

TRACE METAL CONTAMINATION OF LAKES AND PONDS IN LONDON

Thesis submitted for the degree of Doctor of Philosophy,
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I, Charlotte Jane Hall, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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ABSTRACT

Few studies of metal pollution in lakes have been carried out in urban environments. This research aimed to determine both temporal and spatial changes in metal concentration in sediments of lakes in London, and identify the current extent of contamination in lake ecosystems as a whole. The novel use of sediment archives to reconstruct potential toxicity was also explored. Sediment cores were taken from seven lakes across London and analysed for Ni, Cu, Zn, As, Pb and Hg concentrations. The cores were dated using a combination of radiometric and SCP dating, and lake age. Temporal trends were found to vary within and between sites, due to metal behaviour, catchment disturbance and the proximity to and type of metal source. PCA showed that there was some evidence for a regional pattern of contamination. Across all sites metal concentrations were very high, exceeding guideline values both in the past and at present. At various times the concentration of Pb had reached levels that were over 2000% higher than the guideline value. Increasing levels of enrichment and flux towards the surface of the cores also showed that contamination was not declining. Metal concentrations were also determined in deposition, water, and biota at one of the lakes. The concentration of Pb was found to exceed guideline values in both water and fish. The extent of Pb contamination in London lakes is therefore a major cause for concern. The potential toxicity of the combination of metals analysed in the sediment cores was reconstructed, through the calculation of mean toxicity quotients. Every core exceeded the potential toxicity threshold at all depths. Comparison to laboratory toxicity test data carried out on sediments from the OPAL lakes showed that the sediments were likely to be toxic, which would have implications for lake ecosystems should they be disturbed.

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CHAPTER 1: INTRODUCTION

1.1. Introduction

The aim of Chapter 1 is to provide the context for this research in terms of the Anthropocene and the impact that human activity has had and continues to have on the environment as a whole, and on freshwaters in particular. The need for research specifically aimed at metal pollution in urban lakes will be explained, and the particular aims and objectives of this project will be outlined. The current scientific understanding of metal pollution in aquatic environments, in both a global context and in relation to London in particular will be reviewed. This will be followed by some background to metal behaviour and toxicity in lake ecosystems.

1.2. Human impacts on the freshwater environment

1.2.1. The Anthropocene

The onset and expansion of industrialisation over the last 200 years has resulted in a dramatic increase in the impact of human activity on the environment. This period of growth has been termed the 'anthropocene' (Crutzen, 2002). Crutzen argued that the influence of human activity has been so great that the planet has moved out of the Holocene into a much less climatically stable age. The rapid expansion of mankind and the exploitation of the Earth's resources are causing irreversible changes to the environment, some of which are likely to leave a stratigraphically significant mark on the geological record.

Factors cited by Crutzen include the escalation of anthropogenic emissions of carbon dioxide and methane, the disappearance of rainforests, an increase in species extinctions, the increase in water use and the building of dams, overfishing of the seas and a steep rise in energy use (Crutzen, 2002). Subsequent work by Steffen et al (2004) has highlighted this further by depicting some of the key indicators of the Anthropocene, all of which show a steep increase occurring from the mid twentieth century onwards, known as 'The Great Acceleration' (Figure 1.1). The notion of the Anthropocene is of particular relevance at present because there is much ongoing scientific debate surrounding the issue (Vince, 2011). The Anthropocene Working Group was set up in 2009 by the International Commission on Stratigraphy to investigate the proposed new geological epoch and is due to deliver a final report in 2016 (Vince, 2011).

Whatever the outcome of such a proposal, the impact that humans are having on the environment is of great importance. This is exemplified by records of emissions to the atmosphere from anthropogenic sources. A wide range of gases and other compounds are released through human activity. These include greenhouse gases (carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O)), persistent organic pollutants (POPs), heavy metals and various other aerosols and air quality pollutants (such as sulphur dioxide (SO₂), particulate matter (PM₁₀ and PM_{2.5}), carbon monoxide (CO), benzene (C₆H₆), nitrogen oxides (NO_x) and ammonia (NH₃)).

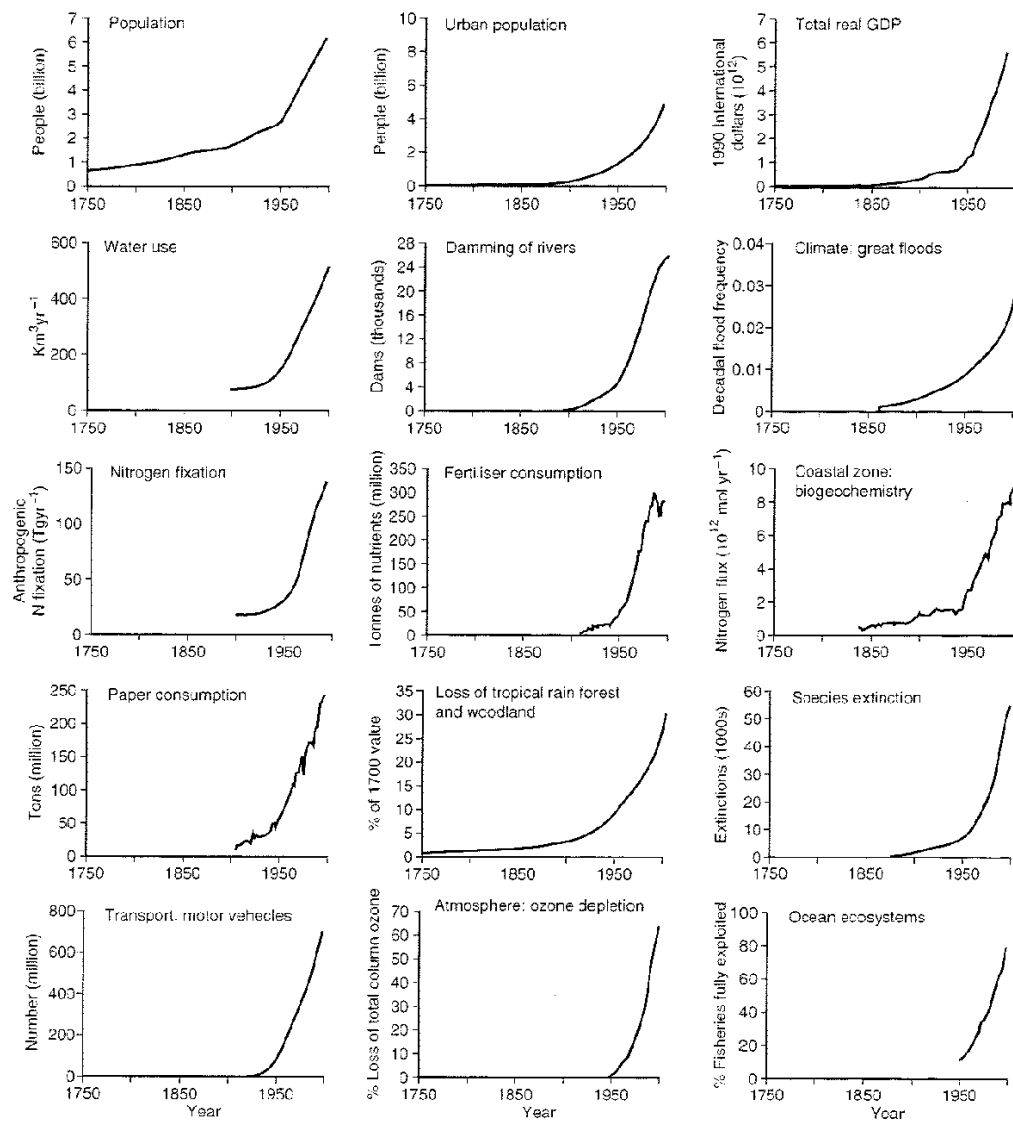


Figure 1.1 – key indicators of the Anthropocene, showing the rising trends from the mid twentieth century onwards (from Oldfield, 2005 (compiled and adapted from Steffen et al, 2004))

Greenhouse gases, metals and other air quality pollutants are emitted from a variety of sources. One of the most important is the combustion of fossil fuels in power stations, other industry and transport. Carbon dioxide, nitrous oxide, nitrogen oxides, sulphur dioxide and metals are all released in this way. Particulate matter and ammonia are produced from transport in particular, whilst the production of benzene is related to both the combustion and evaporation of petroleum products. Carbon monoxide is released through the incomplete combustion of fuel. A second key source of contamination is agriculture. Methane, nitrous oxide and ammonia are all produced from agricultural processes, with emissions from livestock being important in the case of the former, and livestock, fertiliser, crops and the decomposition of agricultural vegetation all contributing to the emissions of the latter. Other sources of pollutants include waste disposal (producing methane and ammonia), biomass burning (nitrous oxide, sulphur dioxide), coal mining (methane), quarrying and construction (particulate matter), the chemical industry (benzene) and other industrial processes (nitrous oxide, sulphur dioxide) (collated from Murrells et al, 2010). There are many different kinds of POPs which can be separated into a number of groups. These include polycyclic aromatic hydrocarbons (PAHs), dioxins and furans (PCDD/F), polychlorinated biphenyls (PCBs), pesticides and polybrominated diphenyl ethers (PBDEs). Each of these sub categories contains large numbers of different chemicals, and therefore the sources of POPs are extremely varied and widespread. PAHs are primarily produced by combustion in power stations, industry and transport. Dioxins and furans enter the atmosphere through the burning of waste. PCBs are found in electrical equipment and therefore the use and destruction of such appliances contribute to PCBs in the environment. They also enter it from landfill sites and during metal production. PBDEs are used as flame retardants and are found in a wide variety of materials. They can enter the atmosphere at any point between the production and disposal of materials. Pesticides are emitted during manufacture and application, and by volatilisation after application (Murrells et al, 2010).

Raynaud et al (2003) used a combination of ice core data and more recent direct measurements to reconstruct past atmospheric concentrations of greenhouse gases and sulphur dioxide (Figure 1.2). The mean global atmospheric CO₂ concentration has increased from 280 ppm in the 1700s to 380 ppm in 2005, at a progressively faster rate each decade. This growth is due to a combination of the rise in CO₂ emissions from fossil fuel combustion and industrial processes, from 11 Mt in 1751 to 32,000 Mt in 2008 (Figure 1.2) and the CO₂ flux from land use change, primarily land clearing (Raupach et al, 2007).

Figure 1.2 shows that the atmospheric concentrations of N₂O, CH₄ and SO₄²⁻ (sulphate from SO₂) have also increased over the last 1000 years, and similarly to CO₂, more dramatically in the last 200 years. Concentrations of N₂O have increased from pre-industrial levels of 270

ppb to 314 ppb in 2001, largely as a result of both the expansion and intensification of food production and modifications to the global nitrogen cycle (Oldfield, 2005). This is reflected by the increase in emissions from 2.15 Tg in 1890 to 9.70 Tg in 1995 (Figure 1.2). An estimate of emissions in 2000 shows a continuation of this increase, with a figure of 12 Tg (Olivier et al, 2005).

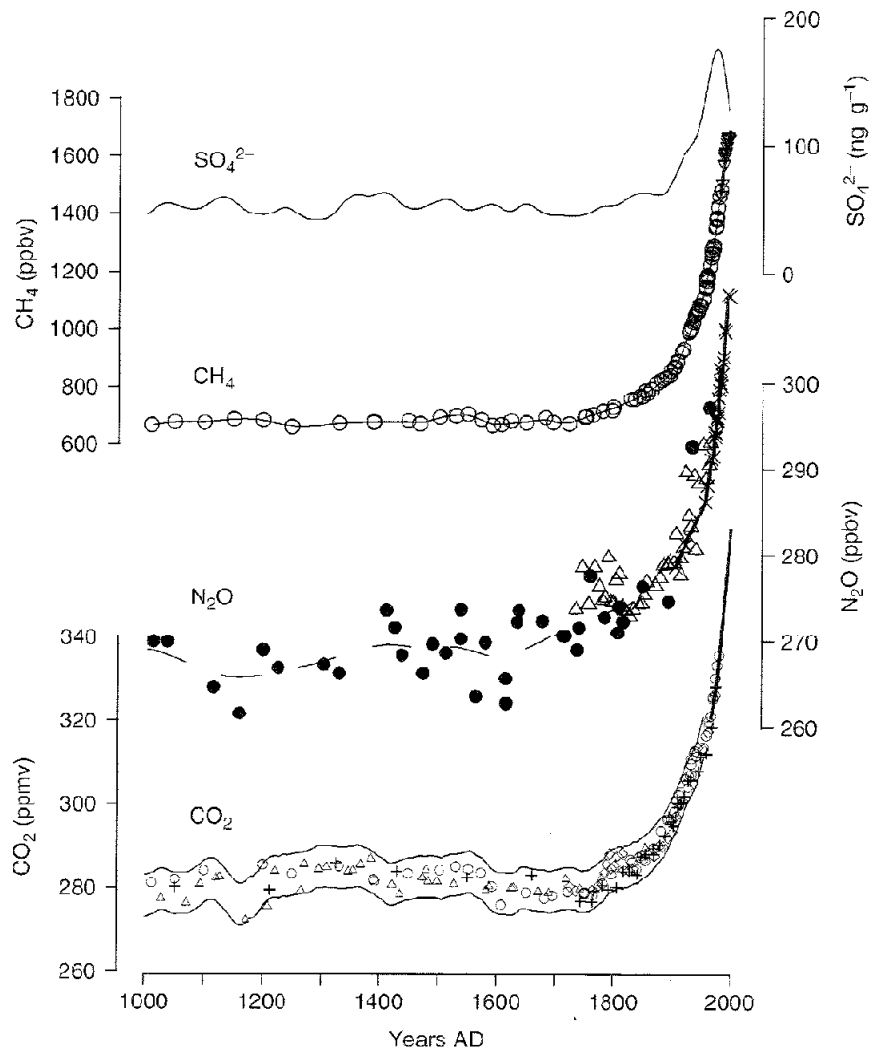


Figure 1.2 – Atmospheric trace gas (CO_2 , N_2O , CH_4) and sulphate (SO_4^{2-}) concentrations over the last 1000 years (from Oldfield, 2005 (modified from Raynaud et al, 2003)), showing a step increase since ~ AD 1800

It is thought that human activities are responsible for about two thirds of global CH_4 emissions. Atmospheric concentrations of CH_4 have more than doubled since 1700, from approximately 700 ppb to over 1600 ppb in 2001 (Raynaud et al, 2003). Figure 1.3 shows that CH_4 emissions also increased between 1860 and 1994, from 79 Tg in 1860 to 371 Tg in 1994 (Stern & Kaufmann, 1998), with more recent estimates in 2000 putting the figure at 320 Tg (Olivier et al, 2005). However, it is thought that this decline may only be temporary, as

emissions are rising again due to the growth of the Chinese economy (Bousquet et al, 2006).

Sulphate atmospheric concentrations peaked at 110 ng g^{-1} at the end of the 1960s, compared with 26 ng g^{-1} in pre-industrial times (Raynaud et al, 2003). The profile of SO_2 emissions between 1890 and 1995 (Figure 1.3) shows a slightly later peak of 146 Tg in about 1980, before declining. However, a recent study by Smith et al (2011) suggests that there has been a further increase in global emissions since 2000. This is because of increased emissions in China, international shipping, and developing countries in general.

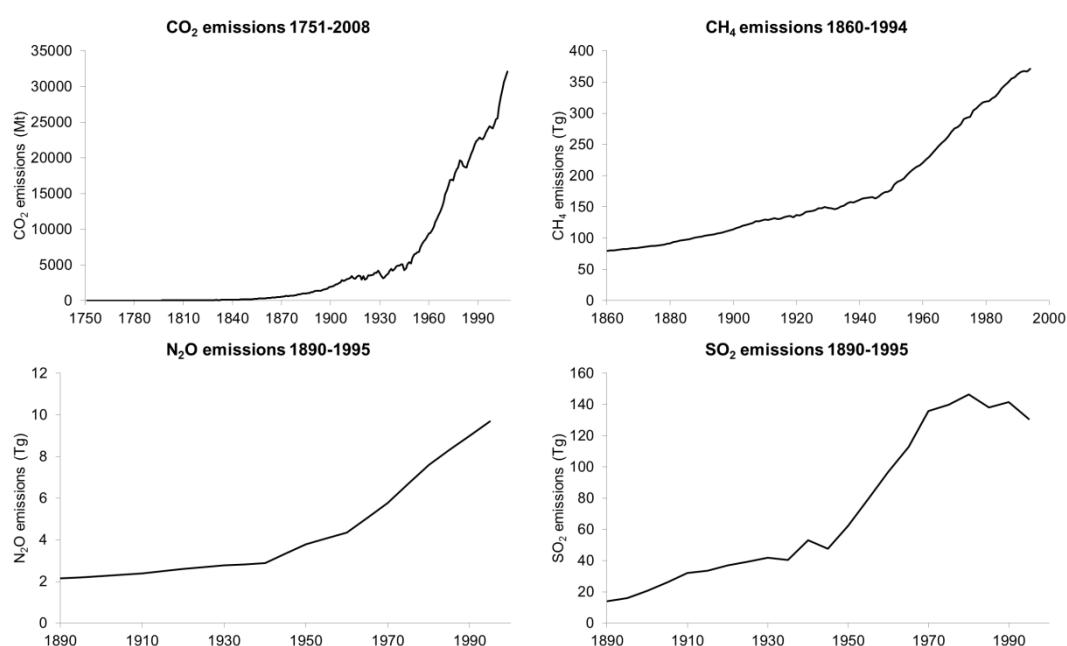


Figure 1.3 – Profiles of CO₂ emissions 1751-2009 (data from Boden et al, 2011); CH₄ emissions 1860-1994 (data from Stern & Kaufmann, 1998); N₂O emissions 1890-1995 (data from Asadoorian et al, 2006); SO₂ emissions 1890-1995 (data from Asadoorian et al, 2006)), all showing an increase in emissions, in particular from the mid-20th century

The data for CO₂, CH₄, N₂O and SO₂ reflects the scale of the increase of anthropogenic emissions over the last 200 years and the impact that this has had on atmospheric concentrations. Similar information is available for the other pollutants. Figure 1.4 shows emissions data for CO, NO_x, NH₃ and volatile organic compounds ((VOCs) which include C₆H₆) between 1890 and 1995 (Asadoorian et al, 2006). All of the emissions show similar increases, with a more rapid rise occurring post 1950.

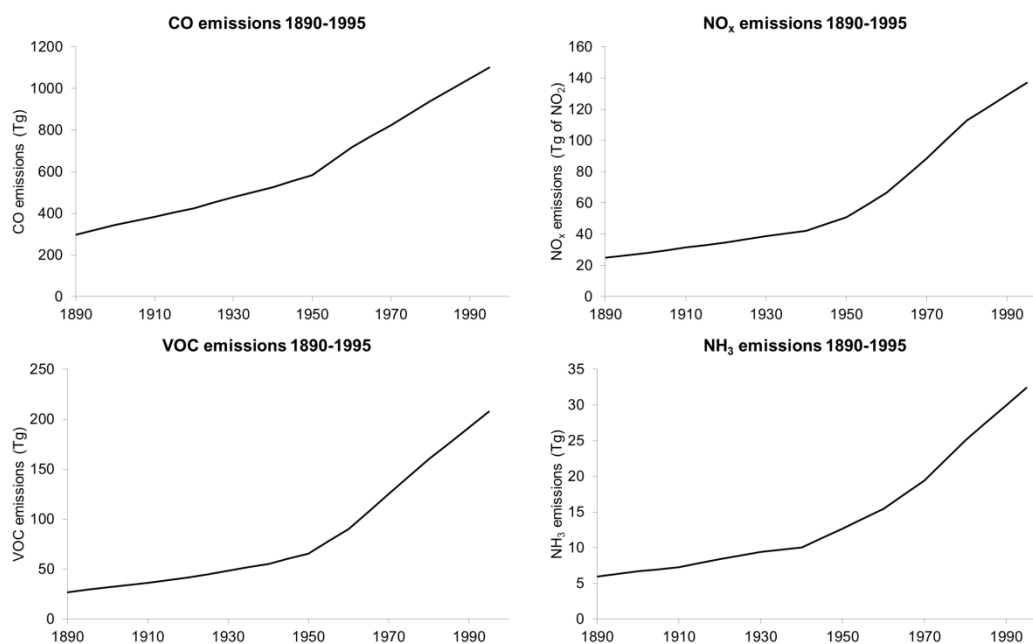


Figure 1.4 – Emissions profiles for CO, NO_x, VOCs and NH₃ 1890-1995 (data from Asadoorian et al, 2006), showing an increase in emissions, in particular from the mid-20th century

The histories of production of metals and POPs fall across three main timescales. Metals such as Pb and Cu were first exploited in prehistory and the long record of their changing atmospheric concentrations have been reconstructed from ice cores and peat bogs (e.g. Hong et al, 1994 and 1996; see Section 1.5.4 for more details). Metals such as Cd and Cr are more closely linked to industrial processes that began during the Industrial Revolution, and therefore increases in these metals first appear during the nineteenth and early twentieth century. POPs have an even more recent history as deliberate synthesis only began in the early 20th century. They are also produced accidentally as by-products of other chemical and industrial processes. Therefore, combined with the numerous types of POPs in existence, reliable estimates of historical and contemporary emissions are very difficult to achieve (Jones and de Voogt, 1999). Figure 1.5 shows a general emission trend that could be applied to many classes of POPs. The profile shows a steep increase in the 1950s and 1960s, following the widespread use of POPs in Europe and North America at that time. A peak in emissions occurs in the 1970s. Concerns over environmental persistence and food chain accumulation in the late 1960s/early 1970s resulted in restrictions in usage, and the subsequent reduction in emissions is shown in the profile as a decrease in the 1980s and 1990s. However as with CH₄ and SO₂, it should be noted that the recent decline may begin to slow, as POPs start to be used more extensively outside of Europe and North America in the newly industrialised nations (Jones and de Voogt, 1999).

It has been shown that there has been a dramatic increase in the emissions of a wide variety of substances to the atmosphere from human activity over the last 200 years. The atmosphere is closely linked to the aquatic and terrestrial biospheres, and therefore changes in the atmosphere affect the oceans and freshwaters, as well as the land. The impacts of anthropogenic emissions are varied, complex and often damaging, and can be both global and more localised.

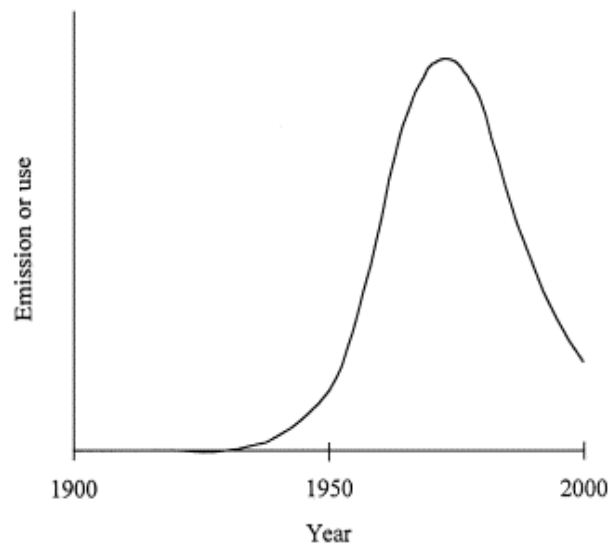


Figure 1.5 – General emission profile for POPs (from Jones and de Voogt, 1999), showing a steep increase between the 1950s and 1970s, followed by a sharp decline to the 2000s

Global temperatures have increased over the last century, by 0.35°C between the 1910s and 1940s, and then more strongly from the 1970s to the present day, rising by 0.55°C (IPCC, 2007). Warming of the Earth is thought to be forced by three factors – solar variability, explosive volcanicity and atmospheric greenhouse gas concentrations. Mann et al (1998) reconstructed a record of northern hemisphere temperature change since 1400 using a multiproxy approach (Figure 1.6). They calibrated a range of temperature proxies from ice cores, trees and corals with instrumental temperature data collected since 1902. The degree to which the temporal changes in temperature correlated with the three forcing factors was assessed. They concluded that the strongest correlations for the changes in temperature before c. 1920 were with solar and volcanic variability, whereas after that date there was an increasing tendency for the changes to correlate with rising greenhouse gas concentrations. Other studies have supported the findings of Mann et al (e.g. Tett et al, 1999) and it is now generally agreed that increased anthropogenic emissions of greenhouse gases and sulphate aerosols are the main cause of the present rise in global temperatures (IPCC, 2007).

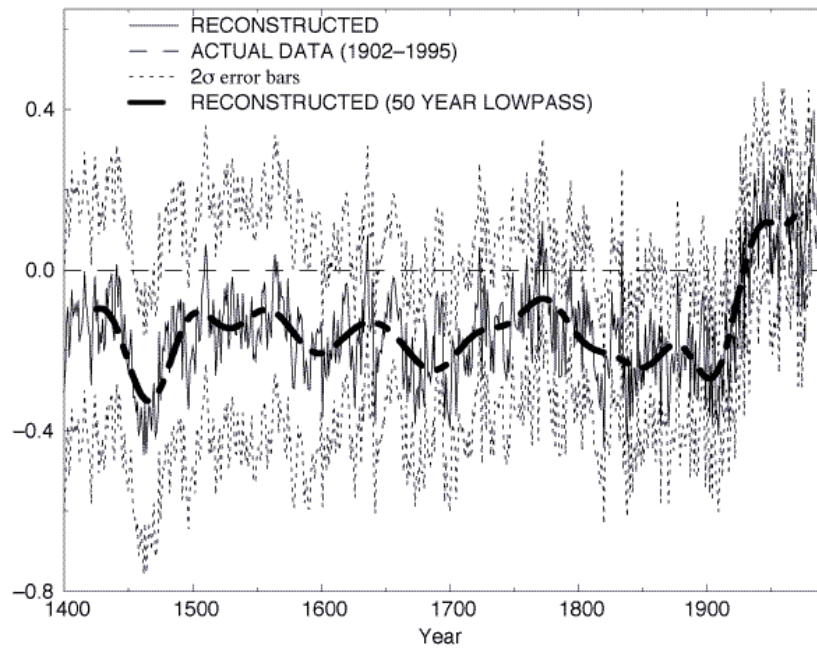


Figure 1.6 – Reconstruction of northern hemisphere temperatures since AD 1400 (from Mann et al, 1998), showing the steep rise in temperature in the 20th century

The warming of the Earth has a wide range of implications. Ice loss has been recorded in polar regions with the thinning of both the Greenland and West Antarctic Ice Sheets (Rignot and Thomas, 2002). Permafrost has been thawing in the Alps, northern Europe and Russia. This has consequences for the construction and operation of roads, bridges and pipelines, and the enhanced likelihood of landslides. It is also thought that melting permafrost can release large amounts of stored carbon back into the atmosphere (Schiermeier, 2003). Glaciers are also in retreat and a study by Reichert et al (2002) has shown that this is a consequence of anthropogenic forcing rather than of internal variability in the climatic system. The oceans are also getting warmer (Levitus et al, 2000). Some climate models suggest that the anthropogenic increase in CO₂ will lead to changes in ocean circulations, and studies have shown that the slowing of some systems is already occurring (Bryden et al, 2005). This could have a big impact on both climate and marine and coastal ecosystems. A combination of ice melt and ocean warming may lead to global sea level rise. A study by Gehrels et al (2002) on the Gulf of Maine found that sea levels had risen by 0.3-0.4 m since AD 1800, and at an unprecedented rate in the twentieth century. The rise has been interpreted as a combination of thermal expansion of the Gulf of Maine and the North Atlantic sea surface and glacioeustatic changes from polar and glacial ice melt. Rising seas will impact upon the land, with low lying areas being at increased risk of flooding and extreme weather events, and possibly permanent inundation (IPCC, 2007).

Both aquatic and terrestrial ecosystems will be affected by changing climates. A key indicator of ecosystem response is phenology, or the timing of seasonal processes in plants and animals. Various indications of shifts in phenology have already been reported for the boreal and temperate zones of the northern hemisphere (Menzel and Estrella, 2001), which suggests that ecosystems are already changing because of climate. It has been suggested that species extinctions are likely to increase and that there will be a loss of biodiversity. The impact on humans is difficult to ascertain, but possible outcomes include changes in food and water supplies, and population health (IPCC, 2007).

Greenhouse gases, aerosols and other air pollutants can have additional impacts to those of global warming. Much of the CO₂ that is released into the atmosphere is absorbed by the oceans. However, the big rise in CO₂ emissions means that uptake by the oceans is also increasing, and this is leading to acidification of the seas (Caldeira and Wickett, 2003). This will potentially lead to adverse consequences for marine biota. It has been found that SO₂ emissions also lead to acidification of freshwaters. The realisation that the pH of many freshwater bodies in Scandinavia and western Britain, as well as northeastern North America, had declined first came to prominence in the 1980s. Lake sediment based evidence was used to determine that the cause of the change was from acid precipitation resulting from industrial processes (Battarbee, 1990). Cultural eutrophication has been on the increase since the mid nineteenth century in both marine (e.g. Andrén et al, 1999) and freshwaters (e.g. Battarbee, 1978). The key nutrients responsible for eutrophication are phosphorus and nitrogen, the latter of which is contributed to by emissions of N₂O, NO_x and NH₃.

The impacts of particulate matter, carbon monoxide, benzene, POPs and metal emissions are primarily to specific ecosystems and human health. The effects can be both localised and far from the source of the pollution. Epidemiological studies show a consistent increase in cardiac and respiratory morbidity and mortality from exposure to particulate matter, which is estimated to kill more than 500,000 people each year (Nel, 2005). Benzene is a carcinogen, exposure to which gives rise to an increase in the risk of developing leukaemia (Snyder, 2002). Carbon monoxide is poisonous, binding to haemoglobin in the blood and starving the body of oxygen (Kampa and Castanas, 2008). POPs have been found to accumulate in food chains, which has led to concerns about their impacts on top predator species, including humans. They can affect reproduction and damage immune systems (Jones and de Voogt, 1999). Some metals, such as mercury, are also able to bioaccumulate. Metals can be toxic to biota, and at high concentrations, to humans (see Section 1.5.2).

In conclusion, it has been shown that emissions to the atmosphere from human activities have increased dramatically over the period known as the Anthropocene. The impacts that humans are having on the environment are vast and not yet fully understood. It is important to study the way in which terrestrial and aquatic environments respond to these changes in order to determine how well they are able to cope, and if any subsequent effects are likely to be felt in the future.

1.2.2. Freshwaters, pollution and the urban context

Freshwater makes up only 2.5% of all the water on the planet. Of this, about 70% is stored in the form of ice and permanent snow cover in mountainous regions, the Antarctic and Arctic regions. The remainder is stored in lakes, rivers and groundwater. The total useable freshwater supply for ecosystems and humans is less than 1% of all freshwater resources (UNEP, 2013).

Humans utilise freshwaters in a wide variety of ways (from Postel & Carpenter, 1997):

- Water supply: drinking, cooking, washing and other household uses; manufacturing, thermoelectric power generation and other industrial uses; irrigation of crops, parks, golf courses etc; aquaculture
- Supply of goods other than water: fish; waterfowl; clams and mussels; pelts
- Nonextractive: flood control; transportation; recreational swimming, boating etc; pollution dilution and water quality protection; hydroelectric generation; bird and wildlife habitat; soil fertilisation; enhanced property values; non-user values (cultural, spiritual and aesthetic value)

It is estimated that wetlands around the world provide goods and services to people worth an estimated US\$70 billion per year (Schuyt & Brander, 2004). However, human activity is leading to the degradation of freshwater ecosystems. Since 1950, the number of large dams (over 15 metres in height) has increased from 5700 worldwide to 41,000, creating extensive habitat fragmentation in nearly 60% of the major river basins (Revenga et al, 2000). Agriculture has a disproportionate impact on water flow, water quality and alteration of freshwater habitats (Johnson et al, 2001). Globally, water pollution is increasing – in developing countries an estimated 90% of waste water is discharged directly into rivers and streams without treatment (Johnson et al, 2001). In consequence, biodiversity of wetland ecosystems is being lost. Between 1970 and 2008, the populations of freshwater species on

the WWF Living Planet Index fell by 37% - a larger decline than for marine and terrestrial ecosystems (WWF, 2012).

There are a number of types of water pollution, each with different causes, sources and effects. Eutrophication has become the primary water quality issue for most of the freshwater and coastal marine ecosystems in the world (Smith & Schindler, 2008). It is caused by nutrient (nitrogen and phosphorus) enrichment, primarily from agriculture, effluents and sewage, and urban runoff, but also from emissions of N_2O , NO_x and NH_3 (see Section 1.1). Enrichment leads to an increase in productivity of the waterbodies, with visible impacts being the growth of algal blooms (Smith & Schindler, 2009). Oxygen can become depleted, which can potentially have detrimental effects upon habitats for fish and macroinvertebrates (Foley et al, 2012; Jones et al, 2008). Species diversity can decrease (e.g. Hillebrand & Sommer, 2000) and biomass can increase (e.g. Harding & Perry, 1997). Sedimentation rates have also been found to increase (Cooper & Brush, 1993). Acidification of freshwaters was described in Section 1.1, primarily caused by SO_2 emissions from power stations, industrial plants, vehicle exhausts and agriculture. Acidification leads to fish kills at extremely low pH and consequently declining populations. Scandinavian fish populations have declined hugely over the 20th century due to acid deposition (Rosseland et al, 1986). Species diversity, not only of fish, but of other biota such as phytoplankton is also known to decrease with increasing pH (e.g. Findlay, 2003). Acidic conditions are also known to bring toxic metals, stored in lake and river sediments, into solution (Miao et al, 2006), thereby providing a secondary source of pollution.

Other types of pollutant are directly responsible for damage to freshwater ecosystems. Metal pollution will be discussed in more detail in Section 1.3. Thermal pollution, primarily caused by electricity generating power stations, raises the temperature of freshwaters which can result in direct damage to organisms, as well as oxygen depletion which can subsequently lead to further impacts (Langford, 2001). Radioactivity from the nuclear industry and nuclear weapons testing can cause acute toxicity. Long term exposure, such as has occurred to biota in the Chernobyl accident exclusion zone, can cause genetic defects (Williams et al, 2001; Gudkov et al, 2006). Radioactive elements can also bioaccumulate and biomagnify up the food chain. The release of oil into aquatic environments from road runoff, illegal disposal, irrigation pumps and boats, and accidents, spillages and vandalism, can be toxic to organisms. It can also cause chronic effects such as neurosensory disruption, behavioural and developmental abnormalities and reduced fertility. Respiratory function of organisms can be reduced, and photosynthesis, feeding, floating and growth of organisms can also be affected (Bhattacharyya et al, 2003). Damaging oil spills, such as that from the Exxon Valdez in Alaska in 1989, can have impacts on the local ecosystem for many years beyond

that of the incident itself (Peterson, 2001). Organic pollution from domestic sewage, industrial and farm effluents, and urban runoff, leads to oxygen depletion and changes in community structure (Mojtahid et al, 2008), as well as high levels of suspended solids and the presence of ammonia (Davies & Hawkes, 1981). Persistent organic pollutants (POPs) from industry, agriculture, forestry, domestic sewage and urban and rural runoff can be toxic to organisms (Yen et al, 2002). They can also cause sublethal effects such as deformity, and impair the growth of organisms (Debruyn et al, 2007). POPs also bioaccumulate and biomagnify in aquatic food webs (e.g. Voutsas et al, 2002; Wu et al, 2009).

Global population is set to grow from 6.1 billion in 2000 to 8.9 billion in 2050 (UN, 2004). As Figure 1.1 shows, the rise in both population and urban population, particularly from the mid-20th century, are two of the key indicators of the Anthropocene. In 1910, only 20% of people lived in urban areas. By 2010, this had risen to more than half of the world's population. This is only set to continue. By 2050 70% of people will live in urban areas, equating to approximately 6.4 billion people (WHO, 2013). An increasing population and the growth of urban areas will put more pressure on urban freshwater resources, both in terms of utilisation and degradation. Urban areas are also commonly the source of much freshwater pollution as they are centres for industry and transport, which increases the likelihood of enhanced degradation occurring. Awareness of localised impacts of pollution on the urban population is also likely to increase. Therefore, the study of pollution levels, patterns and processes in the urban environment is currently of real importance. Lakes are essential freshwater ecosystems and are often found in urban areas. Aside from their value as a water source, lakes are also useful because their sediments provide records of historical pollution. Sediment cores from lakes have been widely used to reconstruct temporal patterns in pollution and in particular, of metal contamination (see Section 1.7.3). However, few studies of metal contamination in urban areas have been carried out, and in particular very few which explore temporal changes in metal pollution. This study aims to remedy that situation.

1.3. Research aims and objectives

The aim of this project is to explore the metal pollution history of London lake sediments and find out if there is a relationship between the levels of metal contamination within the sediments and the wider lake ecosystem. The potential toxicity of metal mixtures in the sediments both in the past and at present will be assessed in order to ascertain if metal pollution is likely to pose problems to ecosystems in the future. The overall aim of the project will be achieved through a number of sub-aims and objectives.

Sub-aim 1: Identify metal concentrations in the sediments of London lakes and describe the temporal changes that occur.

Objective 1a. Sediment cores will be taken from a number of lakes in London. Chronologies will be developed for the cores using a range of techniques including radiometric dating and spheroidal carbonaceous particle analysis.

Objective 1b. The concentrations of a number of metals and other elements within the sediments will be determined, and the 'anthropogenic' pollution component will be identified. Other factors which may influence metal concentrations in sediments such as organic matter and sediment accumulation rate will also be described. Temporal changes in metal concentrations will be related to sediment quality guideline values.

Sub-aim 2: Explain any variation in metal concentrations within and between sediment cores and identify whether the changes in metal pollution across the city reflect a regional pattern or if they are more localised, to ascertain the importance of different pollution sources within the city.

Objective 2a. The influence of metal behaviour, metal sources and the individual lake catchments on metal concentrations at each of the sites will be examined with reference to previous studies and documented histories of each of the lakes.

Objective 2b. Simple correlations and principal components analysis will be used to compare the concentrations of metals at the different lakes in order to determine if there is a regional pattern of contamination across the Greater London area.

Sub-aim 3: Identify and explain trends and levels of metal contamination in recent sediments.

Objective 3a. Recent changes in metal pollution in the sediments will be compared to records of metal emissions and deposition in the UK.

Objective 3b. The levels of contamination found in the lakes in this study will be put into a wider context through comparison with metal concentrations found in other studies of both London and urban lakes worldwide.

Sub-aim 4: Identify metal concentrations in other parts of the lake ecosystem and explore the relationships between the sediments and the rest of the ecosystem.

Objective 4a. Metal concentrations will be determined in recent sediments, deposition, water, macrophytes, benthic algae, zooplankton and fish at one London lake to provide a snapshot of the degree of contamination in an urban lake.

Objective 4b. The variability in concentrations both within and between the different components of the ecosystem will be discussed with reference to previous studies.

Objective 4c. The concentrations of metals in sediments, water and fish will be compared to guideline values.

Sub-aim 5: Reconstruct the potential toxicity of the sediments from each of the London lakes.

Objective 5a. The potential toxicity of surface sediments from the OPAL lakes (see Section 1.9) will be calculated and compared with the results from toxicity tests carried out on the same sediments.

Objective 5b. The potential toxicity of both historic and contemporary sediments in cores from the OPAL lakes and the lakes in London will be calculated.

Objective 5c. The potential toxicities within the cores will be related to guideline thresholds for toxicity to gauge the potential impact future disturbance of the sediments could cause.

1.4. Thesis structure

The chapters in this thesis are sequenced in order to address the aims and objectives of the research project in approximately the same order as they are listed in Section 1.3. The beginning of Chapter 1 provides the context for the study in terms of the Anthropocene and the impact that human activity has had and continues to have on the environment as a whole, and on freshwaters in particular. The need for research specifically aimed at metal pollution in urban lakes is explained. The rest of Chapter 1 reviews the current scientific understanding of metal pollution in aquatic environments, in both a global context and in relation to London in particular. This is followed with some background to metal behaviour and toxicity in lake ecosystems. Chapter 2 introduces the lakes and ponds in London that are studied in the project and explains the reasons for their selection. This is followed by the history and known background of each of the sites.

Chapters 3 and 4 cover the investigation into the sedimentary archives of each of the lakes. Chapter 3 specifically addresses objective 1a, outlining the methods used to obtain chronologies at each of the sites and discussing the problems with dating sediments from

urban lakes. Chapter 4 describes the methods used to obtain the sediment cores and analyse the concentrations of metals within them. The chapter then addresses the rest of sub-aim 1, sub-aim 2 and sub-aim 3, first describing and explaining the changes and variations in metal concentrations, then using statistical techniques to ascertain if there is a regional pollution signal, before discussing the most recent changes in metal contamination.

Chapter 5 introduces the contemporary study carried out at one specific London lake, addressing the objectives of sub-aim 4. It begins with an outline of the field and laboratory methods used to obtain the data. Metal concentrations in both abiotic and biotic components are discussed, both individually and in relation to one another. The implications of the levels of contamination found at the site are also considered. Chapter 6 focuses on sub-aim 5, investigating the potential toxicity of the London lakes. Toxicity data from surface sediments taken from the nine OPAL lakes (see Section 1.9) are introduced. Toxicity quotients calculated for the surface sediments are compared to those calculated for the core sediments from the same sites, and then discussed in relation to potential toxicity in the London lake sediments. Chapter 7 provides a synthesis of the key findings of this research project, together with the implications for management highlighted by the study. Some areas in which further research would be beneficial are also suggested.

1.5. Metal contamination in a worldwide context

1.5.1. Defining trace metals

Metals are loosely defined as having a lustrous appearance, being good conductors of heat and electricity and generally entering chemical reactions as positive ions, or cations (Sharp, 1990). Of the 90 naturally occurring elements in the Periodic Table (Figure 1.7), 67 are considered to be metals. However, these encompass a wide range of physical and chemical characteristics which means that the properties of metals can vary wildly, for example, all metals are solid at room temperature, with the one exception being mercury (Hg). Within the Periodic Table, metals are split down into smaller groups which are defined by the particular properties that they hold. The alkali and alkali earth metals are chemically reactive base metals that are very electropositive and form M^+ and M^{2+} ions respectively (see Figure 1.7). Transition metals are characterised by having variable oxidation states, coloured ions and a tendency to form complexes (see Figure 1.7). The elements defined as 'other metals' in Figure 1.7 include post-transitional metals Ga, In, Sn, Tl, Pb and Bi, metalloids Ge, Sb and Po, and Al. In general, these metals tend to be softer, have lower melting and boiling points and higher electronegativity than the transition metals. Smaller sub-groups are often defined within the larger groups, for example the 'precious metals' Ag, Au, Pt, Pd and Ir, which are

used in coinage and jewellery. However, not all of these metal groups are necessarily considered in the study of environmental pollution.

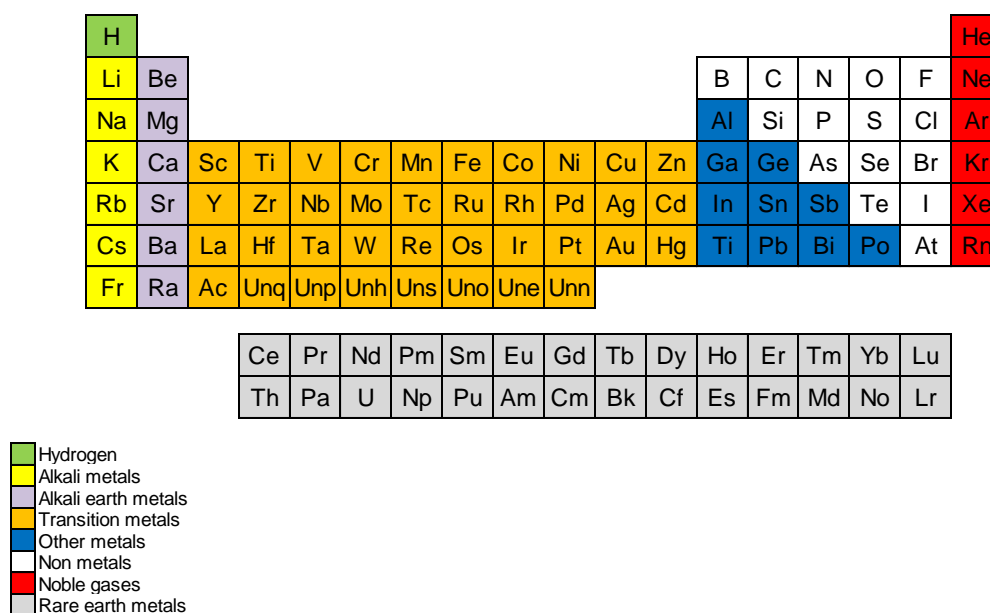


Figure 1.7 – Periodic Table of the Elements outlining the different metal groups

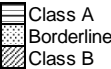
Only some metals are considered to be of importance when studying the biological, ecological and toxicological behaviours of metals, most of which are found within the transition metal group. However, such environmentally important metals cannot be defined just by this group as some key characters like Pb would not be included. Two terms often used in environmental studies are 'heavy metals' and 'trace metals'. Heavy metals are usually described as those with a specific gravity of 4 or more. However, there has been some criticism of the term because this definition would include some of the heavier Group 1 and Group 2 metals and the lanthanides, none of which are usually considered in studies of environmental metal contamination. The actual definition of heavy metals used also varies from publication to publication (Duffus, 2002) and therefore more recently the term has started to fall out of use.

Instead, the term 'trace metal' is now more commonly used within the literature to group these metals. However, its definition and therefore use is also somewhat arbitrary and varies quite widely between studies. The description 'trace' implies that the metal is present in only very small concentrations. Where defined, the concentration amounts to a limit of 0.01% (for example by dry weight in an organism), also expressed as 100 ppm, $\mu\text{g g}^{-1}$ or mg kg^{-1} . However, in some cases metal concentrations can be much higher than this, for example as a result of bioaccumulation. An element of essentiality is also often included as a

requirement of the definition – the metal is required in small doses for the proper functioning of the organism. However, this definition excludes metals such as Pb and Hg and these are frequently described as trace metals in the literature as well (Luoma & Rainbow, 2008).

In order to take into account this variability, a definition will be provided for the specific purposes of this project. The Lewis acid classification system of metals devised by Nieboer and Richardson (1980) and subsequently utilised by Luoma and Rainbow (2008) will be followed. In this method, metals are split into Class A, Class B or Borderline categories depending upon their degree of ‘hardness’ or ‘softness’ as acids and bases, or the affinity that metal ions have for other elements. The classification is related to atomic properties and the solution chemistry of ions, the latter of which is particularly important in a biological context. Class A metal ions are Lewis hard acids (‘more ionic’) and preferentially seek out O containing ligands, Class B are Lewis soft acids (‘more covalent’) with an affinity for N or S containing ligands, and Borderline lie somewhere between the two. Using this method, those that are in Class B or the Borderline group are considered to be trace metals (see Figure 1.8) and will be defined as such within this project.

H																	He																												
Li	Be											B	C	N	O	F	Ne																												
Na	Mg											Al	Si	P	S	Cl	Ar																												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																												
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																												
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																												
Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno	Une	Uun																																				
<table border="1"> <tbody> <tr> <td>Ce</td> <td>Pr</td> <td>Nd</td> <td>Pm</td> <td>Sm</td> <td>Eu</td> <td>Gd</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> </tbody> </table>																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																



 Class A
 Borderline
 Class B

Figure 1.8 – Periodic table of the Elements, with the classification of metal ions into Class A, Borderline and Class B categories based upon Lewis acid properties (from Nieboer and Richardson, 1980)

1.5.2. Problems caused by metal contamination

Metal pollution has a variety of effects on the aquatic environment, which are enhanced by the complex nature of the system. The impact of metals on humans is also an important issue and is often related to the metal concentrations of water sources.

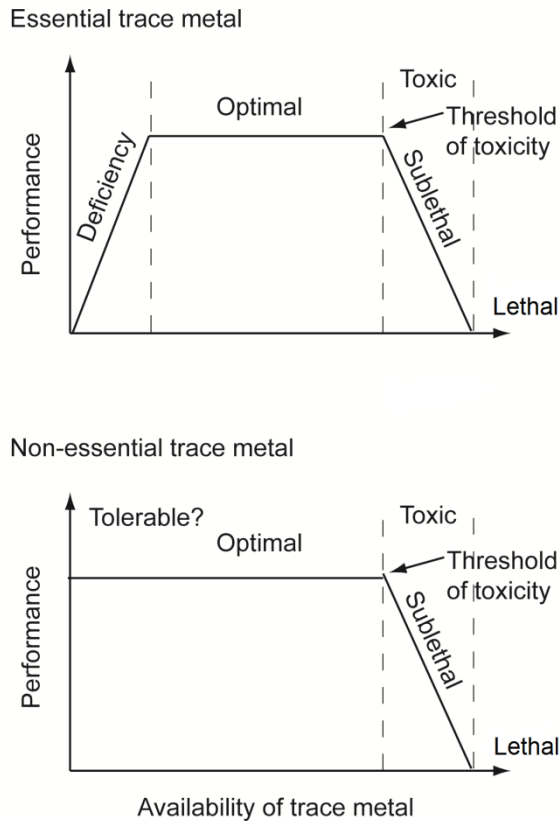


Figure 1.9 - The effect of increasing availability of essential and non-essential trace metals on the performance, e.g. growth, production, fecundity, survival, etc., of an organism (adapted from Förstner & Wittman, 1979)

In Section 1.5.1, the idea of essentiality was touched upon in relation to defining trace metals. Some trace metals are required in very small doses for the functioning of the metabolism of organisms and are therefore considered to be 'essential' (Luoma & Rainbow, 2008). These generally include Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Sn and Sb and are readily incorporated into the proteins of organisms. However, other non-essential trace metals can also be taken up by organisms, including Pd, Ag, Cd, Pt, Au, Hg and Pb. All trace metals can potentially be toxic if the rate of entry of a trace metal into an organism exceeds the combined rates of its excretion and detoxification by that organism (Rainbow, 2002). Therefore, in an environment that is suffering from enhanced metal loadings the likelihood of metals becoming toxic to the inhabitants is much increased.

Figure 1.9 shows the general effects that an increase in the availability of essential and non-essential trace metals will have on organisms. For essential trace metals, at low availability organisms can show a metal deficiency. Optimal performance is achieved as the availability increases, but if the threshold of toxicity is reached the effect on the organism can be

sublethal. The case is much the same for non-essential trace metals, except that because they are not required to enable the organism to function properly, there is no level at which the organism becomes deficient. It should be noted that the concentration at which the onset of toxic effects occur varies greatly between organisms for the same trace metal, and between trace metals for the same organism. Some metals are more toxic than others, although the exact order may vary. However, non-essential trace metals are not necessarily more toxic than essential trace metals.

Within a lake system, the potential toxicity of trace metal contamination is dependent upon both the concentration of metals and the processes that occur within the water, sediment and biota. Of course, metals can only be toxic to living creatures, but the concentration of metals in sediment and water are important because together with other biota, they are the sources of metals for aquatic organisms. Metals move around the lake via the interactions that take place between each of these constituents. For example, metals in lake sediments can be both remobilised back into the water where they are taken up by zooplankton and other organisms as well as being absorbed directly from the sediment, often by benthic organisms. The concentration of the metals can change as they move around the within the system, and hence their toxic effect can also vary. Three processes are important when considering the toxicity of metals in lakes. The first is bioaccumulation – when metals are taken up and stored by organisms. It is defined as the net retention of a contaminant by an organism over time i.e. the influx of the contaminant exceeds its efflux. The second is bioconcentration, which refers to the uptake and accumulation of a substance from water alone. The third process is biomagnification, the phenomenon whereby contaminant concentrations increase in organisms at successively higher trophic levels along a food chain (Hare, 1992). Put more simply, when some organisms consume others the concentration of metals they store is much greater than the metal concentration of the creature that was consumed.

As the graphs in Figure 1.9 showed, when metal availability to organisms increases beyond a certain level it can become sublethal, too low to cause rapid death but high enough to impair the organism from functioning properly. At even greater concentrations metals can become lethal. There are many types of sublethal effects because of the large number of organism species and the variety of metals. Metals can cause changes in the appearance of organisms. A study of diatom communities at a number of points downstream of the abandoned Coval da Mó mine in Portugal showed that diatom growth did not occur close to the mine because of the toxic effect of high metal concentrations. Slightly further downstream diatom communities existed, but more than half the valves counted were found to have asymmetrical abnormal and bent valves (Ferreira da Silva et al, 2009). A

toxicological study by Di Veroli et al (2012) showed that when chironomid larvae were exposed to sediments spiked with a mixture of metals (Zn, Cr, Cd, Ni, Cu, Pb), a clear correlation was found between metal concentrations in the sediment and incidence of mouthpart deformities in the organisms (correlation coefficients ranged between 0.997 and 0.999 and were significant ($P = <0.01$ for all metals except Cd). Another effect of metal contamination is that histological changes in organisms can occur. Enhanced Cu exposure to the macrophyte *Potamogeton pusillus* was investigated (Monferrán et al, 2009). Redox cycling between Cu ions (and other metals) catalyzes the production of reactive oxygen species. If the production of these species is greater than the antioxidant capacity, the imbalance is known as oxidative stress, which can cause enzymes to stop working, proteins to degrade, DNA damage and cell death. In the study in question, at slightly lower concentrations the plants responded positively by induced activity of some antioxidant enzymes. However, at higher concentrations oxidative stress occurred and cell structures were damaged (Monferrán et al, 2009). The effect of Pb toxicity on another aquatic macrophyte *Elodea canadensis* showed that Pb accumulation in tissues increased with increasing Pb concentrations, and that the contents of chlorophylls, carotenoid and protein were adversely affected by Pb accumulation. Pb accumulation also caused oxidative stress (Dogan et al, 2009).

Abnormalities in fertilisation and reproductive processes, delays to sexual maturity and a restriction to growth can also be a sublethal effect of metal pollution. The toxicity of Cu to *Daphnia magna* was investigated in a laboratory experiment by comparing daphnids exposed to both low and high dietary concentrations of Cu. The daphnia which were fed high levels of Cu ($3000 \mu\text{g g}^{-1}$ dry wt) in their diet experienced a 38% reduction in growth, a 50% reduction of reproduction (total number of juveniles produced per daphnid) and only produced three broods versus four broods by the control daphnids (De Schamphelaere et al, 2007). The reproductive output of zebrafish fed the polychaete *Nereis diversicolor* collected from a metal-impacted estuary, Restronguet Creek, Cornwall, was compared to fish fed *N. Diversicolor* from a non-metal impacted estuary, Blackwater, Essex. The results showed that fish fed the metal laden polychaete for 68 days showed reduced reproductive output, characterised by reduced cumulative egg production (47%), cumulative number of spawns (30%) as well as reduced average number of eggs produced per spawn and % hatch rate. The element responsible for the changes in reproduction was found to be a potentially toxic inorganic As species, which accumulated in the tissues of the zebrafish (Boyle et al, 2008). As a final example, the effects of metals on embryonic development of the Ramshorn snail *Marisa cornuarietis* was investigated by exposing embryos to varying concentrations of Cu, Pb, Li, and Pd (Sawasdee & Köhler, 2010). Compared to the control, a significant delay was found in the formation of tentacles and eyes, heart rate decreased, hatching was delayed (although exposure to Cu induced earlier hatching) and body weight was reduced.

As with freshwater organisms, different metals affect humans in different ways and cause a variety of illnesses (Järup, 2003). For example, Pb poisoning can affect the nervous system and the brain, causing acute psychosis, confusion and reduced consciousness. Long term exposure can result in memory deterioration, prolonged reaction times and reduced ability to understand. It can also cause renal failure and kidney damage and is a possible carcinogen. Acute inorganic Hg exposure can cause lung damage and eczema. Chronic poisoning is characterised by an array of neurological and psychological symptoms. However, organic mercury (methyl mercury) is also dangerous, causing nervous system damage and death. Inorganic As is acutely toxic and can lead to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems and death. There is also an increased chance of mortality from lung, bladder, kidney and skin cancer (Järup, 2003). Biomagnification is also an important factor. One of the most famous cases was the illness known as 'Minamata Disease' which infected many inhabitants of Minamata Bay in south western Kyushu, Japan in the 1950s. Research found that the illness was caused by mercury poisoning. Methyl mercury had been discharged into a drainage channel leading to the bay from a number of chemical plants in the vicinity. The methyl mercury entered the food web and biomagnification occurred. The inhabitants who ate seafood in the area absorbed much higher doses of Hg than were present in the water, and suffered a range of symptoms including sensory disturbances, ataxia, dysarthria, visual and auditory disturbances, tremor, brain lesions, and death (Takeuchi et al, 1962; Harada, 1995). The wide variety of health implications shows that it is important that metal contamination of the environment is taken very seriously.

1.5.3. Sources of metal contamination to the aquatic environment

Figure 1.10 provides a general outline of source types and the cycle of metals with particular reference to a lake environment. As outlined in Section 1.5.1, there are a large number of metals which can be considered when exploring metal contamination. Each metal has a range of sources, often specific to the metal in question, although some sources will produce more than one metal. Metals also move around the environment in a variety of different ways. This makes identifying the causes of metal contamination extremely complex and case specific. Because of this, only the general source types and transport mechanisms shown in Figure 1.10 will be discussed in this section.

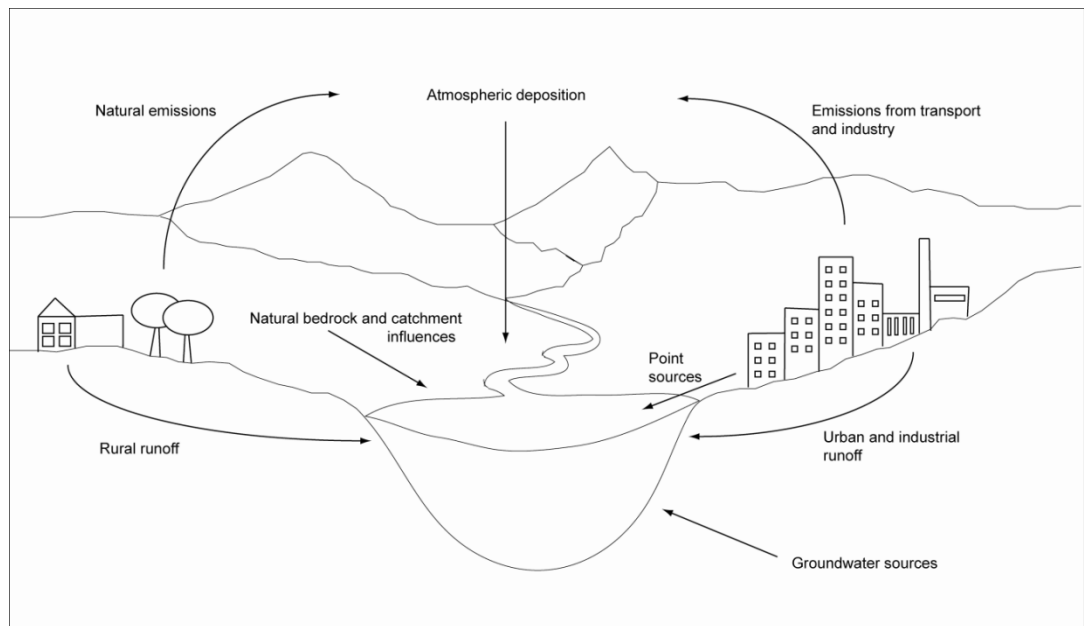


Figure 1.10 – General sources and transport mechanisms of metals in an aquatic system

Metal sources can be split down into those that are natural and those which are caused by human activity. One of the chief natural sources is the weathering of bedrock, which provides a background concentration of metals in the environment. Material produced in this way is often further eroded and transported into lakes. In areas characterised by metal-bearing formations these metals will also therefore occur at enhanced levels in waters and sediments (Förstner and Wittmann, 1979). A number of other natural sources contribute metals directly to the atmosphere including wind-borne soil particles, seasalt sprays, volcanoes, wild forest fires and biogenic particulates (Nriagu, 1989). The metals then reach the land and water through atmospheric deposition. The proportion of natural input varies depending on the metal in question. For example, Nriagu (1989) calculated that in 1983 natural sources of lead to the atmosphere accounted for $12 \times 10^9 \text{ g yr}^{-1}$ out of a total of $344 \times 10^9 \text{ g yr}^{-1}$ - only about 4 per cent. In contrast, 89 per cent of manganese was emitted through natural processes. Overall however, the impact that humans have had on the levels of metals in the environment is much more significant than that of natural sources (Pacyna et al, 1995).

