72 – 8.30
Llyn Cwm Mynach	24.0 – 24.5	6.3 – 8.2	7.67 – 8.13
Llyn Llagi	24.0 – 24.5	6.1 – 8.3	7.63 – 8.06
Loch Chon	24.0 – 24.5	6.1 – 8.1	7.59 – 7.98
Loch Doilet	24.0 – 24.5	6.0 – 8.1	7.61 – 8.06
Lochnagar	24.1 – 24.9	6.1 – 8.3	7.64 – 8.20
Scoat Tarn	24.3 – 25.0	6.1 – 7.9	7.71 – 8.16
Tooting Common Lake	24.3 – 25.3	5.2 – 7.4	7.97 – 8.15

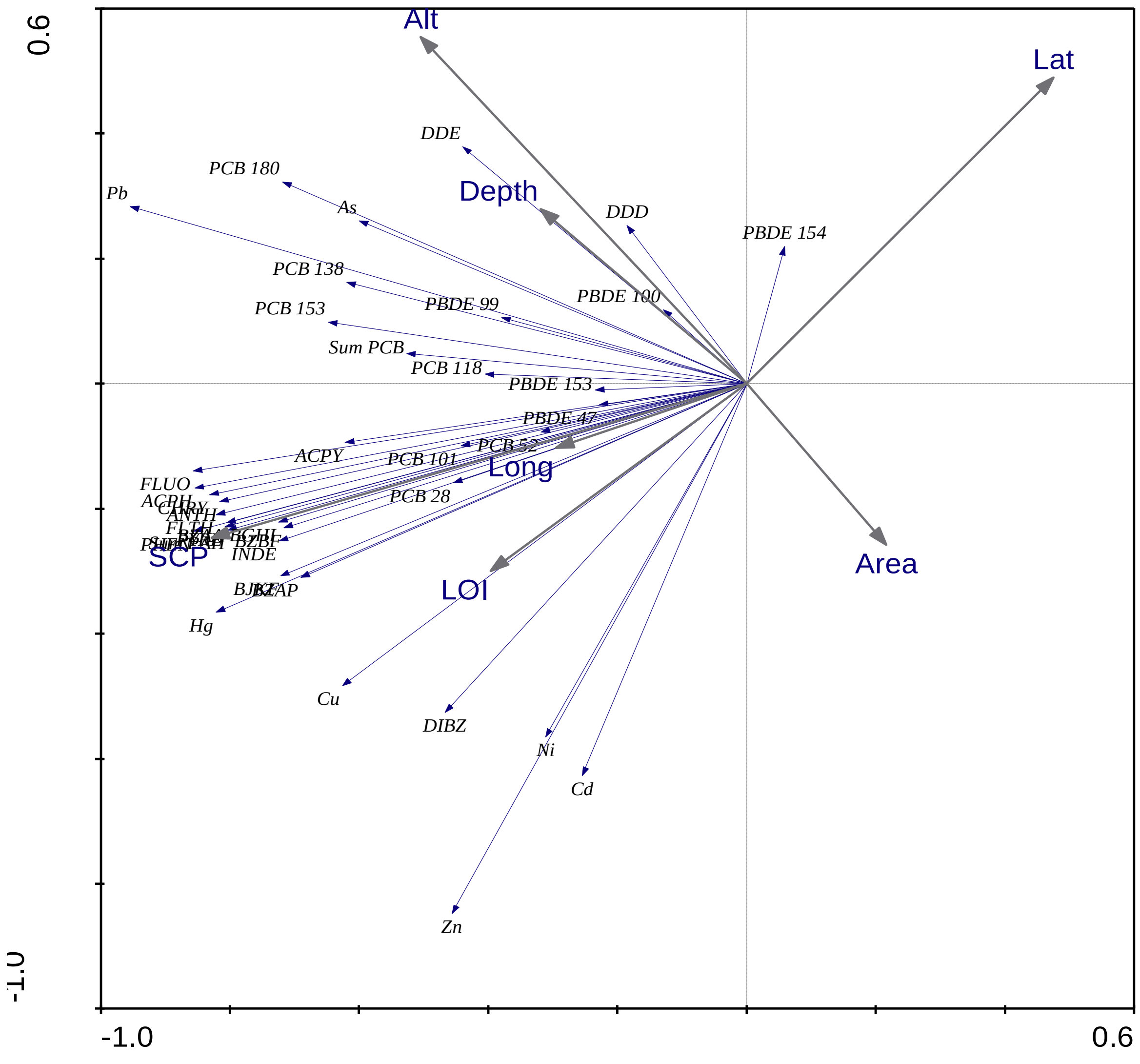
6. DISCUSSION

6.1. Pollutant distribution

Principal components analysis (PCA) can be used to provide a summary of the relationships between the 40 determinands measured on the ten sediment samples and see how these might be explained by environmental and morphological site data. Figure 4 shows the bi-plot of the first two principal component axes. PCA Axis 1 appears to be strongly related to SCP and PAH concentrations whilst Axis 2 is related to altitude, latitude and depth.