Figure 1.10 highlights the chief source types and transport routes of anthropogenic metal contamination. Atmospheric emissions from transport and industry are an important diffuse (indirect) source of contamination. As noted above, a large proportion of the lead emitted to the atmosphere in 1983 was anthropogenic (Nriagu, 1989), with the primary source being the leaded petrol used by road transport at that time. It has been calculated that for 1984, 76% of atmospheric lead came from road transport. Since then however, the introduction of

worldwide legislation to prevent the use of leaded fuel has resulted in emissions levels dropping considerably, from nearly 8000 tons in the UK in 1984 to approximately 1500 tons in 1996 (von Storch et al, 2003). Road transport is also responsible for the emission of a number of other metals such as Ni, Mn and Cd, although to a much lesser extent than Pb (Pacyna, 1984). Industrial emissions include those from power plants, mining, non-ferrous metal production, iron and steel manufacturing and cement production. In Europe in 1979, industries such as these accounted for the emission of 18900 t y⁻¹ of Cr, 15500 t y⁻¹ of Cu, 17600 t y⁻¹ of Mn, 16000 t y⁻¹ of Ni and 80000 t y⁻¹ of Zn, as well as considerable amounts of As, Cd, Co, Mo, Pb, Sb, V and Zr (Pacyna, 1984). However, since the 1990s emissions across Europe have fallen extensively. Emissions of Pb decreased by 89% between 1990 and 2010, Hg by 63% and Cd by 60% (EEA, 2012). All of these figures reflect the general variety of trace metals that are produced through a wide range of industrial sources.

As with natural atmospheric sources, anthropogenic metals emitted to the atmosphere are then deposited on the earth. Metals emitted to the atmosphere are not necessarily deposited close to their source, but often can travel great distances before falling out of the atmosphere. This emphasises the diffuse nature of atmospheric deposition. Studies have been carried out in remote lakes far from industrial sources that show increased concentrations of metals that can only have come from the long range transport and deposition of anthropogenic metals. For example, sediment cores from 12 lakes in the subarctic region of Sweden were analysed for Hg and the results showed a significant increase in concentrations corresponding to the previous 100-150 years, despite there being no local sources of Hg in the area. The increase occurred simultaneously with the increase in Hg emissions produced as part of the industrialisation of Europe and North America during the same period (Lindeberg et al, 2007). Such trans-boundary contamination is problematic both for the impact that the pollution can have, as well as the difficulty in identifying those responsible and being able to legislate against it.

Other diffuse sources of metals include those which enter the aquatic system via runoff and groundwater (Figure 1.10). The addition of fertilisers and the spread of slurry as part of the agricultural process deposits metals on the ground. These can either leach downwards to the groundwater level and thereby reach the aquatic system, or run directly off the land into lakes and streams. In industrial and urban areas, the same processes can occur, although the sources are more varied. Mine tailings from mining operations, storm drainage from roads, landfill, incineration and sewage treatment plants, industrial processing plants, power stations and domestic housing all contribute metals to groundwater and runoff, as will deposition from the atmosphere (Foster & Charlesworth, 1996). Runoff is particularly important in an urban setting because of the built up nature of the area. Roads and buildings

prevent the infiltration of water directly back into the ground and therefore the amount of runoff is high. Combined with high levels of traffic and industry, the input of metals via this route can be considerable (Davis et al, 2001). As before, the diffuse nature of these sources makes it difficult to pinpoint the specific cause of pollution in a particular area.

Some metals are deposited in the aquatic system more directly, via point sources. Point sources usually take the form of industrial and domestic effluents which are discharged into rivers, lakes and the sea, and can be acute or chronic in nature. Point sources can have considerable localised effects on water quality. A study by Cobelo-Garcia & Prego (2004) of the Ferrol Ria in north west Spain analysed the concentrations of a number of metals in surface sediments. Observed concentrations of Zn, Cu and Pb were much higher in the vicinity of point sources. Similarly, in the River Tamar catchment in the UK, a well known area of mining, seven specific sources of the 25 adits and streams surveyed accounted for more than 75% of the estimated total discharge of Fe, Mn, Cu, Zn and As per year from the catchment (Mighanetara et al, 2009). Mines and mine workings can be a considerable point source of metal pollution. The previous study was an example of chronic contamination. An example of acute contamination occurred in the River Carnon, west Cornwall in January 1992. Several million gallons of highly polluted water from the abandoned Wheal Jane tin mine was discharged into the river. A water quality study that took place over the two years following the incident showed that although the water quality improved, fluctuations in concentration continued to occur which suggested that the ecosystem had not fully recovered (Neal et al, 2005). Although this was an extreme event, the importance of point sources to metal contamination of aquatic ecosystems should not be underestimated. It is often easier to identify point sources, which makes control of metal contamination from these sources a little more straightforward.

It has already been noted that metals deposited from the atmosphere or other diffuse sources will enter lakes via run off from the catchment. However, more recently it has been suggested that catchments also act as a secondary source of contamination. Metals and other pollutants which have been deposited previously and stored in catchment soils are released back into the aquatic environment when catchments are disturbed. A study of peat erosion in the southern Pennines, UK (Rothwell et al, 2005) showed that erosion of the upper peat layer was releasing high concentrations of industrially derived Pb (and by inference, other metals associated with industrial particulates) into the fluvial systems of the southern Pennines. This 'legacy' pollution is likely to become an increasingly important source of metal contamination in the future.

In conclusion, the sources of metal contamination are varied and the methods by which they are transferred are important. Industry, transport and urban areas are key anthropogenic sources of metals, although rural areas also contribute and natural sources play a part as well. With particular regard to the aquatic environment, the direct or indirect way in which metals reach the system also has an important role.

1.5.4. Worldwide metal contamination – past and present

Anthropogenic metal pollution has been occurring for as long as humans have been using fire for domestic purposes, the burning of firewood resulting in the deposition of small amounts of trace metals (Nriagu, 1996). The discovery of metals and early mining and metal processing techniques in ancient times enhanced the levels of localised metal contamination, as well as polluting areas further afield through atmospheric emissions and deposition. Contamination close to metal working areas has been identified from sites that are Roman in origin. Peat columns taken from either side of the remains of a Roman road in Belgium have been analysed for Pb and Zn. The results showed an increase in concentration of both metals at depths corresponding to between AD 19 and AD 328, and are thought to be the result of contamination from the transport of Pb-Zn rich material along the road from nearby ore deposits (Renson et al, 2008).

However, it is metals that have been deposited from the atmosphere that have shown the clearest long term trends of contamination. The first indication of atmospheric deposition of Pb pollution dates to between 2000 and 1500 BC in southern Sweden, reflected by a decline in $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratios recorded in lake sediments, and an increase in Pb concentrations in ombrotrophic peat bogs from the area. The rise in atmospheric pollution is attributed to early metal production, with the annual world production of Pb increasing from a few tonnes in 3000 BC to about 300 tonnes in 700 BC (Renberg et al, 2000). Lead concentrations recorded in Greenland ice cores also show an increase, starting about 2500 years ago, or about 500 BC, from background levels of 0.55 pg g^{-1} up to about 2 pg g^{-1} . Concentrations remained at this level for about 800 years, corresponding with the flourishing Greco-Roman civilisations of the period (Hong et al, 1994). Similar patterns have also been found for Cu (Hong et al, 1996). Because of Greenland's remote location, the metals recorded in the ice cores must have been emitted to the atmosphere from mining and smelting processes in the Mediterranean and subsequently deposited. The same studies show a slight drop in Cu and Pb concentrations in the latter half of the Roman period as metallurgy went through a slight decline, followed by an increase from approximately AD 500, which has continued up until the present day. Other studies have confirmed the global nature of contamination since ancient times. Another study of lake sediments from Sweden showed that atmospheric Pb deposition increased above background levels more than 2600

years BP. The subsequent peak that reached about five times over background concentrations, and which was detectable all over Sweden, was dated in six lakes to 2000 years BP (Renberg et al, 1994). Similar results have been found for salt marsh deposits in Iceland, where a low level (0.1 to 0.4 $\mu\text{g g}^{-1}$) Pb enrichment signal was isolated which dated to AD 50-150. The isotopic signature and timing of this signal suggested that Roman metal working industries were the source (Marshall et al, 2009).

By far the most substantial increase in metal contamination has occurred over the last 150-200 years as a result of the Industrial Revolution which took place in the 18th and 19th centuries. Figure 1.11 shows that since 1850 both the quantities of Cu, Pb and Zn produced from mines globally and anthropogenic emissions of trace metals to the atmosphere have increased, with a slight decline in from the 1970s onwards (Nriagu, 1996). The impact of such an increase in air pollution has been reflected in a variety of deposits, including ice cores, peat bogs and lake sediments. For example, Candelone et al (1995) analysed ice cores from Greenland for Pb, Zn, Cd and Cu, all of which showed a significant increase from 1850 to the 1970s. Concentrations at depths dated to 1773 for each of the metals were found to be 7.6, 16, 0.27 and 2.8 pg g^{-1} respectively. Maximum concentrations, all of which occurred in the 1950s, were 126, 155, 3.3 and 17 pg g^{-1} respectively, in all cases more than a fivefold increase, some much greater. A study of cores from ombrotrophic peat bogs in remote locations in Sweden and Norway showed that deposition of Cd, Cu, Pb and Zn increased between 1800 and 1970 (Jensen, 1997), and Birch et al (1996) showed that concentrations of Pb, Zn and Cd in the sediments of Lake Cadagno in the Swiss Alps increased from fairly constant background levels in the late 19th century to peaks of approximately 270, 400 and 3 $\mu\text{g g}^{-1}$ between 1976 and 1983. Although the Industrial Revolution mainly involved the more developed countries of the northern hemisphere, studies from other areas have reflected the worldwide nature of metal contamination. Wolff and Suttie (1994) examined Pb concentrations in snow sequences cut from Coats Land in Antarctica, obtaining a 70 year record, starting in the 1920s. Concentrations rose from 2.5 pg g^{-1} at the base of the section to a peak of over 6 pg g^{-1} in the late 1970s. The rise was attributed to emissions from vehicles and metal production processes in the southern hemisphere.

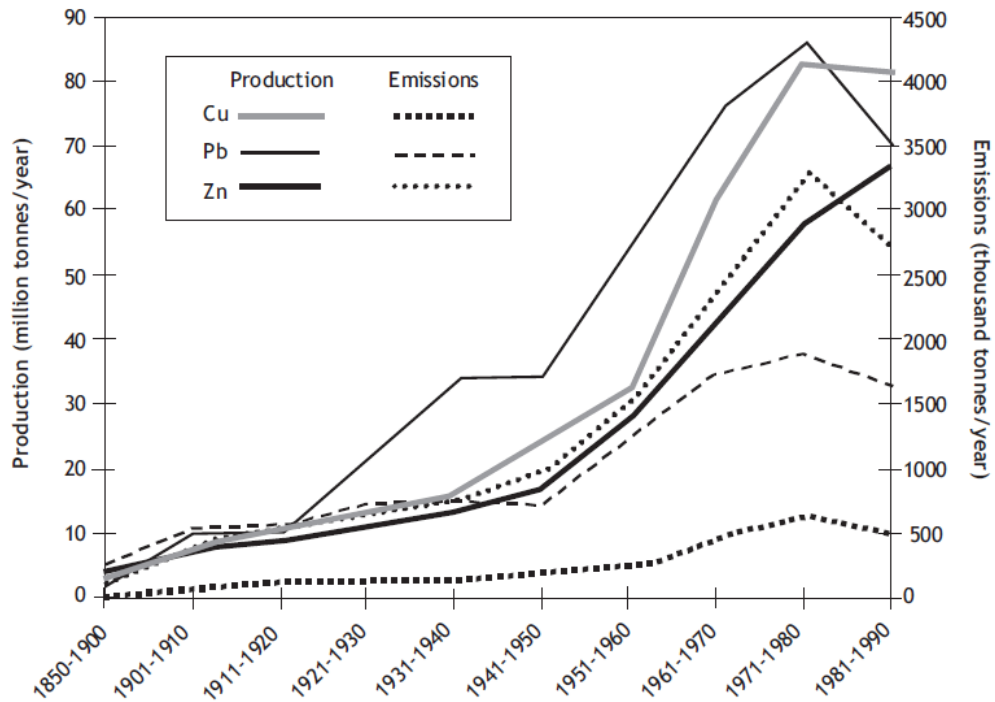


Figure 1.11 – Cu, Pb and Zn production from mines and atmospheric emissions between 1850 and 1990 (from Nriagu, 1996). Both production and emissions increased considerably over the course of the 20th century.

The decline in metal emissions in the 1970s and 1980s shown in Figure 1.11 has continued in the UK, Europe and North America throughout the 1990s and 2000s (e.g. Pb, Figure 1.12), chiefly because of controls put in place by governments to limit them. The 1979 United Nations Convention on Long-range Transboundary Air Pollution aimed to limit and, as far as possible, gradually reduce air pollution including long-range transboundary air pollution. It was the first international legally binding instrument to deal with problems of air pollution on a broad regional basis (UNECE, 2012). The Convention has been extended by a number of protocols, one of which is the 1998 Protocol on Heavy Metals. The basic obligation of the Protocol is to reduce emissions of Cd, Pb and Hg below their levels in 1990, using various means. The Protocol was amended in 2012 to adopt more stringent controls of heavy metals emissions and introduce flexibilities to facilitate accession of new Parties, notably countries in Eastern Europe, the Caucasus and Central Asia (UNECE, 2012). Legislation has also been introduced in many countries to prevent the direct contamination of the environment through improper disposal of metal containing waste materials. More detail on legislation specifically relating to London and the UK is provided in Section 1.6.

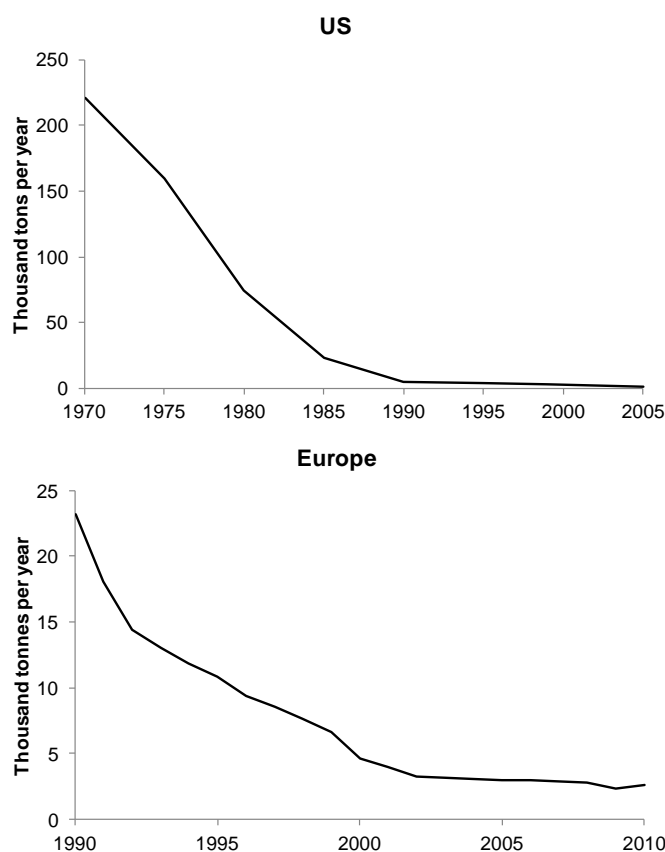


Figure 1.12 – Pb emissions in the United States from 1970 to 2005 (USEPA, 2008) and Europe from 1990 to 2010 (EEA, 2012), showing the decline in emissions in recent decades

However, metal emissions have not declined in all areas of the world. In a recent study by Li et al (2012), atmospheric Pb emissions in China were estimated over the period 1990 to 2009. Although a substantial decline occurred in 2001 due to the phasing out of leaded gasoline, emissions of Pb from other sources, in particular coal combustion and non-ferrous smelting, increased from approximately 3000 tonnes in 2001 to almost 10,000 tonnes in 2009. Consequently, metal contamination of the environment has not decreased in some places. Studies of sediments from Lake Taihu in the more industrialised eastern side of China have shown an increase in the contaminants Cu, Cd, Pb and Zn, beginning in the 1960s and continuing right up until the present day (Rose et al, 2004). Analysis of lake sediments for Hg in the remote Tibetan Plateau at the western edge of China has also shown a marked increase in concentration since the 1960s, probably exacerbated by the close proximity of the area to India (Yang et al, 2010). Nriagu (1992) reviewed the impact that toxic metals are having on ecosystems in Africa. It was found that concentrations are increasing and starting to reach very high levels – in Nairobi the Pb concentrations in soils exceed $4000 \mu\text{g g}^{-1}$ in the industrial areas and $2000 \mu\text{g g}^{-1}$ in the city centre (Onyari et al, 1991), on a par with the most polluted locations in Europe and North America. These studies

show that even if metal contamination in some parts of the world are in decline, increases in other areas mean that global metal pollution is still a problem.

1.5.5. Metal contamination in the urban environment

Metal contamination will be greater in urban environments due to the focusing of large amounts of transport and industry. Urban environmental geochemistry has become more important as the world's urban population continues to grow. Wong et al (2006) reviewed the state of trace metal environmental geochemistry in urban environments with particular focus on soils, showing that research began in the more industrialised countries of Europe and North America in the 1970s and 1980s. However, more recently it has spread to other continents reflecting the current urbanisation of these regions. At the present time research into urban metals spans much of the globe. Soils have been examined in a wide range of urban areas. Morton-Bermea et al (2009) reported on the degree of metal pollution in 135 urban topsoil samples from Mexico City. Lead, Zn and Cu were found to be most enriched over the area. Similarly, a study of the distribution of metals in soils in Hong Kong (Luo et al, 2011) also showed that Pb, Zn and Cu were enriched, and that Pb was particularly influenced by vehicular emissions. A study of soils in Annaba, Algeria (Maas et al, 2010) showed that Pb pollution was a particular problem in the centre of the city, with concentrations reaching $823 \mu\text{g g}^{-1}$. A study in Turin, Italy by Biasioli et al (2006) also showed that Pb was the most enriched metal within the city. Lu & Bai (2006) studied the content of Cu, Zn, Cd and Pb in urban soils of Hangzhou City, China. The degree of contamination was found to follow the order; industrial area > roadside > public parks > residential for Cu and Pb, and the order; industrial area > roadside > residential > public parks for Zn and Cd. Despite the varied geographical locations, the elevated concentrations of metals (particularly Pb, Cu and Zn) that have been found reflect the impact that an urban location can have on metal contamination.

Apart from soils, a variety of other terrestrial media have also been investigated. Street dusts from Dhaka city, Bangladesh have shown enhanced levels of Zn ($261 \mu\text{g g}^{-1}$), Cu ($304 \mu\text{g g}^{-1}$), Ni ($54 \mu\text{g g}^{-1}$) and Cr ($203 \mu\text{g g}^{-1}$) in industrial areas and of Pb ($205 \mu\text{g g}^{-1}$) in commercial areas. The latter result was put down to higher numbers of vehicles in the commercial areas. All metal concentrations exceeded the maximum permissible limits for common soil (Ahmed & Ishiga, 2006). In contrast, in Birmingham (UK), Pb concentrations of street dust have been found to be in decline, from an average of $1300 \mu\text{g g}^{-1}$ 30 years ago to only $48 \mu\text{g g}^{-1}$ in the present day (Charlesworth et al, 2003). The impact of metals on urban plants has also been investigated. In Aqaba city, Jordan, palm leaves (*Phoenix dactylifera* L.) were analysed from urban, suburban, industrial, highway and rural sites, with the industrial areas having the highest content of Zn ($56 \mu\text{g g}^{-1}$), Cr ($3.97 \mu\text{g g}^{-1}$) and Fe ($265 \mu\text{g g}^{-1}$) and the highway

samples having the highest content of Pb ($177 \mu\text{g g}^{-1}$), Cu ($39 \mu\text{g g}^{-1}$) and Ni ($40 \mu\text{g g}^{-1}$) (Al-Khlaifat & Al-Khashman, 2007). Similarly, a study carried out in Vienna, Austria, by Simon et al (2011) showed that elemental concentrations of leaves of *Acer pseudoplatanus* were significantly higher in the urban area than suburban or rural. Tree bark was analysed for trace element concentrations in the cities of Strasbourg and Kehl in the Rhine Valley. The bark was found to be strongly enriched in Mn, Ni, Cu, Zn, Cd and Pb within the urban areas, with elevated levels of Ni and Pb particularly noticeable in barks sampled close to traffic axes (Guéguen et al, 2012). Mosses of the genus *Haplocladium* from Shanghai, China have been analysed at intervals over a 40 year period, between 1965 and 2005. The metal content reflects the increase in industrialisation in south east Asia, with concentrations of Cu, Pb, Cd, Zn and Cr all rising over the period and especially since the 1980s (Cao et al, 2008).

With particular regard to the aquatic environment, some information exists for metal contamination in rivers flowing through urban areas. The Illinois River has been severely impacted by domestic and industrial wastes from Chicago and other cities located along its shores. Sediments, water, fish, clams and tubificids from the river were analysed for metals (Mathis & Cummings, 1973). Using Pb as an example, concentrations in sediments averaged at $17 \mu\text{g g}^{-1}$ and were closely reflected by the tubificids which also had a mean concentration of $17 \mu\text{g g}^{-1}$. The clams had lower concentrations (3.7 , 2.7 and $2.2 \mu\text{g g}^{-1}$ for three different species), with carnivorous and omnivorous fishes containing even less (0.57 and $0.64 \mu\text{g g}^{-1}$ respectively). The water had the lowest metal concentration of all at $0.002 \mu\text{g g}^{-1}$. More recently, sediments of three rivers in Huludao City, northeast China were analysed for metal contamination. Levels of metals were high overall, with Hg exhibiting average concentrations of up to $33.07 \mu\text{g g}^{-1}$, Pb up to $454.1 \mu\text{g g}^{-1}$, Cd up to $250.3 \mu\text{g g}^{-1}$, Zn up to $5595 \mu\text{g g}^{-1}$ and Cu up to $217 \mu\text{g g}^{-1}$ (Zheng et al, 2008).

There is also a small amount of information available regarding metal contamination of urban lake sediments. Arsenic levels in Spy Pond, Arlington (MA, USA) have been studied and show a steep increase in sediments corresponding to the 1960s. In this case, the contamination appears to correspond with the historical application of arsenical herbicides in the 1950s (Durant et al, 2004). More diffuse contamination of lake sediments has been shown in Lake Michigan, where the impact of atmospheric deposition has been investigated. Although Lake Michigan cannot be described as truly urban because of its vast size, the extent of industrial activity and urban conurbation to be found on its shores have impacted upon it greatly. The more urbanised southern basin in this study showed greater levels of atmospheric deposition than the northern basin, with atmospheric loading of Pb amounting to $5.0 \times 10^5 \text{ kg yr}^{-1}$ in the south compared to $1.4 \times 10^5 \text{ kg yr}^{-1}$ in the north. Similar trends were found for Zn, Cu, Cd and Mn (Eisenreich, 1980). Elsewhere, analysis of lake waters and

sediments in Stockholm, Sweden has been carried out to model metal loadings from the urban surroundings. Mean concentrations of Pb, Cu and Zn in sediments were 161.6, 255.6 and 518.5 $\mu\text{g g}^{-1}$ respectively and in water were 1.50, 3.19 and 7.85 $\mu\text{g L}^{-1}$ respectively (Lindström & Håkanson, 2001).

It is difficult to relate levels of metal contamination in different parts of the world. An area such as Europe, where there are many cities quite densely packed together which have been industrialised for a long period of time, is likely to have a higher concentration of metals than those which are in low density areas that have only recently become industrialised, such as Annaba in Algeria. For many of the examples outlined above, urban metal concentrations have been compared to rural concentrations within the same country, and therefore the 'high' or 'increased' levels of metals that have been found are in comparison to background levels in that particular area. Therefore, although some of the concentrations cited may not appear to be very high within the global context, in a local context the increase may be substantial.

Although the examples given within this section highlight the breadth and scale of global urban contamination, more work is still required in a number of areas. The impact of metal contamination on lakes in urban areas has not been assessed to any great degree, with the majority of lake studies being carried out in more remote locations. Of particular interest to this project is the fact that very little information exists on the extent of metal contamination in lakes in London (see Section 1.6). Given that London has long played an important role in trade and industry and the population is still increasing, the lack of exploration into this particular issue provides an intriguing area for further investigation.

1.6. Metal contamination in London

This section will focus on two aspects of pollution in London. As outlined in Section 1.5.3, metals enter lakes from the atmosphere and through water sources. The former deposits metals across a wide area whereas the latter are more localised. In an urban area such as London, the temporal patterns of concentration recorded in lake sediments will be a reflection of both sources. Therefore it is important to identify the histories of both pollution types so as to be able to fully interpret the palaeolimnological data.

1.6.1. History and legislation of air pollution

There has been human settlement in the London area since prehistoric times (Ackroyd, 2000). Atmospheric pollution from the burning of fuel for domestic and industrial purposes would have occurred to a small extent even at this early stage. However, it is thought that air pollution started to increase more significantly in the Medieval Period, at the beginning of the thirteenth century. At this time, the main fuel used in industry (and for lime production in particular) underwent a change from wood to sea-coal (Brimblecombe, 1977). Pollution from coal was considered such a serious matter that a commission was set up in 1285 to investigate the problem and find a solution. Records from the early fourteenth century show that although attempts were made to ban the use of sea-coal, they were largely unsuccessful. Pollution at this time was largely a seasonal event, especially as lime was mostly produced in the summer months. This is reflected by the fact that the number of recorded complaints of air pollution also increased during the summer (Brimblecombe, 1988).

The use of coal as a domestic fuel increased very slightly throughout the fourteenth and fifteenth centuries, as the availability of wood and charcoal near to the city declined. The shortage of timber meant that prices began to rise (Nef, 1932), so that by the Tudor period more and more people were being forced to heat their homes with coal. By the end of the reign of Elizabeth I in 1603, 50,000 tonnes of coal was used each year (Brimblecombe, 1988). Consequently, this change in fuel usage resulted in the further deterioration of air quality in London. A number of investigations were made to try to reduce the effects of coal smoke on the city at this time, among them when 'John Thornbrough, the Dean of York, was granted a seven year privilege 'to correct the sulphurous nature' of coal in 1590. The quantity of coal used continued to grow quite dramatically throughout the seventeenth century, partly because of its newfound necessity as a domestic fuel and also as a result of population growth. It has been estimated that between 1580 and 1680 the amount of coal imported into London increased about twentyfold (Brimblecombe, 1988).

Criticism of the air pollution brought about by coal consumption became more prominent in the mid-seventeenth century. The earliest scientific works on air pollution began to appear in this period, the most notable author being John Evelyn. He produced a book called 'Fumifugium' or 'The Inconveniencie of the Aer and the Smoak of London Dissipated' in 1661. In it he describes London's air pollution as 'the Aer...is here Ecclipsed with such a Cloud of Sulphure, as the Sun itself...is hardly able to penetrate and impart it'. The book describes the effects of pollution on the population, as well as on other entities such as buildings and plants. Arsenic is mentioned as a contaminant along with sulphur, with the main cause being industry. Evelyn then goes on to outline possible remedies, the chief one

of which was to move all industry outside of the city, or to 'propose therefore, that by an Act of this present Parliament...all those Works be removed five or six miles distant from London below the River of Thames' (Evelyn, 1661). Although a draft of this Act was produced, nothing more of it was heard afterwards and London's air pollution continued unabated.

In the eighteenth century, the quantity of coal used continued to increase as the population grew, although the rise was not as dramatic as that of the preceding century. The fact that the city did not expand to encompass the rising number of people meant that the population density increased as well. Therefore more fuel was being burnt but in the same area of space. This enhanced the effects of the high levels of air pollutants in the city at the time. During the latter part of the century pollution became particularly bad because of increasing industrialisation. The impacts of air pollution started to garner more scientific interest during the eighteenth century and a variety of literature was published on the subject. However, very little interest was taken in actually improving the air quality (Brimblecombe, 1988).

As air pollution continued to rise with industrialisation into the nineteenth century, awareness of the problems that it caused finally started to increase and become a public concern. Smoke abatement legislation began to be introduced in the 1820s and was designed to put controls on smoke emissions from industry. The Smoke Nuisance Abatement Act was passed in 1853 and probably met with localised success. The full impact of the Act is difficult to ascertain as pollution in London was not monitored on a regular basis during this period. Smoke clauses were also included in the Sanitary Acts of 1858 and 1866 and in the Public Health Acts of 1875 and 1891. It is thought that the levels of black soot may have declined following this legislation, but that in general much of the pollution still remained. This was due to the fact that the controls on industry were very specific. They only concentrated on reducing 'black smoke' produced by burning coal which in practice was very difficult to define. Many a factory owner escaped punishment by claiming that the smoke from their chimneys was of a different colour. Nor did the Act take into account domestic emissions (Brimblecombe, 1988). The late nineteenth century saw an increase in the frequency of 'London Fogs'. These were a mixture of natural fog and air pollution and became quite common in the latter years of the century. There was a decline in their frequency in the early twentieth century, although they did not disappear altogether; 'The Great Smog' of 1952 is still recalled as one of the worst incidents of air pollution within the city (Ackroyd, 2000).

Following the various Acts introduced in the nineteenth century, a further piece of legislation called the Public Health (Smoke Abatement) bill was passed in 1926, which included tighter constraints on industry but still did nothing to control domestic emissions (Brimblecombe,

1988). However, it was The Great Smog that provided the turning point for the control of pollution in the city. Between 3500 and 4000 deaths were attributed directly to the fog, and such an impact could no longer be ignored (Ministry of Health, 1954). In 1956 the Clean Air Act was enacted. For the first time, domestic sources of pollution were controlled as well as those of industry, although the law was still restricted to smoke. Smokeless zones were created which allowed only the burning of smokeless fuels such as anthracite or gas. Power stations were also relocated to rural areas. The Clean Air Act was remarkably effective and the levels of airborne particles emitted from fossil fuel production in the UK have decreased by 70 per cent since then (ApSimon, 2005). A revision of the Act in 1968 also legislated for the use of tall chimneys for burning coal, liquid or gaseous fuels. The lack of inclusion of sulphur dioxide in the Act did mean that sulphur emissions still remained a problem, although the introduction of cleaner fuels and increase in the use of electricity and gas helped to reduce levels to some extent (Brimblecombe, 1988).

In the late 1970s and 1980s there was a substantial increase in the number of motor vehicles in urban areas and consequently a significant rise in the pollutants produced from them. These include lead (Pb), nitrous oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO₂), ground level ozone (O₃), hydrocarbons (including Benzene) and particulate matter (PM₁₀ and PM_{2.5} – particles with an aerodynamic diameter of less than 10 microns and 2.5 microns respectively (ApSimon, 2005)) (LAQN, 2010). The focus for concern shifted towards these as the use of coal in industry and for domestic fuel started to decline. Sulphur dioxide (SO₂) is also produced from motor vehicles but because of the simultaneous reduction in coal use, the impact of road traffic on sulphur levels was less pronounced. Also, in 1972, the Corporation of the City of London obtained a right to limit the sulphur content of fuel under the City of London (Various Powers) Act. The control of sulphur dioxide emissions were then included as a whole under the Control of Pollution Act 1974 (Brimblecombe, 1988).

Recent legislative activity has focused on controlling vehicle emissions, as well as those from significant point sources such as power stations. The trans-boundary nature of air pollution has also become a bigger concern, with a number of European Commission directives in place to limit the amount of pollution across the European Union (see Section 1.5.4). These require national governments to monitor air quality to show that the standards are not exceeded (EC, 2010). In line with these requirements, the UK government introduced a National Air Quality Strategy in 1997 (revised in 2000) which makes it the responsibility of local authorities to use monitoring information to assess air quality in order to show that Air Quality Standards will not be exceeded in their area by certain deadlines. Air Quality Standards are set at particular levels for each contaminant, below which concentrations are considered acceptable in light of what is known about their effects on

health and the environment. In London, this means that each Borough council is responsible for monitoring NO₂, SO₂, CO, CO₂, O₃, Pb, hydrocarbons (including Benzene), PM10 and PM2.5. Much of this information is collated by the London Air Quality Network which was set up in 1993 to aid the coordination and improvement of air pollution monitoring in London (LAQN, 2010). Alongside this another national legislative programme, the Environmental Protection Act, was established in 1990. This required the Environment Agency and local authorities to be responsible for controlling waste management and emissions (OPSI, 1990).

Air pollutant concentrations are controlled using a combination of international and national measures, regulation of industrial processes and action taken at a local level. For example, the main source of lead in the atmosphere has historically been from the combustion of petrol. The phasing out of leaded petrol in Europe and elsewhere has resulted in a large fall in lead concentrations over the last 10 years (see Figure 1.12) (LAQN, 2010). In London, schemes such as congestion charging and converting buses to hybrid varieties are more localised attempts to reduce air pollution (GLA, 2010). It is generally thought that pollutant levels (excepting lead) peaked in the mid 1990s and are subsequently in decline as a result of the measures and controls that have been put in place. However, also since the 1990s, seasonal (wintertime and summertime) photochemical smogs have become an issue, which unlike the fogs of the nineteenth and early twentieth century are caused by chemical reactions between pollutants and sunlight (LAQN, 2010). Additionally, concentrations of PM10s and NO₂ frequently exceed Air Quality Standards (ApSimon, 2005) – as of June 2010, the City of London was in exceedance of standards of PM10s and was unlikely to be able to reduce levels enough before the next deadline (Vidal, 2010). This shows that air quality in London is still a significant problem.

1.6.2. History and legislation of water pollution

The history of water pollution in London is mainly focused upon the River Thames. This is unsurprising given the important role the Thames has had in the functioning of the city. From the earliest times, boats were used to carry food, trade goods and people up the river into the city and further into England. By the middle ages the river was an important resource for transport, waterpower and food. For a long time, the river was also the main source of drinking water for the population. In 1581 water wheels were erected under London Bridge to supply water to the City, and from the early 18th century private water companies used largely untreated water straight from the river to supply the growing population (MOL, 2012). Further industrialisation in the 18th and early 19th centuries, combined with the rising population resulted in heavy pollution of the river.

In the first half of the 19th century, the inhabitants of London experienced a series of recurring epidemics of cholera and typhoid. This was caused by increasing amounts of sewage being dumped into the river. The river became deprived of oxygen and fish stocks virtually disappeared (Oosthoek, 2005). The Metropolitan Commission of Sewers had responsibility for the situation, but didn't have the power to impose sufficient taxes to resolve the problem (Daunton, 2004). In the late 1840s the London Board of Health eliminated cesspools, and a Metropolis Water Act of 1852 forced water companies to move their intakes upstream and regulate their filtration and storage. Drinking water showed significant improvement by the 1850s, yet a daily influx of 260 tons of raw sewage did little to assuage the pollution problem (Oosthoek, 2005).

It should be noted that freshwater pollution was not just confined to the Thames, but also occurred in its tributaries. Pollution of the river Fleet, which joined the Thames near Blackfriars, was described by Jonathan Swift at the beginning of the 18th century in *A description of a City Shower* published in 1710:

“Now from all parts of the swelling Kennels flow, And bear their Trophies with them as they go: Filth of all Hues and Odours seem to tell, What Street they sail'd from, by their Sight and Smell.”

The Fleet began to be covered over in the late 18th century, and by the end of the 19th century had purposefully been turned into a sewer. A similar process occurred with the Westbourne which joined the Thames in Chelsea, and the Walbrook at Southwark Bridge (Clayton, 2010).

The water pollution crisis came to a peak in the 'Great Stink' of London in 1858. The stench from the Thames was so great that MPs were forced to abandon the House of Commons (MOL, 2012). A bill was rushed through Parliament to provide money to construct a massive new sewer scheme for the city, which took 16 years to build and was completed in 1874 (Daunton, 2004). In addition, the London Metropolis Water Act of 1871 forced water companies to cover all reservoirs within 8 km of St Paul's, filter all domestic supplies through sand beds and only take water from the Thames above Teddington Lock (Clayton, 2010). Although all of these measures resulted in a significant drop in mortality in central London, and cholera became a thing of the past, it only slightly reduced the level of pollution in the river waters. Sewage continued to be discharged into open water outside of cities, and air pollution was also still a large problem (see Section 1.6.1) that contributed to the quality of the water (Oosthoek, 2005).

The Metropolis Water Act of 1902 created a Metropolitan Water Board that took over the eight private water suppliers, and allowed the building of large scale reservoir and waterworks buildings (Clayton, 2010). The creation of a permanent, clean water supply combined with the new sewerage system led to the neglect of water pollution problems in the Thames. Throughout the first half of the 20th century the quality of the water deteriorated, and by the 1950s the river was again little more than an open sewer. In 1957 the Thames was declared biologically dead. It was only in the 1960s, with the closure of the docks, that efforts began to be made to clean up the river (MOL, 2012).

A number of pieces of national legislation were introduced over the following decades that led to improvements in the water quality of the Thames (and also to other UK rivers) (Water UK, 2013). In 1963 abstracting and impounding of water resources became regulated on a national basis with the implementation of the Water Resources Act. The Act created 'River Authorities' with responsibility for enforcing the law relating to water resources, river pollution, land drainage, fisheries and water space recreation. It was the beginning of river basin management. The administration of water law remained local until the Water Act 1973, which created ten regional water authorities whose areas were defined by river basins. For London, the authority was called the Thames Water Authority (later Thames Water). These authorities had overall responsibility for water supply, sewage disposal and river basin management. They were, however, also required to work to some extent through the statutory water companies and the local authorities. Privatisation of the ten water authorities' water supply and sewerage functions came with the Water Act 1989 and with it transfer of the river functions to a newly created National Rivers Authority (NRA). The NRA was later to be subsumed within the Environment Agency (Environment Act 1995). Still, however, much of the substantive law remained unchanged (Water UK, 2013).

Since 1989 water law in England and Wales has been consolidated and to some extent updated by a number of Acts of Parliament. The Water Industry Act 1991 (as principally amended by the Water Industry Act 1999 and the Water Act 2003) deals with matters such as economic regulation of water and sewerage companies, and water supply and sewage disposal powers. The Water Resources Act 1991 (as principally amended by the Water Act 2003) provides for the regulation by the Environment Agency of water resource management and water quality standards and pollution control. Water and sewerage companies have to take into account other national legislation and EC environmental directives as they relate to regulation by the Environment Agency of waste, land contamination, protected areas, air quality, flood defence, fisheries and water space amenity (Water UK, 2013).

The companies now also have to regard the qualitative and quantitative water standards imposed via 'River Basin Management Plans' under the Water Framework Directive 2000/60/EC (WFD). The WFD sets the goal of achieving a 'good status' for all of Europe's surface waters and groundwater by 2015. The Directive defines 'good ecological and chemical status' in terms of low levels of chemical pollution as well as a healthy ecosystem. To achieve good ecological status, Member States will have to address the factors harming water ecosystems. Pollution is one, so are morphological changes such as dams built on rivers. The extraction of water for irrigation or industrial uses can also harm ecosystems if it reduces water levels in rivers or lakes below a critical point. There are separate, less stringent goals for artificial and heavily modified water bodies. The lower stretches of the Thames, which are modified by embankments and other public works as they flow through London were identified in the UK's 2005 river basin report as heavily modified. Monitoring to assess the health of the ecosystems as well as chemical contamination was set up in 2006 and river basin management plans were due in 2009 (EU, 2008). A variety of components in surface waters are being monitored, including for chemical status, 'priority substances' as outlined in the 2008 EU Priority Substances Directive; and for ecological status, physical, chemical and biological elements (e.g. nutrients, pH, dissolved oxygen, ammonia, phytoplankton, macroalgae, fish, invertebrates), specific pollutants (e.g. metals, organic compounds) and hydromorphology (e.g. depth, width, flow, structure) (EA, 2009).

The River Basin Management Plan for the Thames River Basin District encompasses all larger water bodies within London – rivers, canals, lakes and reservoirs. However, smaller water bodies are not part of the monitoring network. The history of water pollution of smaller water bodies in London is not widely known and is very site specific. Most small lakes in London are either managed by the local borough councils and are covered and protected by local byelaws, or by other organisations who own the surrounding land, such as the Corporation of London and Hampstead Heath. Water quality monitoring is or has been carried out at such sites. For example, Wandsworth Borough Council set up the London Lakes Project in 1993 in response to a noticeable decline in water quality at a number of the Borough's lakes. Three lakes, in Battersea Park, Tooting Common and King George's Park were chosen for rehabilitation work. A variety of methods were used to restore the lakes, including reducing nutrient inputs, managing fish populations and improving bankside and aquatic planting (Wandsworth Borough Council, 2008). Water quality testing of various kinds is carried out on the ponds on Hampstead Heath. For example, regular phosphorus testing has been carried out since 2006 and dissolved oxygen levels have been recorded since 2007. For the bathing ponds in particular, the Environment Agency has carried out tests since 1998 as part of the requirements of the EC Bathing Water Directive. Additional microbiological sampling has been carried out by the Corporation of London since 2006

(Brooker, 2009, pers. comm.). However, the small amount of information that is available about water quality in London's lakes highlights the necessity of a study such as this one.

1.6.3. Previous research into metal pollution in London

The study of air pollution encompasses a wide range of scientific disciplines, particularly because of the variety of different effects it can have on both humans and the environment. At the most basic level, the direct monitoring of pollutants provides a contemporary record of the levels of pollutants that are present in the air of the city, and depending on the method of collection, what is being deposited. Information obtained through monitoring helps to ensure that emissions targets are being adhered to and to provide additional support for passing new legislation (LAQN, 2010).

Air pollution in London only really began to be monitored on a regular basis at the start of the twentieth century. In the late nineteenth century, periodic collections of rainfall were made which were analysed for chloride, sulphate, nitrate and ammonia. In 1910, the Coal Smoke Abatement Society installed a trial network of deposition gauges, which was closely followed by the formation of the Advisory Committee on Atmospheric Pollution. Atmospheric deposition began to be collected on a regular basis, with the results being published each year by the Meteorological Office. In London, data from monitoring deposition in this manner continued to be assimilated up until the 1970s, giving a remarkably constant record of the decline in soot and sulphate deposits in the capital. Suspended particulates also began to be recorded in the early twentieth century, followed by the introduction of sulphur dioxide analysis in the 1930s (Brimblecombe, 1988). More recent legislation which requires local authorities to be responsible for the air quality in their area has meant that monitoring is now carried out on a regular basis and for a variety of contaminants (LAQN, 2010).

Within London, research has tended to focus on air pollutant emissions levels as well as the effects on human health, rather than the secondary impacts that air pollution has on the environment. A number of research papers have been produced using monitoring data and concern temporal changes in the levels of pollutants produced (Eggleston et al, 1992), outlining the recent history and using a variety of modelling approaches to predict what future emissions will be like (Beevers et al, 2001; Carslaw et al, 2001). The focus has primarily been on NO₂ and PM10s because of the present difficulties in reducing emissions of these pollutants. The effectiveness of measures put in place to curb emissions have also been reviewed, such as the impact that congestion charging has had on air pollution (Beevers & Carslaw, 2005; Atkinson et al, 2009). Spatial patterns in particulates have also been studied to assess the movement of pollutants from known industrial sources (Berry,

2001). With regard to the impacts on humans, a number of studies have been produced, varying from assessing the levels and types of exposure to which people in London are subjected (Adams et al, 2001; Kaur et al, 2005), to the specific health implications from such exposure (Anderson et al, 1995; Hajat et al, 2002).

Particulate matter is of more interest to this project and in particular the trace metal component of it. Studies of metal contamination and its impacts in London have been relatively sparse, although varied. One of the first projects to investigate metal pollution in the city was published in 1983, where atmospheric deposition was analysed for a variety of metals across nine sites in London over a ten month period, using total deposit collectors and moss bags. They found that in general the four inner city locations had much higher levels of deposition, with average Pb deposition being almost double that found at any of the more suburban locations (Duggan et al, 1983).

Quite a number of research projects have investigated the levels of metals in dusts, particularly with regard to those produced and deposited at street level. Schwar et al (1988) investigated the spatial distribution of metals in dusts across the city and found elevated levels of Cd, Cu, Zn, Pb and Fe in patterns that corresponded to both centres of population and general industrial activity. Dusts collected from Deptford in south east London were used in bioassays to investigate toxicity (Wang et al, 1998), both on plant seed germination and root growth, dinoflagellate green algae and luminescent bacteria. It was found that the smaller particles had the most toxic effect because they had the highest levels of metal contaminants. The rise in vehicle emissions since the 1970s and 1980s resulted in several studies focusing in on the impacts of dusts at roadsides, in Haringey (Harrop et al, 1990), Bethnal Green (Leharne et al, 1992) and Greenwich (Serrano-Belles & Leharne, 1997). Further out from the city centre, the impact of the M25 motorway on the aquatic environment and local vegetation, soil, dust and air has also been investigated (Ward, 1990; Sriyaraj & Shutes, 2001).

The wider effects of metal contamination on the London environment have been investigated to a degree, although not comprehensively. Specific components of the urban environment have been explored, although few have considered the movement of metals within a system as a whole. An exception to this is an urban catchment study that was carried out by Revitt et al (1990). They analysed the metal content (Cd, Cu, Pb and Zn) of airborne particulates, deposition, surface dust and stormwater run off in a small urban street catchment in South Oxney, on the north western outskirts of London. A mass balance was constructed from the data to show how each metal moved between the different components. Other terrestrial

studies have included the analysis of soils in Richmond, south west London, to assess the importance of land use on metal content (Kelly et al, 1996). Lower metal concentrations were found in soils taken from areas of open space, with higher values obtained from built up areas and in samples taken close to roads. The impact of road pollution on plants has also been investigated at two central London locations, Brompton Square and Park Square Gardens, assessing the possible effects of airborne metal contamination on toxicity (Peachey et al, 2009).

Investigation into trace metal contamination of the urban aquatic environment has been similarly limited in London. However, there is limited information available about metal contamination of any kind, although the pollution of lake sediments has been explored to a small extent. A study of spatial contamination was made by Yang et al (2001), who took surface samples from 29 lakes across Greater London and analysed them for a variety of elements. The results showed large ranges in concentrations for Hg, Pb, Zn, Cd, Cu, Cr, Ni, As, V, Se and Sn, although it was generally found that sites close to industrial areas, roads or commercial areas had the highest concentrations of these elements. Temporal changes in trace metal contamination have also been assessed using a sediment core taken from Banbury Reservoir in north east London (Yang & Rose, 2003; Yang & Rose, 2005). Compared to other remote lake sites that were also examined, the concentrations of metals (Hg, Cd, Ni, Pb, Zn, Cu) were much greater and is probably indicative of the lake's urban location. Related to the research carried out at Banbury Reservoir is a study of the catchment of the River Lee, the lower part of which includes a large part of Greater London and also the reservoir. The metal concentrations of the river water and effluents from point sources including sewage, industry and a fish farm were examined, the former having notably higher levels in the urban part of the catchment. Sewage effluents were the chief source of Pb and Zn to the catchment, and industrial effluents contributed much of the Fe (Snook & Whitehead, 2004). Other investigations into metals in the aquatic environment have been carried out for Borough Councils by external consultancies, as part of specific site management plans. Examples of these include a silt and water survey of Wimbledon Park Lake (Mid Kent Fisheries, 2008) and baseline chemical survey and assessment of South Norwood Lake (EAC Ltd, 2000). However, the results from surveys such as these are not usually publicly available. The lack of comprehensive data on metal contamination of the aquatic environment in London provides scope for a wide range of further exploration in this area.

1.7. Metals within a lake system: deposition, water, sediment and biota

Natural background and anthropogenic sources of metal contamination enter lake systems via atmospheric deposition and through the movement of water. Once within the system,

metals are stored and transferred between the water, sediment and biota (see Section 1.5.3). In a study concerned with both the past levels of metal contamination and the potential toxicities of present concentrations, all of these lake components are important.

1.7.1. Metals in atmospheric deposition

The importance of metals emitted to the atmosphere and then deposited on land and in lakes has been described previously (Section 1.5). However, little has so far been said about the physical and chemical processes that are involved during this type of metal transfer. Metals are released into the atmosphere in either gaseous or particulate form. Gaseous metals can exist in both the elemental or molecular form (e.g. Hg° and HgCl_2). However, the majority of heavy metal containing compounds are associated with particulates (Henderson, 1999).

After they have been emitted, chemical changes can occur when metal particulates react with other compounds in the atmosphere, extending the range of available contaminants. Studies have identified compounds of lead in the air that are not known to be released directly from vehicle exhausts (such as $\text{PbSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$), which suggests that their appearance is due to chemical reactions in the atmosphere (Harrison, 1986). Physical changes also happen, such as coagulation. This occurs when two particles collide and coalesce, increasing the size of the metal particulates. Single particles can also increase in size through growth processes such as condensation and dissolution which occur in the presence of atmospheric water and other vapours (Jacobson, 2002). All of these kinds of speciation (chemical form, size, plus elements such as solubility etc) are important factors because they can affect the potential toxicity of the metal in question. They also have a large influence on the environmental pathways and fate of a metal (Harrison, 1986).

Speciation can also affect the residence time of metals in the atmosphere, although external factors such as temperature will also play a part. There are two ways in which metals are removed from the air – dry deposition and wet deposition. Dry deposition itself occurs in two ways. The first is by sedimentation, when particles become large enough and heavy enough to fall (sediment) out of the atmosphere. The second method is when particles are carried by molecular diffusion, turbulent diffusion or advection and rest on/bond/react with the surfaces they come into contact with, such as trees, buildings, lakes etc. Wet deposition occurs when aerosol particles coagulate with raindrops, which subsequently fall to the ground (Jacobson, 2002). Wet and dry deposition is collectively known as bulk deposition.

1.7.2. Metals in water and sediment

Both water and sediment are sources of metals for biota that live in lakes and can be potentially toxic. Transfers of metals between the two components occur continuously, although sedimentation of particulate material means that many metals that have been deposited in the past are locked away at the bottom of the lake. Figure 1.13 shows the types of metal species found in sediment and water and the transfers that occur between the two.

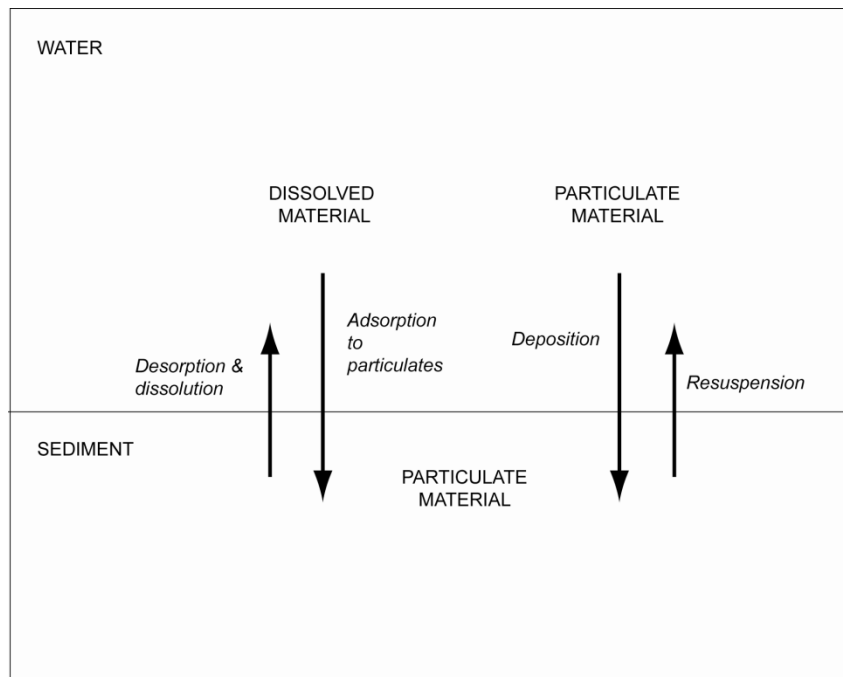


Figure 1.13 – Speciation of metals in lakes, including transfer mechanisms (in italics) between the water and sediment

As with atmospheric deposition, the speciation of metals in water is an important factor when investigating the potential toxicity of such contaminants. It also has an effect on potential sedimentation of the metal. Metals occur in waters as particulates and dissolved species, the latter of which usually includes colloids (Chapman, 1996). Operationally, dissolved metals are defined as those which can pass through a 0.45 μm filter, while particulate metals are those which are too large. Metals that are captured in the size range 0.10 μm to 0.45 μm are colloidal. Particulates have a higher concentration than dissolved material (Luoma & Rainbow, 2008). Although some particulates will remain in suspension, most will sink to the bottom of the lake and become incorporated into the sediment. For this reason lake sediments are frequently used to reconstruct past changes in metal contamination (e.g. Wong et al, 1984; Hermanson, 1991; Rognerud & Fjeld, 2001; Yang et al, 2002), which will be discussed further in Section 1.7.3. Dissolved metals in the water can also be incorporated into the sediments by adsorption to particulates and subsequent deposition. However, as

Figure 1.13 shows, the process can also work in reverse and metals can be re-dissolved in the water through desorption and dissolution and particulates can be resuspended. Although the sediments are mainly comprised of particulate material, some dissolved concentrations are found within the pore waters of near surface sediments. Living organic material and biogenic organic detritus are also part of the sediment. There is continuous equilibrium between the metals in sediments and the pore waters, water column and biota. This is important as the concentration of metals in each component will affect the bioavailability to organisms higher up in the lake food web (Luoma & Rainbow, 2008).

Determining the concentrations of metals in sediment and water is important to assess the levels of contamination in a lake. However, there are a number of processes which can affect the concentrations and which need to be considered if data is to be interpreted correctly. These are described for sediments in Section 1.7.3 and for lake waters in the following paragraphs.

The amount of suspended particulate material in the lake can affect concentrations. The affinity of metals for particulates means that the more suspended particulate material there is, the higher the 'total' concentration of metals in the water will be. It is therefore important to know the contribution of suspended material to the water sample. Alternatively, just the dissolved fraction can be analysed to remove the influence of particulates. Nyguyen et al (2005) compared trace metals in water samples taken in 2000 and 2001 from Lake Balaton, Hungary, by separating the dissolved and particulate fractions and analysing the concentrations of each. Removing the particulate fraction meant that the dissolved data from both years was comparable and that the difference in suspended particulates in each year could also be assessed.

Concentrations of metals can also vary spatially, both across the lake and throughout the water column. A study by Nriagu et al (1996) of dissolved trace metals in the Great Lakes found that higher concentrations were generally found nearer the shore. For example, in Lake Erie, the concentrations of Cu at two nearshore sampling sites were 1061 and 1036 ng L⁻¹, compared to a mean of 870 ng L⁻¹ across all sampling sites. The same study also reflected the vertical variability that there can be, with Zn and Cd both increasing slightly with water depth. Concentrations of metals will also change temporally. Esthwaite Water in the Lake District was analysed for a variety of trace metals in June, August and September of 1991. The results showed that Cr generally decreased across the three month period (Achterberg et al, 1997). The causes of these changes are complex, with physical factors

such as pH and biological processes all playing a part (Mannio et al, 1993; Nriagu et al, 1996).

1.7.3. Sediment core geochemistry

Lake sediments act as a sink for both anthropogenically and naturally derived trace metals. They are the largest store of metals within the ecosystem and are important because analysis of lake sediment cores can provide information about both the baseline state and historical development of metal contamination in a particular area (Boyle et al, 1999). However, inputs from lake catchments and in-lake processes can affect the metal concentration record in a variety of ways.

The natural fluxes of metals to lakes are controlled by biogeochemical cycling in the catchment (Boyle et al, 2004). The weathering of bedrock and in-wash of unpolluted soils form the basis of the sediment matrix and contribute to the natural 'background' concentrations of metals in sediment, along with direct deposition of unpolluted atmospheric particulates (Yang & Rose, 2005). Different sediment sources will have different natural metal concentrations and temporal changes in catchment use will affect the degree to which particular sources are contributing at any one time (Oldfield et al, 2003). The amount of organic matter present in the source sediment can also influence the metal concentrations, as well as indicating the source of the material (e.g. high organic content could indicate erosion from peaty soils (Yang & Rose, 2003)).

The anthropogenic component of lake sediments is also influenced by the catchment. Anthropogenic deposition to the catchment soils will be washed into lakes along with the background component, which can lead to an increase in the anthropogenic accumulation rate in the sediment. The record of direct anthropogenic deposition to the lake will be masked by this increase (Rippey & Douglas, 2004). The size of the catchment area can also have an impact – the larger it is the bigger the store of deposited metals to be transferred (Yang & Rose, 2005). Anthropogenic metals that have travelled from the catchment will not necessarily be recent as erosion at lower soil depths can result in old material being deposited in a present day context (Yang et al, 2002).

In order to be able to assess the anthropogenic impact of trace metals, the background concentrations first need to be identified and removed from the equation. There are a number of ways in which this can be done, the simplest of which is to assume that the

background values will be those found at the 'pre-industrial level' (150-200 years ago) within a sediment core (Verta et al, 1989; Klein & Jacobs, 1995; Engstrom & Swain, 1997). However, this should be done with caution as enrichment can occur prior to the onset of modern industrialisation (Williams, 1991). Alternatively, passive tracer elements (such as Ti, Al and Si) can be used to separate the pollution and natural background signals (Hilton et al, 1985; Norton & Kahl, 1987). The contribution of organic matter to metal concentrations can be removed in a similar fashion by normalising the results to the amount of organic material in the soil (Yang & Rose, 2005).

Metal concentrations can also be impacted by changes in sediment accumulation rate. This can occur as a consequence of forest fires, deforestation or other human-mediated land use changes such as agriculture. Generally an increase in the sedimentation rate will result in the dilution of metal concentrations (Carignan et al, 2003), although in some cases it has been suggested that the overall decline in trace metals emissions and deposition might be obscured by an elevated contaminated sediment load, resulting in no decline or a plateau in metals levels (Yang & Rose, 2005).

A variety of processes can occur which affect the metal concentrations recorded in the sediments after they have entered the lake system itself. Metal deposited onto the lake surface will be concentrated into the deeper water sediments resulting in the highest metal concentrations being found at the deepest point. Sediments in shallow areas can also be resuspended by waves and currents and transported to deeper areas. This process is known as sediment focusing (Blais & Kalff, 1995; Rowan et al, 1995; Yang et al, 2002). The increase in anthropogenic accumulation rate at this point can sometimes exceed the atmospheric flux, which leads to inaccuracies in the data, particularly as sediment cores are frequently taken at the deepest point (Rippey & Douglas, 2004). Because of this effect, results can vary in different cores from the same lake, so sampling a number of cores from a variety of locations within the lake can be beneficial (Yang et al, 2002).

Soluble metals are incorporated into the sedimentary matrix by adsorption, whereas insoluble metals settle (Galloway et al, 1982). Grain size can influence metal concentrations in sediments because fine particles adsorb metals more easily than larger ones as they provide a relatively greater surface area (Förstner & Wittman, 1979; Yang et al, 2002). Some particulates, and those metals which are adsorbed to them, remain in suspension and bypass the lake in the outflow before they can be sedimented (Galloway et al, 1982). pH can also affect the sedimentation of certain elements as acidification of the lake water column may result in decreased adsorption of chemical components onto sedimenting particles. It

can also result in desorption or dissolution of metals from already sedimented material (Norton et al, 1992).

Surface sediments can show a marked enhancement of trace metals towards the sediment-water interface, irrespective of the atmospheric flux (Boyle et al, 1998). Alternatively, reduced concentrations in surface sediments are not always indicative of a fall in deposition rate (Williams, 1991). Post-depositional reactions and processes such as organic matter decay and other redox processes, diffusion, bioturbation and compaction, collectively termed “early diagenesis” can influence sedimentary metal profiles (Carignan et al, 2003). Redox reactions involving metals can increase their mobilisation to porewaters, redistributing them within the sediment column and resulting in their loss to the overlying water column (Boyle, 2001). Metals may reach deeper sediments by diffusion through surficial layers when dissolved metal concentrations are higher in the water column than in the porewaters (Carignan & Nriagu, 1985). This process can create subsurface peaks in sedimentary metals that could be erroneously attributed to variations in metal deposition. Bioturbation which is caused by the burrowing and feeding activities of benthic invertebrates tends to homogenise metal peaks and shifts concentration maxima to deeper sediment layers (Carignan et al, 2003). The quantity of biogenic silica can also influence metal concentrations in sediments by diluting the metal signal (Boyle et al, 1998).

Interpretation of the anthropogenic trace metal record can be difficult for a number of other reasons. As mentioned before, an increase in sediment accumulation rate can result in dilution of metal concentrations. However, this can also impact the dating record. ^{210}Pb is a radioactive isotope often used to date recent sediments (see Section 3.2). An increase in accumulation rate can result in dilution of the radioisotope concentration making the dating record hard to interpret or even unusable. Consequently understanding the temporal changes in metal concentrations is far more difficult. Dredging a lake basin to prevent natural infilling disrupts the natural stratigraphy of sediments and disturbs the metal contamination record. Emptying a lake for a period of time (either purposefully or through natural processes) also interrupts the natural deposition of sediments and therefore affects the metal contamination record.

1.7.4. Metals in biological materials

As outlined in Section 1.5.2, however important the concentrations of metals in sediment and water may be, trace metals can only be toxic to the biological component of lake systems. However, the link between metal contamination and toxicity in biota is complex, particularly because of the large number of different types of organism that have to be considered. Research has been carried out on metal concentrations in phytoplankton (e.g.

Ali et al, 1999), zooplankton (e.g. Watras & Bloom, 1992; Nguyen et al, 2005), a variety of macrophytes (e.g. Stanković et al, 2000; Samecka-Cymerman & Kempers, 2001) and invertebrates (e.g. Hare et al, 2003) as well as fish (e.g. Mason et al, 2000; Rashed, 2001).

A high concentration of metals in sediment and water is not necessarily indicative of a high concentration in associated biota. There are a number of reasons for this, the first of which concerns the 'bioavailable fraction' of the metals in the sediment. This is the proportion of metals within the sediment which can be taken up by organisms. Not all metals stored in sediments are accessible to biota. The availability is dependent on porewaters and sorption behaviour. The higher the bioavailability, the more toxic the metals in the sediment will be (Hartl, 2010). Therefore, sediments with a low level of metal contamination can be just as toxic to biological organisms as sediment with high concentrations of metals, if the bioavailable fraction in the former is high.

Metal concentration also depends upon where and how the organism takes up metals. For example, it has already been stated that sediments are a combination of particulate material and pore water, and therefore contain both particulate and dissolved species of metals (Section 1.7.2). Planktonic organisms obtain their metals from the water column compartment only, whereas benthic organisms live near the interface between the water column and the sediment and can therefore take up metals from either or both of these compartments (Hare et al, 2003). Therefore it might be expected that benthic organisms would contain higher concentrations than planktonic because of the higher affinity of metals for particulates.

However, the source of metals is not the only consideration that needs to be made. How the organism takes up metals is also of interest. Uptake of metals has been studied by Welsh & Denny (1980) using a variety of rooted submerged macrophytes from Ullswater and Coniston Water in the Lake District. Analysis of the plants, sediment and water showed that concentrations of Pb and Cu were high in the shoots and roots of the plants and also the lake sediments, but lower in the lake waters which suggested that in this case the primary uptake route was via the roots rather than through the leaves. Aquatic animals can take up metals both from the water with which they are in contact and from the food that they eat (Hare, 1992). For the former, speciation becomes important again as most metals in water will be in a dissolved form (Section 1.7.2). For the latter, the metal concentration in the food source (whether plants or animal) is important. The uptake of metals also depends on the metal in question.

As mentioned at the beginning, the variety of biota means that metal concentrations can differ greatly. It has been found that accumulated trace metal concentrations in aquatic invertebrates can vary widely, with a low concentration in one type being high for another (Rainbow, 2002). Body weight has been found to play a part in metal contamination, with smaller organisms having higher concentrations than larger organisms (Timmermans et al, 1989). Determination of concentrations is further complicated by the fact that metals accumulate to different levels in different parts of the organism. For example, a study of trout from two rivers in Maryland, USA showed that the concentration of Cd was highest in the kidneys of the fish in both rivers, far more so than any of the other organs sampled. However, for inorganic Hg, although the highest concentrations were found in the kidney of fish from one river, in the other it was the brain that had accumulated most of the metal (Mason et al, 2000).

Lastly, biomagnification (defined in Section 1.5.2) is important in this particular context. Studies have shown that some metals are able to biomagnify as they move successively higher up the food chain. This means that concentrations can become much greater than the sources from which they originally came. For example, analysis of metals in water, zooplankton and fish from lakes in the northeastern United States showed that Hg, Zn and Cd enriched from small plankton to macrozooplankton and Hg and Zn magnified yet again from zooplankton to fish (Chen et al, 2000). All of the factors discussed in this section make determination of metal concentrations in biota very complicated and therefore predicting levels of toxicity is also extremely hard. However, despite these difficulties, many aquatic organisms are used as biomonitors to assess the degree of contamination or 'health' of the ecosystems in which they live (Hare, 1992).

1.8. Toxicity and Sediment Quality Guidelines

The idea of toxicity was outlined in Section 1.5.2. Sediments are both the largest reservoir of metals in a contaminated lake system and also an ecologically important component of the aquatic habitat (Luoma & Rainbow, 2008). Recent sediments may potentially be toxic to biota within the lake system, or if the sediment is removed and deposited elsewhere, to other terrestrial organisms. Therefore management of contaminated sediment is important.

Ascertaining both the concentration of metals within the sediment and its potential toxicity is crucial to management. The toxicity of sediments can be evaluated in a number of ways, usually by testing the survival of a variety of different species, such as *Daphnia magna* (e.g. Dave, 1992) or *Chironomus riparius* (e.g. Lahr et al, 2003). Tier 1 tests involve laboratory based analyses of different components such as pore waters, solid phase, elutriates or

solvent extractions (Hartl, 2010). This kind of test has been used in studies in the Netherlands (Lahr et al, 2003) on lake and river sediments, as well as in the UK on profundal lake sediments (Rippey et al, 2008). However, there are limitations to this method, the chief one being that it doesn't take into account within sediment processes as each part of the sediment matrix is considered in isolation.

Tier 2 tests are also laboratory based, but use whole sediment analysis. This is advantageous because the sediment is brought in from a field site and analysed as a unit and therefore natural within sediment processes can be taken into account. However, handling and transport can be problematic and result in changes in the sediment. Spiked sediments are sometimes used in addition, along with control or reference sediments (Hartl, 2010). Dave (1992 a,b) used Tier 2 tests to investigate the toxicities of lake sediments in Sweden. The most comprehensive way to study toxicity of metals in sediments is to carry out field tests *in situ*, and this is what Tier 3 tests aim to do. However, these are the most complex of the tests as it is difficult to control all the different factors that influence toxicity in a natural environment and therefore Tier 1 and Tier 2 tests are still mostly used in preference (Hartl, 2010).

Determining the toxicity of sediments is only the beginning when it comes to trying to manage metal contamination. Guidelines and limits need to be established in order to be able to place controls on pollutant levels. There are a number of approaches for trying to do this, including direct toxicity testing to areas of concern, creating concentration limits (although this does not take into account bioavailability), using reference concentrations (low or background concentrations), or using effects-based guidelines which relate the concentrations of contaminants in sediment to some predicted frequency or intensity of biological effects (Luoma & Rainbow, 2008). However, there is not yet a general worldwide consensus as to the best method to use and therefore the approaches to sediment management vary widely, from having no specific concentration targets (USEPA) to 'effects-based' regulations based upon total concentration (NOAA, USA) (Babut et al, 2005).

MacDonald et al (2000) developed consensus-based sediment quality guidelines (SQGs) using the results from a range of other SQG studies. The purpose behind the study was to unify the wide variety of SQGs into two consensus-based SQGs that could be used to assess sediment toxicity over a wide range of sediments. This involved the development of the toxicity quotient method, where the toxicity quotient for a chemical is (concentration/PEC) and PEC is the probable effect concentration. The higher the value the stronger the possibility is that the concentration of the chemical is toxic and that the chemical

is at a level of concern. The threshold effect concentration (TEC) is defined as the point below which adverse effects are not expected to occur.

This method was subsequently used in a paper by Rippey et al (2008) which addressed pollution of metals (and POPs) in lake sediments around the UK. Concentrations of Hg, Pb, Cu, Ni, Zn, Cd and As were determined in ten lakes, the results suggesting that Pb, Zn, Cd and As were above background levels and therefore considered as contaminants. The data was then assessed to see if the concentrations found were likely to be toxic to biota, using MacDonald et al's (2000) method. The 'Probable Effect Concentration Quotient (PEC-Q) Mean-metals' was also calculated which is the average of the toxicity quotients for the seven metals outlined above. The values showed that toxicity was likely in five of the lakes. Two Tier 1 sediment toxicity tests were also carried out to provide direct evidence for toxicity, which concluded that four lakes were potentially toxic, mainly through Pb and As.

However, further research is required in the development and use of these kinds of SQGs. There are still many problems to overcome, particularly concerning mixtures of metals and other chemicals where all or some may potentially be toxic to biota, before one single method of managing contaminated sediment is settled upon.

1.9. Open Air Laboratories Project

The Open Air Laboratories Project (OPAL) is a community-driven research programme funded by the Big Lottery Fund, which began in 2007 and ended in May 2013. It is run in partnership with a number of universities and other organisations in England. The main aim of OPAL is to get the public more involved in nature through a range of local and national projects, whilst generating valuable scientific data concerning the state of our environment. The key objectives are to:

- Encourage more people to spend time outside exploring and recording the world around them
- Develop an innovative environmental education programme to support them
- Stimulate a new generation of environmentalists
- Strengthen collaboration between the statutory, voluntary and community sectors
- Gain a greater understanding of the state of the natural environment (Davies et al, 2011)

OPAL is delivered through nine regional programmes, five national centres and a support system. Each of the nine regions is led by a university, and focuses on local issues and local

communities. The five national centres address national research issues and lead on the development of the national public participation surveys. There are six national surveys: Soil, Air, Water, Climate, Biodiversity and the Bugs Count. Each regional and national centre also encourages research through the sponsoring of a PhD studentship (OPAL, 2013). A breakdown of the structure of OPAL is presented in Table 1.1.

Region	University/Organisation
North West	University of Central Lancashire
North East	Newcastle University
York and Humber	University of York
East Midlands	University of Nottingham
West Midlands	University of Birmingham
East of England	University of Hertfordshire
South East	Imperial College London
South West	University of Plymouth
London	Imperial College London
Centre	
Soil	Imperial College London
Air	Imperial College London
Water	University College London
Biodiversity	Natural History Museum Open University
Climate	UK Meteorological Office

Table 1.1 – OPAL regions and centres with key partners leading each

The OPAL Water Centre is based at University College London (Table 1.1). In addition to development of the OPAL Water Survey, the Water Centre had two research concerns. The first was to identify the scale of contamination from trace metals and POPs in the water, wildlife and sediment of ponds and lakes around England and assess the impact of these pollutants on the freshwater ecosystem. The second was to carry out aquatic biomonitoring at a number of lakes in order to investigate general water quality. For both purposes, a lake or pond was identified in each of the nine OPAL regions (Figure 1.14). Sediment cores were taken from each site, along with other samples for analysis such as water and fish. Quarterly visits were made to undertake physical, chemical and biological analysis. Annual aquatic plant and invertebrate surveys were also completed. Field visits were carried out between 2008 and 2012, and data analysis is ongoing. This thesis records the research that has been carried out for the PhD studentship awarded to the Water Centre.

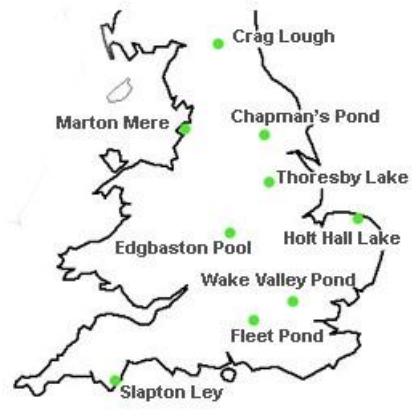


Figure 1.14 – Names and locations of the nine lakes monitored as part of the OPAL project

CHAPTER 2: SITE IDENTIFICATION AND BACKGROUND INFORMATION

2.1. Site identification

Both palaeolimnological and contemporary aspects of the project needed to be considered when identifying which lakes in London were to be studied. The first stage involved the identification of a number of suitable lake sites from which cores could be taken. Of these, one would then be selected for further monitoring. Three key factors influenced the choice of sites for coring.

- 1) For the purposes of the project, London was defined as the area within the M25 orbital motorway. Therefore, the lakes had to be located within this boundary.
- 2) Older lakes were required in order to obtain as long a geochemical record as possible. Lakes which had been in existence prior to the Industrial Revolution were identified so cores could be taken which had at least a 150-200 year sediment history.
- 3) Lakes which had not been dredged were needed so that the sediment record would be uninterrupted.

Potential study sites were identified by cross-referencing Stanford's 1863 map of London with present day Ordnance Survey 1:25 000 maps (Explorer 161 and 173) and the London A-Z. Forty lakes that were visible on both past and present maps were listed as possible sites for investigation. Once the list had been compiled, an internet search of each site was carried out to find out more information and to see if there was any record of dredging. In the majority of cases, this search yielded little information and therefore the present day owners and local conservation groups of each site were contacted. The list was then narrowed down to those lakes which had no record of dredging, although in some cases where there was no written information, the 'record' relied upon the memories of older members of staff.

The lakes that were finally chosen to be investigated further were those which combined both the greatest age and the least chance of having been dredged. Location was also a factor as analysing sediment from across a broad geographical area would show spatial variations in contamination as well as identifying temporal trends in London. The chosen sites were South Norwood Lake and Wimbledon Park Lake in the south of the city, and five ponds on Hampstead Heath just to the north of central London. Wake Valley Pond in Epping Forest was also included because it was the OPAL site for the London region and had already been cored prior to this investigation. In addition, a core was also available that had

been taken from the Highgate Ladies Bathing Pond on Hampstead Heath in 1987 as part of a previous project. Figure 2.1 shows the location of the sites within present day London, along with an approximation of the area that London covered in the middle of the 19th century, highlighting the expansion that the city has undergone over the last 150 years.

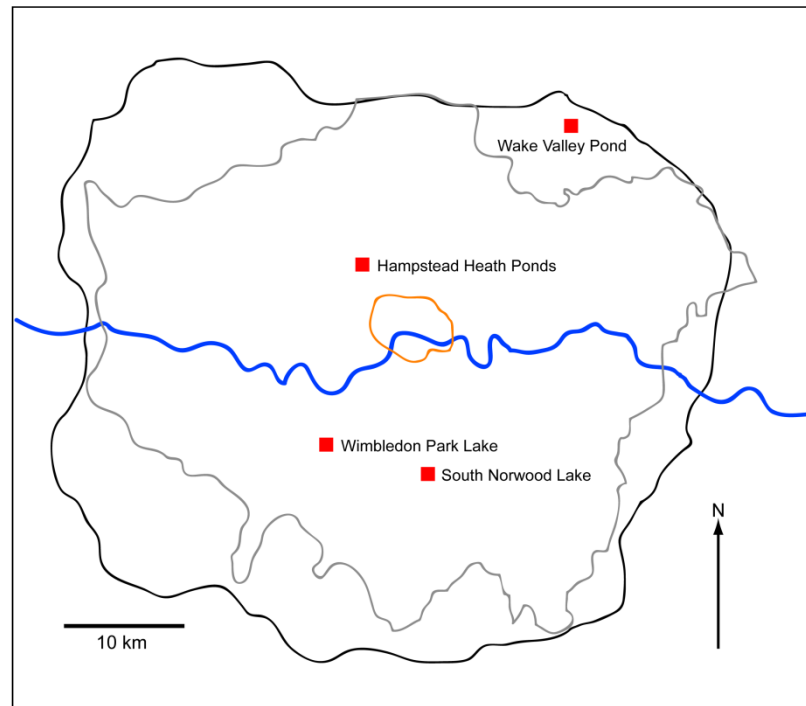


Figure 2.1 – Locations of chosen London lakes. The M25 is shown in black encircling the city, whilst the boundary of Greater London is outlined in grey. The orange line is an approximation of the area that London covered in 1850.

2.2. Preliminary field investigations

Before the cores were taken, preliminary visits were made to each of the potential sites (South Norwood Lake, Wimbledon Park Lake and the five ponds on Hampstead Heath) to assess their suitability for the study. Information on water depth and sediment distribution was obtained (see Figures 2.2, 2.3, 2.5 and 2.6). This allowed areas of maximum sediment accumulation to be identified and potentially collection of the longest sediment record. Although this approach would not necessarily cover the maximum time period, it would at least provide the maximum time resolution. After the preliminary field investigations had taken place the final sites for coring were chosen.

2.2.1. South Norwood Lake

In 2000, a report was issued by the Environmental Advice Centre Ltd, Flintshire, entitled the 'Baseline and Chemical Survey and Assessment of South Norwood Lake'. It included a crude bathymetry and sediment depths along 11 transects across the lake (see Figure 2.2). It showed a maximum water depth of 3.7 m, and sediment depths of between 1 and 2 m. The small size of the lake and the availability of this information negated the need for a pre-coring site visit.



Figure 2.2 – Left - depth contour map of South Norwood Lake; Right - the location of transects used for the assessment of water and sediment depths in 2000 (from EAC Ltd, 2000).

2.2.2. Wimbledon Park Lake

Information from Merton Borough Council suggested that Wimbledon Park Lake had never been dredged, and that current sediment levels were in the order of 2 m deep in places, with the water depth also not exceeding 2 m. A silt and water survey of the lake had been carried out in February 2008 by Mid Kent Fisheries (a division of South East Water). This corroborated the information obtained from the council, although the recorded water and sediment depths varied quite widely across the lake area. An initial visit to the site was made on the 22nd May 2009. During this visit, a boat was taken out onto the lake, and estimates of water and sediment depth were made at various points using an echo sounder (Speedtech Instruments Depthmate Portable Sounder SM-5) and a calibrated metal rod, and their locations recorded using a Garmin eTrex® H (High Sensitivity) GPS. From this information, an approximate bathymetry of the lake was created (Figure 2.3) and the area with the deepest sediment was located. This area was chosen as the location for coring. The

maximum water depth found was 1.8 m, with the maximum sediment depth also being 1.8 m.

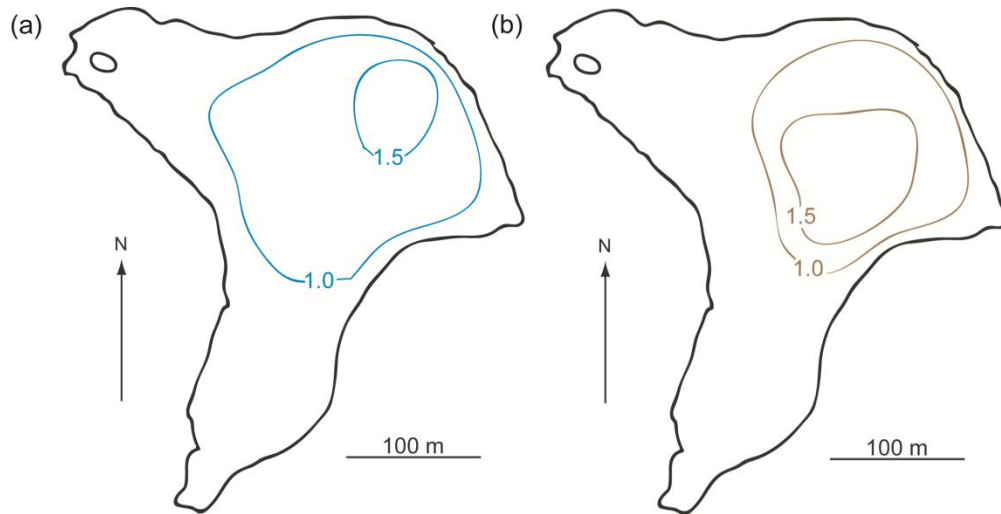


Figure 2.3 – (a) Water and (b) sediment depths (in m) at Wimbledon Park Lake

2.2.3. Hampstead Heath Ponds

There are over twenty five ponds on Hampstead Heath, five of which were thought to have never been dredged. These were Hampstead No.1, Viaduct, Vale of Health, Stock and Highgate No.1 ponds (Figure 2.4). The water depth across the ponds was thought to be between 2 and 3 m, but the sediment depths were largely unknown. Bathymetries were available for Stock Pond and Highgate No.1 Pond from a previous study by the Environmental Advice Centre Ltd, Flintshire (2003).

A site visit was made to the Heath on the 21st May 2009. As with the visit to Wimbledon Park Lake, estimates of water and sediment depth were made at a number of points on each of the five ponds. Figures 2.5 and 2.6 show the water and sediment depths found at each site. Using this information, the ponds that were to be cored were decided upon. Vale of Health Pond was chosen because it contained the deepest sediment record. Stock Pond was picked because it was the only pond to which there was no public access. Viaduct Pond could not be used because the whole lake was full of aquatic macrophytes, including yellow water-lily (*Nuphar lutea*), Canadian pondweed (*Elodea canadensis*), curly-leaf pondweed (*Potamogeton crispus*), stonewort (*Nitella mucronata*), and large amounts of aquatic fern (*Azolla* sp.), which would have made coring very difficult. Hampstead No.1 Pond was chosen over Highgate No.1 because it was the older of the two ponds.

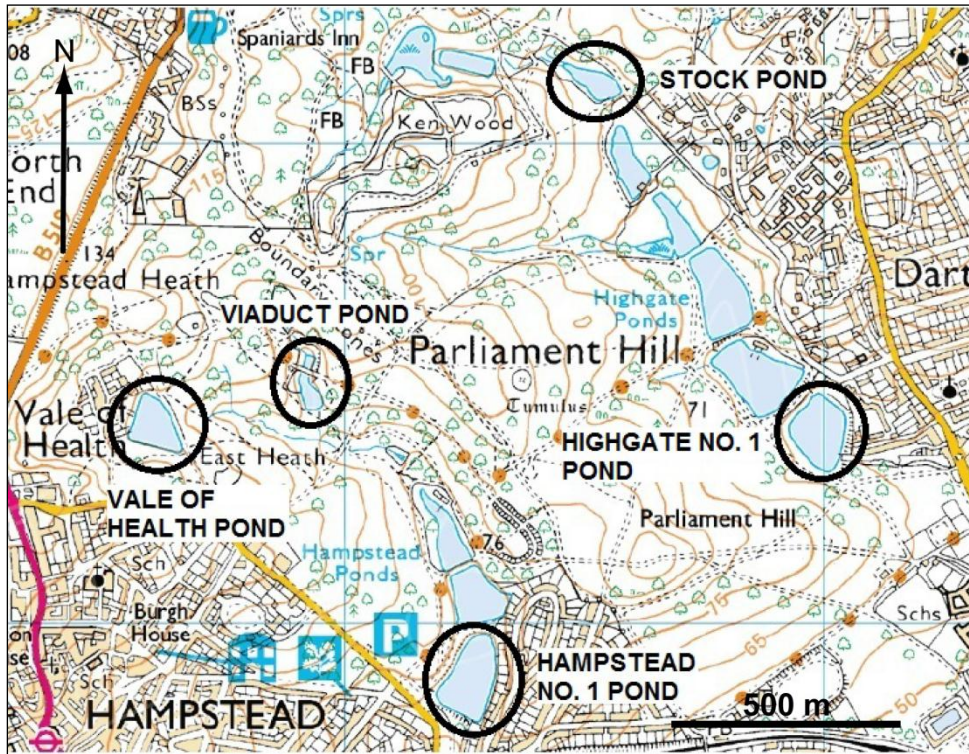
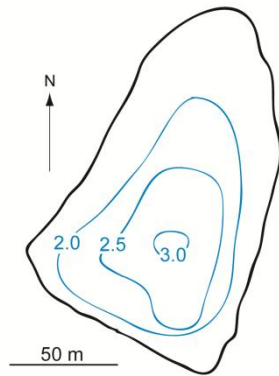


Figure 2.4 – Map of Hampstead Heath showing the locations of the five potentially undisturbed lakes (adapted from OS map available from Edina Digimap, 2011)

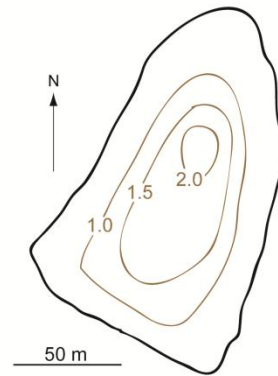
The decision to take cores from more than one pond on Hampstead Heath was made for two reasons. Firstly, Hampstead Heath was the most central of the locations identified, and therefore the closest to the original urban centre of London (see Figure 2.1). This meant that the sediment records from these ponds would be more likely to reflect the trace metal history of the long industrialised city centre than South Norwood Lake and Wimbledon Park Lake, both of which were in rural locations until their absorption into the city in the late 19th century. It was also advantageous to obtain cores from a number of the ponds on the Heath in order to provide a comparison between adjacent sediment records. Similar patterns of trace metal inputs would suggest a regional source of contamination to the area, while differences may be attributed to local catchment inputs. The records from the Hampstead Heath ponds could then be compared to those further away from the centre, to see if changes in metal contamination were the same across the city or subject to more local influences.

Hampstead No. 1 Pond

(a)

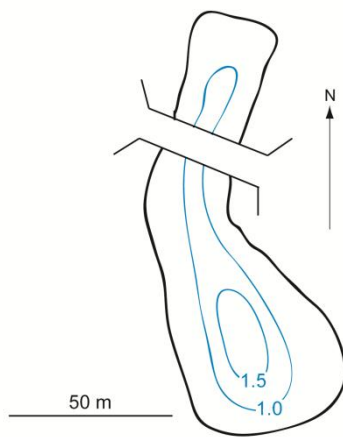


(b)

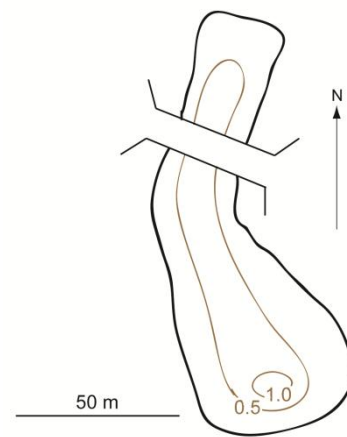


Viaduct Pond

(a)

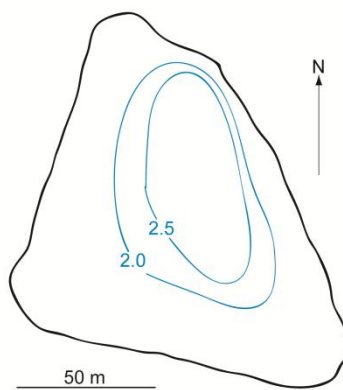


(b)



Vale of Health Pond

(a)



(b)

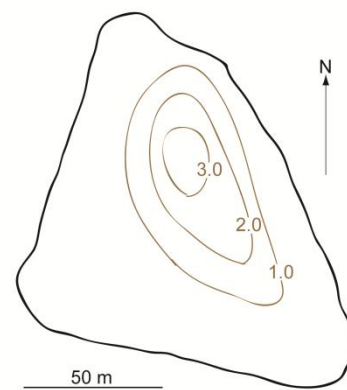
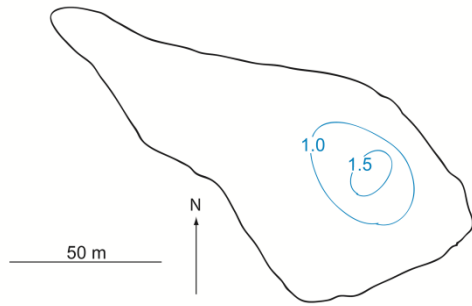


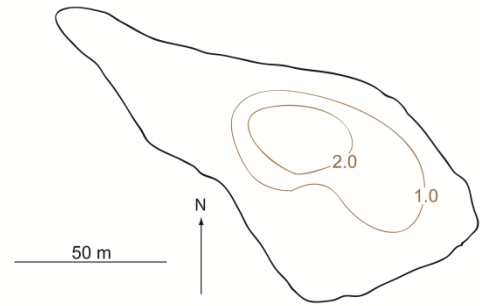
Figure 2.5 – (a) Water and (b) sediment depths (in m) of the Hampstead ponds

Stock Pond

(a)

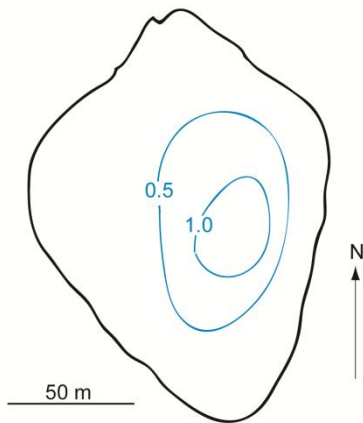


(b)



Highgate No. 1 Pond

(a)



(b)

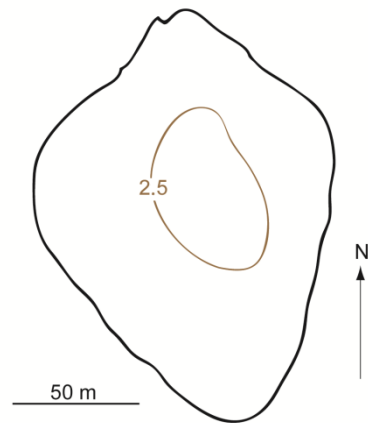


Figure 2.6 – (a) Water and (b) sediment depths (in m) of the Highgate ponds

2.3. Choice of detailed monitoring site

For the second part of the study, a site was selected to be monitored on a regular basis over the course of one year. It was decided that one site should be studied as comprehensively as possible rather than sampling a smaller number of components at a larger number of sites. The intention of the study was to analyse metal concentrations in all components of the lake ecosystem, including atmospheric deposition, water, sediment and biota. The choice of samples would largely be dependent on what was available at the chosen site, although the more ecological compartments that could be encompassed within the monitoring programme the better. The four sites from which cores were taken, South Norwood Lake, Wimbledon Park Lake, the Hampstead Heath ponds and Wake Valley Pond, were all considered as possible monitoring sites, to allow the comparison of contemporary data with that obtained from the analysis of the sediment cores. It was decided that one of the ponds on Hampstead Heath should be used, primarily because of the close proximity of the Heath to the city centre.

Of the Hampstead ponds, previous studies at Stock Pond had shown that it had low dissolved oxygen levels, with a summer mean of 4.40 mg L⁻¹ and a winter mean of 5.46 mg L⁻¹ (Corporation of London, 2007). Consequently there were low fish populations and few aquatic macrophytes or invertebrates present which made the site unsuitable for detailed study. Very little information existed about Hampstead No. 1 Pond, particularly with regard to fish stocks, although in the summer there was a large growth of hornwort (*Ceratophyllum demersum*). The Vale of Health was the only one of the three ponds designated for licensed angling. There were a number of carp (*Cyprinus carpio*) in the pond, as well as a limited number of other species including common bream (*Abramis brama*), perch (*Perca fluviatilis*), pike (*Esox lucius*), roach (*Rutilus rutilus*) and tench (*Tinca tinca*). There were also some visible macrophytes in the pond such as a bed of white water-lily (*Nymphaea alba*) and yellow iris (*Iris pseudacorus*). Therefore, the Vale of Health was considered to be the best choice for a monitoring site because it had a wider range of biota to sample. There was also more information about the fish in the pond than in either of the other two. It was the deepest out of the three ponds with the water depth reaching a maximum of 3m.

2.4. Site histories and background information

2.4.1. South Norwood Lake

South Norwood Lake (Figure 2.7) is located in the London Borough of Croydon, just to the south of Crystal Palace (OS grid reference TQ 340693). The lake was constructed in 1827 as a reservoir to supply water to the newly created Croydon Canal (EAC Ltd, 2000). Due to

the expansion of the railways, transport on the canal declined and it was finally sold to the London and Croydon Railway Company in 1836. The canal was drained and filled in and the lake lay derelict for many years. Figure 2.8 shows the reservoir as it was in 1874. The land to the north of the site was formerly owned by the Archbishop of Canterbury, and latterly by the Ecclesiastical Commissioners. In 1881, Norwood Sports Club leased the lake and the adjacent land, and it was used for fishing, swimming and skating in winter. The lake and grounds were sold to a private company in 1911, and it was then purchased bit by bit by Croydon Council and opened to the public completely in 1969 (London Borough of Croydon, 2009).



Figure 2.7 – South Norwood Lake

The lake is now the only large expanse of open water in Croydon, with an area of 2.83 ha (EAC Ltd, 2000). It is built on London Clay, along with the surrounding catchment (Edina Digimap, 2011). The lake is fed by springs rising on the hillside to the north west where gravels meet the London Clay beneath. These combine to form one small inflow at the western end of the lake which drains the surface water from higher ground, including Howden and Auckland Roads. The outlet is at the eastern corner of the lake and it discharges into a surface water drain that runs parallel to the north east bank of the lake (EAC Ltd, 2000). The water in the lake has a long residence time as for a large part of the year there is no outflow (EHS, 1999). As shown in Figure 2.9, the lake is bordered on two sides by council owned sports grounds. Residential properties line the south eastern side of the lake, and the railway runs along the north eastern edge.

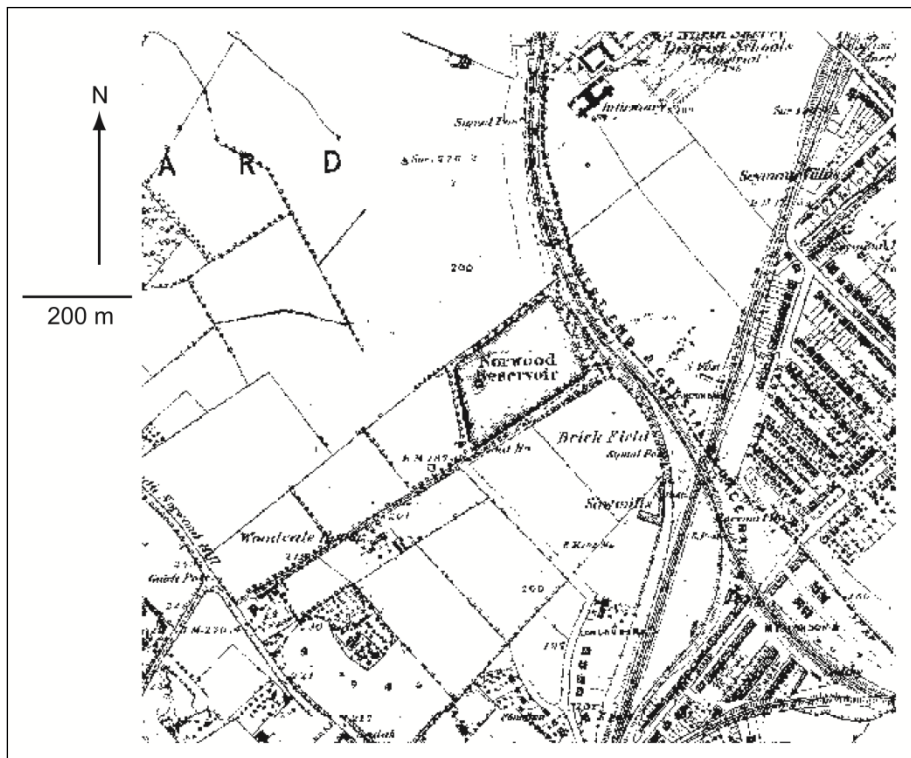


Figure 2.8 – South Norwood Lake as depicted in 1874 (Kent County Series 1:10560, published 1874 (Edina Digimap, 2011))

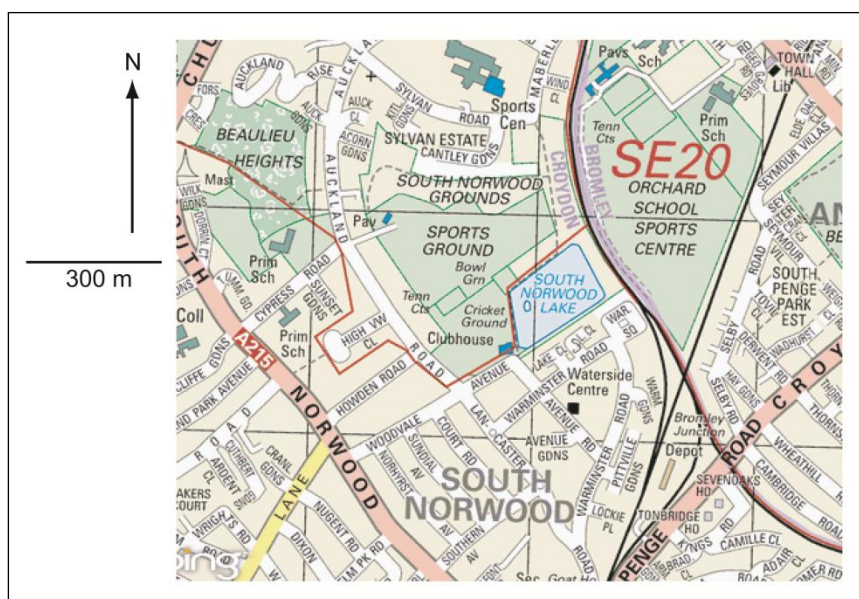


Figure 2.9 – Location of South Norwood Lake in the present day (Multimap Tele Atlas, 2009)

The wider catchment area is also primarily residential. The lake is still used for boating and is the home of Croydon Sailing Club. It is kept stocked with fish and there is a keen

contingent of anglers. A variety of resident and visiting waterfowl can be seen on the lake throughout the year (London Borough of Croydon, 2009).

2.4.2. Wimbledon Park Lake

The lake in Wimbledon Park (Figure 2.10) is owned by and situated in the London Borough of Merton in South West London (OS grid reference TQ 247723). The lake was created in approximately 1764. At the time, the area was a private estate owned by the Spencer family. Earl Spencer employed famed landscape designer Capability Brown to redesign the grounds, part of which included the damming of a marshy stream known as Wimbledon Park Brook to form the lake which is still present today. In 1846 the estate was sold, and much of the land surrounding the lake was developed (Figure 2.11 shows the lake in 1874 before much development had begun). At the turn of the 20th century plans had been made to drain the lake to provide more building land, but at this point the Wimbledon Corporation intervened and purchased the park. A number of smaller changes in ownership of the land surrounding the lake have been made since that time, but the lake itself has remained under the control of the local council since 1914 (Wimbledon Park Heritage Group, 2010).



Figure 2.10 – Wimbledon Park Lake

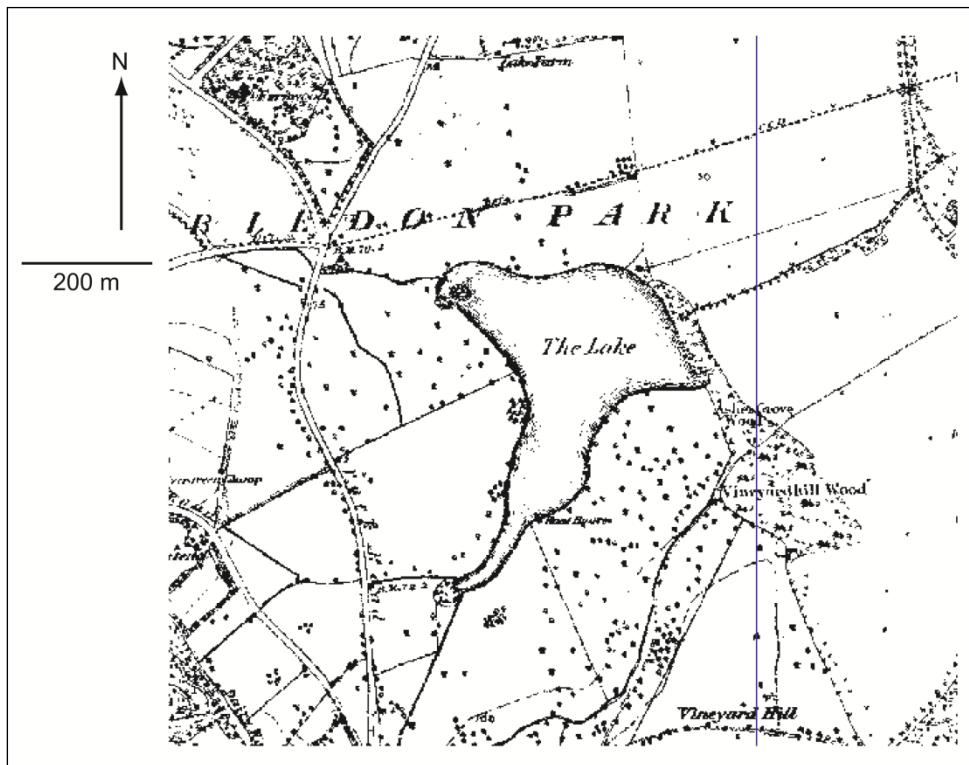


Figure 2.11 – Wimbledon Park Lake as depicted in 1874 (Surrey County Series 1:10560, published 1874 (Edina Digimap, 2011))

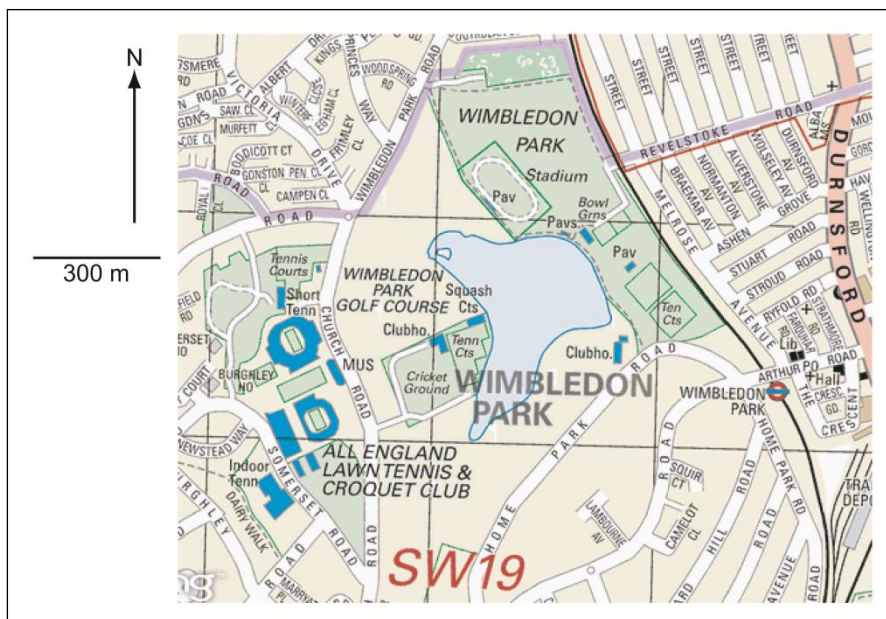


Figure 2.12 – Location of Wimbledon Park Lake in the present day (Multimap Tele Atlas, 2009)

The lake covers an area of approximately 12 ha and is the largest body of water to be found in the Borough. The lake and its catchment are built on bedrock of London Clay (Edina Digimap, 2011). Apart from the north eastern edge of the lake which adjoins Wimbledon

Park, most of the land surrounding the lake is a golf course owned by Wimbledon Park Golf Club (see Figure 2.12). Therefore the land within the immediate area of the lake is primarily grassland. The rest of the catchment is filled with residential housing. The lake has two inlets which supply water and one outlet (Mid Kent Fisheries, 2008). The inlets are located to the north west of lake behind the island and at the lake's most southerly point. The outlet can be found to the north east, near the Wimbledon Park Watersports centre. The centre runs activities such as sailing and canoeing on the water. The lake supports a variety of birdlife and fish (stocked), and is used by anglers on a regular basis (Merton Council, 2009; London Wildweb, 2009).

2.4.3. Hampstead Heath Ponds

Most of Hampstead Heath is situated in the London Borough of Camden, with a smaller area in the London Borough of Barnet. In total it spans an area of 326 ha, the majority of which is managed by the City of London. The heath encompasses a wide range of habitats and includes over thirty ponds of varying size and character (City of London, 2009). The four ponds of particular interest to this study are Hampstead No. 1, Vale of Health, Stock and Highgate Ladies Bathing Pond, labelled on Figure 2.13.

It is not known exactly when the ponds were first made, although in Elrington's 'A History of the County of Middlesex' (1989) he states that "The Hampstead ponds began as a string of reservoirs of the Hampstead Water Co., which was established to supply London in 1692. They were made by damming Hampstead brook, one of the sources of the Fleet, just as Highgate ponds were made from a more easterly source in St. Pancras". This suggests that some of the ponds could have been created as early as 1692. John Rocque's 1745 map 'An exact survey of the Cities of London, Westminster and Southwark and the country near 10 miles around' shows two Hampstead ponds and a string of seven Highgate ponds. This means that Stock Pond and the Ladies Bathing Pond both existed by 1745. Figure 2.14 is part of John Cary's 1786 'Actual Survey of the Country Fifteen Miles Around London' and it shows the Highgate ponds, although they are labelled as 'Hampstead Ponds'. Elrington (1989) then goes on to say that "there were two ponds on Lower Heath by 1703 and in 1745, three by 1786, and four by 1810. The Vale of Health Pond was dammed when the supply system was extended in 1777". This description seems to apply to the Hampstead chain, and so would include Hampstead No. 1 Pond. The location of the ponds shown on Rocque's map (1745) corresponds to the modern location of Hampstead No. 1; therefore the pond may well have existed as early as 1703 and definitely by 1745. The exact date of the creation of the Vale of Health Pond is noted as 1777.

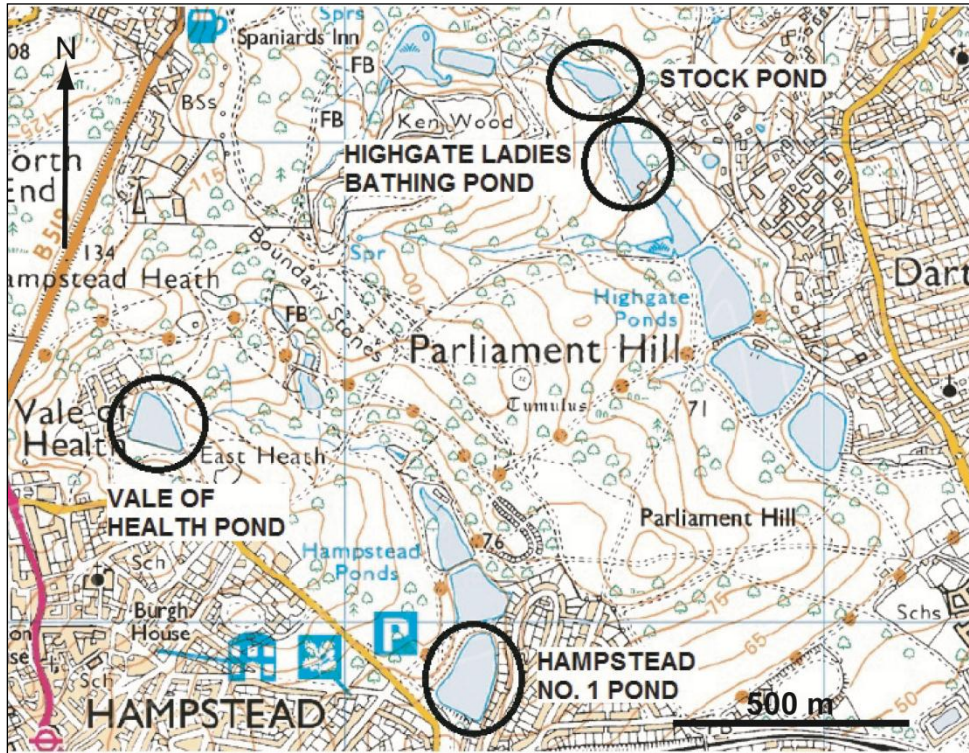


Figure 2.13 – Locations of ponds on Hampstead Heath, with the four chosen for study encircled in black (adapted from OS map available from Edina Digimap, 2011)

As stated above, the ponds on Hampstead Heath were originally leased to the Hampstead Water Company (Elrington, 1989). At this time most of the land was privately owned by the Manor of Hampstead. Some of it was designated as common land by the Manor and started to be dug for sand and gravel by the copyholders (tenants of the Manor with rights over the common land). However, the increasing demand for these materials in the 19th century resulted in the destruction of a large proportion of the natural landscape. The public campaigned against this and in 1871 the Hampstead Heath Act was passed which put specific limitations on what could be done with the land. At the same time the Heath and its ponds were bought by the Metropolitan Board of Works (City of London, 2009). Control of the Heath was passed to London County Council in 1889, which in time became the Greater London Council, then the London Residuary Body and finally the Corporation of London in 1989 (London Parks & Gardens Trust, 2009). The 1871 act combined with over 100 years of continued public ownership has helped to ensure the ponds have been retained for over 300 years.

London Clay forms the base of the geological sequence of Hampstead Heath, although it is also underlain by Bagshot Beds and Claygate Beds. Stock Pond, Highgate Ladies Bathing Pond and Hampstead No. 1 are all built upon London Clay, whereas the Vale of Health

Pond is located on a seam of Claygate Beds which consist predominantly of silts and clays with subordinate sands. The tributaries that flow into the Highgate and Hampstead chains start on the Claygate Beds before flowing over the London Clay formation (Haycock Associates Ltd, 2006).

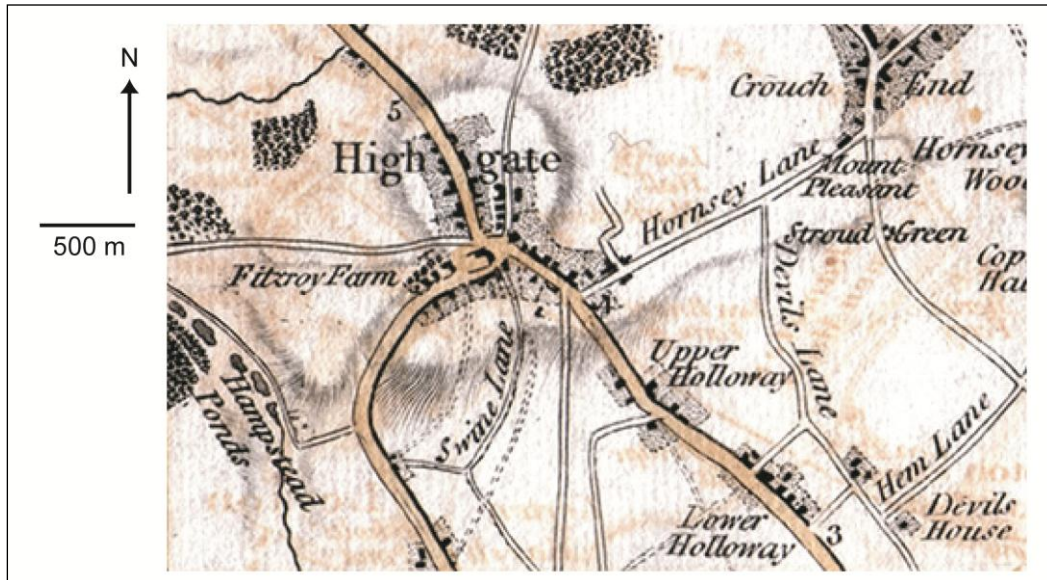


Figure 2.14 – The Hampstead Ponds, from John Cary's 'Actual Survey of the Country Fifteen Miles Around London', published 1786

Of the four ponds of interest to this study, Stock Pond (OS grid reference TQ 275871) (Figure 2.15) is the only one not to have any public access as it is fenced off from the surrounding park. It is relatively small (approximately 0.2 ha) and enclosed on all sides by woodland, which consequently makes it quite shaded. The catchment area of the pond is also small and mostly comprised of heathland. The pond is supplied with water through an inflow at the northern end and there is an outflow via a sluice on the southern side.

Next to Stock Pond in the Highgate chain is the Ladies Bathing Pond (OS grid reference TQ 277870) (Figure 2.16). This is slightly larger than its northerly neighbour, although it is also surrounded by trees. Millfield Lane, which at this point is little more than a muddy track, runs along the north eastern edge. The pond catchment primarily covers the land to the north east which is mainly residential. Water enters the pond from the north through an inflow that comes directly from Stock Pond. Water leaves the pond at the southern end as it continues its journey down the Highgate chain. As its name would suggest, the primary use of this pond is as a bathing pool.



Figure 2.15 – Stock Pond



Figure 2.16 – Highgate Ladies Bathing Pond

Vale of Health Pond (Figure 2.17) is the most westerly of the Hampstead chain (OS grid reference TQ 266864) and is larger (approximately 0.6 ha) than both the Ladies Bathing Pond and Stock Pond. It is also a lot more open with only a few trees and shrubs marking the perimeter. The east of the pond is bordered by a track which is primarily used by people

on foot, although vehicles pass by occasionally. The north western edge is privately owned and is comprised of the gardens of a number of houses and flats. The southerly side of the pond is bordered by open grassland which falls steeply down to the pond edge. The larger catchment area of the pond is a mixture of the residential area and the open grassland. There is no obvious inflow to the pond, although the Hampstead Heath Hydrology Report (Haycock Associates Ltd, 2006) suggests that run off from the Vale of Health road down the grassland bank is a key source of water. There are two outflows, both of which run underneath the track to the east. Vale of Health Pond is one of the Heath's designated sites for fishing.



Figure 2.17 – Vale of Health Pond

Hampstead No. 1 Pond (Figure 2.18) is found at the southern end of the Hampstead chain (OS grid reference TQ 272859) and is the largest of the four ponds that are considered here. As with the Vale of Health, the pond is bordered on one side by the gardens of adjacent houses and on the other with grassland. The catchment area is small and expands to the east, encompassing the housing of South Hill Park. Water enters the pond on the northern side through an inflow from Hampstead No. 2 and exits the pond at the southern end.



Figure 2.18 – Hampstead No. 1 Pond

2.4.4. Wake Valley Pond

Wake Valley Pond (Figure 2.21) is located in Epping Forest (OS grid reference TQ 421988), which straddles the border of north east London and Essex. The pond was created in about 1882, with the “Embankment of the Epping New Road being used as one side” of what was previously a “hollow” (Wheeler, 1998). The exact reason behind the creation of the new pond is unclear, although clay from the south-east end of pond was used in the construction of the embankment of the New Road (Wheeler, 1998). Figure 2.19 shows the pond 15 years after it was made and highlights the proximity of the New Road (now the A104).

The pond has been owned and managed by the City of London since it was built. It has a surface area of approximately 0.8 ha (Wheeler, 1998). Claygate Beds are the underlying geology upon which the pond sits, although there are also outcrops of London Clay and Bagshot Beds in the vicinity (Edina Digimap, 2011). As can be seen in Figure 2.20, Wake Valley Pond is surrounded on all sides by woodland, with the road running along the south eastern edge, and this type of land use is the same for the rest of the catchment area. The pond is fed by a spring that rises on the hill to the north and which feeds down to an inflow at the northern end of the pond. The pond is commonly used for angling as it contains a number of carp, roach, rudd, tench, pike and perch (City of London, 2009).

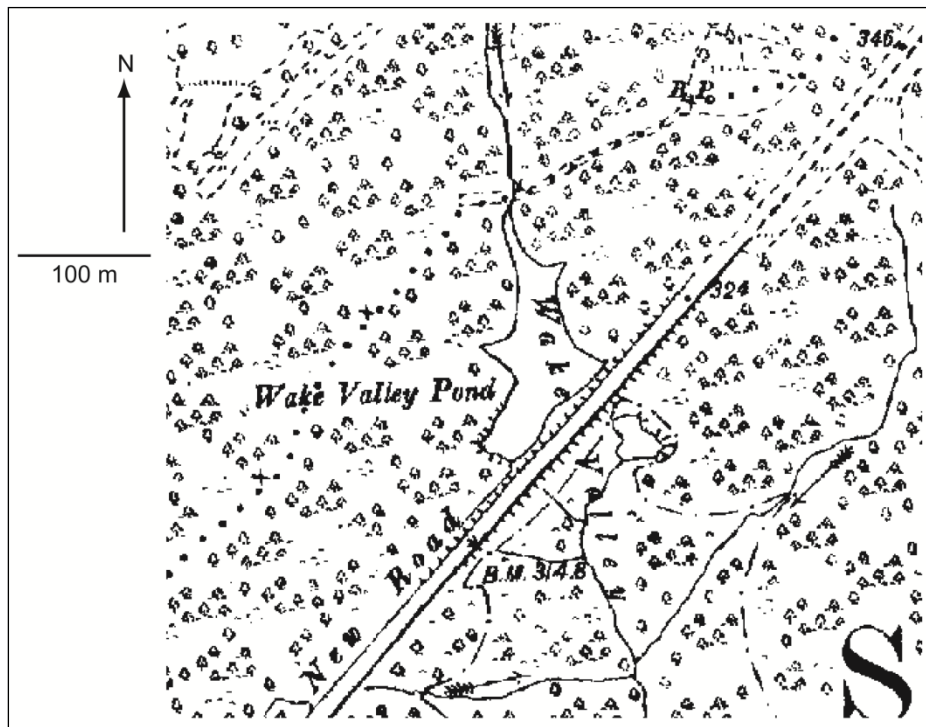


Figure 2.19 – Wake Valley Pond as depicted in 1897 (Essex County Series 1:10560, published 1897 (Edina Digimap, 2011))

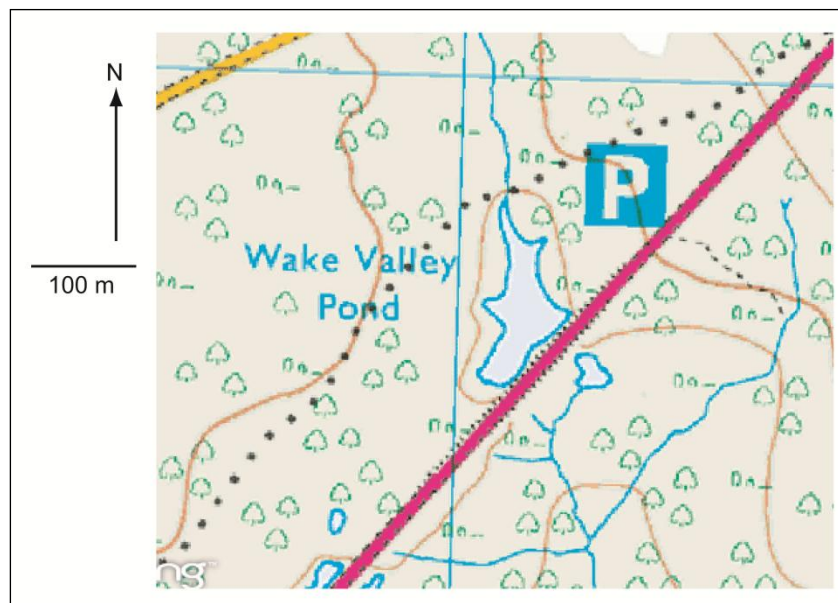


Figure 2.20 – Present day location of Wake Valley Pond (Multimap Ordnance Survey, 2009)



Figure 2.21 – Wake Valley Pond (Photo: Simon Turner)

CHAPTER 3: DETERMINATION OF CHRONOLOGIES FOR LONDON LAKES

3.1. Introduction

The aim of this chapter is to develop chronologies for each of the sediment cores taken from the London lakes discussed in Chapter 2. Accurate sediment chronologies are of crucial importance to the interpretation of trace metal archives in lakes. Recent sediments (from approximately the last 150–200 years) can be dated using a number of methods. These include the use of the natural radionuclide ^{210}Pb , as well as artificial fallout radionuclides such as ^{137}Cs and ^{241}Am (Appleby, 2001), the distribution of spheroidal carbonaceous particles (SCPs) (Rose, 1990), and varve counting (Lamoureux, 2001). The latter requires the presence of annually laminated sediments, a feature that is not found in the lakes of London. In this study, radiometric dating and SCPs will be used to obtain dates for each of the sediment cores and produce chronologies for the lakes which can then be plotted against the concentration profiles of metals and other elements.