As expected the PAH data plot together showing strong inter-compound correlations. SCPs also show a strong relationship with the PAH data and the lighter PCBs (28, 52, 101) and these are inversely related to latitude. This confirms the general distribution trend of higher concentrations in the southern sites and lower concentrations in the north. Hg, Cu and to a lesser extent Ni, Cd and Zn also appear to have a similar distribution, as does loss-on-ignition.

***Figure 4**. PCA of measured determinands and selected morphological and location data.*



As suggested above, the heavier PCBs (118, 138, 153 and especially 180) are related to altitude, probably due to selective trapping (Grimalt et al., 2001) and this is highlighted in the summary figure. DDE and DDD also appear to be related to altitude rather than latitude, as do As, Pb and some of the PBDEs.

Latitude and altitude appear to be important criteria for the distribution of pollutants in UK lake sediments. The inverse relationship with latitude was expected, but less so were the high concentrations of some pollutants in high elevation, remote lake sediments. This is not simply a sediment accumulation rate phenomenon, as it does not occur for all pollutants. However, this is a small dataset and the sampling strategy (i.e. homogenised 0 – 5cm layer) is not ideal for an investigation into pollutant distribution and hence the role of altitude on this distribution within the UK needs to be investigated further.

6.2. Concentrations of heavy metals

Comparison of the 0 – 5 cm concentrations of Pb and Zn with those taken in 1985 – 1990 show a decrease in the period at some sites (Table 34); Pb and Zn at Burnmoor Tarn and Scoat Tarn, and Zn at Llyn Cwm Mynach and Loch Chon. The decrease in Pb is probably due to falling emissions as a result of the widespread use of unleaded petrol; a decrease in Pb concentration in lake sediment cores has been recorded in Scotland (Eades et al. 2002) and the USA (Callender & van Metre 1997). The lack of decline in Pb at Lochnagar is in agreement with the catchment input hypothesis (Yang et al., 2002) whereby in-wash of previously deposited Pb, stored in catchment peats, obscures reductions expected from the decline in emissions observed at other sites.

Table 34. *The concentration of Pb, Cu and Zn in 0-5 cm of sediment measured during the period 1985-90 and in 2002.*

Lake	Pb 2002	Pb 1985-90	Cu 2002	Cu 1985-90	Zn 2002	Zn 1985-90
Loch Coire Fionnaraich [a]	20	51	9.5	11	10.6	52
Loch Doilet	41	56	21.7	36	67	148
Burnmoor Tarn	60	382	17.1	47	178	752
Lochnagar	236	185	22.7	143	74.2	19
Llyn Cwm Mynach	175	220	36.2	55	246	813
Scoat Tarn	398	541	29.5	42	72.7	180
Llyn Llagi	298	230	46.6	50	193	265
Loch Chon	162	221	58.7	74	197	372

[a] 1985 – 1990 data from nearby Loch Coire nan Arr.

The ranges of trace metal concentration are similar to those found in other lake sediments contaminated by deposition from the atmosphere in Europe (Johansson 1989; Rognerud & Fjeld 1993) and the USA (Norton et al. 1992). It is interesting that the trace metal concentrations measured in the lake sediments in 2002 (Table 10) are generally greater than those in estuarine sediments (Field et al. 2002; Long et al. 1998), where there is a great focus of current research.

6.3. Toxicants

The likely contribution of each chemical to toxicity is established using the toxic quotient (Long et al. 1998). This is defined as (concentration/PEC), where PEC is the Probable Effect Concentration, and the higher the value the more likely there is to be toxicity from that chemical. The concentration data (Table 10 & Tables 12-15) and PEC values (Table 1) show that the most important contributors to toxicity in the sediments are trace metals (Table 35) > PAHs (Table 36), and that PCBs and organochlorines (Table 37) are not likely to be important. However, it is interesting to note that, with the exception of Tooting Common Lake, the toxicity quotients for PCBs are highest in the higher elevated sites.