3.2. Radionuclide dating of sediment cores

3.2.1. Background information

^{210}Pb is a naturally produced radionuclide which has a half-life of 22.3 years. ^{226}Ra is released from bedrock as part of catchment erosion and will decay in situ to form firstly ^{222}Ra and then what is known as supported ^{210}Pb . A small proportion of the ^{222}Ra atoms produced by this process escape into the atmosphere where they again decay through a series of short-lived radionuclides to ^{210}Pb . Precipitation or dry deposition then removes this from the atmosphere, and it falls on to the land surface or into lakes and streams where it is incorporated into depositing sediments. This type of ^{210}Pb is known as unsupported ^{210}Pb . The amount of supported ^{210}Pb in sediments will usually be in radioactive equilibrium with the ^{226}Ra . Unsupported ^{210}Pb is determined by subtracting supported activity from the total activity (Appleby, 2001). High unsupported ^{210}Pb activities in the surface sediments derive from their exposure to recent inputs from the atmosphere (Appleby, 2001). A down-profile decline in unsupported ^{210}Pb will be shown in accordance with the natural radioactive decay of the isotope. In most cases equilibrium between total ^{210}Pb activity and the supporting ^{226}Ra is effectively achieved after a maximum of 6-7 ^{210}Pb half-lives, or 130-150 years, which reflects the dating range that can be applied to this method (Appleby, 2001).

^{137}Cs and ^{241}Am are artificially produced radionuclides, the main source of which has been the atmospheric testing of nuclear weapons. Testing started in the 1950s, and reached a

maximum in the late 1950s and early 1960s, after which the 1963 Test Ban Treaty was signed and fallout started to decline. In 1986 the accident at the Chernobyl nuclear reactor in Ukraine led to a significant release of ^{137}Cs and a further peak in fallout of that radionuclide (NEA, 2002). ^{137}Cs is strongly adsorbed onto sediment or soil, and has been incorporated into sediments deposited in the last 30-40 years, with the peaks in fallout of 1963 and 1986 showing up quite clearly in the sediment record in Europe (e.g. Callaway et al, 1996). ^{241}Am was not released during the Chernobyl incident and its presence can therefore be used to distinguish between the 1963 and 1986 peaks in ^{137}Cs . ^{137}Cs acts as an effective tracer suitable for studying soil erosion and sediment accumulation rates during recent decades. It also acts as a support tool for ^{210}Pb dating as it provides a useful way to cross check the accuracy of ^{210}Pb chronologies.

3.2.2. Methodology

Sediment cores were taken from each of the seven London lakes. Details of the cores and the methods used are described in Chapter 4. Subsamples were taken at every 10 cm interval from SNOR1, WIMP1, HAMP1, STCK1, VALE1 and HIGW1 and at every 3cm interval from WAKE1. The samples were analysed for ^{210}Pb , ^{226}Ra , ^{137}Cs and ^{241}Am by direct gamma assay in the Bloomsbury Environmental Isotope Facility (BEIF) at University College London, using an ORTEC HPGe series well-type coaxial low background intrinsic germanium detector (Appleby et al, 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV, and ^{226}Ra by the 295 keV and 352 keV gamma rays emitted by its daughter isotope ^{214}Pb , following 21 days storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV respectively. The absolute efficiencies of the detection system were determined using calibrated sources and standard sediment samples of known activity. Corrections were made for the effect of self absorption of low energy gamma rays within the sample. Core chronologies were calculated using the CRS dating model, which assumes a constant rate of supply over time (Appleby & Oldfield, 1978).

3.3. Spheroidal carbonaceous particles (SCPs)

3.3.1. Background information

Spheroidal carbonaceous particles (SCPs) are produced by the high temperature combustion of fossil fuels such as coal and oil. SCPs are released into the atmosphere and dispersed over wide geographical areas. There are no natural sources of SCPs and therefore they are unambiguous indicators of atmospheric deposition from power generation and other industrial emissions (Rose & Appleby, 2005). Lake sediments provide a record of SCP deposition and have been studied widely across the UK and Ireland (e.g. Rose et al,

1995; Jones et al, 1997; Rose & Harlock, 1998; Rose & Appleby, 2005), in Europe (e.g. Rose et al, 2002; Vukić & Appleby, 2003) and Russia (e.g. Rose, 1995; Rose et al, 1998). SCPs are inert to changes in water and sediment chemistry and consequently the sediment concentration profile of SCPs is both reliable and robust (Rose, 1994). The main profile features can be used as a tool to date lake sediment cores, by relating consistent particle trends in undated cores to those which have previously been dated using a reliable technique such as ^{210}Pb chronology or varve counting. According to Rose et al (1995), the start of the SCP record for UK sites should be attributed to nothing more accurate than the mid 19th century. A rapid increase in SCP concentration occurs after the Second World War, usually dating to the 1950s, and peaks in the late 1970s or early 1980s. These patterns occur due to changes in coal and oil consumption throughout this period. In the same paper, a study of a core from the Men's Bathing Pond on Hampstead Heath places the peak in the SCP profile a little earlier at 1969 ± 2 . More generally, a study of sediment cores from lakes in south and central England place the start of the SCP record at 1850 ± 25 with the peak occurring at 1970 ± 5 (Rose & Appleby, 2005). These dates can be used to place tentative dates on profiles from other lake sediments within the same area.

3.3.2. Methodology

SCPs are composed mainly of elemental carbon and hence are chemically resistant though physically fragile. Unwanted fractions can therefore be removed by the use of strong mineral acids without affecting the particles (Rose, 1994a). SCP analysis followed the method described in Rose (1994a), with each sample being subjected to sequential chemical attack by mineral acids, leaving carbonaceous material and a few persistent minerals. Sediment subsamples were taken from each core at varying resolutions (Table 3.1) depending upon the rate of sediment accumulation determined from the radiometric dating.

Site	Depth (cm)	Sampling interval
HAMP1	0-21	Every 10 cm
	21-50	Every 2 cm
	50-213	Every 10 cm
VALE1	0-45	Every 10 cm
	45-75	Every 2 cm
	75-213	Every 10 cm
HIGW1	0-142	Every 10 cm
STCK2	0-30	Every 10 cm
	30-75	Every 2 cm
	75-155	Every 10 cm
SNOR1	0-35	Every 10 cm
	35-55	Every 2 cm
	55-102	Every 5 cm
WIMP1	0-20	Every 10 cm
	20-40	Every 2 cm
	40-143	Every 10 cm
WAKE1	0-70	Every 3 cm

Table 3.1 – Sediment subsampling resolutions for SCP analysis for each of the seven London lake cores

0.1 – 0.2 g of dried sediment was weighed into 12 ml polypropylene tubes and 1.5 ml of concentrated HNO₃ (laboratory grade) was added to eliminate the organic fraction from the sample. The samples were left to digest overnight, after which a further 1.5 ml HNO₃ was added. The samples were then heated in a water bath at 80°C for 2 hours, removed, topped up with distilled water and centrifuged. The supernatant HNO₃ was taken off and discarded. 3 ml HF was added to each tube to eliminate the siliceous fraction and heated in a water bath at 80°C for 2 hours. The tubes were then removed, topped up with distilled water and centrifuged. The supernatant HF was taken off and discarded. Finally 3 ml HCl (6M) was added to eliminate the carbonate and biocarbonate fractions and the tubes were again heated in a water bath at 80°C for 2 hours. The samples were removed, topped up with distilled water and centrifuged. The supernatant HCl was taken off and discarded. Distilled water was then added to each tube to wash the sample, centrifuged and removed. This step was carried out twice to ensure the sample was clean. A known fraction of the resulting suspension was evaporated onto a coverslip and mounted onto a microscope slide. The number of SCPs on the coverslip was counted using a light microscope at x 400 magnification and the sediment concentration calculated in units of 'number of particles per gram dry mass of sediment' (gDM⁻¹).

3.4. Results

3.4.1. Hampstead No. 1 Pond

The radiometric dating results for HAMP1 are shown in Figure 3.1. Total ²¹⁰Pb activity did not reach equilibrium with supporting ²²⁶Ra within the core (Figure 3.1a). The unsupported ²¹⁰Pb profile could be divided into three sections (Figure 3.1b). In the top 40 cm, unsupported ²¹⁰Pb activity declined exponentially with depth, which was followed by a plateau in activity between 40 and 110 cm. Below 110 cm unsupported ²¹⁰Pb activity declined again. A well resolved ¹³⁷Cs peak was found at 40 cm, with a corresponding peak in ²⁴¹Am at the same depth (Figure 3.1c), which confirmed that the ¹³⁷Cs peak was derived from the 1963 fallout maximum from nuclear weapons testing. The unsupported ²¹⁰Pb and ¹³⁷Cs profiles suggested that the sediments in the top 40 cm of the core had not been mixed. The sediment accumulation rate (Figure 3.1d) from 1963 to the surface of the core was relatively uniform with a mean of 0.167 g cm⁻² yr⁻¹. Below 40 cm, particularly between 40 and 110 cm, there may have been sediment slumping or sediment mixing which affected the sediment chronology.

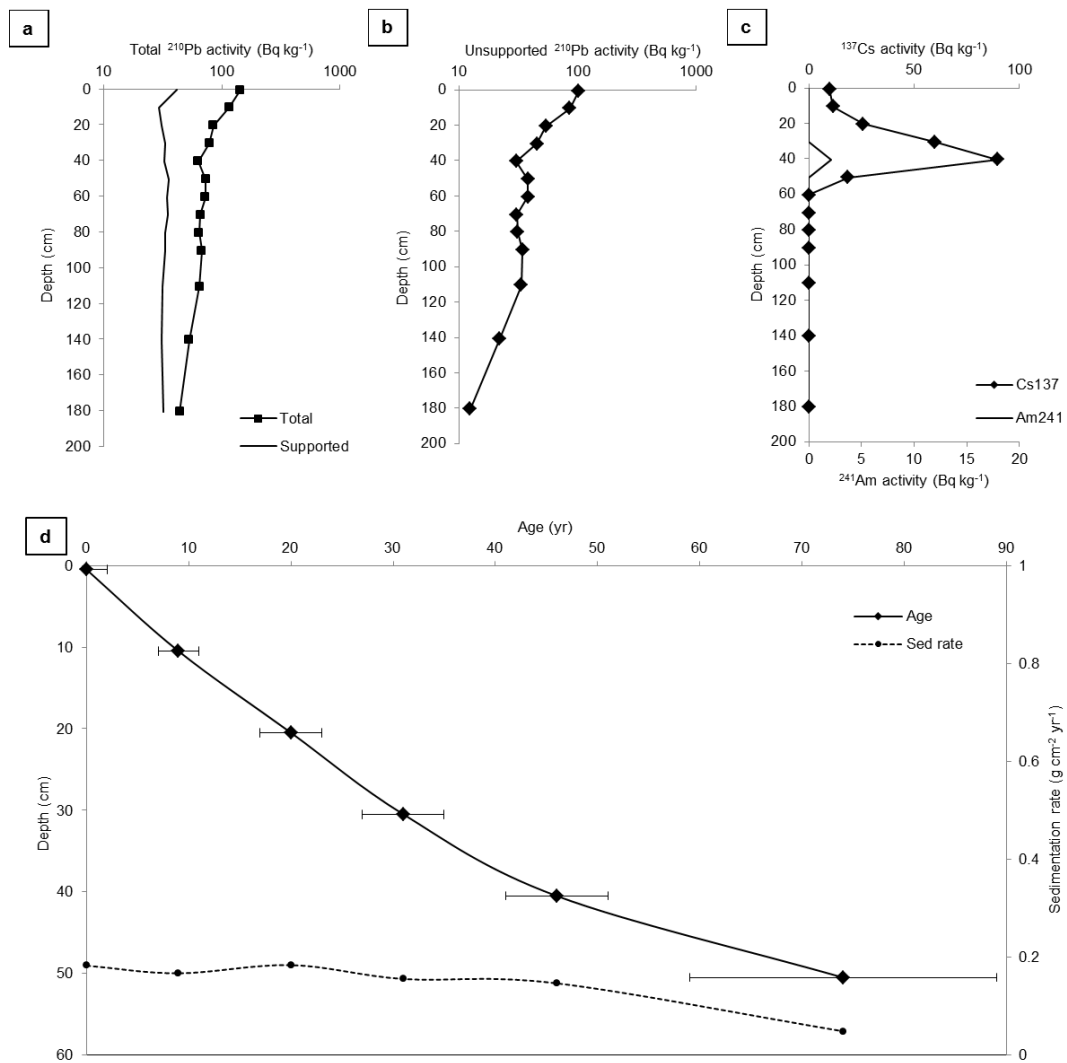


Figure 3.1 – Radiometric dating profiles for core HAMP1 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs and ^{241}Am activity and (d) radiometric chronology and sedimentation rates.

Figure 3.2 shows the SCP concentration profile for HAMP1. SCPs were first detected at a depth of 160 cm, although the concentration remained very low until a rapid increase occurred at a depth of 49 cm. The start of this increase corresponded to the 1950s. The concentration continued to rise until 29 cm when a peak of 50100 g DM $^{-1}$ was reached, corresponding to 1970. From 29 cm to the surface the SCP concentration showed an overall decline to about 11500 g DM $^{-1}$ at the top of the core. The concentrations fluctuated widely throughout the core.

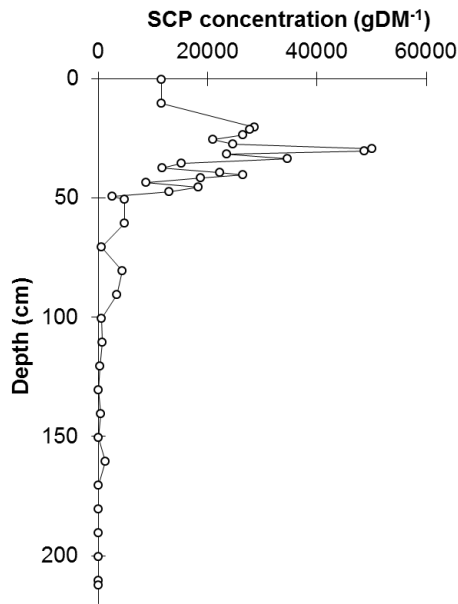


Figure 3.2 – Concentration of SCPs within the sediment core from Hampstead No. 1 Pond, plotted against depth

3.4.2. The Vale of Health Pond

The results from the radiometric dating of VALE1 are shown in Figure 3.3. They showed that equilibrium of total ^{210}Pb activity with supported ^{210}Pb was reached at a depth of between 81 and 90 cm (Figure 3.3a). Unsupported ^{210}Pb activity declined irregularly with depth with a rapid fall at c. 50 cm and below 70 cm (Figure 3.3b). The ^{137}Cs activity profile (Figure 3.3c) showed a well resolved peak at 70.5 cm suggesting a correspondence with the fallout maximum from nuclear bomb tests in 1963. This showed a significant discrepancy from the ^{210}Pb dates which placed 1963 at a depth of 42 cm. This was almost certainly due to incomplete recovery of the ^{210}Pb inventory. Adjusting the dates using the ^{137}Cs date as a reference gave the age-depth profile shown in Figure 3.3d. Sedimentation rates over the last 40 years were relatively stable with an increase in the 1970s. Unsupported ^{210}Pb activities between 70 and 81 cm were quite low, which may suggest that sedimentation rates before the 1960s were high. It is likely that some kind of event (sediment removal) occurred between 80 and 90 cm in the core, with the top 80 cm of the core sediments being deposited on much older sediments or soils.

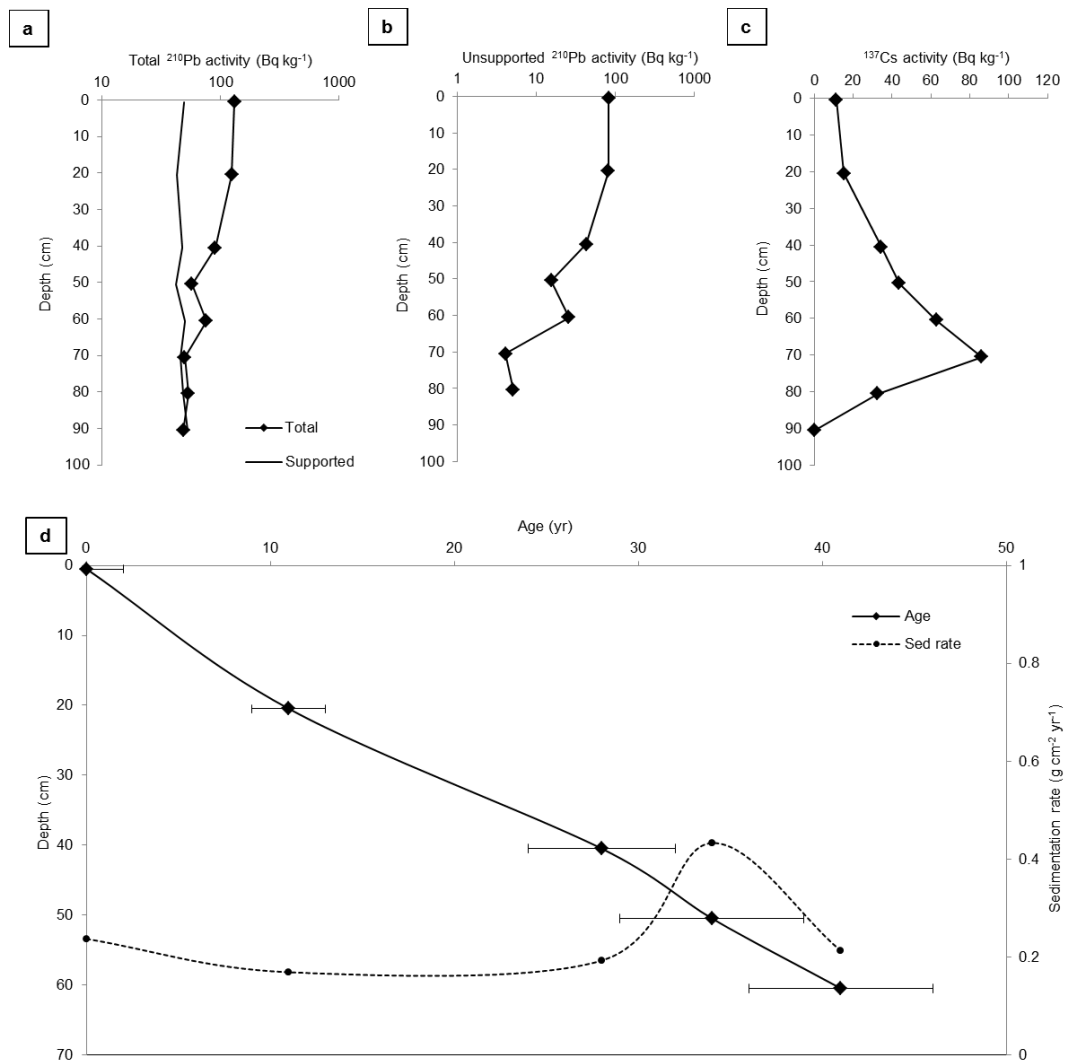


Figure 3.3 – Radiometric dating profiles for core VALE1 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs activity and (d) radiometric chronology and sedimentation rates.

The SCP concentration profile for VALE1 is shown in Figure 3.4. SCPs were first detected at a depth of 130 cm, and showed a clear, rapid increase from 90 cm upwards, which corresponded to the 1950s. Concentrations fluctuated quite widely between this point and the top of the core. However, two major peaks were visible at 70 cm and 51 cm, corresponding to concentrations of 45600 and 40700 g DM $^{-1}$ respectively. It was difficult to ascertain with any certainty which of the peaks corresponded to 1970 because of the variation within the core. Above 51 cm, the concentration began to decline overall but was still in the region of 20000 g DM $^{-1}$ at the surface.

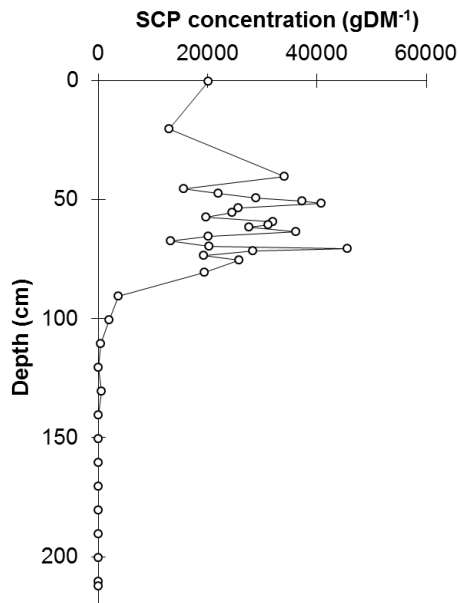


Figure 3.4 – Concentration of SCPs within the sediment core from the Vale of Health Pond, plotted against depth

3.4.3. Highgate Ladies Bathing Pond

The results of the radiometric dating for HIGW1 are shown in Figure 3.5. Total ^{210}Pb activity reached equilibrium with the supporting ^{226}Ra at the base of the core (Figure 3.5a). Unsupported ^{210}Pb activity showed a slow and irregular decline with depth (Figure 3.5b). There were abrupt falls in the profile at approximately 60 cm and 100 cm, which could record episodes of rapid accumulation such as slump events. ^{137}Cs showed a well resolved peak at 39.5 cm corresponding to 1963 (Figure 3.5c). The chronology calculated using the CRS model and the ^{210}Pb data placed the 1963 layer at 49 cm. This was deeper than the ^{137}Cs peak and was possibly due to the impact of a rapid increase in sediment accumulation in recent years. Adjusting the model with reference to the ^{137}Cs peak produced the age-depth profile shown in Figure 3.5d. Overall, the sedimentation rates in this core showed a gradual increase in accumulation, with two peaks in accumulation occurring in the 1920s and 1940s which corresponded to the possible slumping events suggested by the unsupported ^{210}Pb profile.

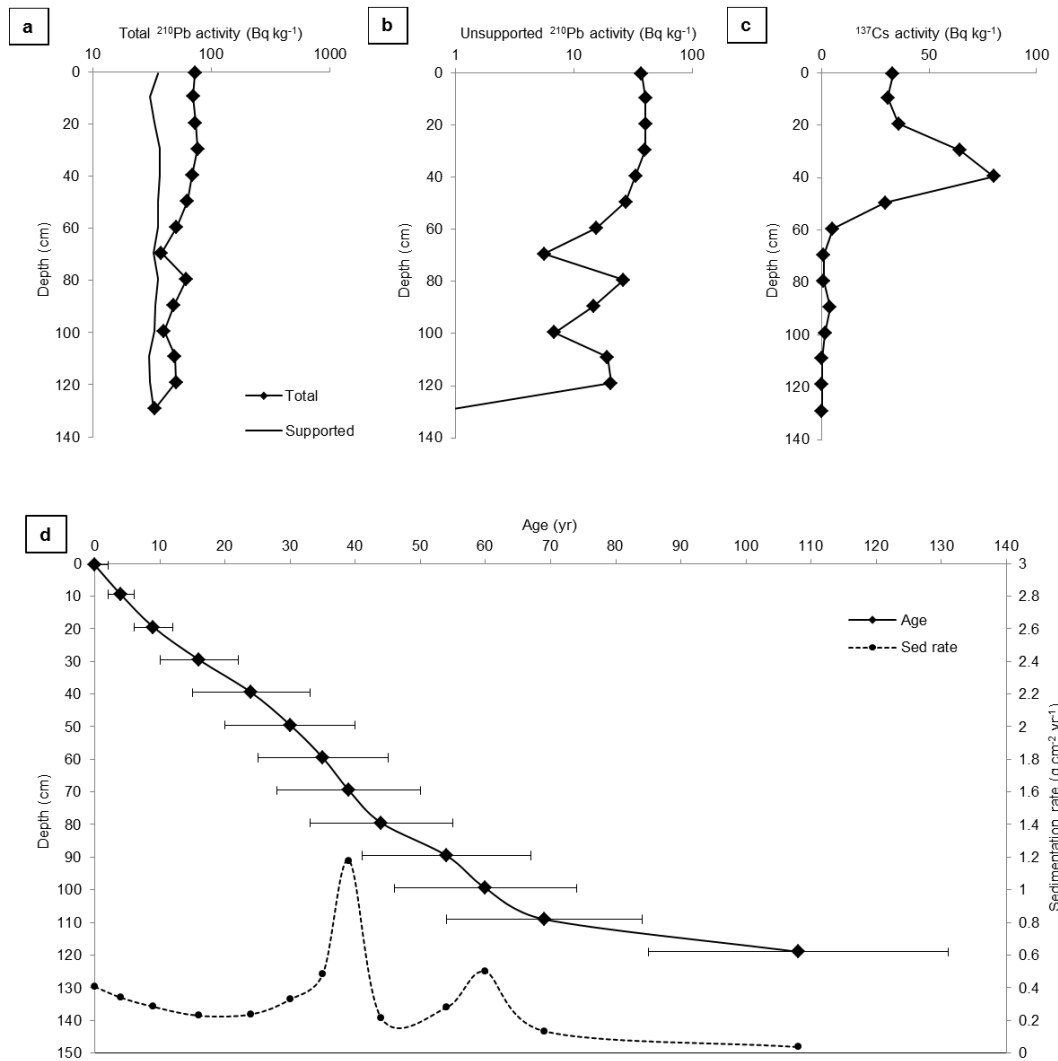


Figure 3.5 – Radiometric dating profiles for core HIGW1 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs activity and (d) radiometric chronology and sedimentation rates.

The SCP concentration profile for HIGW1 is shown in Figure 3.6. Although the concentrations were calculated at more coarse intervals for this core than any of the others, a distinct pattern was still visible. SCPs were present from the base of the core, at a depth of 141 cm, and a rapid increase occurred from a depth of approximately 70 cm which reflected the 1950s. The 1970 peak occurred at about 30 cm with a concentration of 54000 g DM $^{-1}$, after which there was an overall decline to 34200 g DM $^{-1}$ at the surface. The surface concentration in this core was much higher than those found in the other cores. This was probably due to the fact that HIGW1 was retrieved from the lake in 1987, but SCP concentrations have continued to decline throughout the 1990s to the present day.

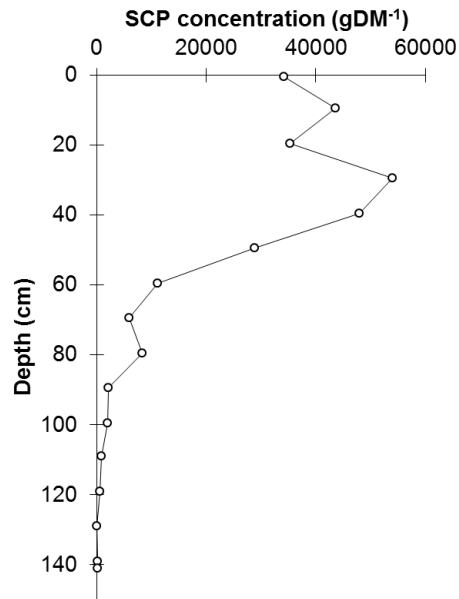


Figure 3.6 – Concentration of SCPs within the sediment core from the Highgate Ladies Bathing Pond, plotted against depth

3.4.4. Stock Pond

The radiometric dating results for STCK2 are shown in Figure 3.7. Total ²¹⁰Pb activity did not reach equilibrium with supported ²¹⁰Pb within the core (Figure 3.7a). Unsupported ²¹⁰Pb activity declined irregularly with depth, with little net decline in the top 50 cm (Figure 3.7b). This suggested that sediment accumulation had increased in recent years. ¹³⁷Cs showed a well resolved peak at 60 cm, which was supported by a smaller peak of ²⁴¹Am at the same depth (Figure 3.7c), suggesting that nuclear weapons testing in 1963 was the cause. Use of the CRS dating model on the ²¹⁰Pb data placed the 1963 layer at a depth of 90 cm, which did not correspond to the ¹³⁷Cs peak. Adjusting the ²¹⁰Pb chronologies to the ¹³⁷Cs peak gave the age-depth profile shown in Figure 3.7d. Sedimentation rates increased from the 1980s following a period of relative stability. The unsupported ²¹⁰Pb inventory yielded a mean flux of 352 Bq m⁻² yr⁻¹ which suggested that the coring location was subject to sediment focusing.

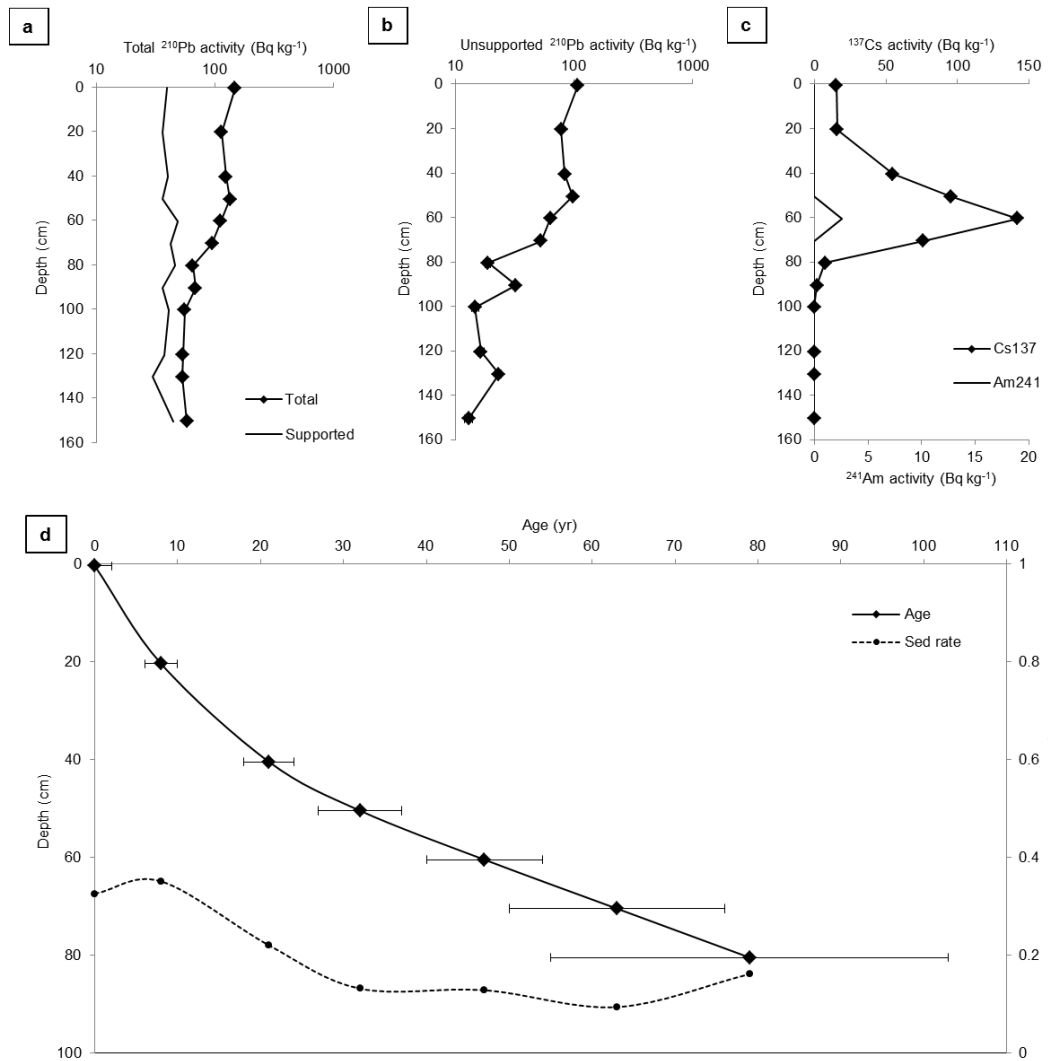


Figure 3.7 – Radiometric dating profiles for core STCK2 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs and ^{241}Am activity and (d) radiometric chronology and sedimentation rates.

The SCP concentration profile for STCK2 is shown in Figure 3.8. SCPs were first detected at a depth of 120 cm and there was a clear, rapid increase beginning at about 80 cm which corresponded to 1950. A peak in concentration occurred at 48 cm with a value of 62200 g DM $^{-1}$, which corresponded to 1970. After this point the concentration declined to about 10000 g DM $^{-1}$ at the surface.

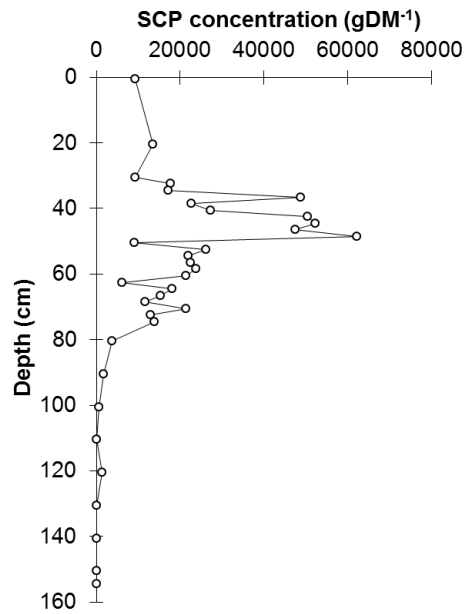


Figure 3.8 – Concentration of SCPs within the sediment core from Stock Pond, plotted against depth

3.4.5. South Norwood Lake

The results from the radiometric dating of SNOR1 are shown in Figure 3.9. Equilibrium of total ^{210}Pb activity with the supporting ^{226}Ra occurred at approximately 80 cm in the core (Figure 3.9a). Unsupported ^{210}Pb activity showed a decline with depth between 45 and 70 cm, but not in the top 45 cm (Figure 3.9b) which suggested that sediment accumulation had changed in recent years. ^{137}Cs activity showed a well resolved peak at 50.5 cm. This was supported by a peak in ^{241}Am in the adjacent deeper sample (55-56 cm), suggesting that the ^{137}Cs peak was derived from the fallout maximum from nuclear weapons testing in 1963 (Figure 3.9c). The raw CRS model using the ^{210}Pb data placed the 1963 layer at 46 cm, above the layer suggested by the ^{137}Cs record. Using ^{137}Cs to correct the dates, the core chronology placed 1930 at 70.5 cm and 1980 at 40.5 cm. ^{210}Pb calculated sediment accumulation rates (Figure 3.9d) showed that sedimentation rates were relatively uniform during this period with an average of $0.14 \text{ g cm}^{-2} \text{ yr}^{-1}$. Over the last 20 years sediment accumulation rates varied but increased overall.

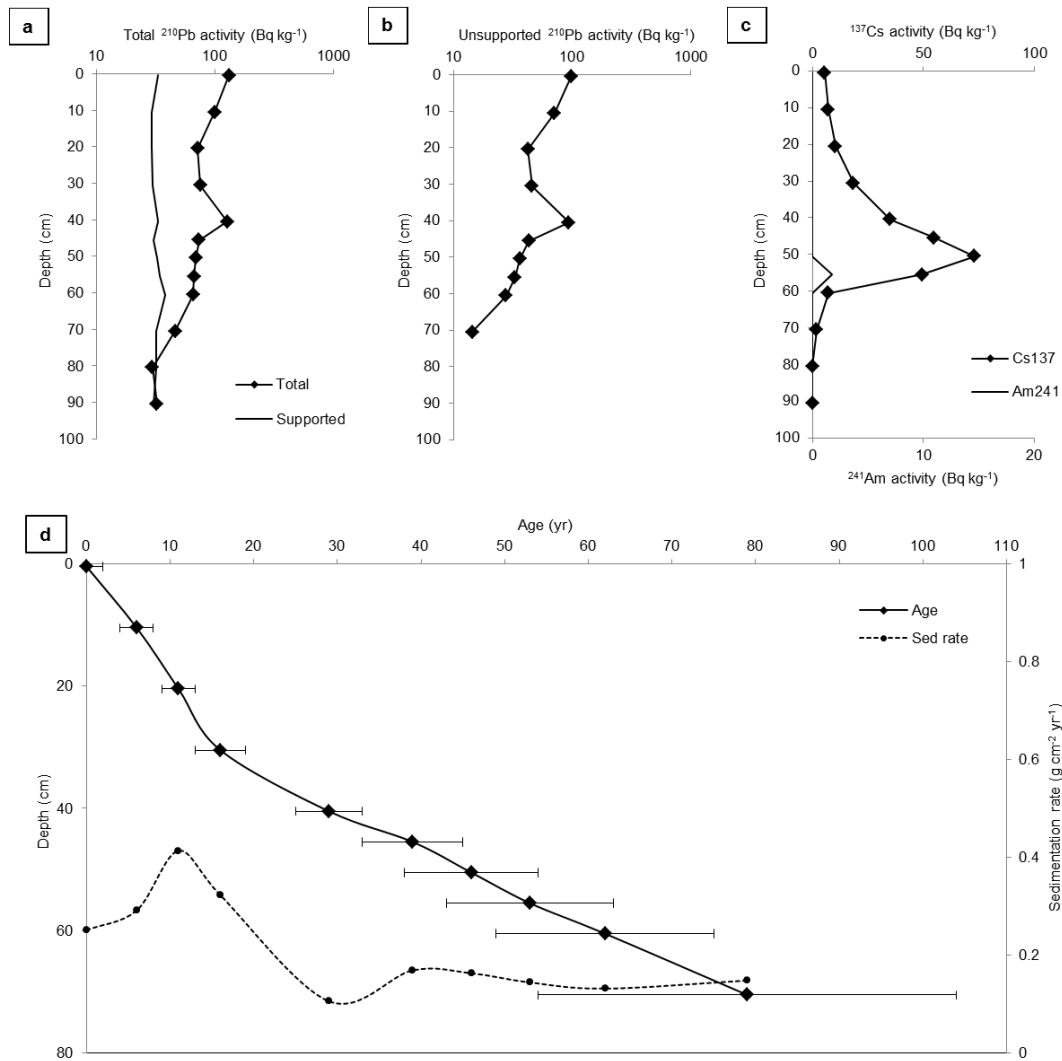


Figure 3.9 – Radiometric dating profiles for core SNOR1 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs and ^{241}Am activity and (d) radiometric chronology and sedimentation rates.

The SCP profile for SNOR1 is shown in Figure 3.10. SCPs were present throughout the entire length of the core with the bottom sample at 101 cm having a concentration of 190 g DM $^{-1}$. However, SCP concentrations started to increase more rapidly at a depth of approximately 70 cm, which corresponded to 1950. There was a peak in concentration of 34100 g DM $^{-1}$ at 47 cm, corresponding to 1970, after which the concentration declined overall. The concentration at the top of the core was in the region of 4000 g DM $^{-1}$.

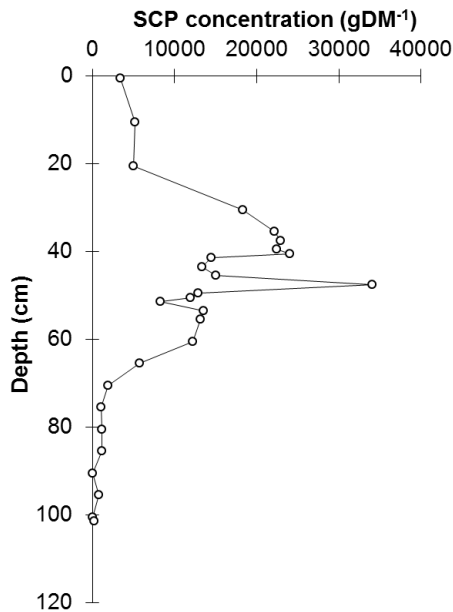


Figure 3.10 – Concentration of SCPs within the sediment core from South Norwood Lake, plotted against depth

3.4.6. Wimbledon Park Lake

The radiometric dating results for WIMP1 are shown in Figure 3.11. Total ^{210}Pb activity reached equilibrium with the supporting ^{226}Ra between the depths of 31 and 40 cm in the core (Figure 3.11a). The unsupported ^{210}Pb activity in WIMP1 declined more or less exponentially with depth until 30cm, suggesting that sediment accumulation rates were relatively uniform in this section (Figure 3.11b). Below 30 cm, there was a very distinct drop in unsupported ^{210}Pb activity. There was a well defined ^{137}Cs peak at 30cm and a smaller peak in ^{241}Am at the same depth (Figure 3.11c), which corresponded to the 1963 nuclear weapons testing maximum. The changes in ^{210}Pb and ^{137}Cs activity within the core suggested that there was a change from old sediment formed approximately 100 years ago at 40cm, to relatively new sediments at 30 cm. This implied that there was a discontinuous sedimentation process between 30 and 40 cm and that the top 35 cm of sediment was formed on much older sediments or soils. Sedimentation rates (Figure 3.11d) have been relatively uniform since the event which must have occurred in about 1960, with a mean of $0.112 \text{ g cm}^{-2} \text{ yr}^{-1}$.

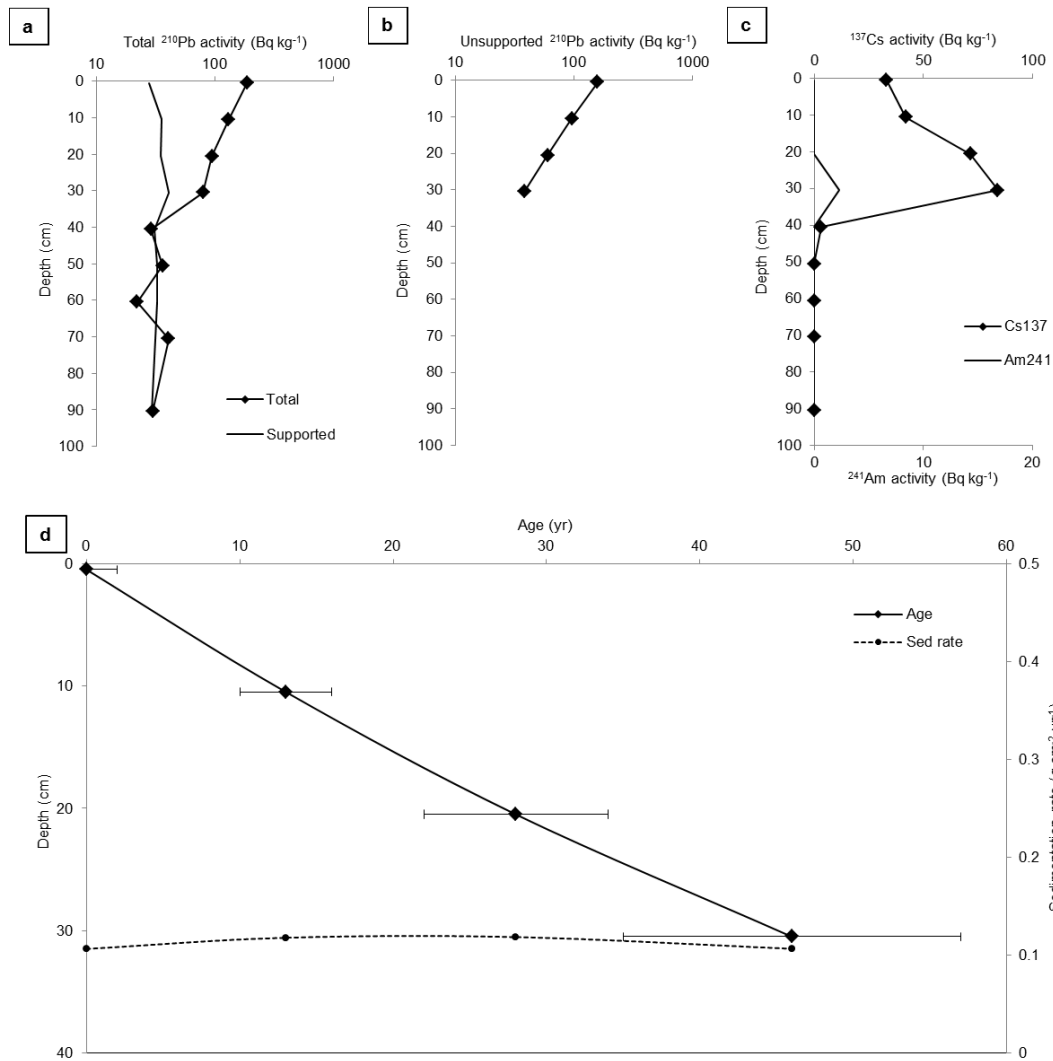


Figure 3.11 – Radiometric dating profiles for core WIMP1 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs and ^{241}Am activity and (d) radiometric chronology and sedimentation rates.

Figure 3.12 shows the SCP profile for WIMP1. Within this core, SCPs were first detected at a depth of 80 cm, although the concentration remained very low until 30 cm. After this point there was a very rapid increase in concentration, which peaked at 25300 g DM $^{-1}$ at a depth of 24 cm. This meant that the concentration of SCPs increased more than six-fold within just 6 cm of sediment. The rapid increase and peak corresponded to the 1950s and 1970 respectively. The concentration declined towards the top of the core and amounted to 8600 g DM $^{-1}$ at the surface.

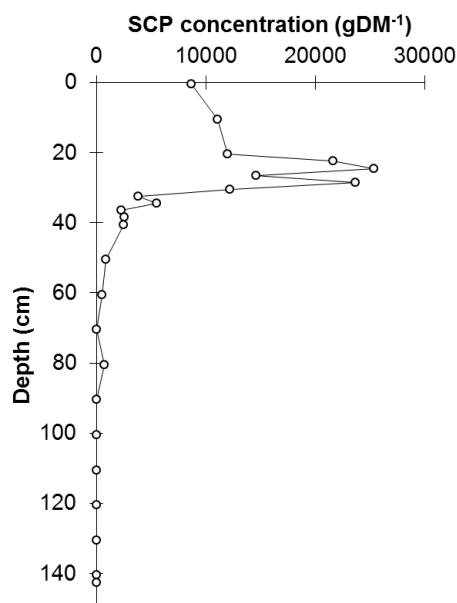


Figure 3.12 – Concentration of SCPs within the sediment core from Wimbledon Park Lake, plotted against depth

3.4.7. Wake Valley Pond

The radiometric dating results for WAKE1 are shown in Figure 3.13. Total and supported ²¹⁰Pb activities did not reach equilibrium depth within the core (Figure 3.13a). The unsupported ²¹⁰Pb activity profile of the core (Figure 3.13b) could be divided into two parts, with the top 30 cm showing little net decline suggesting an increase in sediment accumulation over recent years. Below 30 cm there was a steeper, almost exponential, rate of decline which suggested that sedimentation rates were more stable in this section of the core. There was a peak in ¹³⁷Cs from weapons testing in 1963 at 30.5 cm, although it was not well resolved (Figure 3.13c). The chronology calculated by the CRS model and the ²¹⁰Pb data put the 1963 layer at a greater depth of 38 cm. Calculation of the chronology using the ¹³⁷Cs peak as a reference produced the age-depth profile shown in Figure 3.13d. Sedimentation rates were relatively stable before the 1970s at c. 0.065 g cm⁻² yr⁻¹, followed by a gradual increase to just over 0.2 g cm⁻² yr⁻¹ at the surface.

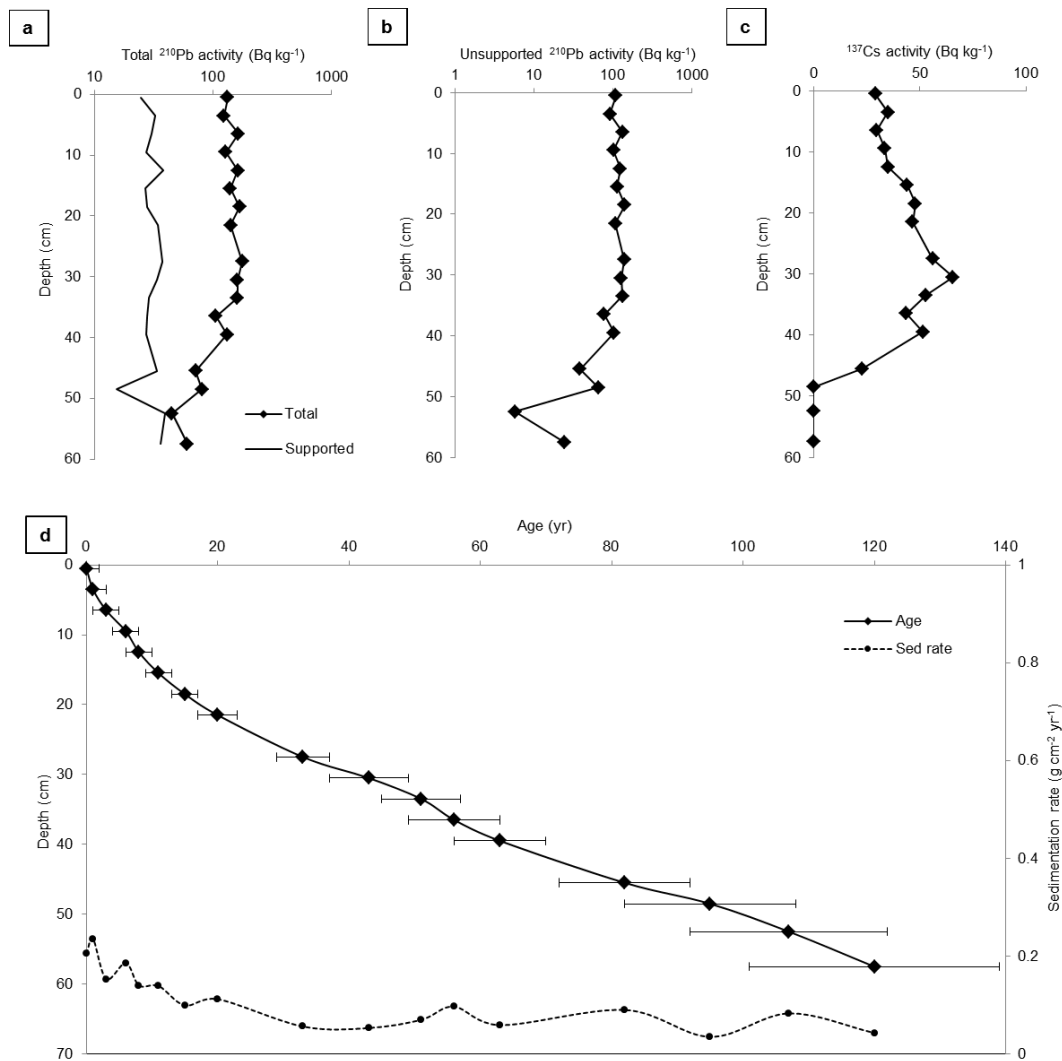


Figure 3.13 – Radiometric dating profiles for core WAKE1 showing (a) total and supported ^{210}Pb activity, (b) unsupported ^{210}Pb activity, (c) ^{137}Cs activity and (d) radiometric chronology and sedimentation rates.

Figure 3.14 shows the SCP concentration profile for WAKE1. SCPs were present throughout the whole core, with the rapid increase of the 1950s occurring at approximately 42 cm. The 1970 peak occurred at a depth of 30 cm with a concentration of 42300 g DM $^{-1}$. Above this layer, the concentration steadily declined to the top of the core, with a value of 8400 g DM $^{-1}$ at the surface.

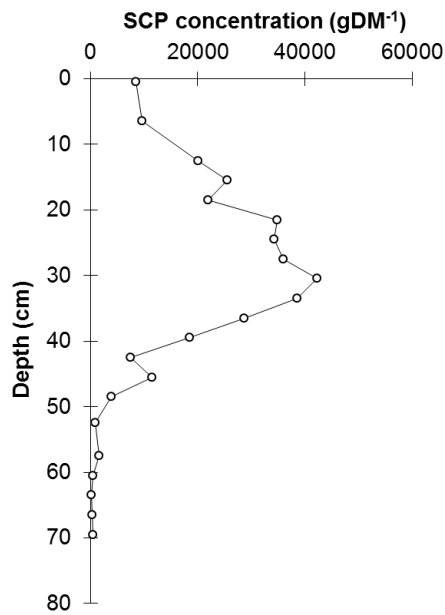


Figure 3.14 – Concentration of SCPs within the sediment core from Wake Valley Pond, plotted against depth

3.5. Discussion

3.5.1. Radiometric and SCP dating

The sedimentation process at each of the London lakes played an important role in the quality of radiometric dating. Interruptions to the ^{210}Pb record at the majority of the sites led to the formation of only short chronologies in most cases. These interruptions had a range of causes. Sediment slumping is an episode of rapid sediment accumulation caused by the collapse of the sediment profile, whilst sediment focusing is the movement of sediment to deeper waters. Changes in the rate of sedimentation such as these are known to affect the ^{210}Pb record, with high accumulation rates leading to dilution of the ^{210}Pb signal (MacKenzie et al, 2011). Sediment mixing can be caused by both physical and biological processes, whilst dredging is the removal of sediment, both of which will interrupt the radioisotopic record. Radiometric dating has also been found to be affected by the supply of radioisotopes to the sediment (Appleby, 2008). Low concentrations can restrict the age of the ^{210}Pb dating horizon, defined as the depth at which unsupported ^{210}Pb concentrations fall below significant levels of detection. Calculation of the unsupported ^{210}Pb inventory of the core can then be highly problematic. This is enhanced at sites with very rapid accumulation (Appleby, 2008). In addition, the supply of radioisotopes to the sediments is not always consistent. A particular case in point is ^{241}Am . In this study, ^{241}Am was only detectable at some of the sites. In a study of a large number of sediment cores by Appleby et al (1991), traces of ^{241}Am was only observed in some of the cores. Where ^{241}Am was observed the peak was

very weak in comparison to the ^{137}Cs peak. This is because ^{241}Am activity is generally much lower than ^{137}Cs activity and therefore is often below the detection limit of the dating method.

The variability in SCP concentration seen in some of the sediment core profiles also reflected changes in sediment accumulation rate. Rapid sediment accumulation can result in dilution of SCPs (Vukic & Appleby, 2003), reflected by low SCP concentrations and broad SCP peaks (Rose et al, 1999). In contrast, a slow sediment accumulation rate can lead to insufficient resolution which masks the true changes in SCP rate (Rose, 1995). Localised sediment focusing can modify SCP patterns by making the profiles noisy or even slightly altering their timing, giving rise to variability (Rose et al, 1999). Mixing caused by physical and biological processes can also influence SCP profiles, often reducing the resolution of the SCP peaks (Rose, 1995). In more rural areas in the UK, SCP profiles have been used to identify the onset of industrialisation, with a date of c. 1850 being attributed to the point in the core where SCPs first start to appear (e.g. Jones et al, 1997; Rose et al, 1995). However, the start of the SCP record in the London lake cores could not be reliably interpreted as the mid-19th century, as the first appearance of SCPs was not followed by a consistent increase in concentration. At sites such as Hampstead No. 1 Pond (Figure 3.2) and Stock Pond (Figure 3.8), the presence of SCPs towards the bottom of the cores was discontinuous, sometimes present at low concentrations and then undetectable in adjacent samples. This may have been a product of both high sediment accumulation rates and low concentrations. In addition, at some of the sites such as Wake Valley Pond, the sediment record did not extend back far enough to encompass the mid-19th century.

3.5.2. Age-depth graphs and chronology formation

In order to formulate a chronology for each of the cores, the dates obtained from the radiometric data and the SCP concentration profiles were plotted together onto age-depth axes (shown in Figures 3.15 to 3.21). The errors associated with each of the dates were also included. In addition, a bottom date for each core was determined by assuming that the maximum sediment depth (obtained during the preliminary field investigations (see Section 2.2)) corresponded to the date the lake was created. In the case of VALE1, WAKE1, SNOR1 and WIMP1 there was no error in the date as the exact age of the lake was known. For HAMP1, STCK2 and HIGW1 the age of the lake wasn't known exactly, but could be confined to a short period of time. Therefore, for these lakes there was a small error associated with the date. At all sites there may have been some error associated with the depth. However, for the purposes of the chronology formation it was assumed that the maximum sediment depth did correspond to the date the lake was created. The graphs were used to compare the results of both dating methods and to provide chronologies for the cores that could be used for the analysis of the metals data.

The age-depth graph for HIGW1 is depicted in Figure 3.15 and shows that the radiometric and SCP dates corresponded extremely well. The 1970 (± 5) SCP peak was 1970 (± 6) in the radiometric record and the 1950 (± 15) SCP increase corresponded to 1948 (± 11). In the case of the other lakes there was some discrepancy between the dates. For VALE1 (Figure 3.16) both of the possible 1970 (± 5) SCP peaks have been plotted, with the higher of the two (51 cm) corresponding to a radionuclide date of 1974 (± 5). The lower SCP peak was at a depth of sediment (70 cm) which was beneath the last calculated radionuclide date. At a depth of 60 cm, the radiometric date was calculated to be 1968 (± 5), so the date at 70 cm must have been earlier than that. For the same reason there was no radionuclide date to compare with the 1950 SCP increase. The age-depth graph for HAMP1 is shown in Figure 3.17. The 1970 (± 5) SCP peak corresponded to a radiometric date of 1977 (± 5). The 1950 (± 15) SCP increase corresponded to a radiometric date of 1935 (± 15). The same pattern was present in the data from WAKE1 (Figure 3.18) and SNOR1 (Figure 3.19). For WAKE1, the 1970 (± 5) SCP peak corresponded fairly closely to the 1965 (± 6) radionuclide date at the same depth, but the 1950 (± 15) SCP increase differed more as the radionuclide date at that depth was 1936 (± 9). In SNOR1, the 1970 (± 5) SCP peak corresponded to 1968 (± 6) in the radiometric record, but the 1950 increase (± 15) at 70 cm was calculated to be 1930 (± 25) by the radionuclide model. WIMP1 (Figure 3.20) also showed a better agreement between the radionuclide chronology and the 1970 (± 5) SCP peak than the radiometric dates and the 1950 (± 15) SCP increase. The former corresponded to a radionuclide date of 1975 (± 8), and the latter to 1964 (± 11). STCK2 showed a slightly different pattern (Figure 3.21) as both SCP dates differed to those calculated using the radionuclide model. The 1970 (± 5) SCP peak corresponded to a radiometric date of 1980 (± 4), and the 1950 (± 15) increase to a date of 1930 (± 24).

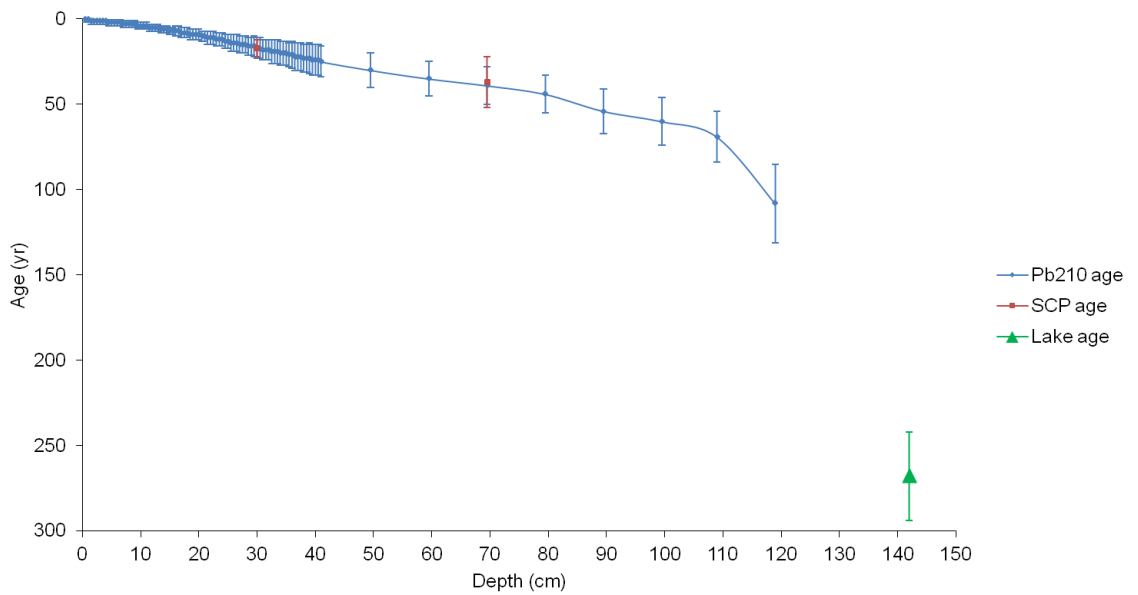


Figure 3.15 – Age-depth graph for HIGW1 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown (errors are included because the exact date is not known).

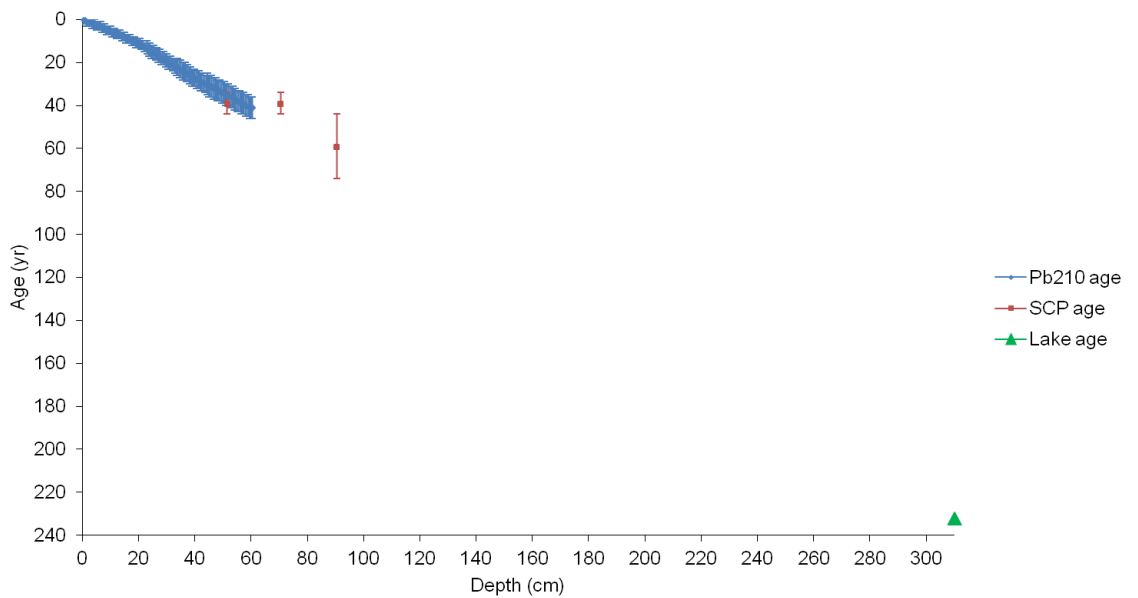


Figure 3.16 – Age-depth graph for VALE1 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown.

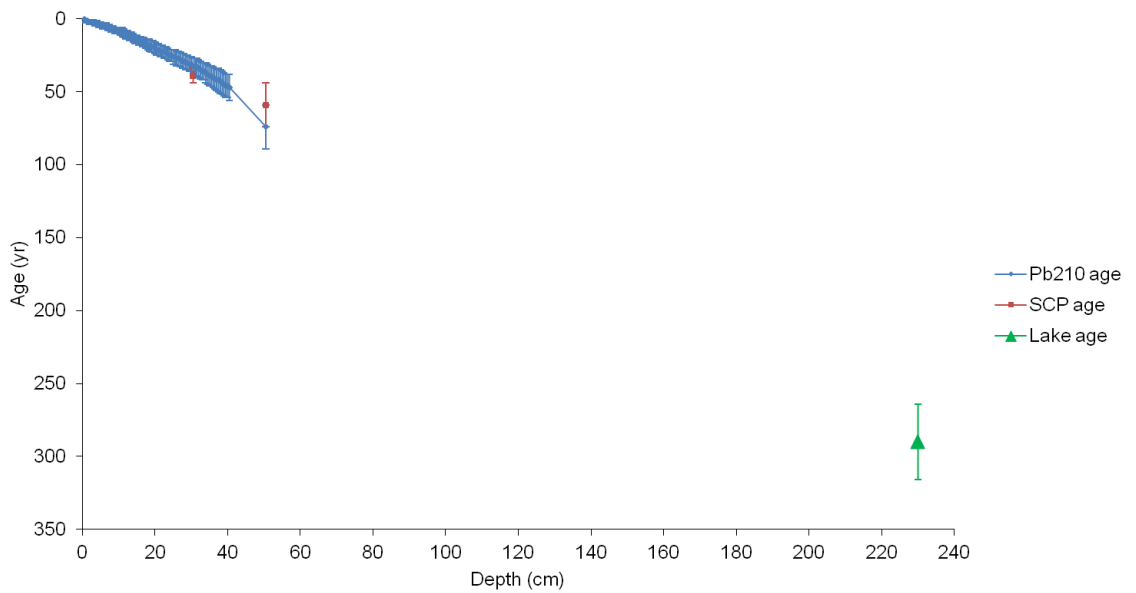


Figure 3.17 – Age-depth graph for HAMP1 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown (errors are included because the exact date is not known).

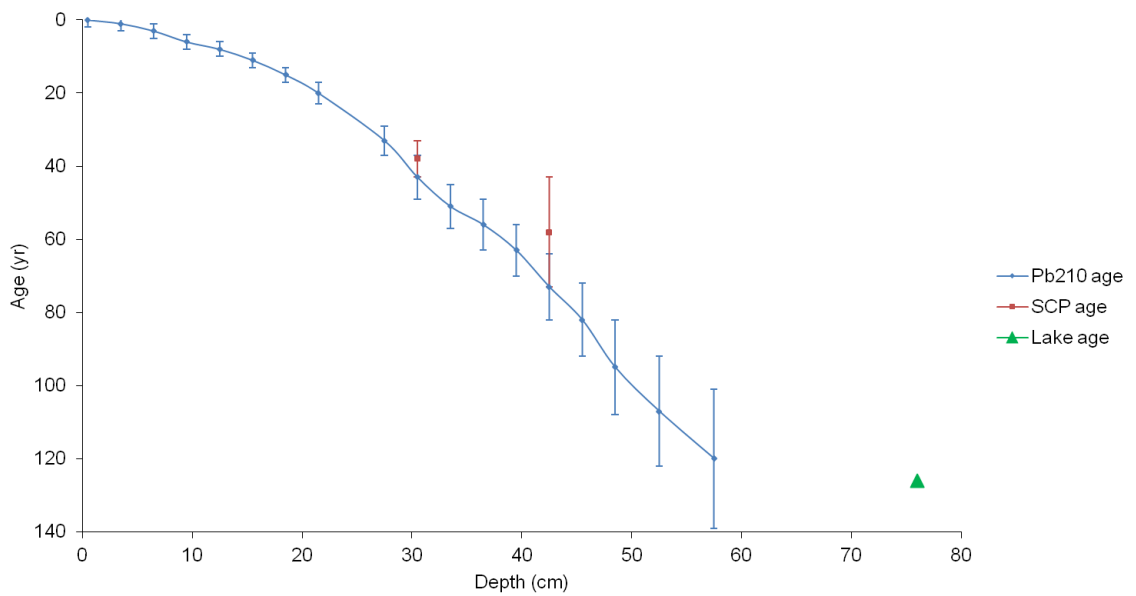


Figure 3.18 – Age-depth graph for WAKE1 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown.

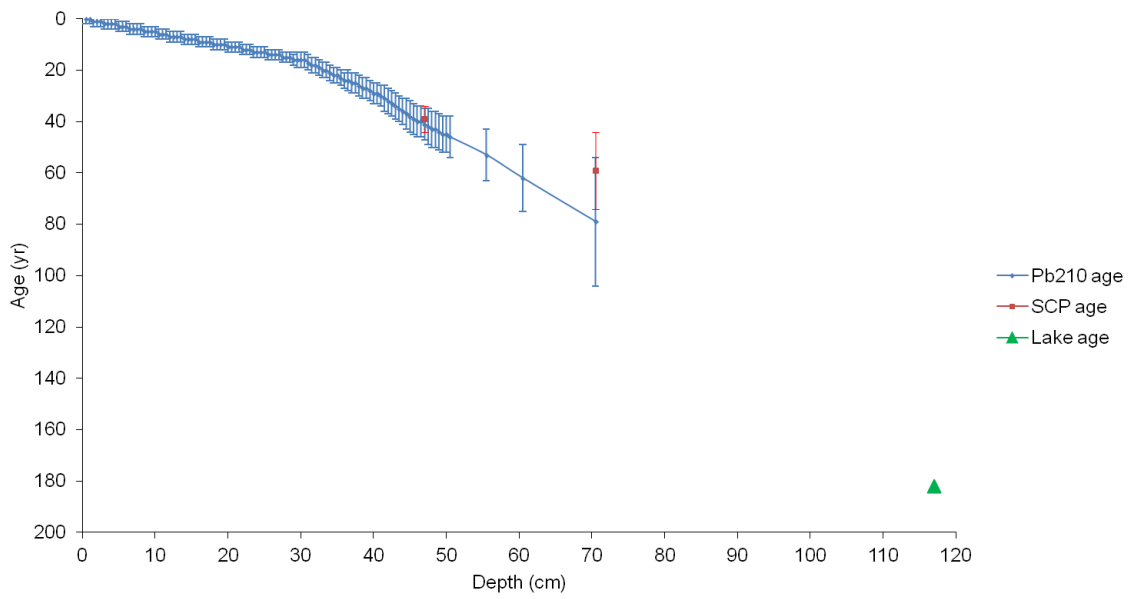


Figure 3.19 – Age-depth graph for SNOR1 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown.

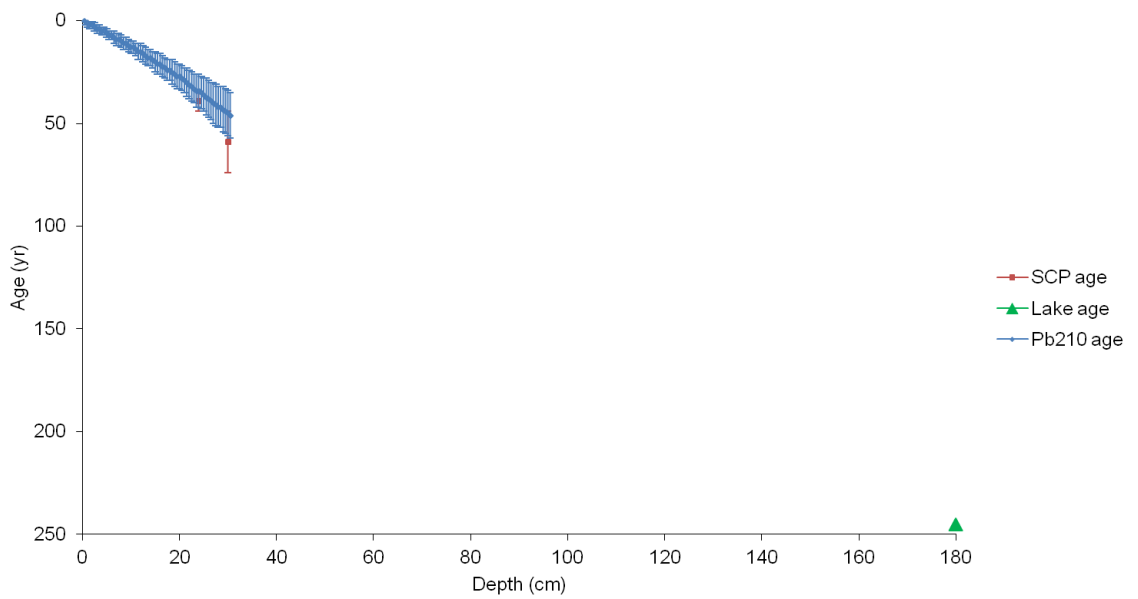


Figure 3.20 – Age-depth graph for WIMP1 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown.

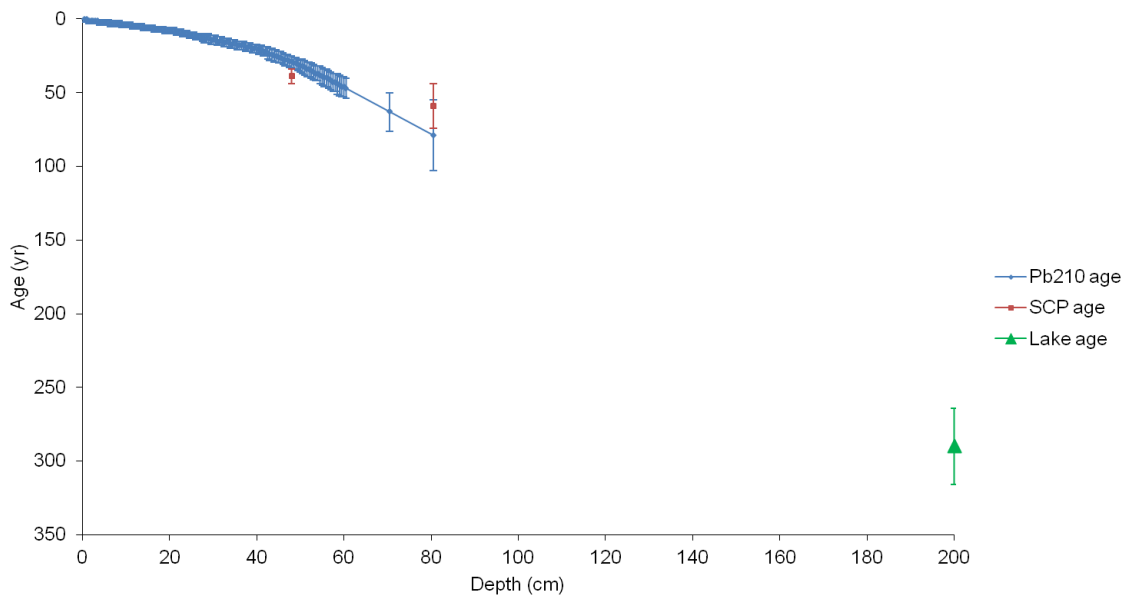


Figure 3.21 – Age-depth graph for STCK2 showing ^{210}Pb and SCP dates, including errors. The date the lake was created is also shown (errors are included because the exact date is not known).

However, as Figures 3.15 to 3.21 show, for all cores the size of the error associated with each date increased as the sediments got older, irrespective of the method. This helped to explain why the 1970 SCP peaks corresponded better to the radiometric dates than the 1950 SCP increases did. Even though some of the dates did not appear to match very well, taking into account the error associated with each one meant that there was an overlap between all the SCP and radiometric dates for all the cores. This suggested that there was reasonable corroboration between the two dating techniques and that a final chronology could be defined for each core.

For HIGW1 and WAKE1 the chronologies calculated using the radiometric models provided dates for the cores back to 1879 (± 23) and 1888 (± 19) respectively. For WAKE1, this meant that the whole history of the lake was contained within the core as the lake was created in 1882. For HIGW1, the same was likely. The age-depth graph shown in Figure 3.15 did support this idea to some degree as the gap between the bottom radiometric date and the age of the lake appeared to be fairly linear, but it couldn't be established with absolute certainty. However, a bottom date of 1879 was practical within the context of studying recent metal pollution because it covered the latter part of the Industrial Revolution. Because the SCP dates fell within the boundaries of the radiometric errors for both of these cores, it was reasonable to assume that the radiometric chronologies could be used as a basis for interpretation of the metals data for both lakes.

For the other five cores, establishing chronologies which covered the entirety of the lakes' histories was more of a problem. The bottom radiometric dates that were calculated for VALE1, HAMP1, STCK2, SNOR1 and WIMP1 were 1968 (± 5), 1935 (± 15), 1930 (± 24), 1930 (± 25) and 1963 (± 11) respectively, which meant that each chronology was relatively short. This was highlighted by the age-depth graphs for each of the cores (Figures 3.15 to 3.21) which showed a cluster of dates in the top half of each core and a single date at the base (corresponding to the date the lake was made), with a large gap in between. Using the SCP dates, an additional date of 1950 (± 15) was applied to a depth of 90 cm within the VALE1 core, which extended the chronology back a little further. However, apart from independent corroboration of the radiometric dates, this was of no additional help to HAMP1, STCK2 and SNOR1 as their radiometric chronologies extended further back than 1950 anyway.

SCP dates were also of little use to WIMP1, albeit for different reasons. As described in Section 3.4.6, there appeared to have been a non-continuous sedimentation process between 30 and 40 cm, which occurred in about 1960, with the sediments beneath this point being much older than those above it. Such a pattern may suggest that the lake was dredged at this point, with the surface sediments at the time being removed to reveal the older sediment layers beneath. If this was the case then it would mean that the rapid increase in SCPs at a depth of 30 cm was not because of an increase in energy consumption in the 1950s, but rather from already high atmospheric concentrations being deposited directly on the old unpolluted sediments. Therefore the 1950 SCP date for this core could be misplaced.

Dates prior to the 1950 SCP date for VALE1 and the bottom radiometric dates for the other four cores could not be ascertained with any certainty. Each of the age-depth graphs for the five cores (Figures 3.15 to 3.21) did however decline fairly steadily with depth, and using the lake age as a reference point for the base of the core, in a relatively linear fashion. If it was assumed that the sediment accumulation rates in each core remained constant over time, then speculative dates could be assigned to the rest of the cores (apart from WIMP1). These dates would have to be treated with caution when interpreting patterns within the metals data, but they would at least act as a point of reference in the undated parts of the cores. Chronologies calculated using this method are shown in Figure 3.22. An extension of the HIGW1 chronology is also included, as is the full chronology for WAKE1.

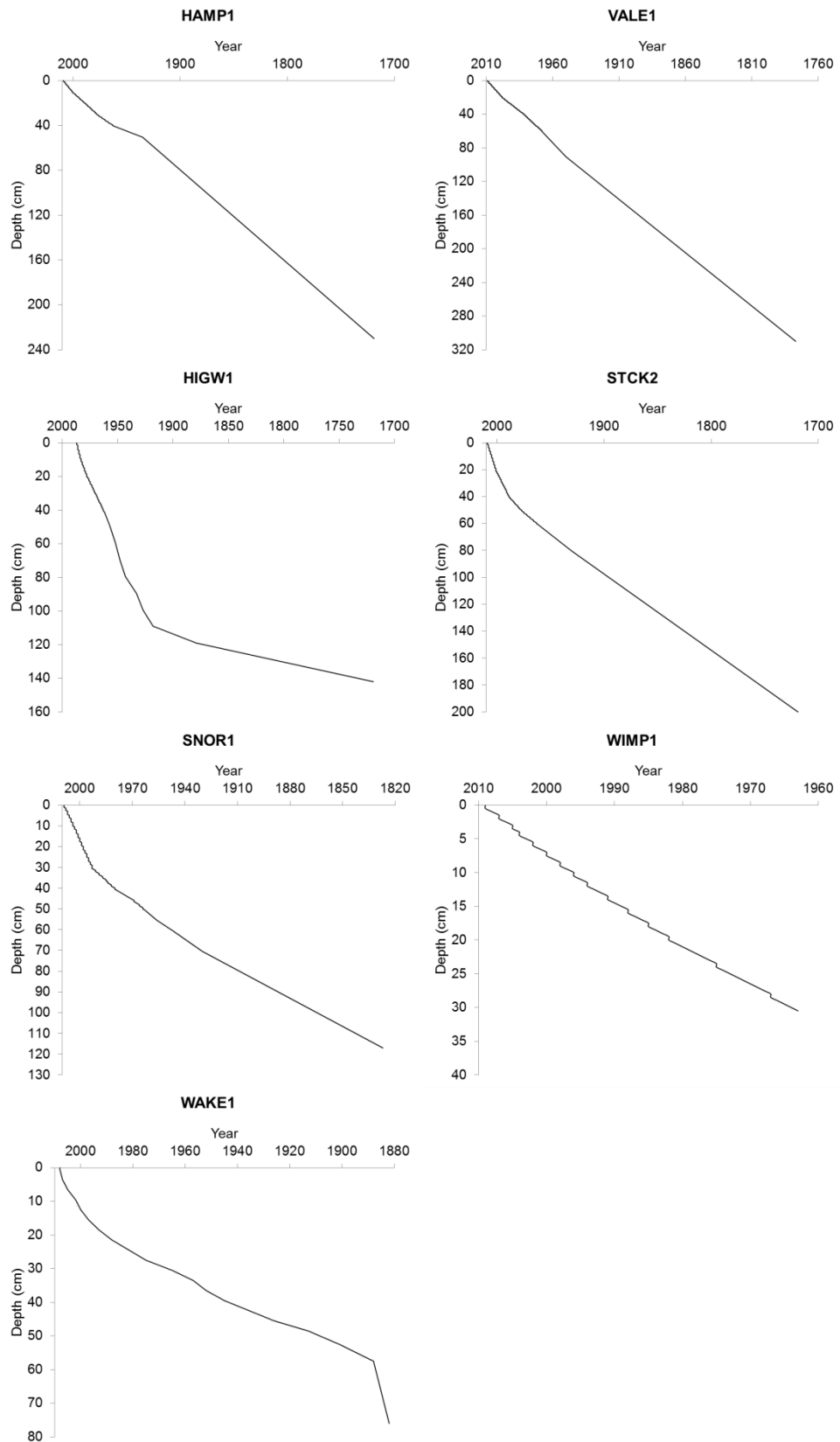


Figure 3.22 – Sediment core chronologies calculated from radiometric and SCP dating together with lake age, for the seven London lakes – Hampstead No. 1 Pond (HAMP1), Vale of Health Pond (VALE1), Highgate Ladies Bathing Pond (HIGW1), Stock Pond (STCK2), South Norwood Lake (SNOR1), Wimbledon Park Lake (WIMP1) and Wake Valley Pond (WAKE1)

The difficulty in establishing accurate chronologies for most of the cores in this study made interpretation of the sediment metals data much more complicated. Therefore, the dates that were determined using the methods described in this chapter needed to be used with care. For all of the cores except WAKE1 and WIMP1, the chronologies fell into two distinct parts – those that were calculated with some certainty and could be assumed to be fairly reliable, and those which were much more speculative. The last reliable date for VALE1 was 1950 (± 15), for HAMP1 was 1935 (± 15), for STCK2 and SNOR1 was 1930 (± 24 and ± 25 respectively), and for HIGW1 was 1879 (± 23). It was logical to split the interpretation of the cores into pre- and post-World War II parts – before 1945 and after 1945. This was also a useful way to analyse the data in terms of the Anthropocene (see Section 1.2), as one of the key stages in this period began at the end of WWII (Steffen et al, 2004). For HIGW1 some of the later dates were also reliable and this was taken into account when the metals data from this core was discussed. WIMP1 had to be treated a little differently because of the problems described earlier, although the more recent 40 years could be discussed with some certainty. WAKE1 could be split into pre- and post-war elements to provide a comparison with the data from the other cores, but it could also be studied as a whole.

3.5.3. Chronology formation in other urban lakes

The difficulty in formulating chronologies in urban lake sediments is not just restricted to the lakes in this study, but is reflected in the wide range of methods that have been used to date sediments in other urban areas. Two of the three methods used to formulate the chronologies in the London lakes – radiometric dating and lake age have been used individually to date sediments in other urban studies. The most comprehensive study of radiometric dating of urban lake sediments was carried out in North America by the US Geological Survey (Van Metre et al, 2004). Forty-seven of the 56 lakes studied were in or near one of 20 US cities. The primary age-dating tool used was ^{137}Cs , along with ^{210}Pb in a smaller number of the cores. The purpose of the study was to date relatively recent sediments (back to the 1960s). Therefore, in contrast to the present study the role of ^{137}Cs was as a depth marker, rather than to confirm the ^{210}Pb dating profile. The urban lakes had higher sedimentation rates than the non-urban sites. It was found that ^{210}Pb age-dating was less useful in high sedimentation rate lakes with developed watersheds. However, despite the poor results obtained from ^{210}Pb dating, the study concluded that the greater the mass accumulation rate of sediment, the more likely the age-dating would be successful. This was because a greater mass accumulation rate improved temporal resolution in core samples, and reduced the effects of postdepositional mixing and diagenesis. However, although the use of ^{137}Cs to date recent sediments was successful in the majority of cases, no attempt was made to date sediments over a longer period of time. The poor ^{210}Pb results suggest that this would have been difficult.

A number of other urban studies have relied on radiometric methods to date sediment cores. Another North American study by Durant et al (2004) used ^{210}Pb to date a sediment core from an urban pond in Massachusetts, but as with the Van Metre et al (2004) study the dating was only required to extend back a short period, to the late 1950s/early 1960s. The core extended back further than the dated levels, but it is not mentioned if the lower core samples were dated. Similarly, both ^{210}Pb and ^{137}Cs activities were used to date the sediments from three lakes in the lower Yangtze River basin, China (Yao et al, 2009). However, although the profiles appear to extend back further, they were only used to obtain sedimentation rates between the 1960s and the 2000s. In contrast, in a more recent paper by Van Metre (2012), atmospheric deposition of mercury to twelve lakes of varying ages near major urban areas was examined. Sediment cores from five of the lakes were successfully dated back to 1860 using the ^{210}Pb record. Similarly, radiometric dating was successfully used in a study of lead contamination in urban lakes in Shanghai, China, by Li et al (2012). Five sediment cores with depths from 24 to 34 cm were retrieved, and the age of the oldest sediments calculated from the ^{210}Pb excess activity profiles ranged from 90 to 125 years old. Sediment accumulation rates at these sites were less than $0.4 \text{ g cm}^{-2} \text{ yr}^{-1}$ throughout the length of the cores, which was not very different to the sedimentation rates calculated for the London cores. However, at these sites, the rate of accumulation did not affect the radiometric record. In one last example, radiometric methods were successfully used to date a sediment core from Lake Ballinger, near Seattle, Washington, USA, back to at least the late 17th century (Thapalia et al, 2010). These examples show that the use of radiometric dating varies widely between different urban sites, depending on the purpose of the research. The success of the dating method also varies, as the quality of the radioisotopic record is site specific. Therefore, the radiometric records obtained from the lakes in this study are not unusual.

The use of just lake age to date sediments is less common, but it has been done. Foster et al (1991) compared the levels of metal contamination and other types of pollution in two reservoirs in Coventry, UK – Wyken Slough and Swanswell Pool. The date that each reservoir was created was known (1850 and 1855 respectively) and was applied to the base of each sediment core. It was assumed that sediment accumulation rate had remained constant since that date, and a chronology was created for each lake accordingly. However, the inaccuracy in the chronology that is likely to occur from assuming a constant sedimentation rate means that this method is not widely used.

It is rare to use only one technique to date urban lake sediments. Although radiometric dating is the most widely used method, it is usually used in conjunction with one or more

additional techniques, as has been the case in the present study. SCPs are often used together with radiometric dating to formulate chronologies, as SCP profile features require confirmation from reliable dating techniques before the dates can be attributed to features in other cores from the same area (see Section 3.3). For example, the dates of features in the SCP concentration profile for the Men's Bathing Pond, Hampstead Heath were confirmed using radiometrically obtained dates (Rose, 1994b). A combination of radiometric and SCP dating was used by Tikkanen et al (1997) to formulate a chronology for a sediment core from a marine site in Helsinki, Finland. However, this was because radiometric dating proved problematic, as the ^{210}Pb activity profile was highly irregular due to rapid sedimentation and vertical migration of the nuclide. However, the SCP and ^{137}Cs profiles corroborated one another well and were used to obtain a chronology for the sediments.

Radiometric dating has been used together with lake age to form chronologies in a number of studies. In the study by Van Metre et al (2004) discussed before, although most of the sites were dated using radiometric dating alone, lake age was included as a base marker in cases when it was known and the bottom of the lake was reached within the core. In a subsequent study of Wyken Slough and Swanswell Pool in Coventry, UK (Charlesworth & Foster, 1999), the sediment chronology was resolved slightly more than it had been in Foster et al (1991) by using the first appearance of ^{137}Cs as a marker representing 1954. Sediment accumulation rate was split into two parts, the first between lake formation and 1954, and the second between 1954 and the present day. A constant rate of sediment accumulation was assumed within each of the two parts. Radiometric dating has also been used in conjunction with lake age at sites where, as with the London lakes in this study, the ^{210}Pb record has not been traceable all the way down the sediment profile. In order to reconstruct a history of air pollution in an urban area of north Cheshire and south Merseyside in the UK, Power & Worsley (2009) extrapolated the dates determined from radiometric analysis of sediments from four ponds, using their known ages as a guide. Chillerud et al (1999) analysed ^{210}Pb and ^{137}Cs activity in a core from Central Park Lake, New York City, USA, but found that the profile was disturbed due to dredging. The date at which the lake was dredged was known, so rather than using lake age to form a chronology, in this case the dredging date was applied to the depth at which the sediments were disturbed, and a chronology was formulated from this point.

Known dredging events were also used in a study by Mayer & Johnson (1994), together with historic records of steel production and radiometric dating to establish the chronology of a core from Hamilton Harbour, Lake Ontario, Canada. Dredging interrupted the radiometric record, but the time interval corresponding to dredged spoil layers (identified by visual inspection and from the bulk density data) was estimated from the unsupported ^{210}Pb

activities immediately above and below the spoils, allowing the chronology to be formed. Other studies have used combinations of radiometric dating, SCPs and varves (Meriläinen et al, 2003); radiometric dating, SCPs and magnetic analyses (Worsley et al, 2006); and radiometric dating and the relationship to visual laminations and elemental profiles in previously analysed cores (Rauch & Hemond, 2003).

The many different combinations of methods that have been used to date urban sediments reflect the complexity of the urban environment and the difficulty in obtaining good chronologies at these sites. The fact that chronologies in the London lake sediments were difficult to determine, and that pre-WWII dates were rather speculative, only reflects the difficulties that have been found at many other urban sites. Although radiometric dating is used in the majority of cases, the additional use of other methods shows the need for site specific interpretations of sediment chronologies in urban areas.

3.6. Conclusion

The aim of this chapter was to develop chronologies for the seven sediment cores taken from the London lakes. The sedimentation process at each of the London lakes played an important role in the quality of both the radiometric and SCP dating. Variation in the sediment accumulation rate caused by a number of factors including slumping events, focusing and mixing, and interruptions to the sediment record such as dredging, influenced both the radioisotope and SCP concentrations recorded in the sediment cores. For all sites apart from the Highgate Ladies Bathing Pond and Wake Valley Pond, the radiometric dating records did not extend back through the whole of the cores, and only at the Vale of Health Pond did the SCP record provide dates older than those calculated from the radiometric dating. However, despite the limitations of both dating methods, for the periods that dates could be ascertained there was good agreement between the dates provided by each method. Chronologies were formed using a combination of the two methods, together with the dates the lakes were constructed, which provided a baseline date for each core. Although the chronologies for Wake Valley Pond and Highgate Ladies Bathing Pond were quite robust, those for the Vale of Health Pond, Stock Pond, Hampstead No. 1 Pond, South Norwood Lake and Wimbledon Park Lake were comprised of reliable post-WWII dates and more speculative pre-WWII dates. However, by being aware of the shortcomings of the method used, the chronologies could be used as reasonable framework for the rest of the study. The difficulty in formulating chronologies in urban lake sediments was not just restricted to the lakes in this study, but was reflected in the wide range of methods that have been used to date sediments in other urban areas. Chronologies also tended to be short, although that may be partly due to the requirements of the research being carried out. The

chronologies constructed in this chapter will be used in the following chapters as a basis for the interpretation of metal concentration and other data analysed in the cores.

CHAPTER 4: THE SEDIMENTARY RECORD OF TRACE METAL POLLUTION IN LONDON LAKES

4.1. Introduction

As outlined in Section 1.5, there are a number of different sources of metals to lakes. These consist of a natural background component and anthropogenic inputs including point sources and atmospheric deposition. Run off and erosion from the catchment can also result in the transportation of both natural and previously deposited metals into lakes. The concentrations of metals in lake sediment cores provide an indication of both historical and contemporary levels of contamination. There are a number of aims to this chapter. The first is to identify metal concentrations in the sediments of London lakes and describe the temporal changes that occur, with reference to the chronologies constructed in Chapter 3. The concentrations of a number of metals and other elements within the sediments will be determined, and the 'anthropogenic' pollution component will be identified. Other factors that may influence metal concentrations in sediments such as organic matter and sediment accumulation rate will also be described. Temporal changes in metal concentrations will be related to sediment quality guideline values. The second aim is to explain any variation in metal concentrations within and between sediment cores and identify whether the changes in metal pollution across the city reflect a regional pattern or if they are more localised, to ascertain the importance of different pollution sources within the city. The influence of metal behaviour, metal sources and the individual lake catchments on metal concentrations at each of the sites will be examined with reference to previous studies and documented histories of each of the lakes. Simple correlations and principal components analysis will be used to compare the concentrations of metals at the different lakes in order to determine if there is a regional pattern of contamination across the Greater London area. The third and final aim of this chapter is to identify and explain trends and levels of metal contamination in recent sediments. Recent changes in metal pollution in the sediments will be compared to records of metal emissions and deposition in the UK and the levels of contamination found in the lakes in this study will be put into a wider context through comparison with metal concentrations found in other studies of both London and urban lakes worldwide.

4.2. Sediment coring methodology

Cores were taken from South Norwood Lake, Wimbledon Park Lake, Hampstead No. 1 Pond, Vale of Health Pond and Stock Pond between the 8th and 11th June 2009. The core from Wake Valley Pond had been taken previously, on the 10th November 2008. The Highgate Ladies Bathing Pond core was retrieved from the ECRC dried sediment archive, having originally been taken on the 15th October 1987, just prior to the dredging of the pond.

Two sediment cores were taken from each lake, apart from Hampstead No. 1 Pond, the Highgate Ladies Bathing Pond and Wake Valley Pond, from which only single cores were retrieved. All cores were taken as near as possible to the area within each of the lakes that contained the deepest sediment (see Section 2.2). The exact locations are listed in Table 4.1.

Lake name and core code	Date taken	Location	Water depth (m)	Length of core (m)
Highgate Ladies Bathing Pond				
HIGW1	15/10/87	TQ 277 870	unknown	1.42
Wake Valley Pond				
WAKE1	10/11/08	TQ 421 988	3.70	0.76
South Norwood Lake				
SNOR1	08/06/09	TQ 34038 69346	2.65	1.03
SNOR2	08/06/09	TQ 34035 69338	2.65	1.00
Wimbledon Park Lake				
WIMP1	09/06/09	TQ 24748 72357	1.50	1.43
WIMP2	09/06/09	TQ 24748 72357	1.50	1.41
Hampstead No. 1 Pond				
HAMP1	10/06/09	TQ 27274 85905	2.70	2.13
Stock Pond				
STCK1	10/06/09	TQ 27539 87131	1.40	1.54
STCK2	10/06/09	TQ 27539 87131	1.30	1.55
Vale of Health Pond				
VALE1	11/06/09	TQ 26602 86444	2.76	2.12
VALE2	11/06/09	TQ 26602 86444	2.75	1.95

Table 4.1 – Core information: dates, locations, water and sediment depths

Coring was carried out using a Livingstone-type piston corer (Livingstone, 1955) fitted with a Perspex tube with an internal diameter of 7.1 cm. Different length tubes were used depending on the amount of sediment to be taken, with a maximum length of 3 m. Table 4.1 provides additional information regarding the water depths and amount of sediment retrieved. All the cores were extruded vertically on site at 1 cm intervals using a stainless steel slicer, apart from STCK1 and STCK2 which were extruded back in the laboratory. HIGW1 was sliced into 1 cm intervals to a depth of 100 cm, after which it was sliced at every 2 cm. The samples had been oven dried before being placed in the archive. The rest of the core samples were stored in the dark in a cold store at 4°C when not in use.

4.3. Sediment core analysis

4.3.1. Lithostratigraphic analysis of sediments

A visual inspection was carried out following the extraction of the cores. During extrusion and subsampling any changes that occurred down the cores were noted, such as major differences in colour and sediment composition. Each of the cores was then subsampled for analysis of wet density, water content, organic content and carbonate content. In the case of HIGW1 from the Ladies Bathing Pond, all of these analyses (excluding carbonate content) had been carried out in November 1987 by the Geography Department at UCL.

The density and water content of lake sediments will vary depending upon the rate of sedimentation, the quality and character of the deposits and the degree of compaction and bioturbation. Variations in their profiles down a sediment core can indicate fluctuations in composition that might be attributed to changes in sediment source (Bengtsson & Enell, 1986). For wet density calculations, the cores were subsampled in proportion to their length. SNOR1 was subsampled every other centimetre to 10 cm, then every third until 50 cm and every fourth thereafter, plus at every 10 cm interval. WIMP1 and STCK2 were subsampled at every other centimetre to 15 cm, then every third until 70 cm for the former and every third until 75 cm for the latter, then both every fourth centimetre thereafter, plus at every 10 cm interval. HAMP1 and VALE1 were subsampled at every other centimetre to 20 cm, every third until 100 cm, and every fourth thereafter, plus at every 10 cm interval. WAKE1 was subsampled every second centimetre to 10 cm and then every third until 50 cm. Finally, HIGW1 was subsampled every centimetre to 10 cm, then every second until 40 cm and every fourth thereafter. All of the cores were subsampled at every centimetre interval for water content, apart from HIGW1 which was sampled every centimetre to 10 cm and then every second centimetre thereafter. Wet sediment density was calculated by measuring the mass of a known volume (2 cm^3) of sediment from core samples. Water content was measured by weighing samples of wet sediment into crucibles, heating at 105°C for 24 hours, leaving the samples to cool in a dessicator and then reweighing them. The loss in mass from the samples was then calculated. This was a standard procedure which followed that of Bengtsson & Enell (1986).

The organic matter content of lake sediments can be both allochthonous and autochthonous in origin (Meyers & Teranes, 2002). The carbonate content in the sample is caused by allogenic, endogenic and authigenic minerals (Bengtsson & Enell, 1986). Therefore, organic and carbonate content of aquatic sediments provides useful information about recent depositional changes and contemporary biogeochemical processes within the sediments (Heiri et al, 2001). Loss-on-ignition is usually used as a measure of organic content and can

also be used to estimate the carbonate content. All of the cores were subsampled at every centimetre interval for organic and carbonate content, apart from HIGW1 which had been sampled every centimetre to 10 cm and then every second centimetre thereafter. Organic content was assessed by combusting a known mass of dried sediment at 550°C in a muffle furnace for a period of 2 hours, leaving to cool in a dessicator, and then reweighing. The amount of organic matter is expressed as a percentage of the dried sediment. Carbonate content was derived by heating the sediment at 950°C for a further 2 hours, cooling in a dessicator and then reweighing. This provides an estimate of how much CO₂ has been lost due to the decomposition of carbonates. The weight loss was multiplied by a conversion factor of 1.36 to obtain the carbonate content (Bengtsson & Enell, 1986).

4.3.2. Analysis of sediments for trace metals using X-ray fluorescence

X-ray fluorescence spectroscopy (XRF) is a non-destructive technique that is used to determine total elemental concentrations in a variety of materials. A large number of elements can be analysed simultaneously, including Ni, Cu, Zn, As and Pb. For this reason it was proposed that it be used for the analysis of the lake sediments in this project. However, the use of XRF in the analysis of lake sediments is not widespread, and the sample preparation methods vary. It was decided that an initial study should be undertaken to compare a number of methods in order to determine which was the most appropriate.

4.3.2.1. Background to X-ray fluorescence

The theory behind XRF is relatively simple. When an atom absorbs a photon of energy, an electron is ejected. An electron from a higher energy level orbital within the atom will then be transferred to the lower energy level from which the electron was lost. During the transition, a photon may be emitted (or fluoresced). The energy of the emitted photon will always be the same between two specific orbitals in a given element, and by determining the wavelength of the photon, the element can be identified. By counting the number of photons that are detected for that element's characteristic energy over a set amount of time, the concentration of the element in question can also be determined.

An early paper by Giauque et al, published in 1977, used energy dispersive X-ray fluorescence to determine twenty six trace metals and two major elements in geochemical specimens. The paper was largely concerned with refining the specifications used in the XRF process in order to make the technique more accurate, with respect to spectrum background concentrations, overlapping x-ray background and standardisation of calibration methods. In the last ten years, however, the focus of investigation has largely shifted to the

different materials to which XRF can be applied. A review of the developments in X-ray fluorescence spectrometry since 2003 (Hill et al, 2003; Potts et al, 2005) has shown it has found many uses in the analyses of water, air, soil, plants, geology and other environmental materials, not to mention a wide variety of industrial, biological, clinical and archaeological settings.

The use of XRF with specific reference to lake sediments has been a little more limited, although it is becoming a more popular method of analysis due to the speed and accuracy of the technique and its non-destructive nature. Boyle (2000) reviewed the use of XRF in lake sediment analysis. In his study, the application of an isotope source XRF method to the multi-element analysis of lake sediments was evaluated by testing the instrument on reference samples of known composition and a lake core previously analysed by atomic absorption spectroscopy (AAS). In the lake core, similar stratigraphic patterns were apparent for both methods, with R^2 values in the range of 0.73 and 0.91. The results from the reference materials were also sufficiently accurate to conclude that XRF was a suitable technique for the analysis of lake sediments. Since then, a number of studies have been carried out on lake sediments using X-ray fluorescence, either solely or in combination with other analytical techniques. These studies have tended to focus on the relative impacts of anthropogenic and natural sources of metals to lakes (e.g. Makundi, 2001; Boyle et al, 2004; Durant et al, 2004; Yang & Rose, 2005).

There are no standard preparation methods for samples that are to be analysed by XRF – they vary from study to study. Samples are usually dried before analysis, although the way in which this is done varies. In some studies the sediment is oven dried, but at an array of different temperatures e.g. 45°C for 48 hours (Makundi, 2001), 60°C (Osan, 2002), 80°C for ≤ 5 days (Durant et al, 2004), 105°C (Trounova et al, 1996). In a study by Yang et al (2002) the sediments were freeze dried and in an investigation by Bichlmeier et al (2002) the samples were dry to begin with. Kido et al (2006) used XRF on wet samples, although this is unusual. The weights of material used for samples and the form in which they are analysed also vary. In most cases, the dried samples are ground to a fine powder and pressed into a tablet with another material which binds the sediment together. The amount of sediment used changes between experiments, from a maximum of 4g (Durant et al, 2004) down to 0.036g (Trounova et al, 1996). In the study by Boyle (2000), 1-2g of disaggregated sediment was used per sample, but it was placed loose in a sample tube rather than compacted into a tablet. Given this variation there was a need to establish a standard methodology to be applied to the sediment samples in this study.

4.3.2.2. Initial study of X-ray fluorescence – methods

The aim of this study was to determine the sample preparation method that would give optimum results. This would be assessed through the comparison of different drying methods, the level of sample disaggregation and sample size. The lake sediment used in this study was taken from Fleet Pond in Fleet, Hampshire (SU 8199 5517), which is one of the OPAL sites (see Section 1.9). Sediment was taken from the centre of the lake using a Glew gravity corer (Glew, 1991) fitted with a Perspex tube. The core was mixed thoroughly after extraction to homogenise the material before analysis. The sediment was stored in the dark in a cold store at 4°C between collection and preparation of the samples.

The sediments were first dried in three ways:

- 1) 400 g of sediment was freeze dried over 3 days.
- 2) 400 g of sediment was placed in a dessicator to air dry. After six weeks, the sediment had still not dried out completely, so it was transferred to a drying cabinet (at 40°C) for one further day.
- 3) 400 g of sediment was dried in an oven at 105°C overnight.

The dried sediments were then prepared for analysis. Four methods were chosen:

- 1) No preparation – dried sediment weighed directly into XRF sample cuvettes. The cuvettes were formed by a polyethylene cylinder on one side of which a thin polypropylene X-ray film was held in place with a polyethylene ring.
- 2) Partially disaggregated - sediment disaggregated with a pestle and mortar, over a time period of 1 minute, and then weighed into sample cuvettes.
- 3) Finely powdered - sediment disaggregated with a pestle and mortar until finely powdered, and then weighed into sample cuvettes.
- 4) Powder pellets - sediment disaggregated with a pestle and mortar until finely powdered, weighed out with 0.9 g Licowax C Micropowder PM (Hoechstwax), homogenised and compressed at a pressure of ~10t to form a tablet of 32 mm diameter.

For each preparation method, samples of 1 g, 2 g and 3 g were measured out, and each was replicated 3 times. This was done in order to be able to compare the variations in results from samples of different sizes. Subsequently, freeze dried, finely powdered sediment was also analysed at masses of 0.10 g, 0.15 g, 0.20 g, 0.25 g, 0.50 g and 0.75 g,

each replicated 3 times. Once the optimum sample size was chosen, 20 replicates of that mass were run to determine the precision of the technique.

The samples were analysed for metals content using a Spectro X-Lab 2000 energy dispersive X-ray fluorescence spectrometer (ED-XRF) with a Si(Li) semiconductor detector. Calibration of the spectrometer was done using an MCA (multi channel analyzer) calibration disc. Standard reference materials (JLK: sedimentary rock; SSP: soil; BRS: Buffalo river sediment) were analysed regularly during sample analyses to assess the accuracy of the analytical method. Recovery ranged between 95.4% and 120% for Ni, Cu, Zn, As and Pb (Table 4.2).

	Ni	Cu	Zn	As	Pb
JLK					
Certified value	35	62.9	152	26.8	43.7
Measured value	34.8	66.9	150.8	29.5	49.0
SD	2.6	1.1	4.0	0.4	1.7
Recovery (%)	99.4	106.4	99.2	110.0	112.1
SSP					
Certified value	37.4	30.9	119	14	41.3
Measured value	37.5	34.9	121.9	16.8	45.1
SD	2.4	1.7	1.1	0.7	1.0
Recovery (%)	100.3	112.9	102.4	120.0	109.1
BRS					
Certified value	42.9	Not listed	408	17	150
Measured value	42.5		401.3	16.2	152.9
SD	1.8		5.5	0.8	4.2
Recovery (%)	99.0		98.3	95.4	102.0

Table 4.2 – Recovery of standard reference materials (n = 4)

4.3.2.3. Initial study of X-ray fluorescence – results

The results for five elements, Ni, Cu, Zn, As and Pb were examined. Figure 4.1 compares the results from the different drying methods. Overall, there was very little to distinguish between the effects of drying the samples in different ways. The range of concentrations for each type of sample (freeze dried, oven dried, air dried) were similar and all overlapped. Oven drying the samples resulted in slightly lower concentrations than either of the other two methods. There was very little difference between the concentrations of the freeze dried and air dried samples. Standard deviations for the oven dried samples (see Table 4.3) were higher than those for the freeze and air dried samples. The smallest deviations were for the freeze dried samples.

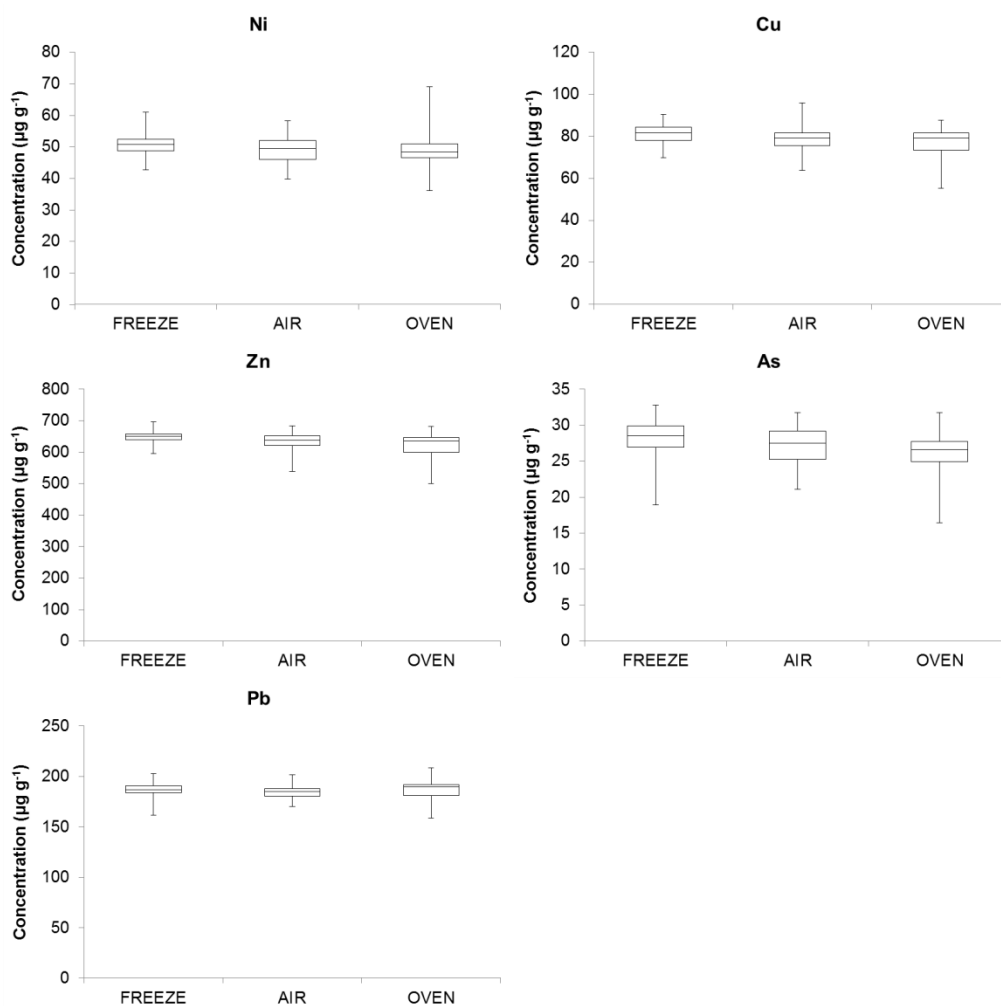


Figure 4.1 – Box and whisker plots showing the median, 1st and 3rd quartiles and range of the metal concentration data from each of the different drying methods; freeze, air and oven drying

		Ni	Cu	Zn	As	Pb
Drying methods	Freeze	3.77	4.70	19.68	2.85	7.23
	Oven	5.51	7.36	43.00	3.27	11.94
	Air	4.65	5.62	29.21	2.89	7.07
Preparation methods	No prep	4.54	5.44	41.13	2.49	7.64
	Part disagg	2.47	2.97	12.24	2.06	3.07
	Fine powder	3.19	3.56	9.74	1.82	2.84
	Pellet	6.83	8.93	39.61	4.07	12.58
Weights	1 g	4.31	5.11	30.56	3.07	8.69
	2 g	5.57	5.80	36.94	3.66	9.22
	3 g	4.40	6.98	33.98	2.42	9.10

Table 4.3 – Standard deviations of drying methods, preparation methods and weights for Ni, Cu, Zn, As and Pb

The results from using different preparation methods are outlined in Figure 4.2. Metal concentrations increased as the preparation methods changed from no preparation, to partial disaggregation to fully powdered. The range of concentrations was also much smaller for the partially disaggregated and powdered samples than for the samples that had no preparation. The results for the samples which were made into pellets had a much wider range than any of the other preparation methods, which encompassed the ranges of concentration determined from all of the other methods. In all cases apart from Zn, the samples that were compressed into pellets had higher standard deviations than any of the other methods (Table 4.3). The samples that had been partially disaggregated or powdered showed the smallest deviations for all the metals.

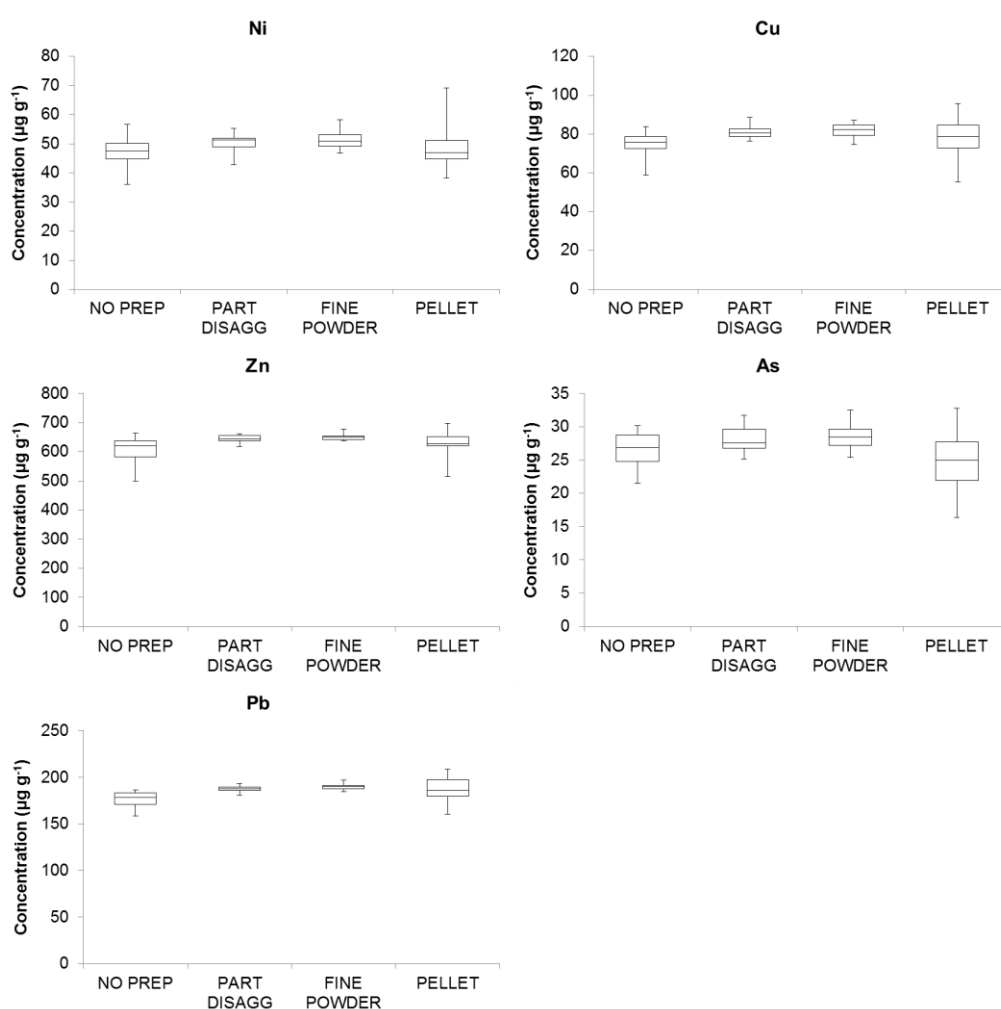


Figure 4.2 – Box and whisker plots showing the median, 1st and 3rd quartiles and range of the metal concentration data from each of the different preparation methods; no preparation, partial disaggregation, finely powdered and powder pellets

The results for samples of different weights are shown in Figure 4.3. There was very little difference between the mean concentrations determined using different sample masses, and

also little difference in the range of concentrations. The standard deviations for the different weights also reflected the similarity between the results, as there were no obvious trends in the data (Table 4.3).

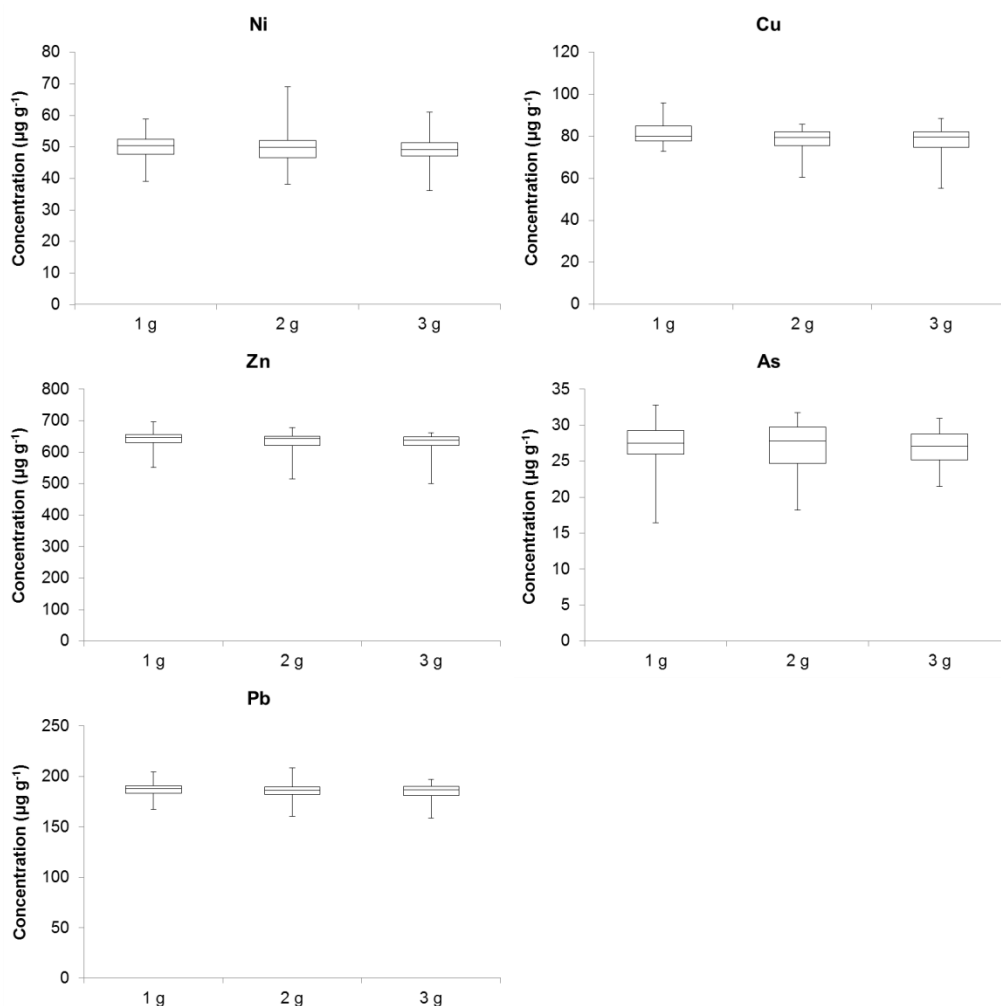


Figure 4.3 – Box and whisker plots showing the median, 1st and 3rd quartiles and range of the metal concentration data from each of the different sample masses used; 1 g, 2 g and 3 g

4.3.2.4. Initial study of X-ray fluorescence – discussion

The slightly lower concentrations that were found for the oven dried samples may be because the metals started to evaporate, due to their volatility at 105°C. Therefore concentrations would be lower in comparison to the freeze or air dried samples. The potential loss of metal recovery due to evaporation meant that oven drying was not a suitable method to use. The results from freeze and air dried samples were more similar to one another as both were dried at low enough temperatures to avoid any evaporation. Of the freeze and air dried samples, the former had the lowest standard deviations, which showed

that method was the more precise of the two. Freeze drying was therefore chosen as the optimum drying method for sediment samples for XRF analysis. Other practical considerations were also taken into account. Air drying was extremely slow, and therefore not a realistic option. Oven drying and freeze drying were both quicker. However, the process of freeze drying breaks up the sediment anyway, which makes disaggregating it much easier.