This evidence, that there may be toxicity from heavy metals and PAHs in some lake sediments in the UK, but not from PCBs and organochlorines, is new and valuable information. Within each of the two toxicant groups, Pb and As are the trace elements and chrysene, pyrene, fluoranthene, phenanthrene and benzo[a]pyrene the PAHs that contribute to the toxicity. However, this evidence for toxicity, based on comparing chemical concentrations with Probable Effect Concentrations, needs to be supplemented by direct evidence.

6.4. Combination of toxicants

There is more than one toxicant in the sediment samples and this is usually the case. How the total toxicity from more than one chemical is derived is a topic of active research. The two main options are concentration-addition models (toxic unit models) (Field et al., 2002) and response-addition models (Smith et al., 2000). The current consensus is that a concentration-addition model should be used when the toxicants act in a similar way, for example for the heavy metals and from the PAH group, while the response-addition model is appropriate when they act in different ways; simple similar action and independent action, respectively.

Table 35. *The toxicity quotient for trace metals in the lake sediment samples, together with the mean and maximum values.*

Sample	Hg	Pb	Cu	Ni	Zn	Cd	As	Mean	Max
Loch Coire Fionnaraich	0.10	0.16	0.06	0.09	0.02	0.02	0.33	0.11	0.33
Loch Doilet	0.18	0.32	0.15	0.57	0.15	0.07	0.09	0.22	0.57
Burnmoor Tarn	0.12	0.47	0.11	0.19	0.39	0.68	1.19	0.45	1.19
Lochnagar	0.19	1.84	0.15	0.09	0.16	0.21	1.05	0.53	1.84
Tooting Common Lake	0.25	0.78	0.19	0.37	0.22	0.16	0.16	0.30	0.78
Llyn Cwm Mynach	0.32	1.37	0.24	0.42	0.54	1.08	1.79	0.82	1.79
Scoat Tarn	0.25	3.11	0.20	0.18	0.16	0.29	3.35	1.08	3.35
Llyn Llagi	0.30	2.33	0.31	0.73	0.42	0.07	0.09	0.61	2.33
Loch Chon	0.20	1.27	0.39	0.84	0.43	0.38	0.92	0.63	1.27
Agden Reservoir	0.25	1.83	0.30	0.92	0.42	0.62	1.77	0.87	1.83

Table 36. *The toxicity quotient for selected PAHs and total PAH in the lake sediment samples. Fl is Fluorene, Ph is Phenanthrene, An is Anthracene, Ft is Fluoranthene, Py is Pyrene, B[a]An is Benzo[a]anthracene, Ch is Chrysene and B[a]Py is Benzo[a]pyrene.*

Sample	Fl	Ph	An	Ft	Py	B[a]An	Ch	B[a]Py	Total PAHs
Loch Coire Fionnaraich	0.003	0.010	0.001	0.008	0.009	0.005	0.018	0.002	0.01
Loch Doilet	0.004	0.014	0.002	0.015	0.018	0.011	0.034	0.008	0.02
Burnmoor Tarn	0.005	0.019	0.003	0.016	0.020	0.011	0.030	0.005	0.02
Lochnagar	0.027	0.168	0.046	0.198	0.168	0.102	0.434	0.104	0.18
Tooting Common Lake	0.062	0.283	0.120	0.390	0.431	0.265	0.317	0.065	0.14
Llyn Cwm Mynach	0.041	0.398	0.074	0.244	0.211	0.125	0.307	0.083	0.15
Scoat Tarn	0.054	0.270	0.060	0.200	0.194	0.126	0.240	0.024	0.09
Llyn Llagi	0.065	0.280	0.079	0.343	0.402	0.226	0.460	0.142	0.21
Loch Chon	0.023	0.225	0.039	0.145	0.149	0.108	0.250	0.053	0.10
Agden Reservoir	0.080	0.303	0.089	0.544	0.689	0.430	0.566	1.194	0.42

Table 37. *The toxicity quotient for total PCBs and selected organochlorines, DDE, DDD and DDT, in the lake sediment samples.*

Sample	PCBs	DDE	DDD	DDT
Loch Coire Fionnaraich	0.001	0.00	0.00	0.00
Loch Doilet	0.002	0.00	0.00	0.00
Burnmoor Tarn	0.001	0.00	0.00	0.00
Lochnagar	0.010	0.20	0.20	0.00
Tooting Common Lake	0.015	0.00	0.00	0.00
Llyn Cwm Mynach	0.006	0.10	0.00	0.00
Scoat Tarn	0.009	0.20	0.10	0.00
Llyn Llagi	0.009	0.00	0.00	0.00
Loch Chon	0.007	0.20	0.20	0.00
Agden Reservoir	0.007	0.00	0.00	0.00