The increase in concentration from samples which had not been prepared at all to those which were completely powdered may be a consequence of the increase in surface area that occurred due to the grinding up of the samples. The more surface area available to the x-rays in the spectrometer, the more accurate the results. The low standard deviations calculated for the partially disaggregated and finely powdered samples reflected the greater precision of results found using these methods. Surprisingly, the most common method for preparing XRF samples, combining sediment with another material to bind into a tablet, gave the biggest range of results and the highest standard deviations, meaning that the method was the least precise of the four. This might be due to the addition of another substance which diluted the signal, or perhaps to the sediment having a smaller surface area in comparison with the more disaggregated samples. Finely powdering the samples was chosen as the optimum preparation method for sediment samples for XRF analysis, as the results gave the highest concentrations, and it was also easier to ensure that the samples would be ground to an even consistency if they were fully powdered, rather than only partially disaggregated. Powdering the sediments but not combining them with wax to make pellets also meant that the samples could be reused for other types of analysis, which is important in cases where only small amounts of sediment are available.

The similarity in the sample mass concentration data showed that 1 g, 2 g, or 3 g of sediment could be used for analysis, with no noticeable difference between the results. Given that the quantity of sediment available for analysis is often quite small, further analysis of smaller sample sizes was carried out on freeze dried, finely powdered sediment to find the smallest sample mass that still provided accurate and precise results. The results are shown in Figure 4.4. They showed that in general, at sample masses of < 0.75 g, metal concentrations began to decline or became more variable, and that the range of concentrations increased. For this reason, 0.75 g of sediment was chosen as the optimum mass to use in this project.

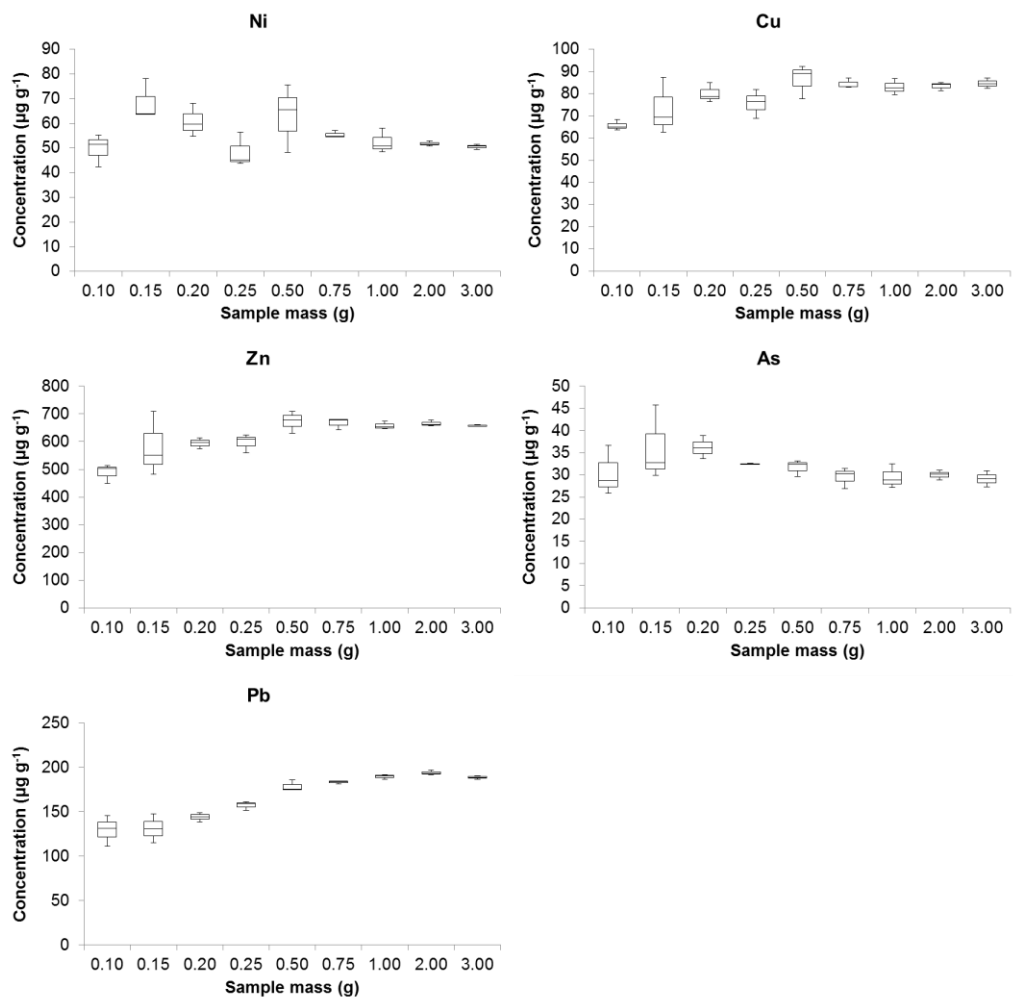


Figure 4.4 – Box and whisker plots showing the median, 1st and 3rd quartiles and range of the metal concentration data from a range of sample masses; 0.10 g, 0.15 g, 0.20 g, 0.25 g, 0.50 g, 0.75 g, 1 g, 2 g and 3 g

4.3.2.5. Chosen X-ray fluorescence methods

HIGW1 and WAKE1 were subsampled as for LOI (see section 4.3.1). The other five cores were subsampled at every centimetre interval for the top 10% of slices calculated from each core length, and then at every two centimetres for the rest of each core. This sampling technique was chosen to obtain a higher resolution of data for the more recent sediments because of the likelihood they would have been subjected to post-depositional changes in concentration. Because of the different core lengths, this was done as a percentage to make sure a similar proportion of each core was analysed at a higher resolution.

Based on the results of the initial study outlined in Sections 4.3.2.2 to 4.3.2.4, a preparation method was chosen for the lake sediments to be analysed by XRF in this study. Samples were freeze dried (apart from HIGW1 which had already been oven dried in 1987) and then

disaggregated until finely powdered. Approximately 0.75 g of each sample was weighed out into XRF sample cuvettes and then analysed as described in Section 4.3.2.2.

4.3.3. Analysis of VALE1 and WAKE1 for Hg

The cores from the Vale of Health Pond and Wake Valley Pond were also analysed for Hg concentrations. For the Vale of Health Pond, this was necessary because Hg had also been analysed in other components of the ecosystem (water, deposition, biota) as part of the investigation into contemporary levels of metal contamination (Chapter 5). Mercury was analysed in the sediments of Wake Valley Pond as part of the wider study into metal contamination at all of the OPAL lakes (Section 1.9). XRF could not be used to determine Hg in sediments because the metal is ordinarily found in very low concentrations which are below the detection limit of the XRF method. The method used to analyse Hg is described in the following paragraphs. However, more detail can be found in Section 5.3.2.

All laboratory equipment used in the preparation of the samples was cleaned prior to use by soaking in a 5% Decon 90 solution for 24 hours, followed by multiple rinses with deionised water and a further 24 hour soak in a 2 % HNO₃ solution bath. The equipment was then rinsed extensively with deionised water again and left in a static air drying cabinet. Subsamples were taken from each of the cores. Samples from VALE1 were taken at centimetre intervals for the top 20 cm, and then at every other centimetre until the bottom of the core. WAKE1 was subsampled at 3 cm intervals down the length of the core.

The samples were freeze dried and then disaggregated and homogenised with a pestle and mortar until finely powdered. Approximately 0.2 g of each sample was weighed into Teflon beakers and 8 ml of an *aqua regia* solution (1:3 conc. HNO₃:HCl) was added. The beakers were then heated on a hotplate at 100°C for 2-3 hours until the samples reached near dryness. The samples were removed from the hotplate and deionised water was added. Then they were left to cool and any undigested material was able to settle out. The digested sediment solutions were decanted directly into sterile polystyrene containers and topped up to 40 ml with deionised water and any remaining undissolved sample was discarded. Samples of reference sediment (Stream Sediment NCS DC 73374) and blanks were digested in the same way with each batch of samples.

The samples were analysed using a PS Analytical Millennium Merlin 1631 atomic fluorescence spectrometer. Internally, extracts are first diluted and subjected to a tin (II)

chloride reduction, which converts Hg (II) into Hg (0) vapour, before the Hg concentrations are detected. The linear dynamic range of the method is approximately 1 ng L^{-1} to $100 \text{ } \mu\text{g L}^{-1}$. The instrumental detection limit varies depending on the selected operating conditions and calibration range. In this instance, the analyser was calibrated to standards of 0, 10, 20 and 40 ng mL^{-1} .

4.4. Results

4.4.1. Hampstead No. 1 Pond

Wet density and dry weight decreased between the 1750s and the 2000s, the former from 1.5 g cm^{-3} to 1.0 g cm^{-3} and the latter from nearly 60% to approximately 10% (Figure 4.5). Both dropped sharply at the base of the core, and were very low in the mid-18th century. Organic matter and carbonate content increased from the base of the core to the surface (Figure 4.5). Organic matter rose fairly steadily from 6% to 17%. There was a period of increased organic matter in the mid to late 18th century, when content reached 10%, and a steady increase from the mid 19th century to the surface. Carbonate content rose from 2% at the base of the core to 7% at the surface. There was a short period of increased carbonate content in the mid 18th century, followed by a longer period between the late 18th and mid-19th centuries. There was also a sharp peak in approximately 1940, when carbonate content reached 8%. The profiles of Al, Si and Ti were all very similar (Figure 4.5), declining very slightly from the bottom of the core to the surface. The concentration of Zr declined sharply at the bottom of the core, the same as in the wet density and dry weight profiles, and then remained fairly steady over the rest of the core.

The metal profiles for Hampstead No. 1 Pond differed quite widely, with each of the metals increasing, peaking and declining at slightly different times (Figure 4.5). Nickel concentrations remained fairly stable with only minor fluctuations. There was a very slight increase from a value of about $55 \text{ } \mu\text{g g}^{-1}$ at the base of the core to a small peak of $75 \text{ } \mu\text{g g}^{-1}$ in the late 1960s, after which the concentration declined to $60 \text{ } \mu\text{g g}^{-1}$ at the surface. The concentration of Cu increased overall from $30 \text{ } \mu\text{g g}^{-1}$ at the base to $90 \text{ } \mu\text{g g}^{-1}$ at the surface. There were two small peaks in the mid to late 18th century, but the concentration started to increase more steadily from the mid-19th century. There was a rapid increase in the late 19th century with the concentration peaking at $130 \text{ } \mu\text{g g}^{-1}$ in about 1900. The concentration declined over the course of the 20th century, apart from a short increase in the 1970s. The Pb concentration increased overall from $70 \text{ } \mu\text{g g}^{-1}$ at the base of the core to $400 \text{ } \mu\text{g g}^{-1}$ at the surface. As with Cu, two small peaks in concentration occurred in the mid to late 18th century. The concentration then increased steadily from the early 19th century to a peak in the early 1900s. There was a slight decline through the 1920s, followed by another increase

to a peak of 640 $\mu\text{g g}^{-1}$ in the early 1970s. The concentration of Zn started to increase steadily from the mid-19th century (the same as for Cu) coming to a broad peak between the 1940s and the 1970s. The highest recorded Zn concentration was 650 $\mu\text{g g}^{-1}$ found in the late 1940s. From the 1970s, the concentration declined to 400 $\mu\text{g g}^{-1}$ at the surface. As with Cu and Pb, there were also two peaks in the concentration of As in the mid to late 18th century. Relative to the As concentrations found in the rest of the core, one of the peaks was actually quite large, reaching 35 $\mu\text{g g}^{-1}$. As with Cu and Zn, the concentration increased more sharply from the mid-19th century, peaking at 42 $\mu\text{g g}^{-1}$ in the early 1900s, before declining to about 20 $\mu\text{g g}^{-1}$ at the surface.

The Pearson product-moment correlations for HAMP1 are shown in Table 4.4. All of the correlations between all of the metals were significant. However, the most positive correlations were between Cu, Zn and Pb. The correlations between Ni and As and the other metals were all slightly lower, and the Ni/As correlation had the lowest value of all.

HAMP1	Ni	Cu	Zn	As	Pb
Ni	1				
Cu	.655	1			
Zn	.717	.950	1		
As	.486	.642	.523	1	
Pb	.610	.943	.911	.572	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Table 4.4 – Pearson product-moment correlations between the metals in HAMP1

Sediment accumulation rate (Figure 4.5) increased from 0.10 $\text{g cm}^{-2} \text{yr}^{-1}$ in the 1940s to approximately 0.17 $\text{g cm}^{-2} \text{yr}^{-1}$ in the mid-1990s. It then declined slightly before increasing to 0.18 $\text{g cm}^{-2} \text{yr}^{-1}$ at the surface of the core. The metal flux profiles were all very similar (Figure 4.5). Flux of all the metals increased from the 1940s to the early 1960s. Nickel and Cu flux remained constant from the 1960s to the surface of the core, with the former fluctuating between 9 and 11 $\mu\text{g cm}^{-2} \text{yr}^{-1}$ and the latter between 14 and 16 $\mu\text{g cm}^{-2} \text{yr}^{-1}$. Zinc flux remained level until the 1970s after which it declined slightly to 70 $\mu\text{g cm}^{-2} \text{yr}^{-1}$ at the surface of the core. Arsenic flux remained at approximately 4 $\mu\text{g cm}^{-2} \text{yr}^{-1}$ until the late 1990s, after which it declined slightly. Lead flux also showed the same pattern, remaining level until the mid-1990s before declining to 70 $\mu\text{g cm}^{-2} \text{yr}^{-1}$ at the surface. Comparison of the SAR and metal flux profiles showed that the increase in flux between the 1940s and 1960s was driven by the large rise in accumulation that occurred during the same period, rather than by metal concentration.

The steady overall decline in wet density and dry weight from the bottom of the core to the surface showed that sediment composition had not changed much over the last 250 years. This was reflected by the Al, Si, Ti and Zr profiles which showed that input of inorganic material from the catchment had also been fairly consistent. The sharp drop in wet density, dry weight and Zr at the base indicated that the bottom of the lake had been reached within the core. The increase in carbonate content in the early 19th century and the mid-20th century corresponded to periods of lower concentration in the Cu and Pb profiles. A greater influx of carbonate to a lake from increased erosion in the catchment can result in the dilution of metal concentrations (Koinig et al, 2003).

Although the composition of the sediments have not changed very much overall, there was a short period in the mid to late 18th century when there was a change, possibly related to the increase in organic matter and carbonate that occurred at the same time. The increase in concentration of Cu, As and Pb during the same period could have been due to a higher affinity of those metals to organic matter, or an actual increase in the amount of anthropogenic enrichment. The same applies to the mid-19th century onwards, when organic matter increased alongside the concentrations of the metals.

Normalising the metal concentrations to organic matter (Figure 4.6) resulted in a big change to the profile of Ni. Rather than increasing over much of the core, the normalised profile decreased in concentration from the bottom of the core to the surface. Two troughs also appeared in the mid to late 18th century, which showed that the increase in organic matter during that period was related to higher Ni concentrations in the original profile. The other profiles did not change to nearly the same extent. In the Cu profile, the two peaks in the mid to late 18th century were no longer discernible, which showed that they were related to organic matter. The concentration also declined more steeply over the 20th century in the normalised profile, again an effect of the increase in organic matter during this period. The Zn, As and Pb profiles did not change very much when normalised, and unlike Cu, the peaks of As and Pb in the mid to late 18th century were still evident in the adjusted profiles. This suggests that As and Pb do not show the same affinity for organic matter as Ni and Cu.

Although the concentrations of Ni and Cu were related to the amount of organic matter in the lake, organic matter was not the main reason for the changes in metal concentrations within the core. Calculation of enrichment factors (Figure 4.6) showed that metal enrichment occurred over the entire length of the core, which meant that the lake had been contaminated by anthropogenic sources of metals for at least the last 250 years. In general,

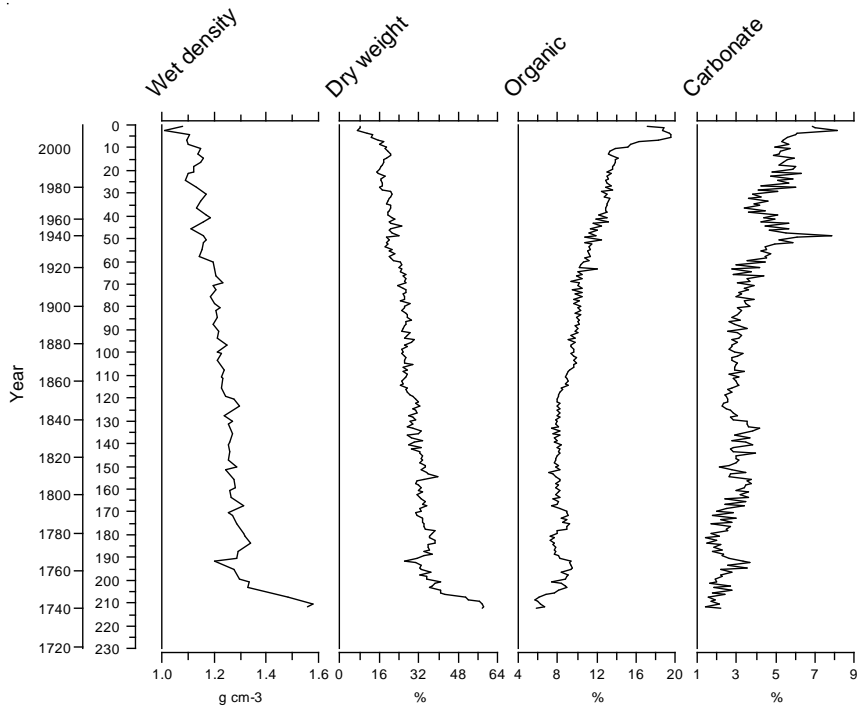
the enrichment profiles were similar to the concentration profiles (Figures 4.5 and 4.6), and in particular the profiles of Pb and As changed very little. However, Ni enrichment steadily increased from the mid-18th century to the surface of the core and the enrichment of Cu and Zn remained steady in the top 30 cm of the core, which was a noticeable contrast to the decline that occurred in the concentration profiles.

Even though the whole core was found to be anthropogenically enriched in metals, the concentrations have not necessarily exceeded SQGs the whole time. However, Ni, Cu, As and Pb have exceeded TECs over the entire length of the core, and Zn rose above the threshold concentration in the early 19th century. In 2009, the concentrations of all of the metals were higher than the TEC (Table 4.5). The relationship between each metal and the PEC varies more. The concentration of Ni exceeded the PEC over the entire length of the core, reaching a maximum in the late 1960s when the concentration was 50% higher than the PEC. Currently, the concentration of Ni exceeds the PEC by 20%. The PEC of Zn was exceeded between the early 1900s and the late 1990s, by a maximum of 40% in the late 1940s, although the concentration had fallen to slightly less than the PEC at the top of the core. The As concentration exceeded the PEC at various points between the late 19th century and the 1950s, although it declined to below the PEC over the last 60 years. The concentration of Pb exceeded the PEC for the whole core apart from at the very bottom and a short period in the early 19th century. The greatest exceedance occurred in the early 1970s when the concentration of Pb was 400% higher than the PEC, but this had dropped to 220% by the surface of the core. In contrast to the other metals, the concentration of Cu has never exceeded the PEC (Table 4.5).

HAMP1	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	2009	Maximum	2009
Ni	230	160	50	20
Cu	300	180	No exceedance	No exceedance
Zn	440	230	40	No exceedance
As	330	100	30	No exceedance
Pb	1690	1040	400	220

Table 4.5 – Percentages by which metal concentrations exceed TECs and PECs at Hampstead No. 1 Pond. The table includes both the maximum exceedance and the exceedance when the core was taken (2009).

a)



b)

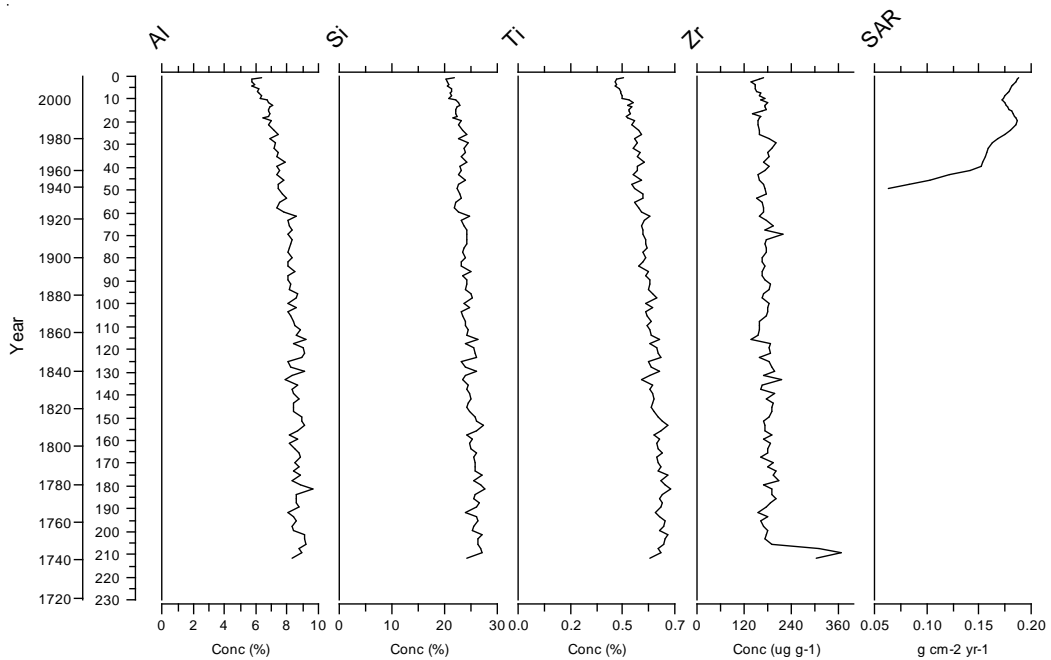


Figure 4.5 – Sediment core profiles from Hampstead No. 1 Pond showing a) lithostratigraphic data – wet density, dry weight, organic matter and carbonate content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth). The short SAR profile reflects the radiometric dating record from the core (see Chapter 3), which was used to calculate SAR.

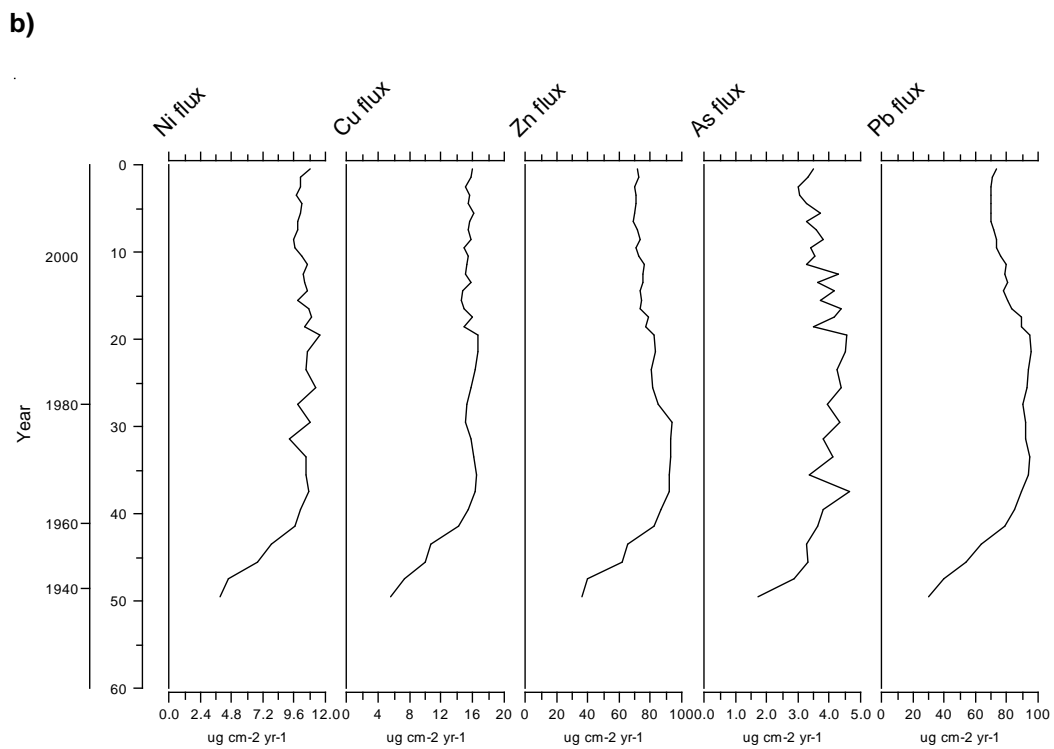
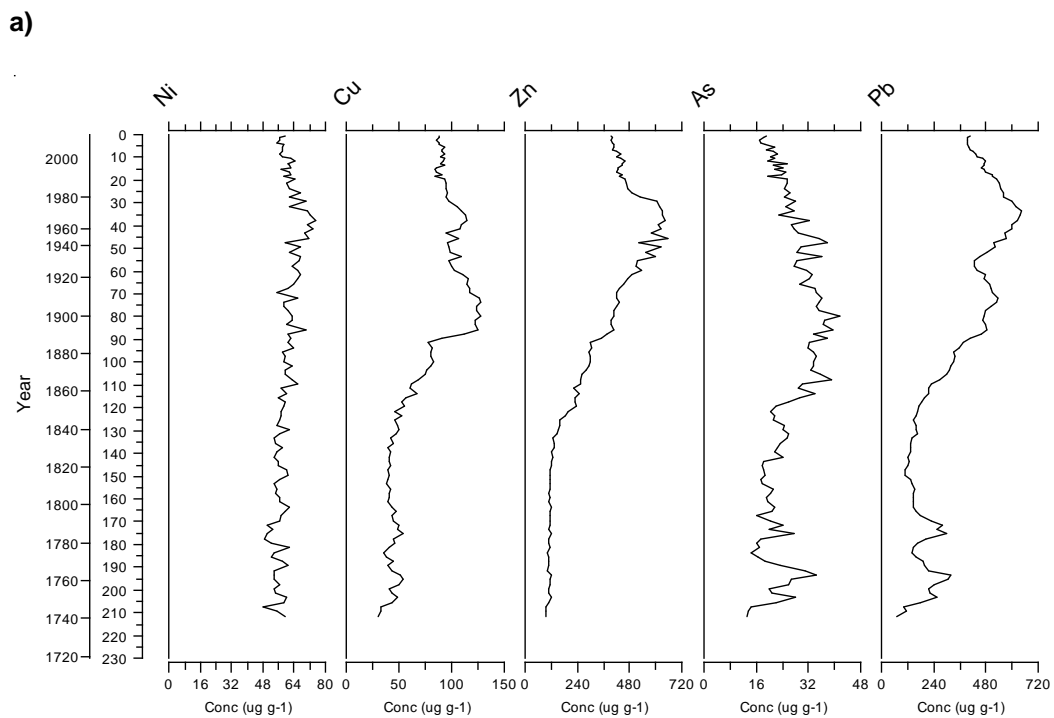
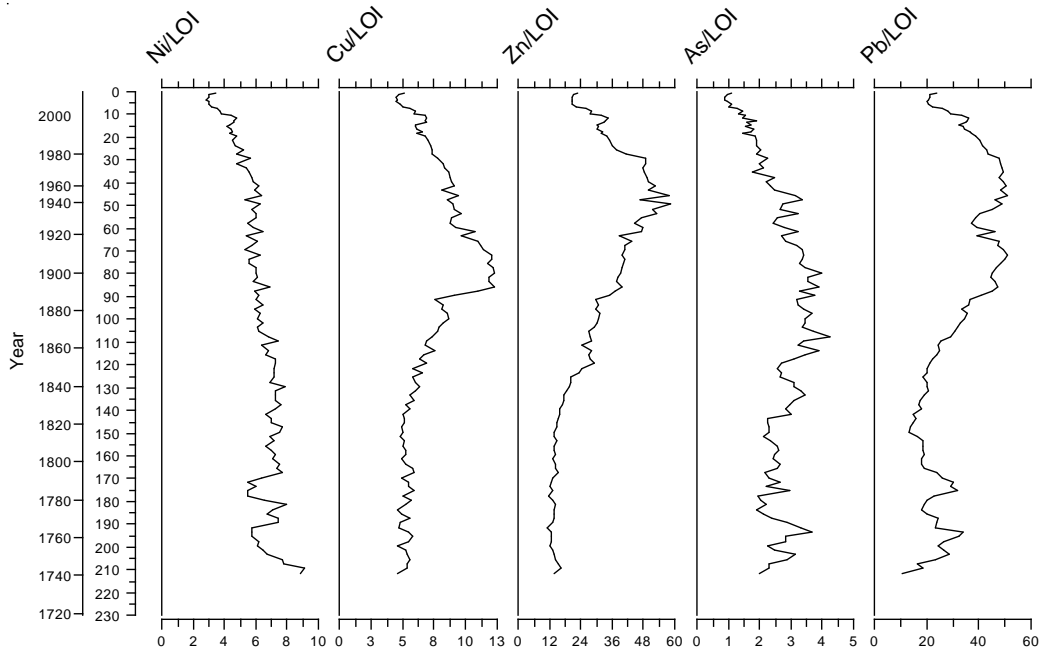


Figure 4.6 – Sediment core profiles from Hampstead No. 1 Pond showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth). The short flux profiles reflect the radiometric dating record from the core (see Chapter 3), which was used to calculate sediment accumulation rate and hence flux.

a)



b)

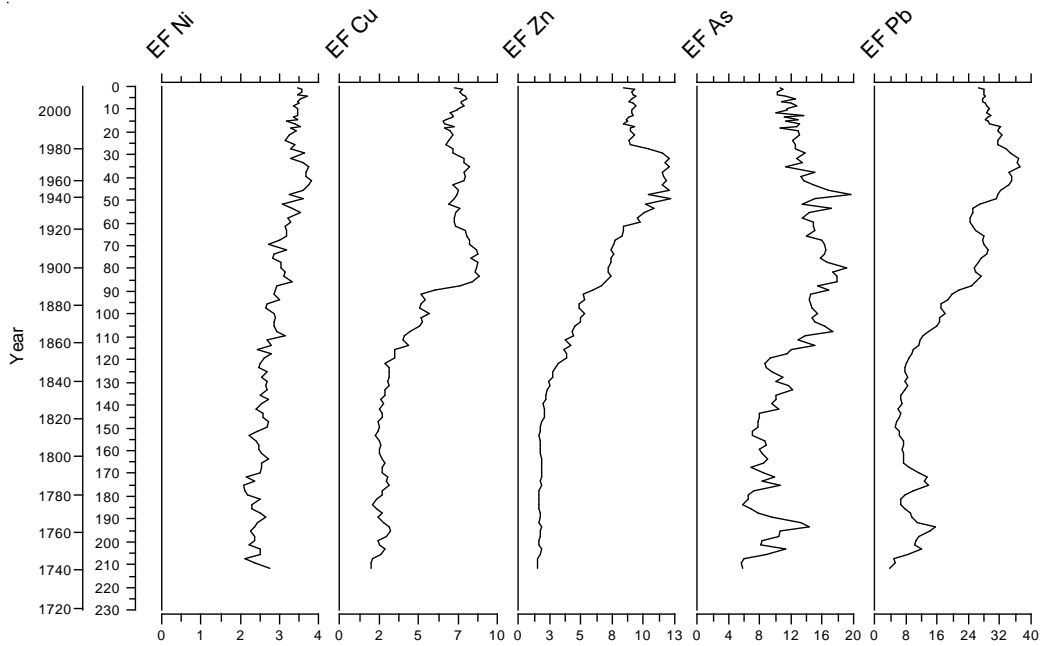


Figure 4.7 – Sediment core profiles from Hampstead No. 1 Pond showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

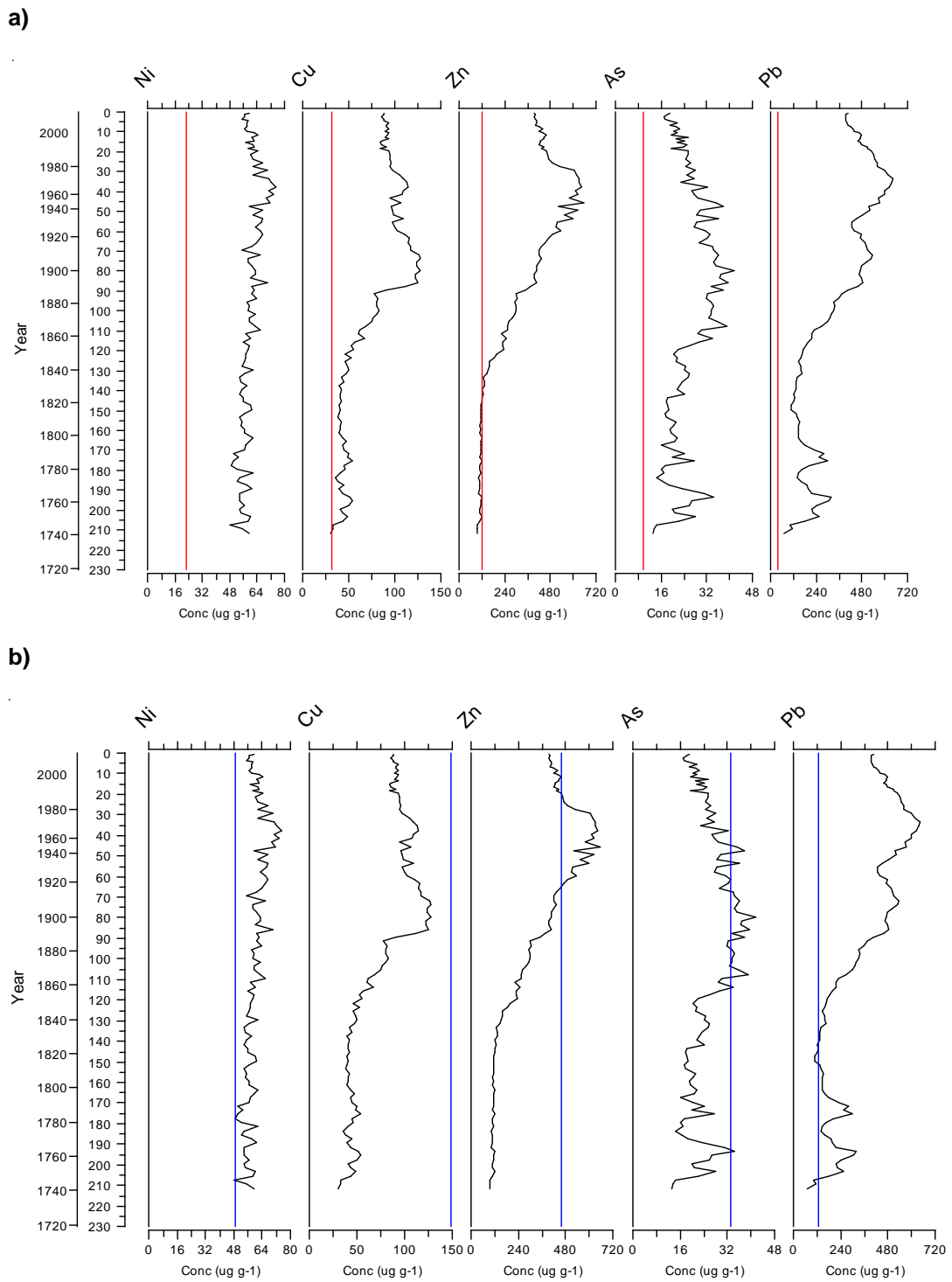


Figure 4.8 – Sediment core profiles from Hampstead No. 1 Pond showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

4.4.2. The Vale of Health Pond

All of the lithostratigraphic profiles showed a distinct change halfway down the core, which corresponded to the middle of the 20th century (Figure 4.7). Wet density was highest in the bottom half of the core, with values consistently over 1.3 g cm⁻³. In the 1940s, wet density fell to 1.2 g cm⁻³ and then decreased steadily up to the surface of the core. Dry weight was also greater in the bottom half of the core (Figure 4.7), dropping from over 30% to 25% in the 1940s, before declining up to the surface. Carbonate content was lower in the bottom half of the core, with values consistently less than 3%. In the 1940s, content rose to 4% and then increased steadily up to the top of the core. The organic matter profile (Figure 4.7) declined initially from 14% in the mid 19th century to approximately 7% in the early 20th century. From the mid-20th century content increased steadily to a peak of 25% in the 1990s, before declining at the top of the core.

The profiles of Al, Si and Ti were very similar to one another (Figure 4.7), all declining slightly between the base of the core and the surface. The three elements also all showed a more pronounced drop in concentration in the 1980s. The Zr concentration profile was very different (Figure 4.7), and showed the same mid-20th century change that was present in the lithostratigraphic indicator profiles. The concentration at the base of the core was similar to the concentration at the surface, approximately 200 µg g⁻¹. However, there was a sharp increase in concentration in the mid to late 19th century, which peaked at 420 µg g⁻¹. The concentration increased sharply again and peaked at 600 µg g⁻¹ in the early 20th century, before declining to 200 µg g⁻¹ in the early 1940s and remaining at that level up to the surface of the core.

The concentration profiles for each of the metals in the Vale of Health Pond looked very different to one another (Figure 4.7). However, significant Pearson product-moment correlations were calculated between most of the metals (Table 4.6). The most positive correlations were between Cu and Pb, and Ni and Zn, although all four metals were well correlated with one other. Mercury was negatively correlated with Ni and Zn, and had the highest positive correlation with As. The metal correlations that showed no significance were between As and Ni/Cu/Zn, and Hg/Cu and Hg/Pb.

VALE1	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.750	1				
Zn	.904	.891	1			
As	-.029	.100	-.123	1		
Pb	.691	.960	.828	.216	1	
Hg	-.383	-.083	-.375	.525	.097	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 4.6 – Pearson product-moment correlations between the metals in VALE1

The concentration of Cu began to rise in the late 19th century and initially peaked at 120 µg g⁻¹ in the early 20th century. The concentration continued to increase reaching a maximum of 140 µg g⁻¹ in the early 1970s, before declining to 100 µg g⁻¹ at the surface. The Pb concentration also increased from the late 19th century to a broad peak in the early 1900s. This was followed by another peak in concentration between the 1930s and the 1950s, which reached a maximum of 950 µg g⁻¹. The concentration then declined overall, apart from a small increase in the mid-1970s. The concentration of Ni increased slightly between the mid-19th century and the mid-20th century. It then rose more rapidly to a maximum of 70 µg g⁻¹ in the 1970s and then declined to 50 µg g⁻¹ at the surface. The concentration of Zn also rose slowly from the mid-19th century, with a more rapid increase in the mid-20th century. The concentration peaked at 1000 µg g⁻¹ in the mid-1970s and then declined to 500 µg g⁻¹ at the surface. The concentration of As in the late 19th century was about 30 µg g⁻¹, which was the same as the concentration in the 2000s. There was a peak in the early 20th century, when the concentration reached 45 µg g⁻¹ before declining. The concentration rose again in the 1930s to 40 µg g⁻¹ and then decreased to the surface. The concentration of Hg increased from the late 19th century to a peak of 3000 ng g⁻¹ in the 1930s. There was a sudden decline in concentration in the 1940s, after which the concentration decreased more steadily up to the surface of the core.

The Vale of Health Pond sediments contained the highest concentration of Pb found at any of the sites. They also contained the highest concentration of Hg, although this was only in comparison to Wake Valley Pond. Examination of the profiles showed that there was a similarity between some of the metals, as Ni, Cu and Zn all reached maximum concentrations in the 1970s, and there was also a peak in the Pb profile at this time. The profiles of As and Hg were very different, and the latter in particular showed evidence of the same mid-20th century change that was visible in the lithostratigraphic and Zr profiles. In addition, all of the metals (excluding Zn) declined sharply at the base of the core, which could have indicated that the bottom of the lake had been reached. However, as was

discussed in Chapter 2, the core did not cover the entire sediment record. The only other profile which showed the same trend was organic matter (Figure 4.7), which suggested that the concentrations of Ni, Cu, As, Pb and Hg might have been influenced by organic content.

Sediment accumulation rate (SAR) increased rapidly from $0.23 \text{ g cm}^{-2} \text{ yr}^{-1}$ at the bottom of the profile (the late 1960s) to a peak of $0.41 \text{ g cm}^{-2} \text{ yr}^{-1}$ in the mid-1970s. It then declined to $0.17 \text{ g cm}^{-2} \text{ yr}^{-1}$ in the late 1990s before increasing again to $0.24 \text{ g cm}^{-2} \text{ yr}^{-1}$ at the surface (Figure 4.7). The profiles of metal flux were very similar to the SAR profile (Figure 4.7). In all cases, flux increased sharply to a peak in the 1970s, declined until the 1990s and then increased slightly up to the surface of the core. The similarity of the SAR and metal flux profiles showed that SAR was the driver of metal flux, rather than metal concentration. This is of interest as it shows that despite metal concentrations being in decline, the flux of metals to the lake sediments has continued to increase over the last 20 years.

The lithostratigraphic profiles all showed that sediment composition changed in the middle of the 20th century. The change was not evident in the profiles of Al, Si, or Ti, which suggested that the cause was not down to an increase or decrease in material from the catchment. However, a similar change was visible in the Zr profile. Zirconium has been found to be associated with a different fraction of mineral matter than Ti (Koinig et al, 2003; Taboada et al, 2006), and a change in the type of the material being transported into the lake, from coarser to finer mineral particles, would change the relative concentration. In the same way, there was a decrease in Al, Si, and Ti in the 1980s that was not seen in the Zr profile, which could be explained by reduced input of the clay fraction of the soil (Taboada et al, 2006). Therefore, a change in the supply of catchment material could have been responsible for the changes seen in the lithostratigraphic profiles.

A change in the supply of catchment material and organic matter can impact upon metal concentration profiles, enhancing or diluting the metal signals. Normalising the metal concentrations to organic matter resulted in changes to the profiles of Ni, Cu, As and Pb (Figure 4.8). The normalised Ni concentration decreased between the 1930s and the 1990s. A similar pattern occurred in the normalised Cu, As and Pb profiles. In the Cu profile, the concentration declined after peaking in the early 20th century. The same occurred in the As profile, although the peak in the early 20th century was sharper in the normalised profile, and the decline to the surface of the core was steeper. There was also a steeper decline in concentration between the 1930s and the 1990s in the normalised profile of Pb than there had been in the original. The profiles of Zn and Hg did not change very much when normalised to organic matter (Figure 4.8). The high concentrations of all the metals at the

bottom of the core (except Zn) were still evident, although they were reduced in size. The normalisation profiles showed that the large increase in organic matter that occurred in the latter half of the 20th century was related to the concentrations of Ni, Cu, As and Pb during the same period, but that the increase had little effect on the concentrations of Zn and Hg. This implied that Ni, Cu, As and Pb bind more easily to organic matter than Zn or Hg.

Calculation of enrichment factors resulted in small changes to the shape of the metal profiles, although the consistency of catchment inputs reflected in the Ti profile meant that there were no great changes in concentration caused by dilution of the sediments (Figure 4.8). The enrichment factors for all of the metals were greater than 1, which showed that there had been enrichment of the lake sediments since at least the 1850s. The main difference between the metal concentration profiles and the enrichment profiles was that whereas the former had generally been in decline over the last 30 years, Cu, As, Pb and Hg enrichment had increased, while Ni and Zn enrichment remained constant. This is similar to metal flux, and suggests that even though emissions have declined, secondary sources of metals from the catchment are still important (see Section 1.5.3). This also has implications for SQGs and toxicity.

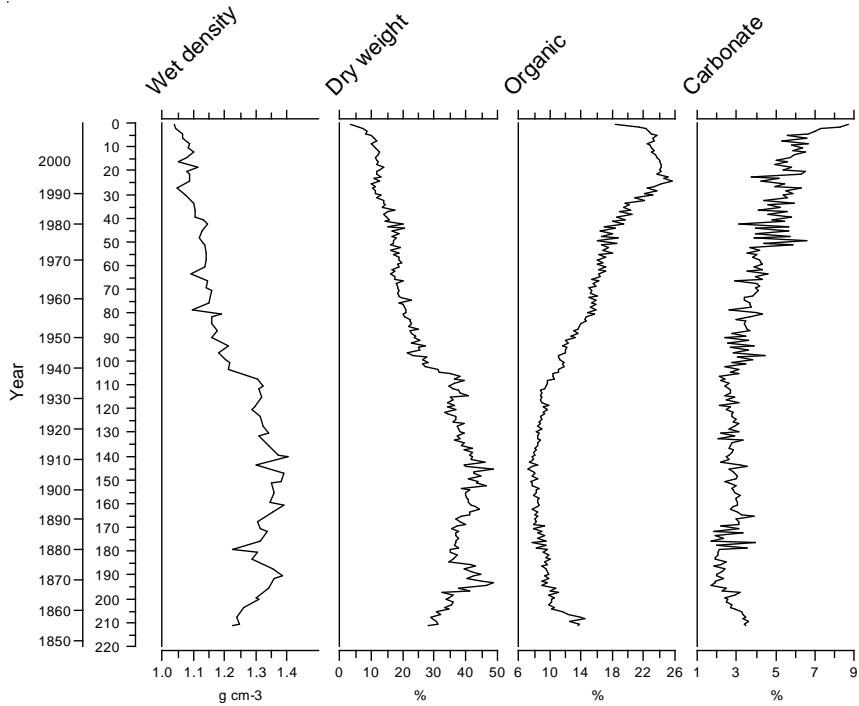
VALE1	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	2009	Maximum	2009
Ni	210	140	40	10
Cu	350	260	No exceedance	No exceedance
Zn	730	370	120	20
As	500	270	80	10
Pb	2540	1640	640	390
Hg	1570	350	180	No exceedance

Table 4.7 – Percentages by which metal concentrations exceed TECs and PECs at the Vale of Health Pond. The table includes both the maximum exceedance and the exceedance when the core was taken (2009).

The metal concentrations recorded in VALE1 exceeded the TECs over the whole length of the core and were still much higher in 2009 (Table 4.7). Lead is the only metal which has also exceeded the PEC over the entire core. The greatest exceedance occurred in the mid-1950s when the concentration was 640% higher than the PEC. In 2009, Pb exceeded the PEC by nearly 390% and the TEC by 1640%. In contrast, Cu has never been higher than the PEC. The other metals have all exceeded the PEC at some point within the core. The concentration of Ni first exceeded the PEC in the 1940s and was 40% higher by the early 1970s, although it had dropped to 10% by 2009. Zinc followed a similar pattern, with the concentration rising above the PEC in the 1940s and peaking in the early 1970s, at 120% of the threshold value. The concentration was still 20% higher than the PEC in 2009. The

concentration of As fluctuated around the level of the PEC over the entire length of the core, but has never been consistently higher for any length of time, although it was just above the PEC in 2009. The concentration of Hg exceeded the PEC between the mid-19th century and the late 1960s. The greatest exceedance occurred in the early 1930s when the concentration was 180% more than the PEC. Of all the metals analysed in VALE1 (apart from Cu), Hg was the only one which did not exceed the PEC in 2009.

a)



b)

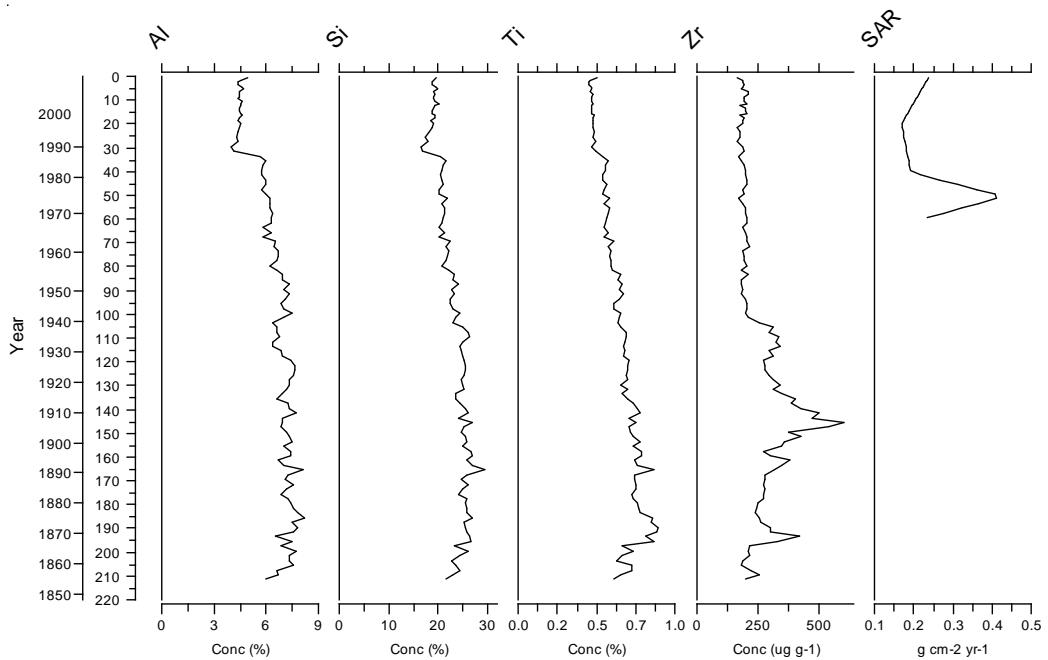


Figure 4.9 – Sediment core profiles from the Vale of Health Pond showing a) lithostratigraphic data – wet density, dry weight, organic matter and carbonate content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth). The short SAR profile reflects the radiometric dating record from the core (see Chapter 3), which was used to calculate SAR.

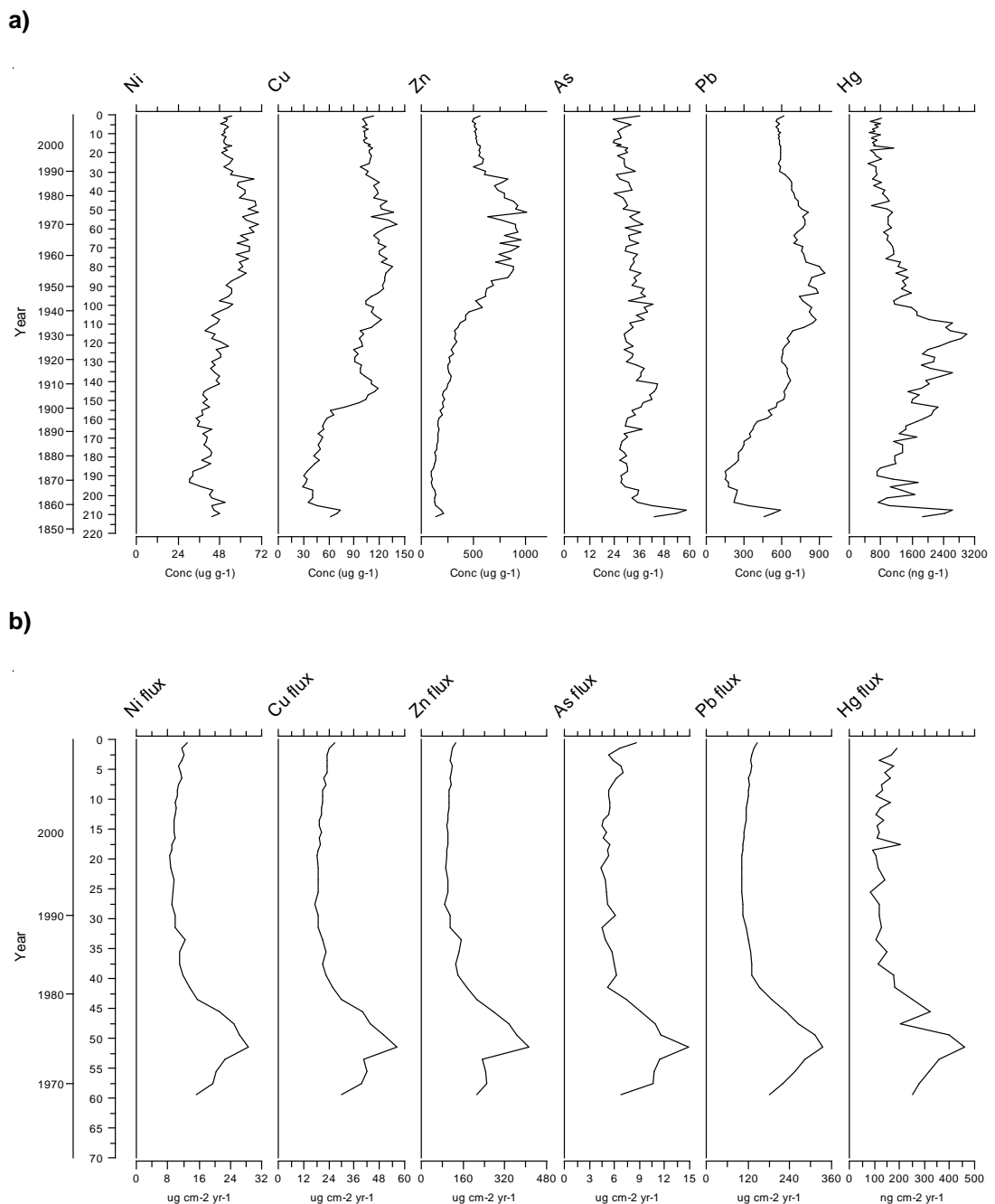


Figure 4.10 – Sediment core profiles from the Vale of Health Pond showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As, Pb and Hg, each plotted against sediment age (and depth). The short flux profiles reflect the radiometric dating record from the core (see Chapter 3), which was used to calculate sediment accumulation rate and hence flux.

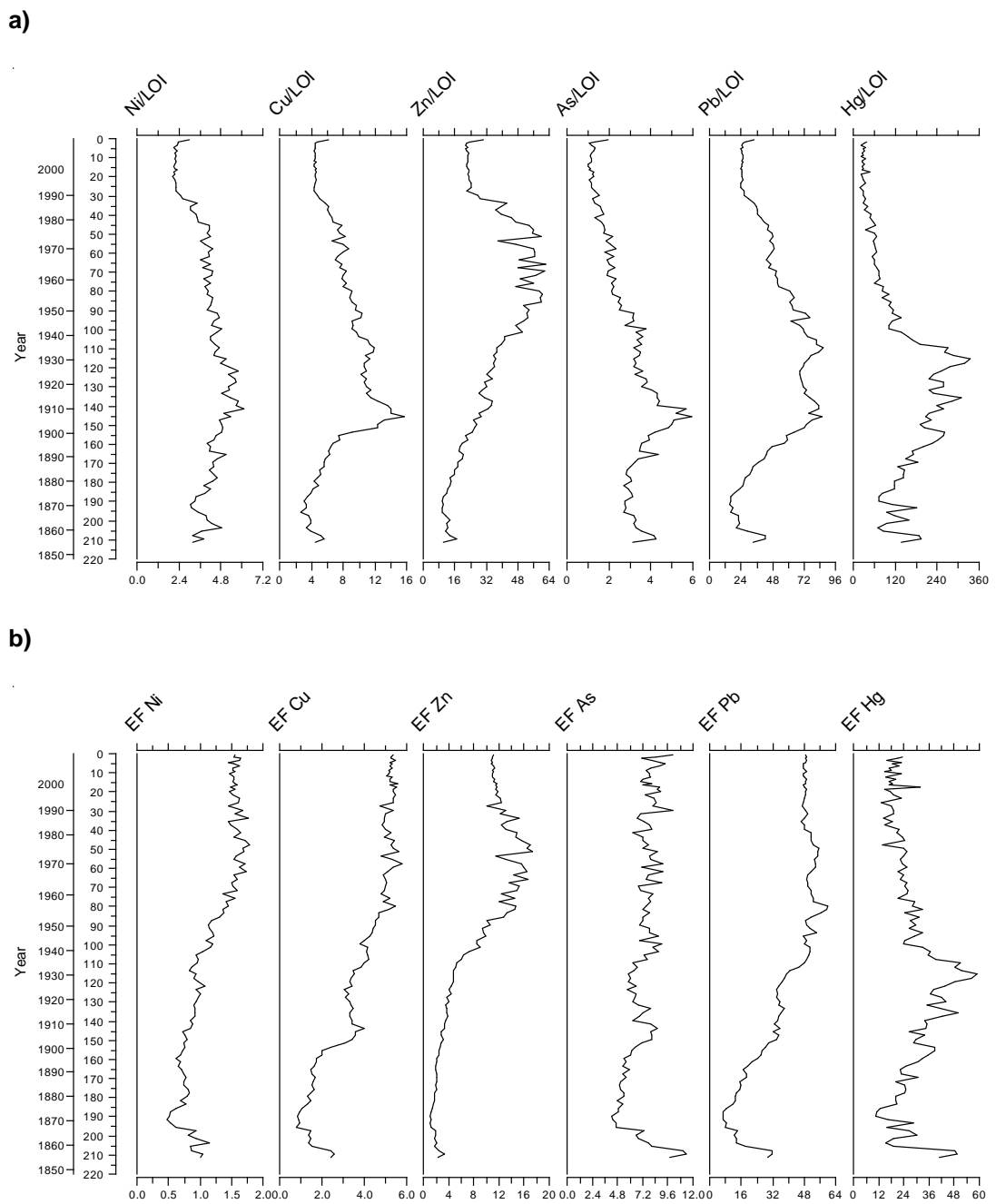
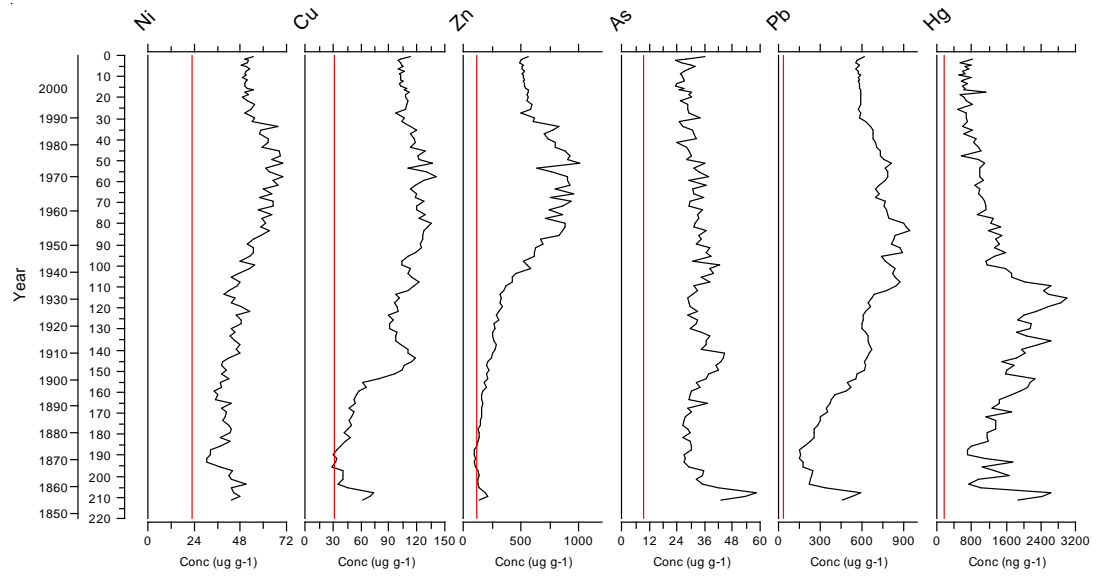


Figure 4.11 – Sediment core profiles from the Vale of Health Pond showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As, Pb and Hg, each plotted against sediment age (and depth)

a)



b)

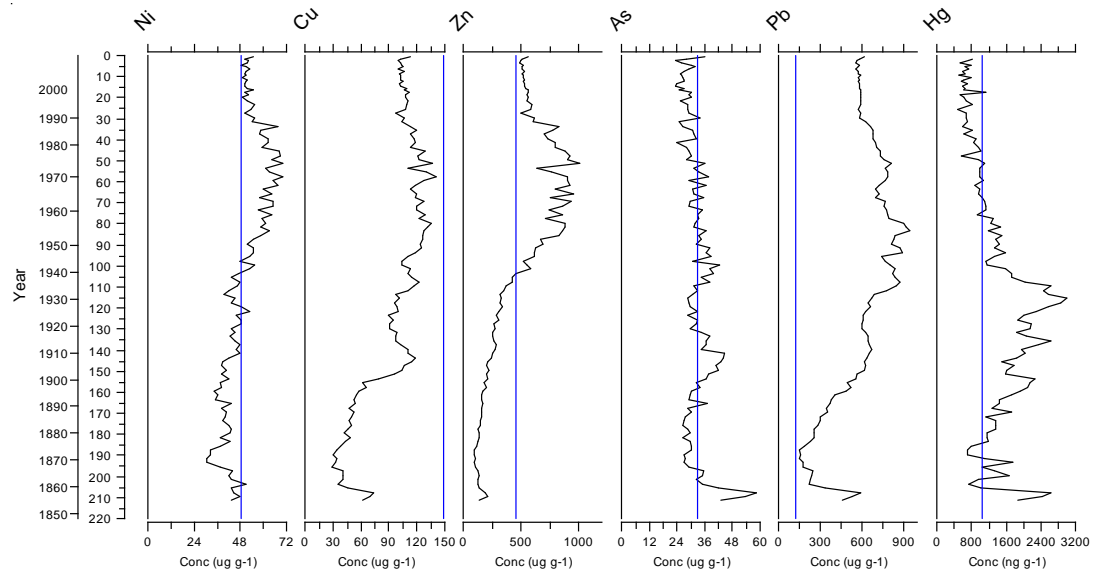


Figure 4.12 – Sediment core profiles from the Vale of Health Pond showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As, Pb and Hg, each plotted against sediment age (and depth)

4.4.3. Highgate Ladies Bathing Pond

Wet density decreased overall from 1.22 g cm⁻³ in the mid-18th century to 1.08 g cm⁻³ in the late 1980s (Figure 4.9). In the 1940s wet density briefly increased to 1.23 g cm⁻³. Dry weight showed the same pattern (Figure 4.9), decreasing up the core from 30% at the base to 10% at the surface. There was also a peak of 30% in the 1940s. The organic matter profile (Figure 4.9) increased overall from 10% in the mid-18th century to 24% in the late 1980s. The increase was interrupted by a drop in the 1940s when organic content briefly fell back to 10%.

The profiles of the lithogenic elements were all very similar (Figure 4.9). The concentrations of Al, Si and Ti all decreased slightly between the mid-18th century and the late 1980s. The decline was interrupted in the 1940s by a small peak in concentration, the same event that was visible in the profiles of the lithostratigraphic indicators. The concentration of Zr remained level throughout the core, at about 180 µg g⁻¹, apart from the same period in the late 1940s when the concentration peaked at 500 µg g⁻¹.

The metal concentration profiles of Ni, Cu, Zn and Pb were very similar, but the profile of As differed (Figure 4.9). The most positive Pearson product-moment correlations (Table 4.8) were found between Cu, Zn and Pb, which were all above 0.9. The correlations of Cu, Zn and Pb with Ni were slightly lower, although still greater than 0.8. The lowest correlations were between As and the rest of the metals. All of the correlations were significant, except for As and Cu, and As and Zn.

HIGW1	Ni	Cu	Zn	As	Pb
Ni	1				
Cu	.806	1			
Zn	.839	.981	1		
As	.374	.154	.205	1	
Pb	.814	.930	.933	.341	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Table 4.8 – Pearson product-moment correlations between the metals in HIGW1

The concentration of Cu began to increase in the early 20th century and peaked at 90 µg g⁻¹ in the late 1930s. The concentration declined to 50 µg g⁻¹ during the 1940s and then increased again to 120 µg g⁻¹ in the late 1960s. After this date, the concentration decreased to the surface of the core. The concentration of Zn also increased from the early 20th century

and peaked at $530 \mu\text{g g}^{-1}$ in the late 1930s. After dropping in the 1940s, the concentration increased again to a peak of $960 \mu\text{g g}^{-1}$ in the late 1950s, slightly earlier than the peak in the Cu profile. The concentration then declined to the late 1980s. As with Cu and Zn, the increase in Pb concentration began in the early 20th century. The concentration peaked sharply at $450 \mu\text{g g}^{-1}$ in the early 1940s and then declined before increasing again to $380 \mu\text{g g}^{-1}$ by the mid-1950s. The concentration remained at this level until the early 1970s, after which it decreased slightly to $300 \mu\text{g g}^{-1}$ at the top of the core. The concentration of Ni increased between the late 1920s and the late 1930s, peaking at $120 \mu\text{g g}^{-1}$. As with Zn, the concentration of Ni declined in the early 1940s, rose again to a peak of about $145 \mu\text{g g}^{-1}$ in the late 1950s and then decreased to the late 1980s. As with Cu, Zn and Pb, the concentration of As increased from the early 20th century, peaking at $60 \mu\text{g g}^{-1}$ in the mid-1930s. However, from then the concentration declined, reaching $20 \mu\text{g g}^{-1}$ by the late 1980s. A series of small peaks occurred in the 1940s and 1950s, but successively decreased in concentration over the period.

Sediment accumulation rate (Figure 4.9) increased from $0.04 \text{ g cm}^{-2} \text{ yr}^{-1}$ in the 1880s to $0.50 \text{ g cm}^{-2} \text{ yr}^{-1}$ in the late 1920s, before declining back down during the 1930s. In the 1940s there was a sharp rise in accumulation rate which peaked at $1.20 \text{ g cm}^{-2} \text{ yr}^{-1}$. SAR then decreased again until the mid-1960s before rising to $0.40 \text{ g cm}^{-2} \text{ yr}^{-1}$ at the surface. The metal flux profiles were very similar to one another (Figure 4.9) and resembled the profile of SAR. This showed that the changes in flux were driven by sedimentation rather than by metal concentration. Metal flux increased from the early 20th century to a small peak in the late 1920s. A steeper increase occurred in the 1940s, when Ni flux peaked at $100 \mu\text{g cm}^{-2} \text{ yr}^{-1}$, Cu at $75 \mu\text{g cm}^{-2} \text{ yr}^{-1}$, Zn at $460 \mu\text{g cm}^{-2} \text{ yr}^{-1}$, As at $60 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ and Pb at $315 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. By the late 1960s metal flux had decreased substantially, but over the 1970s and 1980s metal flux began to increase again and was still rising at the surface of the core.

The consistency of the wet density and dry weight profiles showed that sediment composition had not changed much at the Highgate Ladies Bathing Pond since the mid-18th century. This was reflected in the lithogenic element profiles which showed that input of inorganic material from the catchment had been fairly constant. The amount of organic matter had steadily increased, from either allochthonous or autochthonous sources. The exception to this continuity was a change that occurred in the 1940s which was visible in all of the lithostratigraphic and lithogenic profiles, as well as the profile of SAR. The increase in wet density, dry weight, Al, Si, Ti, Zr and SAR during this period showed that the sediment composition changed through an influx of inorganic material from the catchment. This was supported by the decline in metal concentration which occurred at the same time, as increased sedimentation can result in dilution of the metal signal. The metal fluxes confirmed

that this was the case, as the rate of metal deposition to the sediments in the 1940s increased substantially.

The role of organic matter in binding metals was not clear from the concentration profiles. Normalising the concentrations to organic content resulted in changes to the Ni, Cu and Pb profiles, but not to those of Zn or As (Figure 4.10). This implied that the three former metals had a greater affinity for organic matter than the latter two. The main change to the Ni profile was that the normalised concentration declined overall from the bottom of the core to the top. A third peak also became evident in the 1940s, clearly resulting from the increase in organic matter that occurred at this time. With regard to Cu, a slight increase was evident between the early 20th century and the late 1930s which was the same as the original. However, in contrast, the normalised concentration declined from the 1940s to the late 1980s. The changes to the Pb profile were similar to those of Cu. The bottom half of the normalised Pb profile was the same as the original, due to the lower amount of organic matter in the core. The normalised concentration then declined from the 1940s to the top of the core. Although the Zn and As profiles changed very little when normalised to organic matter, there was a slight adjustment to the latter as the series of peaks that were evident in the 1940s and 1950s in the original profile were consolidated into one peak in the normalised version.

The enrichment factor profiles (Figure 4.10) were very similar to the original concentration profiles. This showed that catchment inputs had little effect on metal concentrations, which was not unsurprising given the consistency of the lithogenic element profiles. The increase in inorganic material from the catchment in the 1940s was small enough not to affect the profiles either. The enrichment factors were greater than 1 for all metals across the whole core, which showed that enrichment of the sediments from anthropogenic sources had occurred at the lake since at least the mid-18th century. In contrast to HAMP1 and VALE1, enrichment did not increase in the top of the core, although in the Cu profile enrichment had stopped declining. However, the increase in enrichment at HAMP1 and VALE1 occurred between the 1980s and late 2000s. HIGW1 was taken in the 1980s and therefore did not contain recent sediments. It was impossible to ascertain from the core if enrichment would have started to rise again, although the increase in metal flux towards the top of the core suggested that it was a possibility.

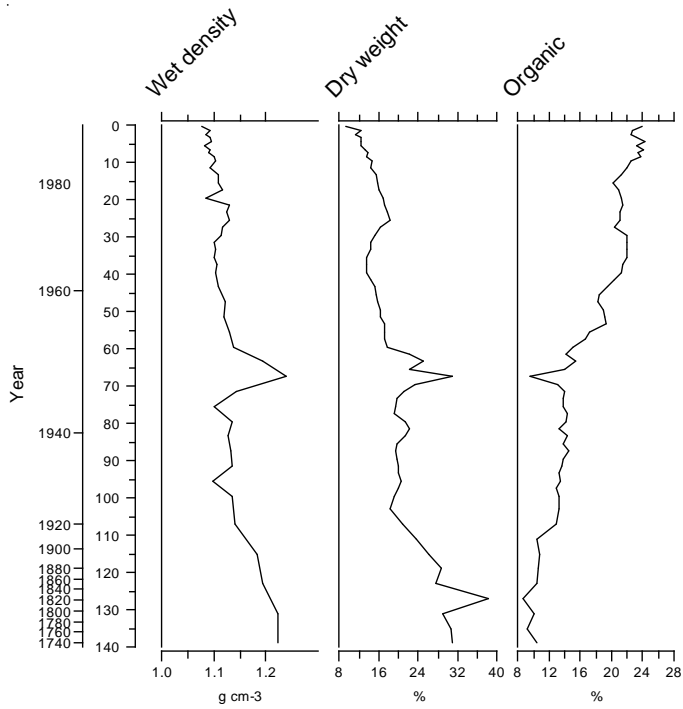
Even though the enrichment factors were generally declining at the top of the core, all of the metals still exceeded the TECs by a minimum of 140% in 1987 (Table 4.9). Ni, Pb and Zn were also still in exceedance of PECs. Ni and Pb had both exceeded the PEC over the

entire length of the core (Figure 4.10). The greatest exceedance of Ni occurred in the late 1950s when the concentration was 200% higher than the PEC, although by the top of the core this had dropped to 90%. The concentration of Pb exceeded the PEC by 250% in the early 1940s, but again this had dropped to 150% by 1987. Zinc had exceeded the PEC slightly for a short period in the late 1930s/early 1940s, and then far more substantially between the early 1950s and the late 1980s (Figure 4.10). In the late 1950s the concentration of Zn was 110% higher than the PEC and was still 50% greater at the top of the core. The concentration of As exceeded the PEC between the early 20th century and the early 1970s (Figure 4.10). The largest exceedance occurred in the mid-1930s, when the concentration was 90% greater than the PEC. As with Hampstead No. 1 Pond and the Vale of Health Pond, the concentration of Cu has never exceeded the PEC. However, the concentration was greater than the TEC for the whole length of the core. The greatest exceedance occurred in the late 1960s when the concentration was 280% more than the TEC. By the late 1980s this had declined slightly to 240%.

HIGW1	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	1987	Maximum	1987
Ni	540	300	200	90
Cu	280	240	No exceedance	No exceedance
Zn	700	460	110	50
As	530	140	90	No exceedance
Pb	1160	790	250	150

Table 4.9 – Percentages by which metal concentrations exceed TECs and PECs at the Highgate Ladies Bathing Pond. The table includes both the maximum exceedance and the exceedance when the core was taken (1987).

a)



b)

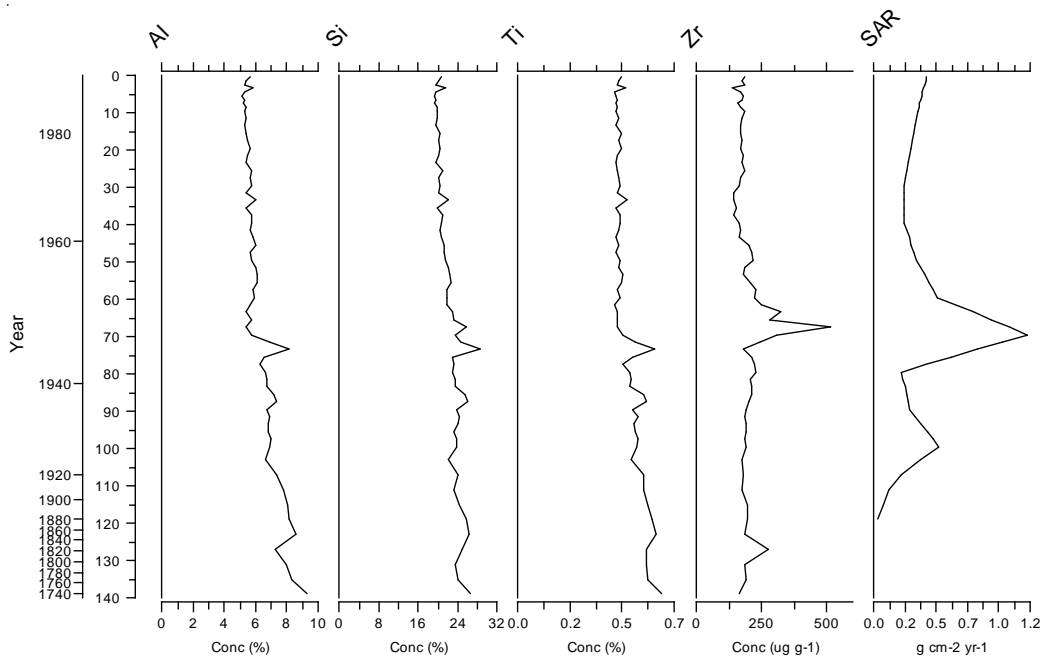


Figure 4.13 – Sediment core profiles from the Highgate Ladies Bathing Pond showing a) lithostratigraphic data – wet density, dry weight and organic matter content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth)

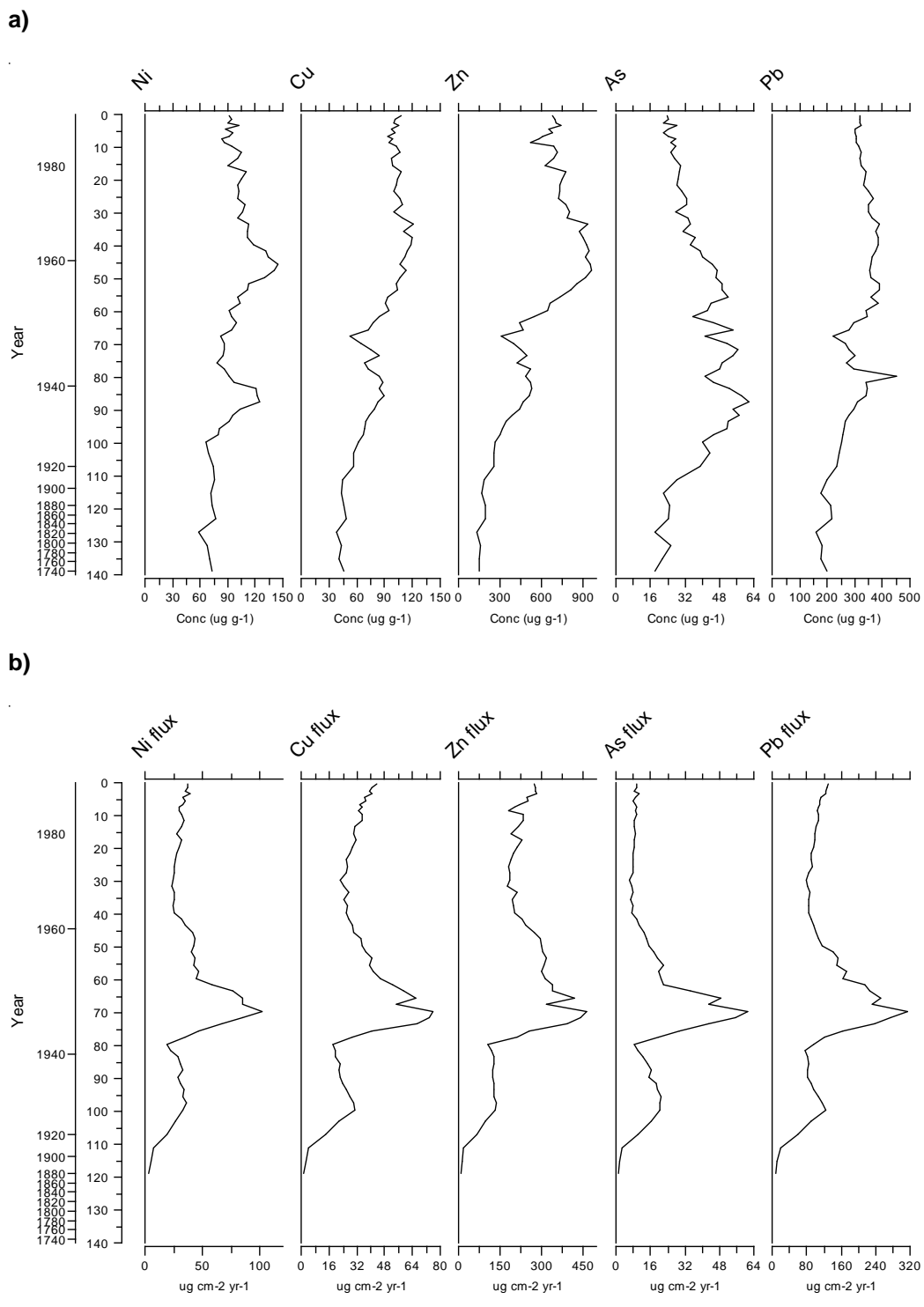


Figure 4.14 – Sediment core profiles from the Highgate Ladies Bathing Pond showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

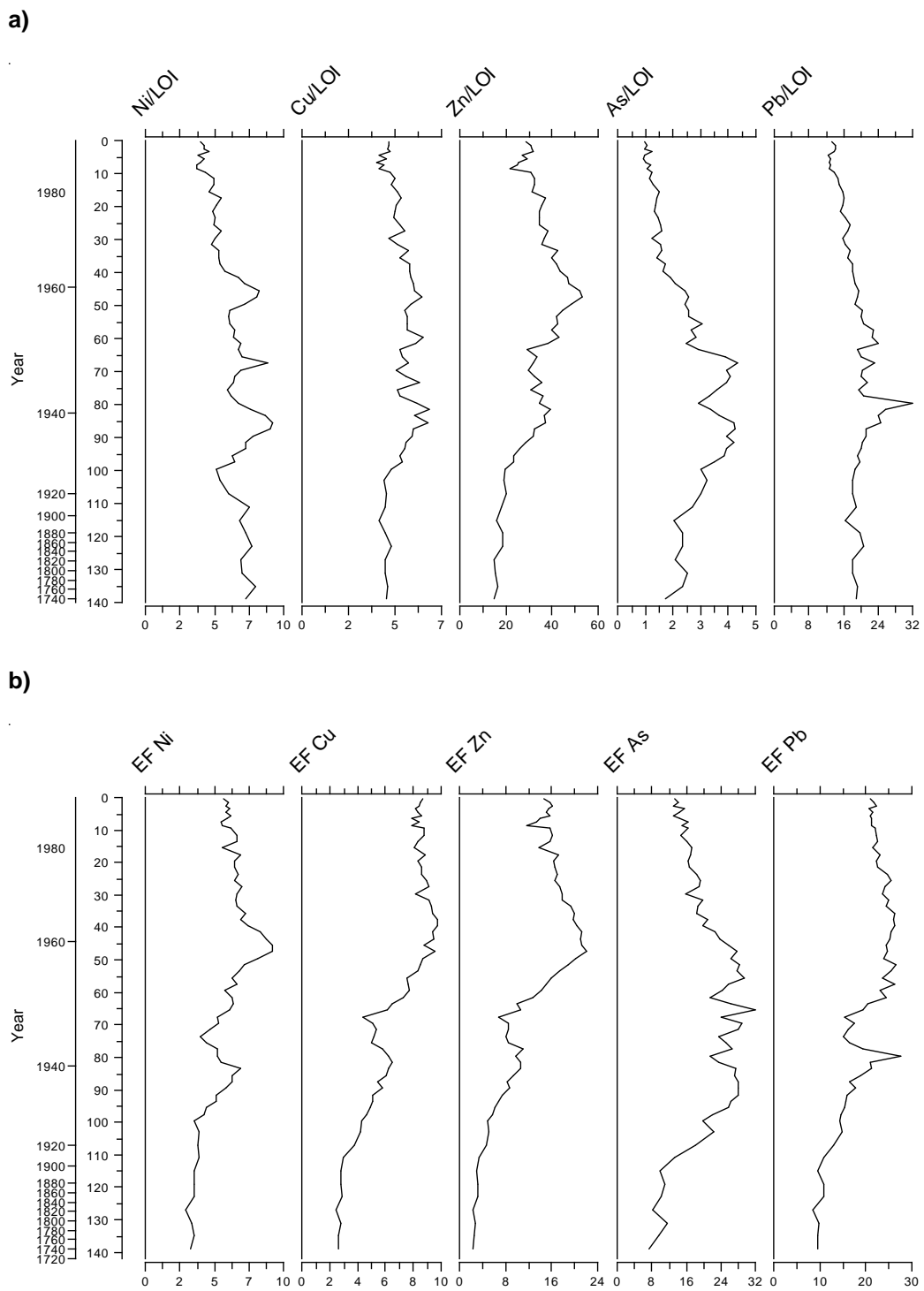


Figure 4.15 – Sediment core profiles from the Highgate Ladies Bathing Pond showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

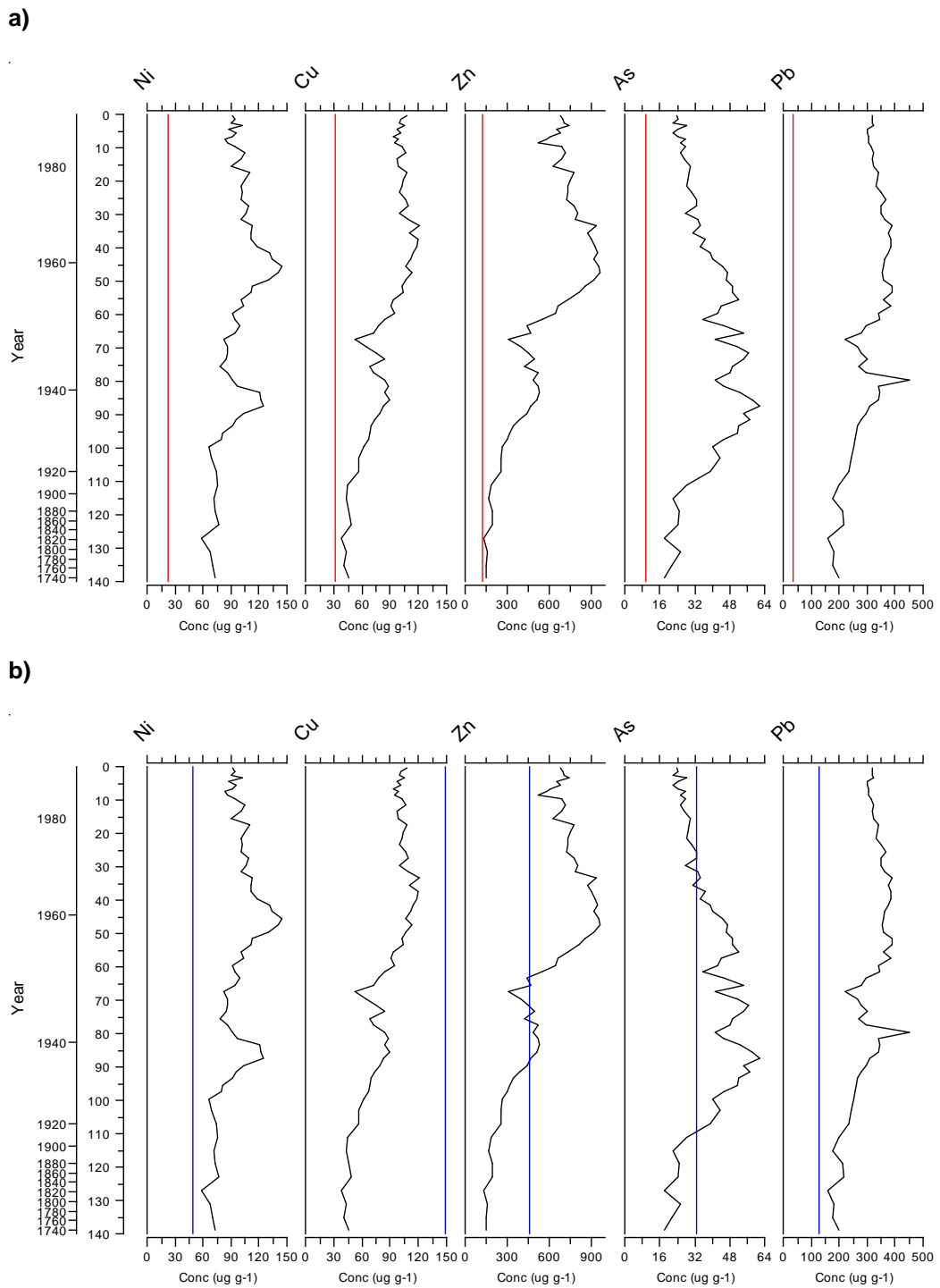


Figure 4.16 – Sediment core profiles from the Highgate Ladies Bathing Pond showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

4.4.4. Stock Pond

In the mid-19th century wet density decreased sharply from 1.20 g cm⁻³ to 1.05 g cm⁻³ (Figure 4.11). This was followed by an increase back up to 1.20 g cm⁻³ by the early 20th century. Wet density then declined up to the surface of the core. The dry weight profile (Figure 4.11) showed the same pattern, declining sharply in the mid-19th century from approximately 30% to 16%, before increasing back up to 28% by the early 20th century and then declining up to the top of the core. Organic matter (Figure 4.11) increased sharply from 10% to 17% in the mid-19th century, but had decreased back to 10% by the early 20th century. The content then increased again up to the surface of the core. Carbonate content (Figure 4.11) increased slightly overall from 3% at the base to 7% at the surface. In the mid-19th century carbonate content briefly increased to a sharp peak of 11%.

The concentration profiles of Al, Ti and Zr were very similar to each other (Figure 4.11). All three declined very slightly overall from the start of the 19th century to the 2000s. There was a sharp decrease in the early to mid-19th century, followed by an increase which peaked in the early 20th century. The concentrations then declined again, remaining fairly constant from the mid-20th century to the surface of the core. Silicon concentration also declined between the start of the 19th century and the present day, and there was a sharp decrease in the early to mid-19th century (Figure 4.11). The concentration then increased again, but peaked slightly later than the other elements, in the mid-20th century. The concentration declined slightly at this point and then remained fairly constant up to the surface of the core.

STCK2	Ni	Cu	Zn	As	Pb
Ni	1				
Cu	.792	1			
Zn	.908	.922	1		
As	.070	<i>.241</i>	.068	1	
Pb	.281	.551	.323	.793	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 4.10 – Pearson product-moment correlations between the metals in STCK2

A broad peak in concentration in the mid to late 19th century was present in all of the metal profiles (Figure 4.11). In the top half of the core, the profiles of Ni, Cu and Zn were also similar, but As and Pb were slightly different. This relationship was supported by the Pearson product-moment correlations (Table 4.10). All of the correlations were significant, apart from As/Ni and As/Zn. The most positive correlations were found between Cu and Zn, and Ni and Zn. The correlation between Cu and Ni was slightly lower. These three metals

correlated least well with As, and only slightly better with Pb. However, As and Pb correlated more positively with each other, which showed that there was a significant relationship between the two elements.

The concentration of Ni peaked at $140 \mu\text{g g}^{-1}$ in the late 19th century and then decreased until the early 20th century. The concentration increased again up to the mid-20th century, remaining high until the 1980s. The concentration peaked at $150 \mu\text{g g}^{-1}$ in the early 1980s and then declined to the surface. The concentration of Cu peaked at $110 \mu\text{g g}^{-1}$ in the late 19th century. It then declined until the early 20th century, before increasing back up to $110 \mu\text{g g}^{-1}$ in the mid-20th century. The concentration remained at about that level up to the surface of the core. The concentration of Zn increased in the late 19th century to a peak of $700 \mu\text{g g}^{-1}$. The concentration then declined until the early 20th century, before increasing again to $900 \mu\text{g g}^{-1}$ in the mid-20th century. The concentration remained at about that level until the early 1990s, before decreasing to the top of the core. The concentration of As peaked at $90 \mu\text{g g}^{-1}$ in the late 19th century, which was the highest concentration of As recorded at any of the London lakes, and then decreased until the early 20th century. The concentration rose again up to the mid-20th century, although it was not as pronounced as the increase in the Ni, Cu and Zn profiles. After peaking at $60 \mu\text{g g}^{-1}$ in the early 1950s the concentration declined up to the surface of the core. The concentration of Pb increased in the late 19th century to a peak of $550 \mu\text{g g}^{-1}$ and then declined until the early 20th century. After that there was a steady increase until the early 1980s, reaching a maximum concentration of $370 \mu\text{g g}^{-1}$. As with As, the rise in concentration wasn't as pronounced as in the profiles of Ni, Cu and Pb. The concentration of Pb decreased between the 1980s and the surface of the core.

Sediment accumulation rate (Figure 4.11) decreased between the early 1930s and the mid-1940s. SAR then rose from $0.1 \text{ g cm}^{-2} \text{ yr}^{-1}$ to a peak of $0.35 \text{ g cm}^{-2} \text{ yr}^{-1}$ in the early 2000s, with a more rapid increase occurring in the 1980s and 1990s. SAR declined slightly between the early 2000s and the surface of the core. The metal flux profiles (Figure 4.11) were very similar both to each other, and to the profile of SAR. As with the other Hampstead Heath ponds, this showed that sediment accumulation was the driver behind flux, rather than metal concentration. Metal flux was quite consistent up until the late 1970s, but during the 1980s and 1990s the rate of flux steadily increased. From the mid-2000s metal flux began to decline. The date at which maximum flux was reached differed between the metals. Nickel flux peaked at $40 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ in the mid-2000s, and Cu flux peaked at $35 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ at the same time. The peak in Zn flux occurred slightly earlier, in the late 1990s, at $250 \mu\text{g cm}^{-2} \text{ yr}^{-1}$, although flux remained high into the mid-2000s. Arsenic and Pb flux both peaked in the early 2000s, the former at $11 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ and the latter at $110 \mu\text{g cm}^{-2} \text{ yr}^{-1}$.

The lithostratigraphic and lithogenic profiles showed that inputs of inorganic material changed for a period in the mid to late 19th and early 20th centuries. The drop in wet density and dry weight showed that sediment composition underwent a change at that time. The profiles of Al, Si, Ti and Zr showed that had been a sudden decline in the amount of inorganic material entering the lake from the catchment in the mid-19th century, but that influx began to increase again during the latter part of the 19th century. The profiles showed that in the early 20th century input from the catchment decreased again. Over the same period as these changes were occurring, there was also an increase in organic matter, an influx of carbonate and a rise in metal concentration. The changes in metal concentration could have been enhanced by the amount of organic matter in the lake, or diluted by the carbonate content. The relationship between SAR and flux further up the core also showed that inputs from the catchment may have diluted the metal signal, as the metal concentrations declined from the 1980s but the flux profiles showed an increased rate of deposition in the 1980s and 1990s.

Normalising the concentrations to organic matter resulted in large changes to the Ni, Cu and Zn profiles, but As and Pb were less affected (Figure 4.12). This showed that there was a relationship between Ni, Cu and Zn and the amount of organic matter in the sediments. The normalised Ni profile increased slightly between the early 19th century and the early 20th century, and then declined towards the surface of the core. The normalised Cu profile increased from the base of the core to a peak in the mid-19th century and then decreased up to the surface. The normalised profile of Zn had the same general shape as the original, but the decline and subsequent increase in concentration that occurred in the early to mid-20th century was no longer as pronounced. The normalised As concentration declined from the peak in the late 19th century to the surface of the core, and therefore the peak in the early 1950s was no longer evident. Similarly, in the normalised Pb profile the concentration also declined directly from the peak in the late 19th century up to the surface of the core, no longer increasing over the course of the 20th century.

The variation in the supply of inorganic material from the catchment recorded in the lithogenic element profiles had little impact on the concentration profiles after enrichment factors had been calculated, as they were all very similar (Figures 4.11 and 4.12). All of the enrichment factors for all of the metals were greater than 1 which showed that, as with the other Hampstead Heath lakes, anthropogenic contamination of the sediments had occurred over the entire length of the core. The small scale pattern of enrichment at the top of the core differed for each of the metals, but was generally the same as metal concentration. From 2000, Ni and Zn enrichment rose slightly and then declined to the surface of the core,

and As and Pb decreased over the whole period. Copper was the only metal which increased between 2000 and the surface of the core.

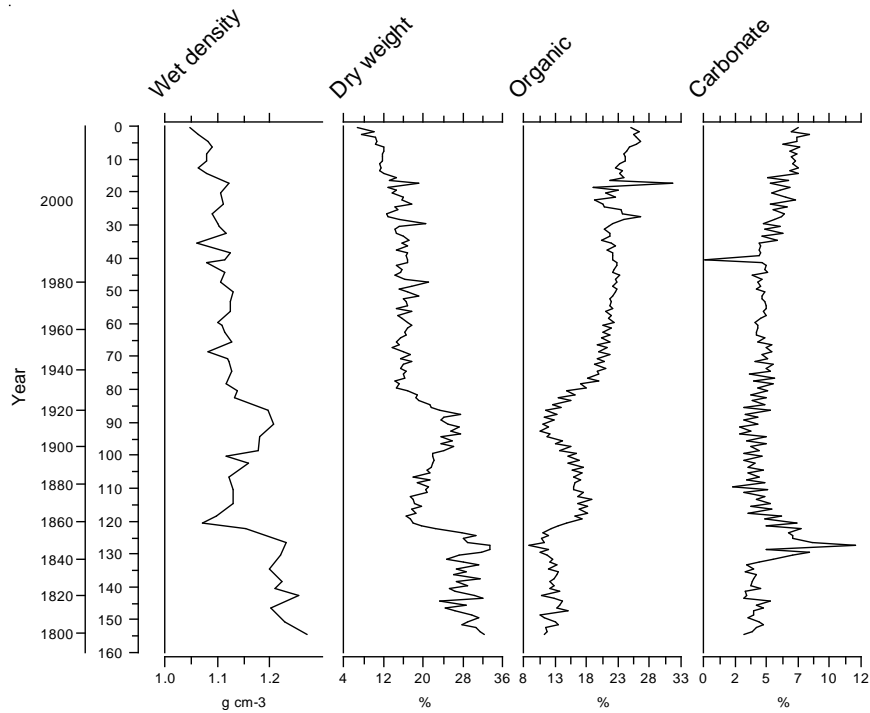
The relationship between enrichment and SQGs (Table 4.11) at Stock Pond was interesting. Despite the fact that enrichment had generally been falling since at least the 1990s, in 2009 the concentrations of Ni and Pb were both still 80% higher than the PEC. However, the concentration of Zn had fallen to the same level as the PEC, and the concentration of As was no longer in exceedance. In contrast, the concentration of Cu had never exceeded the PEC, which was the same pattern that was found at the other Hampstead Heath ponds. This was also despite the fact that enrichment of Cu was still increasing. However, Cu was 180% greater than the TEC in 2009.

STCK2	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	2009	Maximum	2009
Ni	590	280	220	80
Cu	260	180	No exceedance	No exceedance
Zn	660	290	100	Level
As	790	100	170	No exceedance
Pb	1460	550	340	80

Table 4.11 – Percentages by which metal concentrations exceed TECs and PECs at Stock Pond. The table includes both the maximum exceedance and the exceedance when the core was taken (2009).

With regard to the relationships between metal concentrations and SQGs in the past, all of the metals had exceeded the TECs over the entire length of the core (Figure 4.12). Nickel and Pb had also both exceeded the PEC over the whole core. Nickel reached a maximum exceedance in the early 1980s when the concentration was 220% greater than the PEC, whilst Pb peaked in the mid-19th century when the concentration was 340% higher. This reflected the high level of Ni and Pb contamination that was found at the other Hampstead Heath ponds. Zinc exceeded the PEC over two periods, the first in the mid to late 19th century and the second between the early 1920s and the surface of the core. At its maximum, the concentration of Zn was 100% higher than the PEC. The concentration of As was greater than the PEC between the mid-19th century and the early 1980s. The biggest exceedance occurred in the late 19th century, when the concentration was 170% greater than the PEC. Even though the concentration of Cu never exceeded the PEC, maximum exceedance of the TEC occurred in the early 1960s when the concentration was 260% higher.

a)



b)

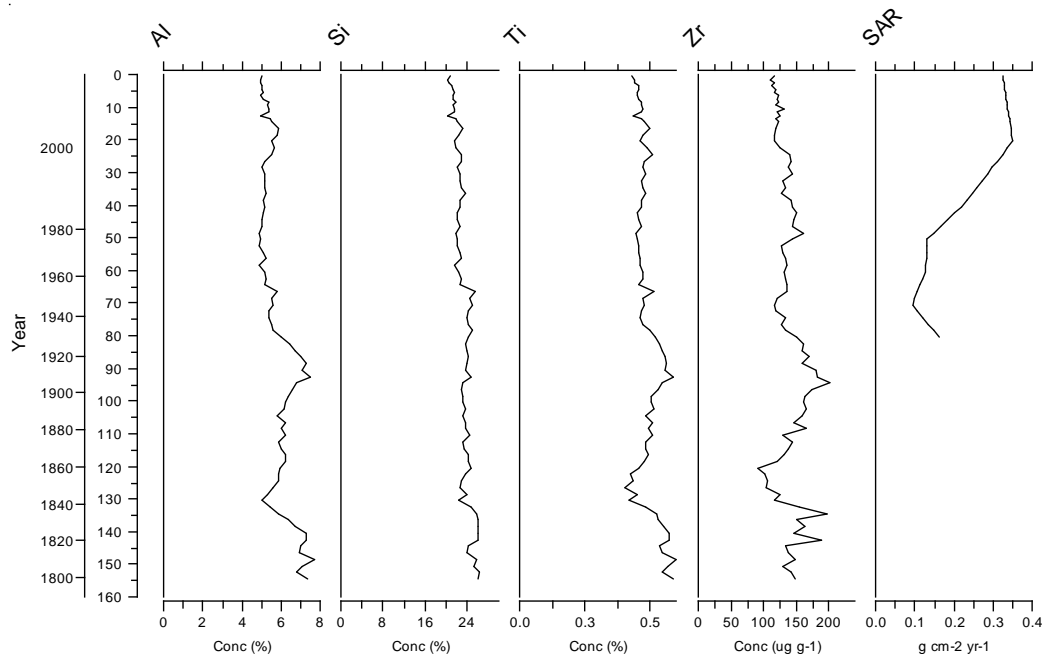


Figure 4.17 – Sediment core profiles from Stock Pond showing a) lithostratigraphic data – wet density, dry weight, organic matter and carbonate content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth). The short SAR profile reflects the radiometric dating record from the core (see Chapter 3), which was used to calculate SAR.

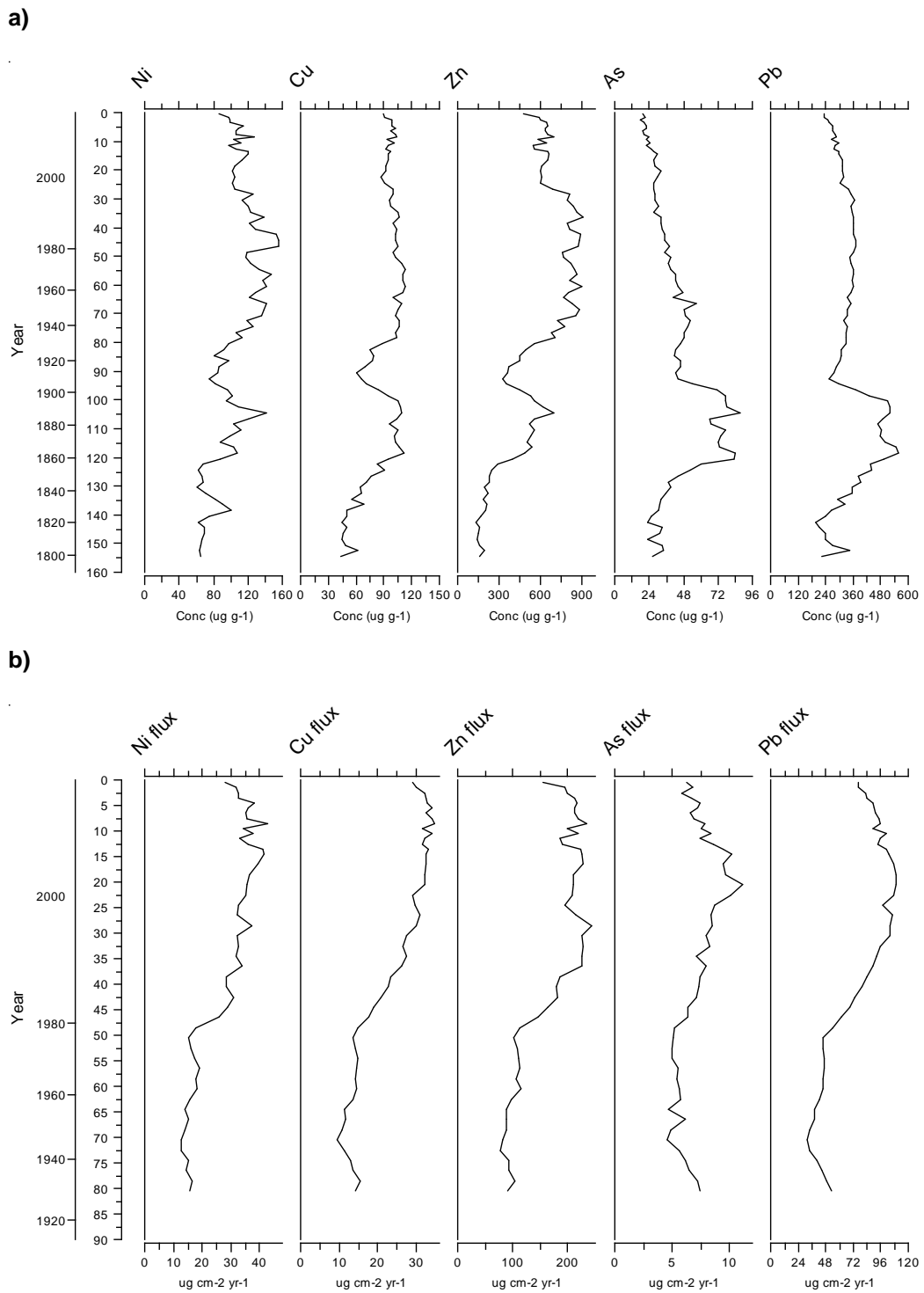


Figure 4.18 – Sediment core profiles from Stock Pond showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth). The short flux profiles reflect the radiometric dating record from the core (see Chapter 3), which was used to calculate sediment accumulation rate and hence flux.

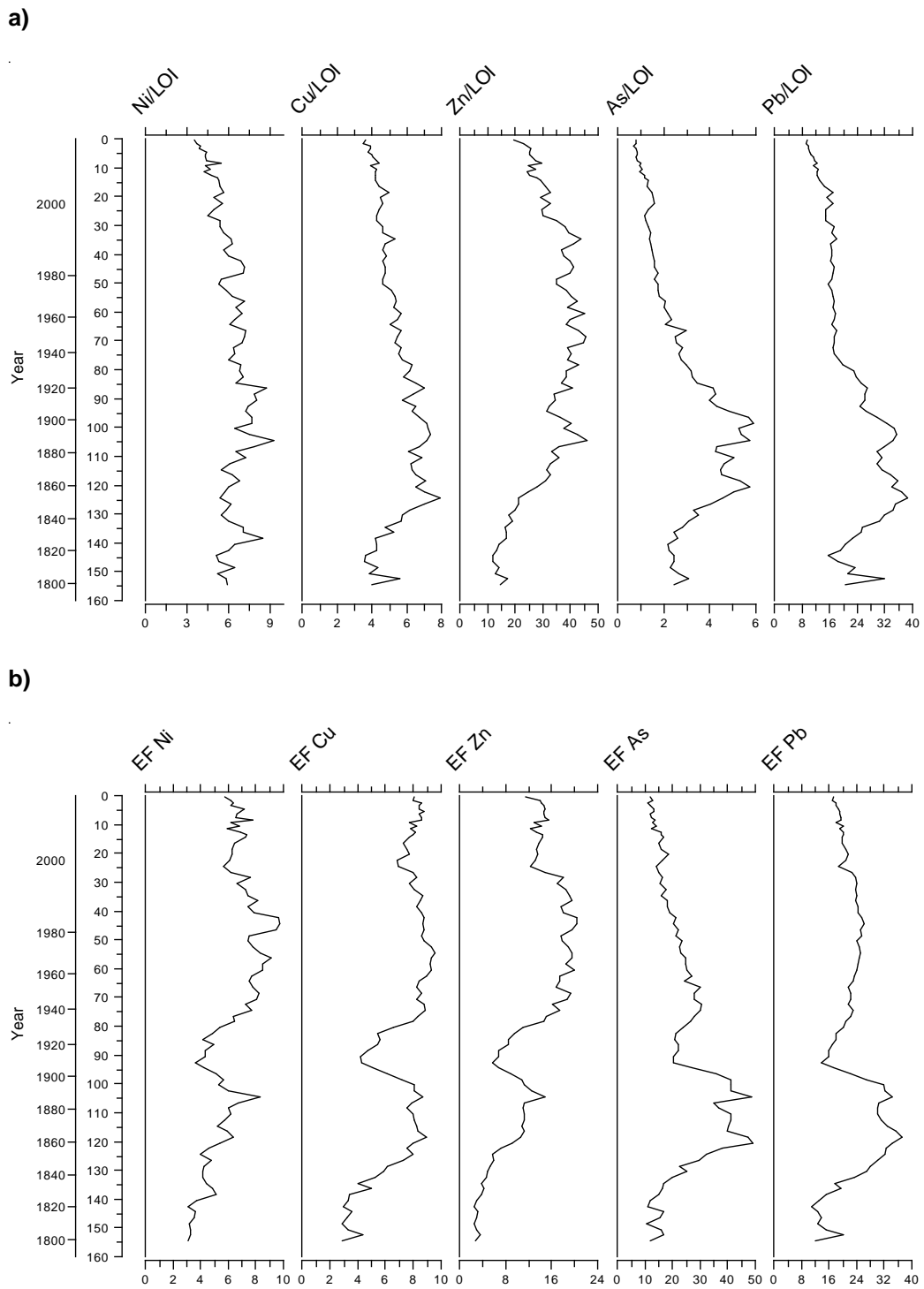
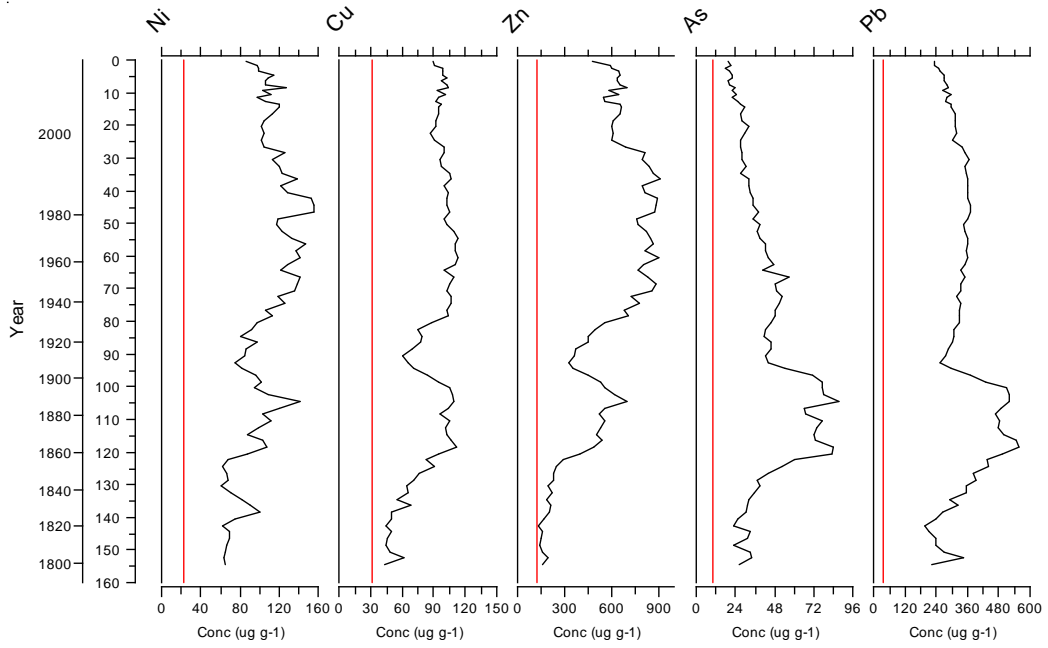


Figure 4.19 – Sediment core profiles from Stock Pond showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

a)



b)

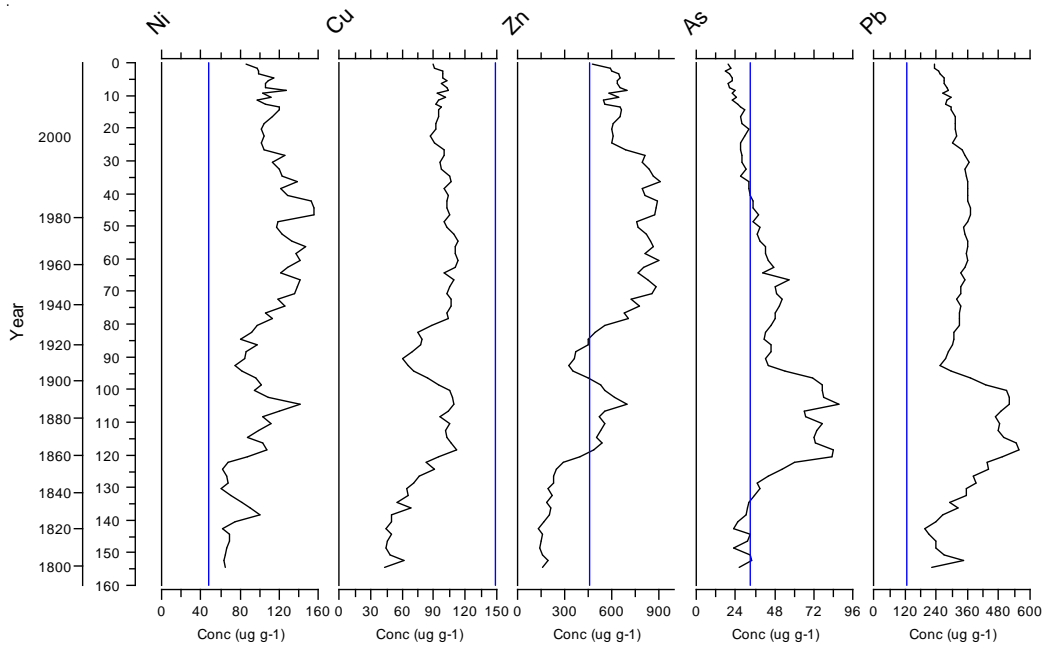


Figure 4.20 – Sediment core profiles from Stock Pond showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

4.4.5. South Norwood Lake

Wet density (Figure 4.13) decreased sharply in the mid to late 19th century, from 1.4 g cm⁻³ to 1.1 g cm⁻³, and then declined slightly further up to the surface of the core. Dry weight showed the same pattern (Figure 4.13), decreasing from 50% to 20% in the mid to late 19th century, before declining to 10% by the surface of the core. Organic matter (Figure 4.13) increased slightly from the base of the core, and then rose more rapidly in the early 20th century, peaking at 25% in the late 1930s. The amount of organic matter dropped to 20% immediately after this date and remained at the same level up to the surface of the core. Carbonate content (Figure 4.13) increased from 2% at the bottom of the core to a small peak of 7% in the early 20th century, before levelling out at 4 to 5%. The amount of carbonate stayed at this level until the surface of the core, when it rapidly increased to 10%. The profiles of the lithogenic elements were very similar to one other (Figure 4.13). The concentration of Al and Ti declined very slightly over the length of the core, whilst the concentration of Si and Zr remained the same. The exception to this was a short period starting in the early 20th century when the concentration of all elements decreased rapidly, and remained lower until the middle of the 20th century.

The concentration profiles differed between each of the metals, although all of them showed a rapid increase in concentration in the early 20th century (Figure 4.13). The concentration of Ni increased from 40 µg g⁻¹ in the early 20th century to a peak of 65 µg g⁻¹ in the 1950s and then declined to 35 µg g⁻¹ at the surface. The most obvious feature of the Cu profile was the large peak in concentration that occurred in the late 1930s, which had a maximum value of 700 µg g⁻¹ (one of two data points with high concentrations from which the peak was formed). This was the highest concentration of Cu found in any of the lakes studied. Such high concentrations masked any other patterns in the core and therefore the profile was also plotted with the high values removed (Figure 4.13). The profile showed a steep increase in concentration in the early 20th century which peaked at 190 µg g⁻¹ in the 1940s and then declined to the surface of the core. Zinc concentrations increased from 150 µg g⁻¹ in the early 20th century to a peak of 730 µg g⁻¹ in the 1960s. The concentration then declined to the surface of the core. The concentration of Pb increased in the early 20th century to a peak of 450 µg g⁻¹ in about 1940, and then remained above 400 µg g⁻¹ until the 1980s, after which it declined to the surface. The As profile differed slightly to those of the other metals as there was an additional peak in concentration that occurred before the rise in the early 20th century. The concentration increased rapidly from the base of the core to a peak of 50 µg g⁻¹ in the late 19th century, and was then followed by the second increase in the early 20th century. This also peaked at 50 µg g⁻¹, in about 1940. As with Ni, Cu and Zn, the concentration then decreased up to the surface of the core.

Even though the profiles differed in some ways, in particular the dates when the metal concentrations peaked, the Pearson product-moment correlations (Table 4.12) showed that all of the correlations between all of the metals were significant.

SNOR1	Ni	Cu	Zn	As	Pb
Ni	1				
Cu	.629	1			
Zn	.735	.894	1		
As	.609	.633	.560	1	
Pb	.649	.913	.962	.615	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Table 4.12 – Pearson product-moment correlations between the metals in SNOR1

Sediment accumulation rate (Figure 4.13) remained fairly constant at approximately $0.15 \text{ g cm}^{-2} \text{ yr}^{-1}$ between the 1930s and the 1970s. In the 1980s and 1990s SAR increased rapidly to a peak of $0.4 \text{ g cm}^{-2} \text{ yr}^{-1}$ and then declined to $0.25 \text{ g cm}^{-2} \text{ yr}^{-1}$ at the surface of the core. The profiles of metal flux were all very similar to one another (Figure 4.13) and followed the same pattern as SAR. This showed that sedimentation was the driver of flux rather than concentration change. Metal flux in all of the profiles was fairly constant between the 1930s and the 1970s, and then increased sharply in the 1980s. This was in contrast to the metal concentration profiles which all showed a decline during the 1980s, and therefore suggested that concentration had been diluted by the influx of material. Metal flux decreased between the late 1990s and the surface of the core, with the exception of As which increased slightly in the very top layers.

Overall, the lithostratigraphic and lithogenic element profiles showed that the lake sediments had not been much affected by changes to the catchment. The profiles of wet density and dry weight showed that sediment composition at South Norwood Lake had been quite consistent since the mid-19th century, apart from at the very bottom of the core. The decrease in wet density and dry weight at this time was not reflected in any of the other profiles, and could have been connected to the degree of sediment compaction. Erosion of carbonates from the catchment had been fairly consistent overall, and the lithogenic element profiles showed that inputs of silicates and other inorganic matter from the catchment had also changed little since the mid-19th century. However, there was an exception to this. In the early 20th century the amount of inorganic matter coming from the catchment changed, dropping briefly before rising again. This change coincided with a substantial increase in metal concentration, which suggested that the two were connected. However, the metal concentrations could also have been enhanced by the increase in organic matter that

occurred during the same period. Although all the metal concentrations increased between the 1920s and the 1940s, the large peak in Cu in the late 1930s was not reflected in any of the other profiles, which suggested that there was a local input of Cu to the lake during this period.

Normalising the metal concentrations to organic matter changed all of the metal profiles to some extent, especially Ni and As (Figure 4.14). The concentrations of Cu, Zn and Pb still increased in the early 20th century, but this rise was no longer as well defined in the As profile and had disappeared completely in the Ni profile. It showed that the increase in organic matter did enhance some of the metal concentrations. Normalising Ni to organic matter changed the profile so that it decreased from the bottom of the core to the surface. The normalised As profile still showed a peak in concentration in the late 19th century, but the second increase in the early 20th century was less pronounced. The normalised Cu and Pb profiles were very similar to the originals, except that the peak in the early 19th century was sharper for the former and broader for the latter. The normalised Zn profile showed only very small changes from the original.

The consistency of the lithogenic element concentrations meant that the enrichment factor profiles were very similar to the concentration profiles (Figures 4.13 and 4.14). All of the enrichment factors were greater than 1 which showed that the lake sediments had been contaminated by metals from anthropogenic sources since at least the mid-19th century. As with the concentration and flux profiles metal enrichment declined overall up to the surface of the core. However, closer examination of the top layers of the core showed that whilst the concentrations decreased, Cu and Pb enrichment has remained constant since the early 2000s and Zn and As has increased slightly. The results for As corresponded with the slight increase in As flux that was also visible at the surface of the core. If metal enrichment of the lake is not decreasing, this would have implications for both the site and for policy. However, as the change in enrichment only occurred in the top layers of the core it is difficult to be certain if it is a long term change. The fact that metal flux has declined suggests that metal contamination of the site may also begin to decrease in the near future.