The total toxicity is therefore estimated by calculating the average toxicity quotient for each of the two toxicant groups, trace metals and PAHs, and then deriving the mean and the sum of the two quotients (Table 38). In this way, the similar action of the toxicants that form the trace metal group and those that form the PAH group is averaged and the independent action of each group is combined. The mean of the average toxicity quotient for the trace metals and the PAHs is also calculated and the rank order of the samples using this value, and that using the sum of the two quotients, is identical (Table 38). The relative toxicity of the samples as represented by both the mean and sum of the average toxicity quotients for heavy metals and PAHs is Agden Reservoir > Scoat Tarn > Llyn Cwm Mynach > Llyn Llagi > Loch Chon > Lochnagar > Burnmoor Tarn > Tooting Common Lake > Loch Doilet, with toxicity only likely in the first four or five samples as toxicity is only expected when the mean toxicity quotient is ≥ 0.5 (MacDonald et al., 2000). While this approach based on a chemical evaluation does provide useful guidance on biological effects (O’Connor et al. 1998); this evidence needs to be supplemented by direct evidence for toxicity which is evaluated in the next section.

Table 38. *The mean toxicity quotient for trace metals and for PAHs in the lake sediments and the mean and sum of the two values. The ranking of sample toxicity based on the mean and sum of the toxicity quotient for heavy metals and for PAHs is also given.*

Sample	Trace metals	PAHs	Mean	Sum	Rank, mean	Rank, sum
Agden Reservoir	0.87	0.42	0.64	1.29	1	1
Burnmoor Tarn	0.45	0.02	0.23	0.47	7	7
Llyn Cwm Mynach	0.82	0.15	0.49	0.97	3	3
Llyn Llagi	0.61	0.21	0.41	0.81	4	4
Loch Chon	0.63	0.10	0.37	0.73	5	5
Loch Doilet	0.22	0.02	0.12	0.23	9	9
Lochnagar	0.53	0.18	0.36	0.71	6	6
Scoat Tarn	1.08	0.09	0.58	1.17	2	2
Tooting Common Lake	0.30	0.14	0.22	0.45	8	8

6.5. Evaluation of sediment toxicity

The evaluation of the chemical evidence for toxicity found that the trace metal and PAH concentrations determined in the lake sediments are large enough in some of the samples to produce toxicity. Further assessment of the toxicity quotients indicated that there might be toxicity in Agden Reservoir, Scoat Tarn, Llyn Cwm Mynach and Llyn Llagi, and possibly Loch Chon. The evaluation of toxicity test results found evidence for toxicity in Agden Reservoir, Llyn Llagi, Loch Doilet and Scoat Tarn.

Combining the chemical and sediment toxicity test evidence shows that there are biological effects in sediment when the mean toxicity quotient for heavy metals and PAHs is greater than approximately 0.40 and when the sum of the quotients for trace metals and PAHs is greater than approximately 0.80. Loch Doilet is an exception, as the sediment toxicity test shows evidence of toxicity, yet the concentration of the toxicants (Table 10 & Tables 12-15) and the toxicity quotients (Tables 35 - 38) are very low. We currently have no explanation for this finding. The values for Llyn Cwm Mynach are above the 0.40 and 0.80 critical values, yet the toxicity test results indicate that there is no toxicity. This behavior is not uncommon, as chemical evidence for toxicity does not always produce toxicity (Dave, 1992a; Dave, 1992b; Besser et al., 1996; O'Connor et al., 1998; Long et al., 1998; Field et al., 2002; Smith et al., 2003).

Our assessment of the chemical and toxicological evidence from lake sediments that cover the range of contamination by trace metals, PAHs, PCBs and organochlorines in the UK is that there is toxicity in some lakes due to trace metals and PAHs. Toxicity was found to be likely when the mean toxicity quotient for heavy metals and PAHs was greater than approximately 0.40 and when the sum of the quotients was greater than 0.80. Both values are provisional. The most important toxicants are likely to be Pb and As within the trace element group and chrysene, pyrene, fluoranthene, phenanthrene and benzo[a]pyrene within the PAHs.

6.6. Evaluation of ecological effects

Chemical concentrations above Probable Effect Concentrations or above critical toxicity quotients do not always lead to toxicity in sediments (Dave 1992a; Dave 1992b; Besser et al. 1996; O'Connor et al. 1998; Long et al. 1998; Field et al. 2002; Smith et al. 2003) and evidence of toxicity from sediment toxicity tests does not always lead to ecological effects in the sediments of a lake (Besser et al. 1996; Long et al., 2001). Whilst good correlations between contaminant concentrations, sediment toxicity test results and benthic community characteristics, including hazard quotients, are found (Besser et al., 1996; Long et al., 2001), and ecologically relevant losses in abundance and diversity of benthic fauna frequently correspond with reduced survival in laboratory tests, these are statistical relationships. Variability of response, toxicity test result with toxicant concentration and ecological change and toxicity test result, means that extrapolation to ecological effects must be completed carefully. Ideally, a substantial dataset of toxicant concentrations, toxicity test results and ecological effects should be evaluated. The most complete dataset is that of Long et al. (2001), but this is for estuarine sediments, and the only one for freshwater sediments is that of Besser et al. (1996); that of Dave (1992b) has data for eight sites, but cannot be used here as the sediment toxicity test results are given as EC_{50}s. Besser et al. (1996) has toxicant concentrations, sediment toxicity test results and ecological effects for five channel samples. They use an early and crude toxicity quotient, but it can be converted to the one used here by dividing their values by ten. If we use this conversion, then Besser et al. (1996) found that trace metal toxicity quotients greater than 0.7 and PAH toxicity quotient greater than 1.0 consistently caused severe toxicity in sediment toxicity tests and ecological effects. This is in agreement with our findings; toxicity is likely when the trace metal toxicity quotient is greater than approximately 0.6 (Table 38); this is also equivalent to a mean toxicity quotient for trace metals and PAHs greater than approximately 0.40 and the sum of the quotients for trace metals and PAHs greater than 0.80. While this assessment of ecological effects must be considered uncertain, it suggests that there may be ecological effects in the sediments of Agden Reservoir, Llyn Llagi and Scoat Tarn.

7. CONCLUSIONS

The findings from this pilot investigation are that there is toxicity in the sediments of Agden Reservoir, Llyn Llagi and Scoat Tarn due to trace metals and PAHs, mainly Pb, As, Chrysene, Pyrene, Fluoranthene, Phenanthrene and Benzo[a]pyrene, that may lead to ecological effects.

Provisional toxicity quotients that may be used in risk assessment have also been derived; mean toxicity quotient for heavy metals and PAHs of approximately 0.40 and sum of the quotients for trace metals and PAHs of 0.80.

Two of the sites for which toxicity has been demonstrated are upland lakes removed from direct effects. The role of altitude in the distribution of pollutants within the UK remains to be confirmed, however, the results do indicate that concentrations of trace metals and PAHs towards the heavier end of the range, found in remote lake sediments in the UK today, do cause toxicity which possibly results in ecological effects. The central London site showed no toxicity but this may be due to rapid sediment accumulation rates diluting pollutant concentrations.

Further, upland lakes tend to have slow sediment accumulation rates and therefore, given the active burrowing depth of benthic invertebrates, it is likely that these sites will continue to contain pollutants at toxic concentrations for decades to come. This may be exacerbated, particularly at upland lakes, by the in-wash of previously deposited pollutants from catchment soils. The predicted effects of climate change may increase this in-wash.

8. RECOMMENDATIONS FOR FURTHER WORK

Greater confidence in the provisional toxicity quotients is desirable and this can be achieved by increasing the number of sites in the toxicant concentration-sediment toxicity test database and including additional sediment toxicity tests. Increasing the amount of data allows statistical significance to be derived. As the extension of the toxicity test data to ecological effects is uncertain for lake sediments, it is also desirable to include assessment of the benthic community in the lakes. It is recommended that the dataset on the trace metal and PAH concentrations in the sediments and sediment toxicity be increased by the inclusion of additional lakes and sediment toxicity tests and that assessment of the benthic community is also included.

The dataset has also shown the intriguing possibility that altitude may play a significant role in pollutant distribution in the UK. Our data have shown that altitude appears to be important for the distribution of, especially the heavier, POPs. This has been demonstrated for high altitude lakes in Europe, but given the lack of data available, this is the first time that this has been shown for UK lakes. Biological communities in upland lakes are sensitive to pollutant inputs and hence the role of altitude could be significant. However, given the small dataset, further data are required for confirmation.

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