The surface sediments at South Norwood Lake were enriched in metals irrespective of whether or not the level of enrichment was increasing. Correspondingly, in 2009 the concentrations of all metals exceeded the TECs by at least 60% (Table 4.13) and had exceeded them over the entire length of the core. The relationship between metal concentrations and the PECs varied (Figure 4.14), and in 2009 only Pb was still higher than the PEC.

SNOR1	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	2009	Maximum	2009
Ni	190	60	40	No exceedance
Cu	2140	180	380	No exceedance
Zn	500	150	60	No exceedance
As	440	150	60	No exceedance
Pb	1160	490	250	70

Table 4.13 – Percentages by which metal concentrations exceed TECs and PECs at South Norwood Lake. The table includes both the maximum exceedance and the exceedance when the core was taken (2009).

The concentration of Ni was in excess of the PEC between the 1930s and the late 1980s, and briefly in the late 1990s. The greatest exceedance occurred in the mid-1950s when the concentration of Ni was 40% higher than the PEC. Copper exceeded the PEC between the late 1920s and the late 1970s. The large peak in Cu concentration that occurred in the late 1930s was almost five times higher than the PEC. However, when this event was removed from the profile, the maximum exceedance of the PEC was by 30% in the early 1940s. The concentration of Cu decreased to below the level of the PEC in the 1980s. The concentration of Zn was above the PEC between the early 1930s and the early 1990s. At its maximum in the early 1960s, the concentration of Zn exceeded the PEC by 60%. The concentration of As exceeded the PEC in the early 1900s, and then again from the early 1920s to the late 1980s. At its maximum, the concentration of As was 60% greater than the PEC. The concentration of Pb exceeded the PEC from the early 1900s up to the surface of the core. The greatest exceedance occurred in the late 1930s when the Pb concentration was 250% higher than the PEC, although the concentration remained at a similar level until the 1990s. In 2009 the concentration of Pb still exceeded the PEC by 70%.

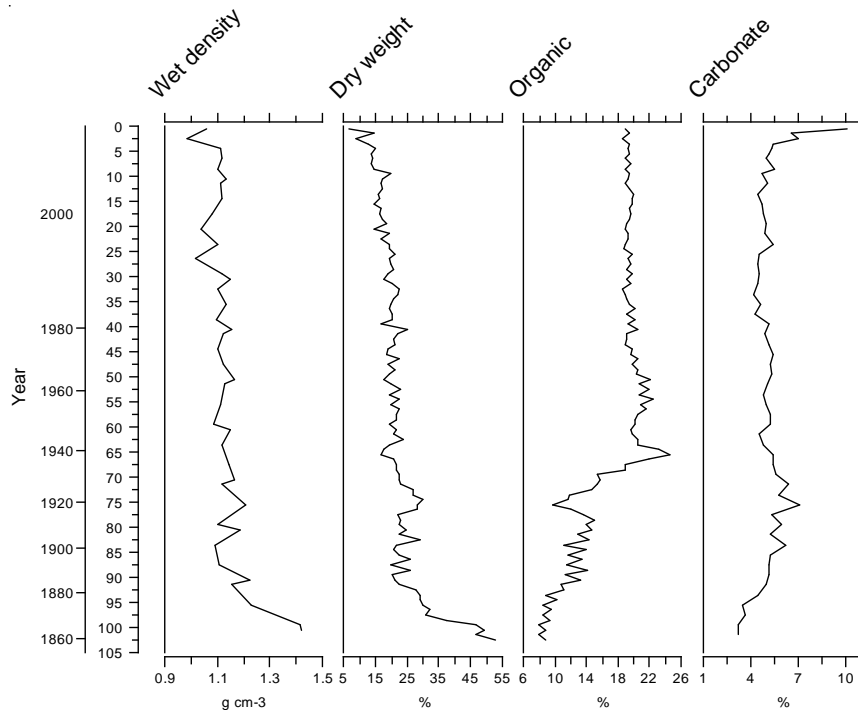
A previous study was carried out at South Norwood Lake in 2000. The 'Baseline Chemical Survey and Assessment of South Norwood Lake, Croydon' was completed by the Environmental Advice Centre Ltd. Composite surface sediment samples were analysed for a range of elements. The results showed that the sediments contained elevated concentrations of Pb and Zn, possibly caused by inputs from road drainage. The range of concentrations found for each of the metals of particular interest to this study are shown in Table 4.14, alongside the values obtained from the core SNOR1 at a depth corresponding to the same year. In all cases the concentrations in the core were higher than those found in the surface sediments in 2000, although the maximum value in each range was not dissimilar. The results contrasted with those from this study as they showed that Pb and Zn were the only metals of concern at the lake, whereas this study has shown that enrichment

of Ni, Cu, Zn, As and Pb has occurred at all levels in the sediments and concentrations were still in exceedance of SQGs at the surface.

Element	Conc ($\mu\text{g g}^{-1}$)	Conc ($\mu\text{g g}^{-1}$)
	EAC Ltd	SNOR1
Ni	<5-20	44.5
Cu	19-74	103
Zn	72-289	364.7
As	4-23	27.6
Pb	51-203	264.9
	Conc (ng g^{-1})	Conc (ng g^{-1})
Hg	180-680	N/A

Table 4.14 – Range of concentration values found in the 2000 survey of South Norwood Lake surface sediments (EAC Ltd, 2000), compared to the values in SNOR1 at a depth corresponding to the same year

a)



b)

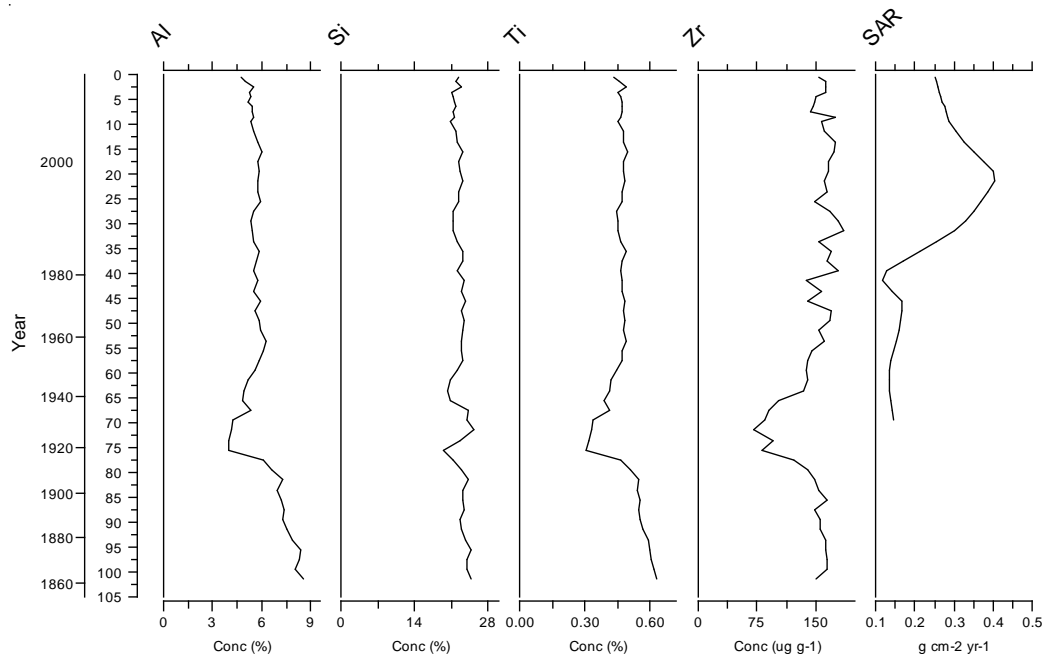


Figure 4.21 – Sediment core profiles from South Norwood Lake showing a) lithostratigraphic data – wet density, dry weight, organic matter and carbonate content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth). The short SAR profile reflects the radiometric dating record from the core (see Chapter 3), which was used to calculate SAR.

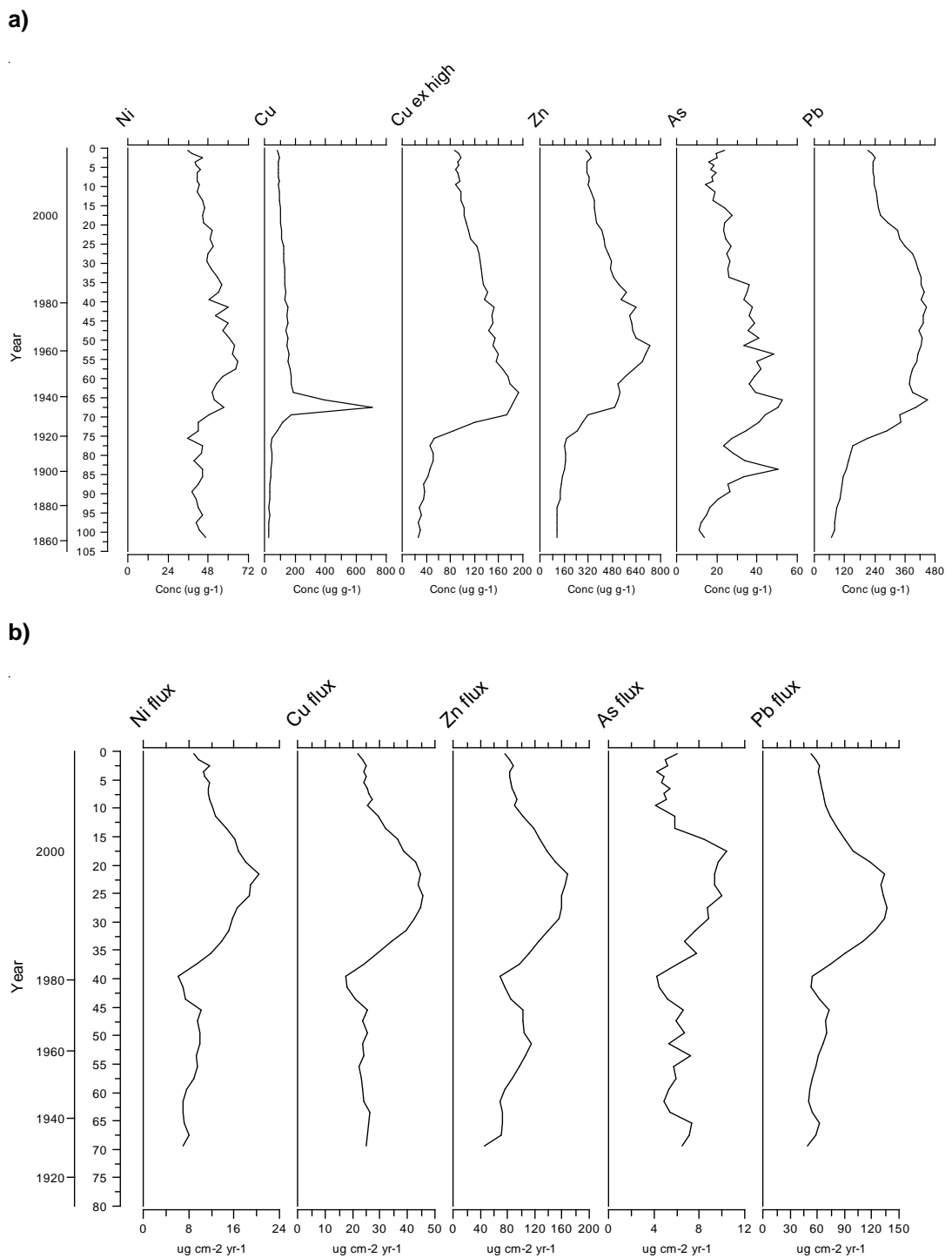
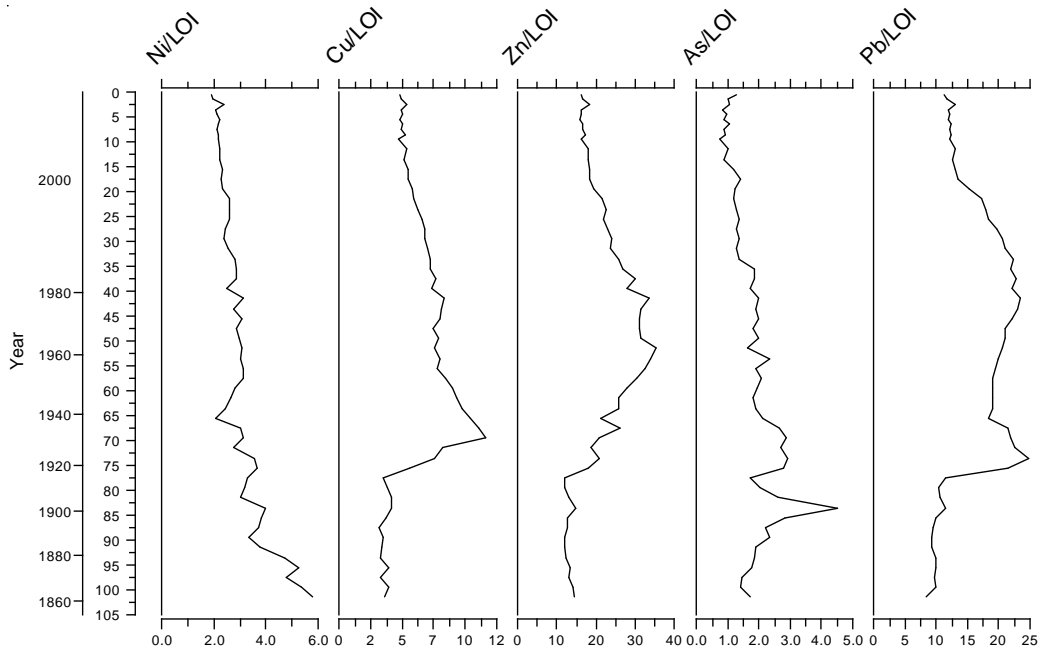


Figure 4.22 – Sediment core profiles from South Norwood Lake showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth). The profile of Cu concentration is shown twice, with one graph showing the large peak in concentration in the 1930s ('Cu') and a second graph showing the profile with the large peak removed ('Cu ex high'). The short flux profiles reflect the radiometric dating record from the core (see Chapter 3), which was used to calculate sediment accumulation rate and hence flux.

a)



b)

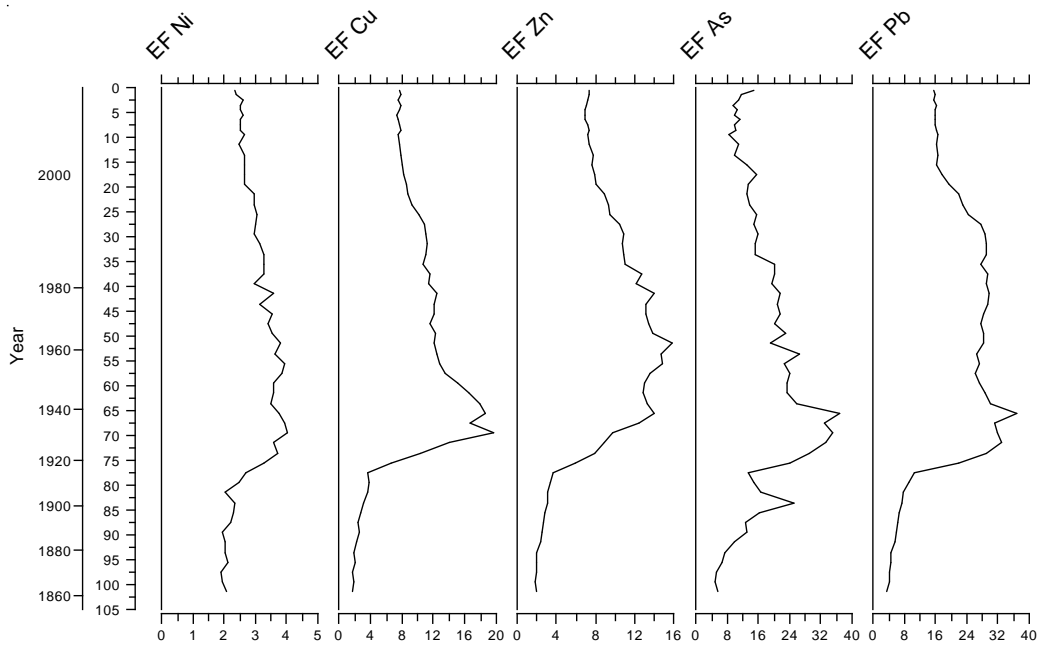
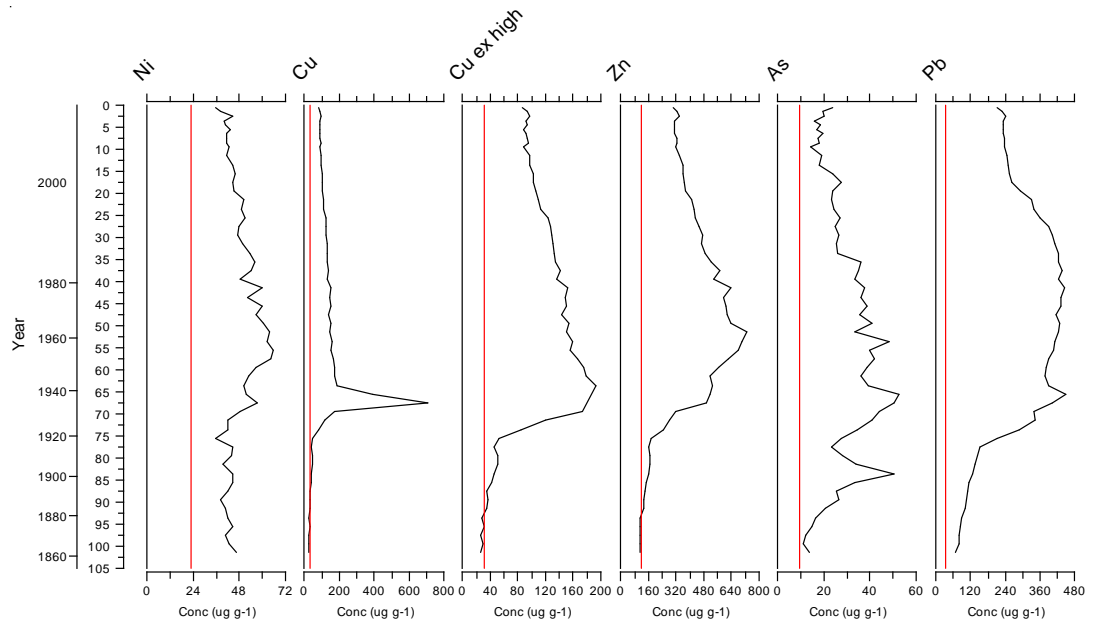


Figure 4.23 – Sediment core profiles from South Norwood Lake showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

a)



b)

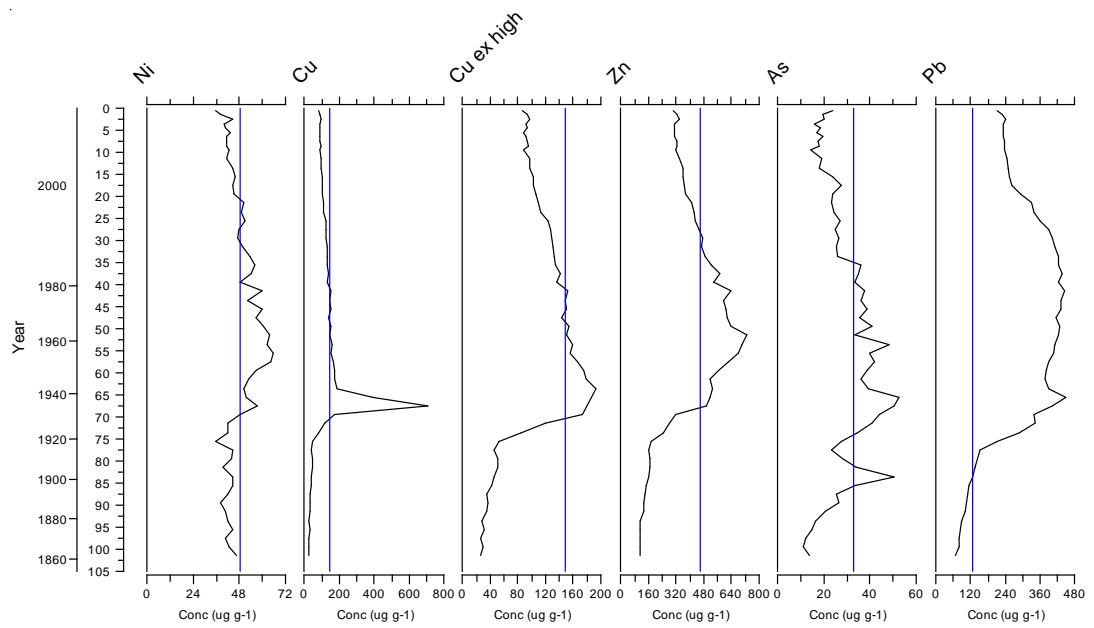


Figure 4.24 – Sediment core profiles from South Norwood Lake showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth). The profile of Cu concentration is shown twice, with one graph showing the large peak in concentration in the 1930s ('Cu') and a second graph showing the profile with the large peak removed ('Cu ex high').

4.4.6. Wimbledon Park Lake

Wet density decreased from 1.3 g cm⁻³ at the base of the core to 1.0 g cm⁻³ at the surface (Figure 4.15). The decline was mostly steady apart from a period between 40 and 60 cm deep when wet density increased. Dry weight also decreased from the base of the core to the surface, from about 35% to 15% (Figure 4.15). As with wet density, the decline was fairly steady apart from a period between 40 and 60 cm deep when dry weight increased. The amount of organic matter in the bottom half of the core was very low, between 7-8% (Figure 4.15). There was a small peak between 60 and 75 cm deep, when the amount of organic matter almost doubled, followed by another increase from about 40 cm, which peaked at 18% in the mid-1960s. The organic matter content remained at just below that level until the 2000s, after which it decreased slightly up to the surface of the core. Carbonate content (Figure 4.15) increased steadily from 2% at the base of the core to 10% at the surface. The lithogenic element profiles were all very similar to each other (Figure 4.15). The concentration of Al, Si, Ti and Zr declined very slightly between the base of the core and the surface. The profiles were all very consistent, with no major changes occurring at any point.

The metal concentration profiles were also quite similar to one another (Figure 4.15). All of the Pearson product-moment correlations between all metals were significant (Table 4.15). The most positive correlations were between Ni, Cu, Zn and Pb, where all of the correlations were greater than 0.9. Arsenic was less well correlated with the other metals although the values were still significant.

WIMP1	Ni	Cu	Zn	As	Pb
Ni	1				
Cu	.912	1			
Zn	.944	.990	1		
As	.840	.668	.731	1	
Pb	.922	.986	.985	.732	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Table 4.15 – Pearson product-moment correlations between the metals in WIMP1

In general, the concentration of metals was low in the bottom half of the core and then increased rapidly from a depth of about 40 cm. The concentrations peaked and then declined up to the surface of the core. However, there were variations as to when those changes occurred. The concentration of Ni in the bottom two thirds of the core was about 40 µg g⁻¹ and began to rise from about 60 cm. The concentration rose more sharply from a depth of 40 cm and peaked at 100 µg g⁻¹ at about 30 cm, which corresponded to the late

1960s. From that date the concentration declined to $60 \mu\text{g g}^{-1}$ at the surface. The Zn concentration was about $100 \mu\text{g g}^{-1}$ in the bottom two thirds of the core. At a depth of 45 cm the concentration rose steeply and peaked at $1500 \mu\text{g g}^{-1}$, also in the late 1960s, before declining to $980 \mu\text{g g}^{-1}$ at the surface. The concentration of Cu increased sharply at a depth of 45cm, from $30 \mu\text{g g}^{-1}$ to a peak of $180 \mu\text{g g}^{-1}$ in the late 1970s. It remained at that level until the top of the core, where it declined slightly to $160 \mu\text{g g}^{-1}$. The concentration of Pb increased slightly between 80 and 45 cm deep, from $60 \mu\text{g g}^{-1}$ to $150 \mu\text{g g}^{-1}$. A sharp rise in concentration occurred between 45 cm and 25 cm and peaked at $900 \mu\text{g g}^{-1}$ in the late 1970s, the same time as Cu. The concentration then declined to $650 \mu\text{g g}^{-1}$ at the surface. The concentration of As increased rapidly between 50 cm and 40 cm and peaked at $50 \mu\text{g g}^{-1}$. The date at which the peak occurred was unknown as it came before the lowest dated level in the core. The concentration declined quite sharply after 1960 to about $20 \mu\text{g g}^{-1}$ at the surface.

The SAR did not change between the 1960s and 2009, remaining constant at $0.1 \text{ g cm}^{-2} \text{ yr}^{-1}$ (Figure 4.15). The profiles of Ni, Zn and As flux were similar to each other, but differed to the flux profiles of Cu and Pb (Figure 4.15). Nickel flux decreased slightly from $10 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ in the late 1960s to $6.5 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ at the surface of the core. Zinc and As flux also decreased between the late 1960s and the surface of the core, the former from $160 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ to $100 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ and the latter from $5 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ to $2 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. The flux of Cu increased slightly between the mid-1960s and the late 1970s, from $16 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ to $21 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. From the late 1970s to the late 1990s Cu flux remained quite constant at about $20 \mu\text{g cm}^{-2} \text{ yr}^{-1}$, and then declined to $17 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ at the surface. Lead flux also increased between the mid-1960s and the late 1970s, from $80 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ to $105 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. From the late-1970s to the surface of the core Pb flux declined overall to $70 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. The fact that SAR did not change between the 1960s and the late 2000s meant that it was not the driver of metal flux. Instead, metal flux was driven by changes in metal concentration. The concentrations of Ni, Zn and As all peaked in the late 1960s or before, and the flux profiles reflected the subsequent decline in concentration that each metal then underwent. The increasing concentrations of Cu and Pb peaked slightly later, in the late 1970s, which corresponded to the rise in flux that occurred between the 1960s and 1970s. The decline in Pb flux from the late 1970s matched the fall in concentration. The concentration of Cu remained constant until the 1990s and then declined, and that was also reflected in the flux profile.

As discussed in Chapter 3, there was clear disturbance to the sediments from Wimbledon Park Lake. Interpretation of the radiometric data from the core showed that the sediments in the top 40 cm were newer and had been deposited since the 1960s, and that the sediments

at greater depths were much older. The suggested cause of this was that the lake had been dredged just prior to the 1960s, although no record of this had been found.

This hypothesis was supported by the metal profiles from the core, all of which showed a substantial increase in concentration at approximately 40 cm. Very low concentrations were found in the undateable part of the core (from 40 cm to the bottom), which indicated that those sediments were older and deposited at a time when there was less anthropogenic contamination. The abrupt rise at 40 cm was interpreted to be the result of deposition of new contaminated layers of sediment. The organic matter profile also showed the same rise at 40 cm. The amount of organic matter in the other London lakes increased up the cores – newer sediments were more organically rich than older sediments. Assuming that this would also have been the case at Wimbledon Park Lake, the steep increase at 40 cm could also be attributed to the deposition of newer sediments on older. The earlier increase in organic matter (60-75 cm) was not reflected in any of the other profiles, but it was possible that such a rise may have contributed to the need to dredge the lake. The similarity of the organic matter profile to the metal profiles suggested that the former may have enhanced the metal concentrations. The wet density and dry weight profiles showed that sediment composition had remained quite consistent, apart from a slight change just prior to when the lake was presumably dredged. The decline in both profiles between 40 and 50 cm might indicate the difference between older, more compact sediments and newer, less dense material. In contrast, no interruption to the sediment record was visible in the profiles of the lithogenic elements. The consistency of the profiles showed that inputs of inorganic material from the catchment did not change, and this was also true for the amount of carbonate erosion to the lake. The lack of change in inorganic inputs could be explained by the fact that removal of sediments would not impact upon input from the catchment.

Normalising the metal concentrations to organic matter resulted in a large change to the profile of Ni (Figure 4.16). The increase at 40 cm was no longer present, and instead, between 30 cm and 50 cm the normalised concentration was fairly level. However, as with the original profile, the concentration still declined between the late 1960s and the surface of the core. The steep increase in organic matter at 40 cm clearly enhanced the increase in Ni at the same time. However, the other metals were not affected in the same way, as the normalised profiles of Cu, Zn, As and Pb were very similar to the originals (Figure 4.15).

The consistency of the lithogenic element concentrations meant that the enrichment factor profiles were very similar to the concentration profiles (Figure 4.16). All of the enrichment factors were greater than 1, even in the older sediments in the undated part of the core.

However, it seemed unlikely that the older sediments were contaminated by anthropogenic pollution given the consistently low concentrations in that part of the core, and the results may have been a consequence of the crustal abundances overestimating enrichment. Enrichment increased rapidly for all metals between 40 and 50 cm. As with concentration, Ni and Zn enrichment peaked in the late 1960s and then declined to the surface of the core. Lead enrichment peaked in the 1970s and then also decreased to the surface. Enrichment of As peaked just prior to the dated part of the core and then declined to the surface. Only Cu showed a slightly different pattern. The large increase in enrichment from 40 cm levelled out in the 1970s, but rather than peaking and then falling, subsequently increased very slightly up to the top of core, with the highest levels of enrichment being found at the surface. The similarity of the enrichment and concentration profiles reinforced the interpretation that the sediments in the top 40 cm of the core were much more recent than those beneath them.

WIMP1	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	2009	Maximum	2009
Ni	350	170	110	30
Cu	480	410	20	10
Zn	1190	720	240	120
As	450	110	60	No exceedance
Pb	2430	1770	610	420

Table 4.16 - Percentages by which metal concentrations exceed TECs and PECs at Wimbledon Park Lake. The table includes both the maximum exceedance and the exceedance when the core was taken (2009).

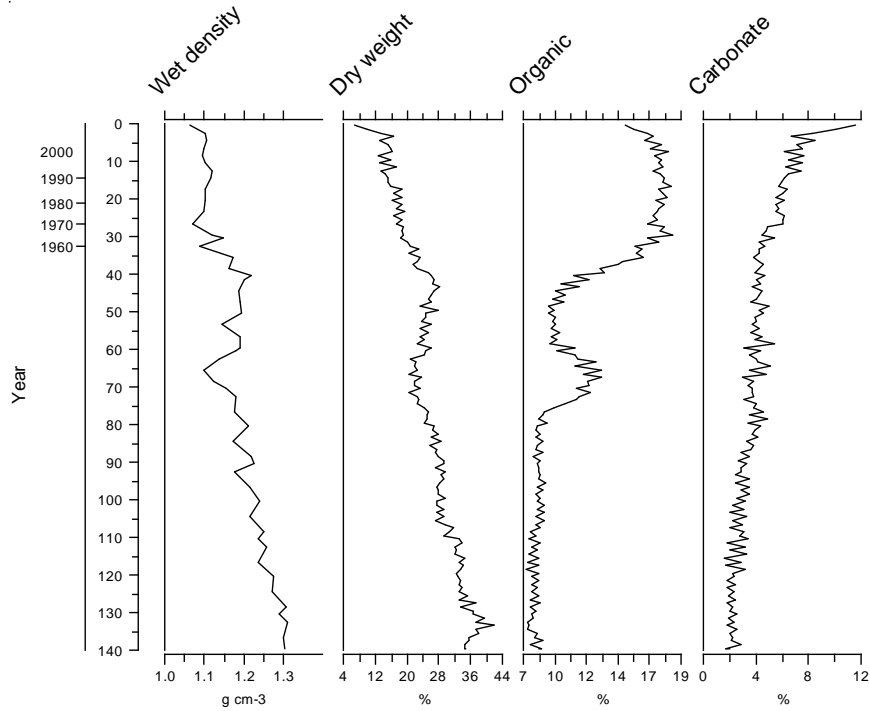
The metal concentrations in the top 40 cm of WIMP1 have always exceeded the TECs (Figure 4.16). The timing and extent to which the concentrations have exceeded the PECs varied between metals (Figure 4.16; Table 4.16). There has been a lot of Pb contamination at the site. Lead has exceeded the PEC since the 1960s, and in the late 1970s was 610% higher. At the surface of the core Pb was still 420% greater than the PEC. Nickel and Zn have also exceeded the PEC since the 1960s. The greatest exceedance was in the late 1960s when the concentration of Ni was twice that of the PEC, and the concentration of Zn was 240% higher. Both metals were still in exceedance of the PEC at the surface of the core, Ni was 30% greater and Zn was 120% higher. The concentration of Cu has also exceeded the PEC since the 1960s, although not to the same degree as Pb, Ni or Zn. In the late 1970s the maximum exceedance was 20% higher than the PEC, and at the surface this had dropped to 10%. The concentration of As exceeded the PEC from before the 1960s up until the 1980s. The greatest exceedance occurred at a depth of 40 cm when the concentration of As was 60% higher than the PEC.

A previous 'Silt and Water Survey' of Wimbledon Park Lake was carried out in 2008 by Mid Kent Fisheries. Surface silt samples were taken and analysed for a number of metals. Contamination was found to be 'high', especially around the inlets, with the probable cause being cited as road run off. The results from the silt survey are shown in Table 4.17, alongside the results from the 2008 level in the WIMP1 core. The concentrations from WIMP1 are within the range of values determined in the 2008 silt survey.

Element	Conc ($\mu\text{g g}^{-1}$) MKF	Conc ($\mu\text{g g}^{-1}$) WIMP1
Ni	42-440	59.6
Cu	Not analysed	
Zn	Not analysed	
As	11-19	17.6
Pb	110-710	646
	Conc (ng g^{-1})	Conc (ng g^{-1})
Hg	470-1700	N/A

Table 4.17 – Range of concentration values found in the 2008 survey of Wimbledon Park Lake surface sediments (Mid Kent Fisheries), compared to the values in WIMP1 at a depth corresponding to the same year

a)



b)

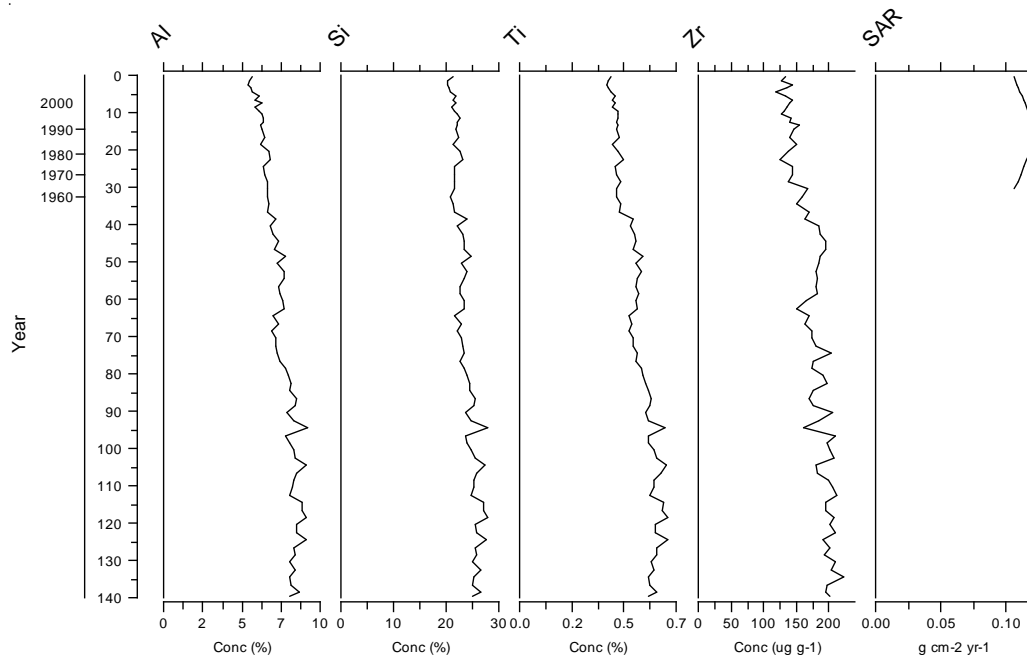
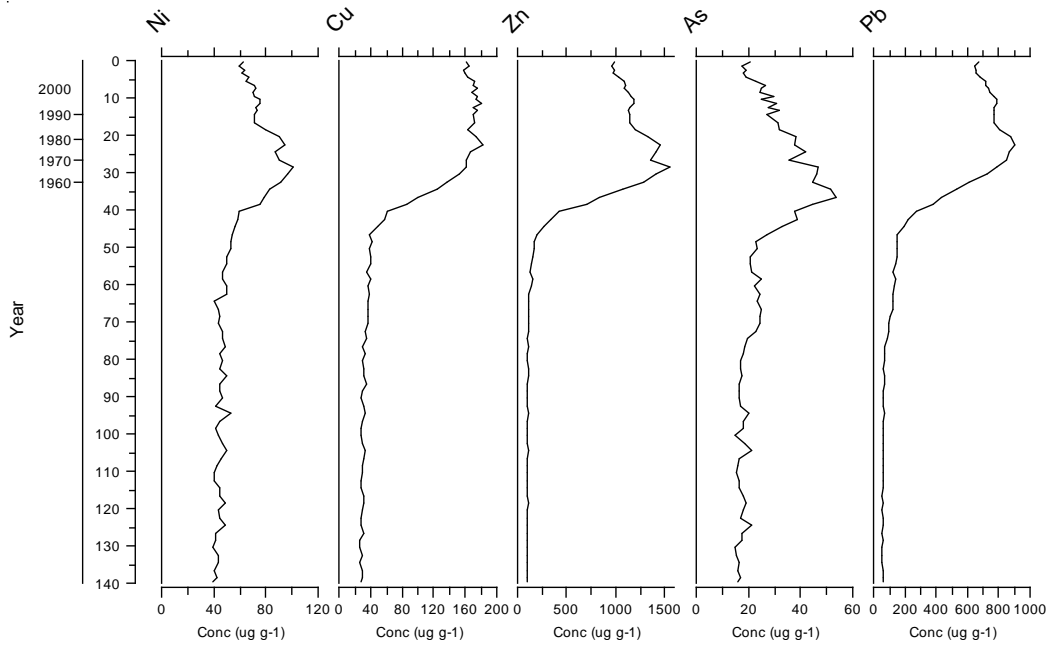


Figure 4.25 – Sediment core profiles from Wimbledon Park Lake showing a) lithostratigraphic data – wet density, dry weight, organic matter and carbonate content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth). The short SAR profile reflects the radiometric dating record from the core (see Chapter 3), which was used to calculate SAR.

a)



b)

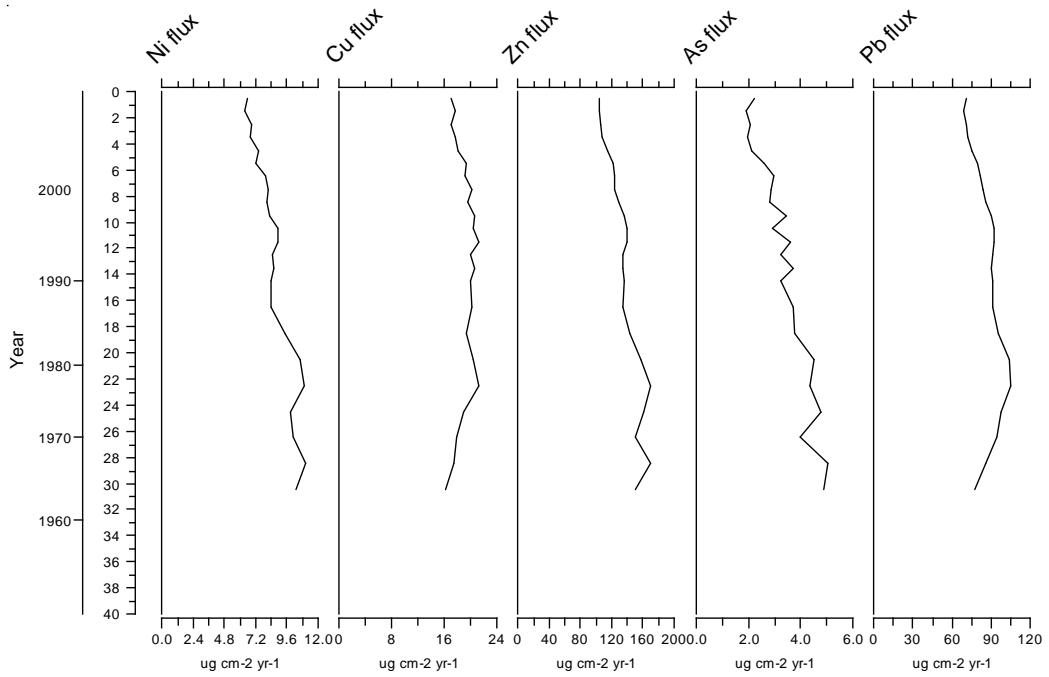


Figure 4.26 – Sediment core profiles from Wimbledon Park Lake showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth). The short flux profiles reflect the radiometric dating record from the core (see Chapter 3), which was used to calculate sediment accumulation rate and hence flux.

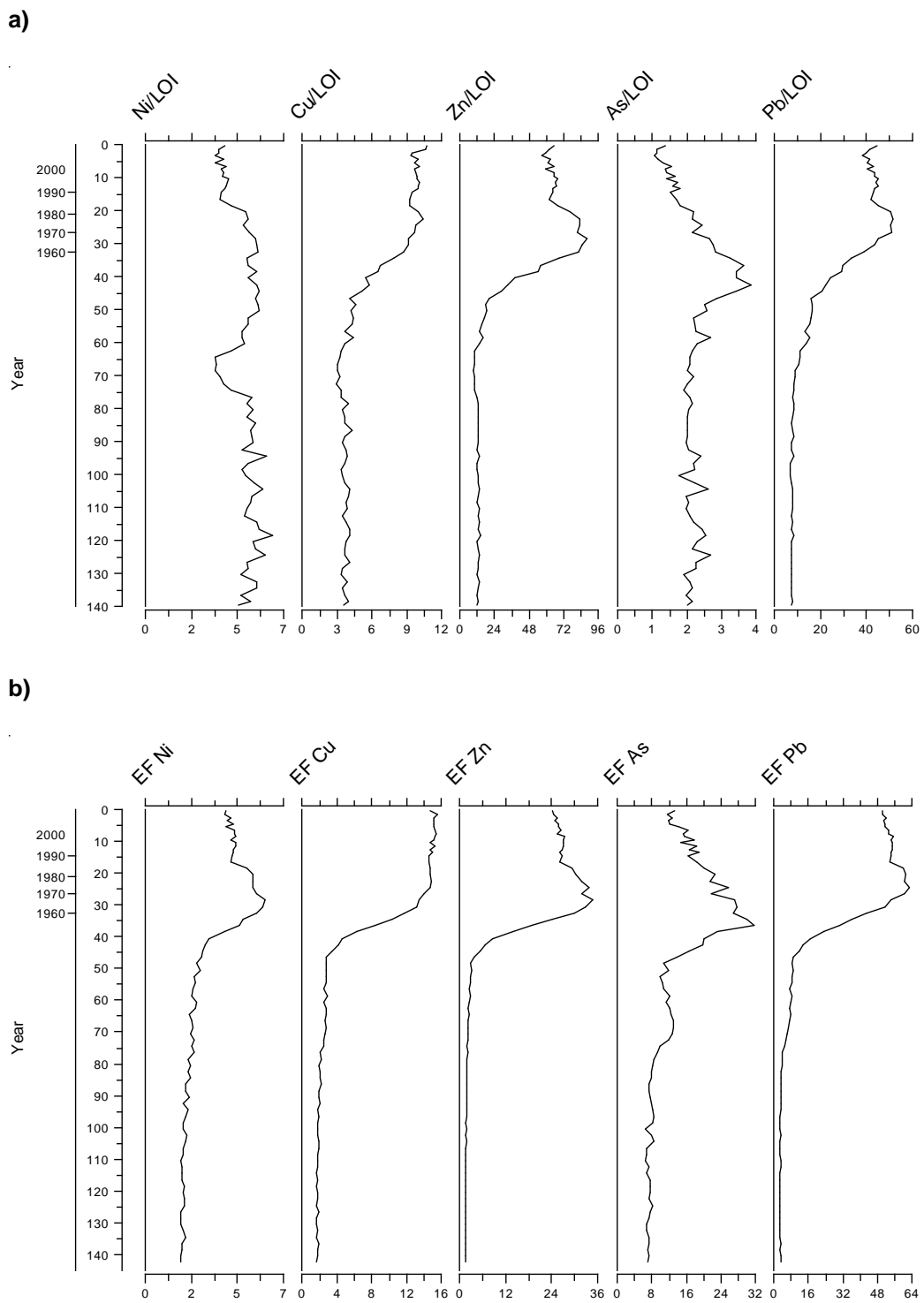


Figure 4.27 – Sediment core profiles from Wimbledon Park Lake showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

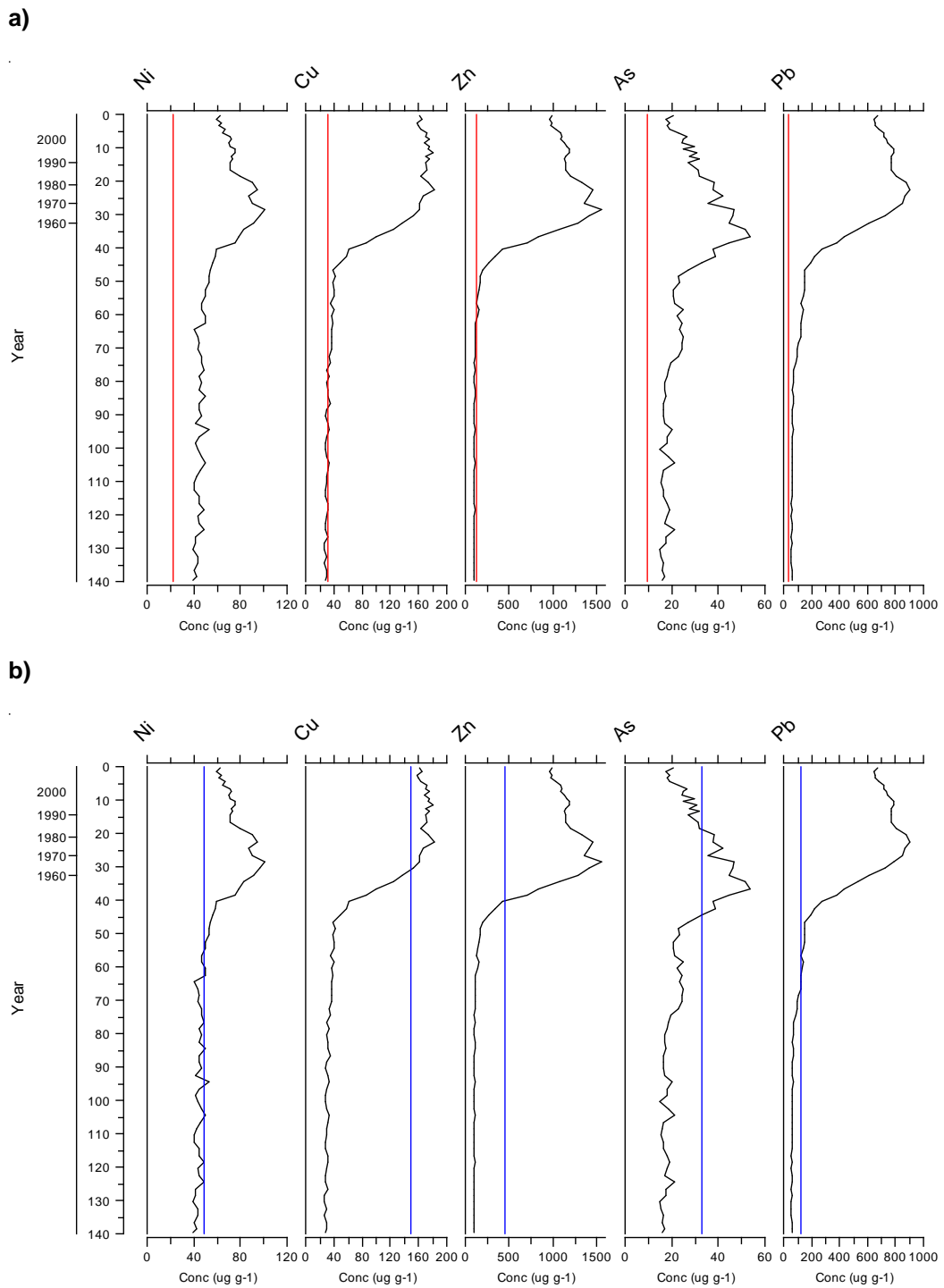


Figure 4.28 – Sediment core profiles from Wimbledon Park Lake showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As and Pb, each plotted against sediment age (and depth)

4.4.7. Wake Valley Pond

Wet density decreased overall from 1.17 g cm⁻³ in the early 20th century to 1.10 g cm⁻³ in the 2000s (Figure 4.17). Dry weight (Figure 4.17) decreased sharply at the bottom of the core, from 55% to 25%, and then continued to decrease more steadily to 6% at the surface of the core. The amount of organic matter (Figure 4.17) increased from 7% at the base of the core to 18% in the late 19th century. The content then declined slightly before increasing again to a peak of 37% in the 1950s. The amount of organic matter fell to 28% in the 1970s and then decreased very slightly to 25% at the surface of the core. Carbonate content remained fairly constant over the length of the core, with an average content of 4%.

The profiles of Al, Si and Ti were very similar to one another (Figure 4.17). The concentrations decreased slightly between the late 19th century and the mid-1960s. Two short, sharp peaks in concentration occurred in the 1880s and early 1900s. In the late 1960s the concentrations increased and then remained fairly constant up to the present day. The concentration of Zr (Figure 4.17) declined sharply at the base of the core, which matched the profile of dry weight. The concentration then decreased more steadily until the 1950s, after which it increased up to the surface of the core. As with the Al, Si and Ti profiles, there were small peaks in the profile in the 1880s and early 1900s.

The metal concentration profiles of Ni, Cu, Zn, Pb and Hg were similar to each other, but the profile of As was very different (Figure 4.17). These relationships were reflected by the Pearson product-moment correlations (Table 4.18). The correlations between Ni, Cu, Zn, Pb and Hg were all significant. The most positive correlations were between Ni, Cu, Zn and Pb, with all the values above 0.9, whilst the correlations with Hg had slightly lower values. Arsenic was negatively correlated with all of the other elements and of these, only As/Cu and As/Pb were significant.

WAKE1	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.925	1				
Zn	.975	.972	1			
As	-.040	-.324	-.213	1		
Pb	.935	.989	.983	-.308	1	
Hg	.867	.771	.821	-.094	.791	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Table 4.18 – Pearson product-moment correlations between the metals in WAKE1

Although the metal concentration profiles of Ni, Cu, Zn, Pb and Hg showed the same overall pattern, the dates at which changes in concentration occurred varied slightly between the metals. The concentration of Ni increased from the base of the core to $100 \mu\text{g g}^{-1}$ in the late 19th century before declining slightly. The concentration increased more rapidly in the early 20th century and peaked at $260 \mu\text{g g}^{-1}$ in the late 1940s, which was the highest concentration of Ni found in any of the London lakes. The concentration then decreased to $90 \mu\text{g g}^{-1}$ at the surface. The concentration of Cu increased slowly from the bottom of the core until the early 20th century when a more rapid increase occurred. The concentration peaked at $190 \mu\text{g g}^{-1}$ in the mid-1940s and then declined overall to $90 \mu\text{g g}^{-1}$ at the top of the core. As with Cu, the concentration of Zn increased slightly in the late 19th century and then rose more rapidly in the early 20th century. The concentration peaked at $2100 \mu\text{g g}^{-1}$ in the late 1940s, which was the highest concentration of Zn found at any of the London lakes, but had declined to $500 \mu\text{g g}^{-1}$ by the 2000s. The concentration of Pb also increased slightly over the late 19th century and then rose more rapidly in the early 20th century. A sharp increase occurred in the mid-1930s and the concentration peaked at $420 \mu\text{g g}^{-1}$ in the late 1950s, before declining to $180 \mu\text{g g}^{-1}$ at the surface of the core. The resolution of the Hg data from WAKE1 was coarser than for the other elements. The concentration of Hg increased more steadily than the other metals, from 160ng g^{-1} in the late 19th century to a peak of 430ng g^{-1} in the mid-1960s. The concentration then declined to 180ng g^{-1} at the surface of the core. In contrast, the concentration of As increased rapidly from $11 \mu\text{g g}^{-1}$ to $30 \mu\text{g g}^{-1}$ at the bottom of the core, the opposite to the pattern seen in the dry weight and Zr profiles. From a peak of $37 \mu\text{g g}^{-1}$ in the late 19th century the As concentration decreased up the core to $15 \mu\text{g g}^{-1}$ at the surface.

Between the late 19th century and the late 1960s the SAR remained fairly steady at less than $0.1 \text{g cm}^{-2} \text{yr}^{-1}$ (Figure 4.17). The SAR began to increase from the early 1970s reaching $0.2 \text{g cm}^{-2} \text{yr}^{-1}$ by the surface of the core. The flux profiles of Cu, Pb and Hg were very similar to each other (Figure 4.17). Flux increased from the early 20th century to a peak in the early 1950s, which was then followed by a decline to the mid-1970s. From the late 1970s flux increased again up to the surface of the core. The flux of Ni and Zn (Figure 4.17) also increased from the early 20th century, but peaked slightly earlier in the late 1940s. Flux declined until the mid-1970s and then increased again, although never reaching the level achieved in the 1940s. In the early 1980s flux stabilised and remained at the same level up to the surface of the core. The profile of As flux differed to the others, although it showed the same overall increase between the base of the core and the surface (Figure 4.17). From the late 19th century until the late 1960s As flux remained fairly constant, increasing between the early 1970s and the surface of the core. Comparison between the metal concentration, SAR and metal flux profiles showed that between the late 19th century and the late 1960s metal flux was driven by concentration. During this period SAR did not change but concentration did, and this was reflected in the changes to the flux profiles. However, from the 1970s up to

2008, SAR became the main driver as fluxes increased even though concentrations had declined. The decrease in concentration was in part connected to dilution caused by increased sedimentation.

The consistency of the dry weight profile showed that the composition of the sediments in Wake Valley Pond had changed little since the late 19th century. This was supported by the same overall decline in the wet density profile. The sharp decline in dry weight at the bottom of the core matched the same decrease in Zr concentration, and given the radiometric chronology of the core was interpreted as basal material. Inputs of inorganic matter from the catchment were also fairly consistent over the length of the core. The lithogenic element profiles showed that there were two short periods in the late 19th century when influx increased. There was also an increase in the 1960s, although this was not reflected in the profile of Zr which suggested that there had been a rise in the input of a particular fraction of the soil. The amount of carbonate being eroded to the lake was also fairly consistent over the length of the core. The rise in organic matter in the early 20th century corresponded to the increase the concentrations of Ni, Cu, Zn, Pb and Hg, which suggested that these metal signals may have been enhanced by organic content.

However, normalising the concentrations of Ni, Cu, Zn and Pb to organic matter did not change the general pattern of the profiles (Figure 4.18). The normalised concentrations still increased in the early 20th century and then declined up to the surface of the core, although there was more variation in the profiles and some of the changes in concentration were less well defined. This showed that the amount of organic matter in the core did not affect the concentrations of Ni, Cu, Zn or Pb to any great extent. In contrast, normalising the concentration of Hg to organic matter dramatically changed the shape of the profile (Figure 4.18). The normalised profile decreased overall from the base of the core to the surface. There were some periods when the normalised concentration increased, such as in the late 19th century and in the 1950s, but the rise in the early 20th century was no longer present. This showed that Hg had a higher affinity for organic matter than the other metals. Even though the profiles of As and organic matter weren't very similar, normalising As concentration to organic content did result in some changes to the profile, which showed that As was actually influenced by the amount of organic matter in the core. The normalised As profile decreased between the bottom of the core and the mid-20th century, and then remained constant up to the surface (Figure 4.18). The normalised profiles of As and Hg were similar to one another.

The enrichment factor profiles of Ni, Cu, Zn, Pb and Hg were very similar to the concentration profiles, although the mid-20th century peak in concentration became more

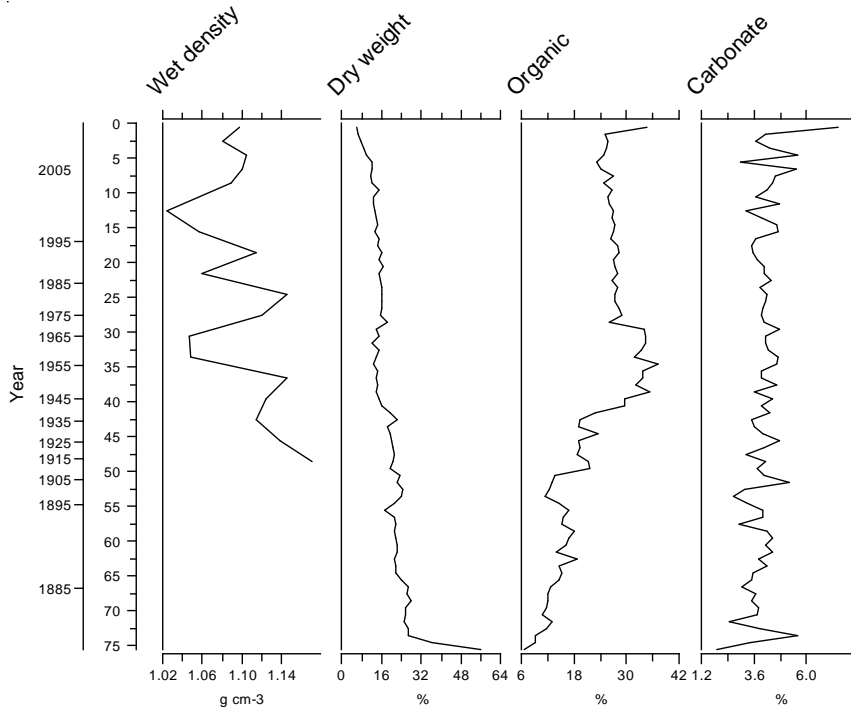
pronounced (Figure 4.18). The similarity was unsurprising given the general consistency of the lithogenic element concentrations. The enrichment profile of As changed slightly from the original, becoming more similar to the profiles of the other metals (Figure 4.18). There was a peak in enrichment in the mid-1950s which was not present in the original concentration profile. All of the enrichment factors for all of the metals were greater than 1 which meant that there had been anthropogenic contamination of the lake since it was built in the late 19th century. Enrichment of Ni, Cu, Zn, Pb and Hg increased dramatically over the middle decades of the 20th century, but has since declined to levels only slightly higher than those found at the bottom of the core. Enrichment of As had been high since the late 19th century, but at the surface of the core enrichment was at the lowest it had ever been.

WAKE1	TEC exceedance (%)		PEC exceedance (%)	
	Maximum	2008	Maximum	2008
Ni	1060	300	440	90
Cu	510	180	30	No exceedance
Zn	1640	330	360	10
As	280	70	10	No exceedance
Pb	1080	370	230	30
Hg	140	Level	No exceedance	No exceedance

Table 4.19 – Percentages by which metal concentrations exceed TECs and PECs at Wake Valley Pond. The table includes both the maximum exceedance and the exceedance when the core was taken (2008).

Even though enrichment has declined, the concentrations of all metals have exceeded the TECs over the entire length of the core, apart from at the very bottom (Figure 4.18). The relationship with PECs has varied (Figure 4.18; Table 4.19). The concentration of Ni exceeded the PEC for the whole core, with the greatest exceedance occurring in the late 1940s when the concentration of Ni was 440% higher than the PEC. By 2008, this had dropped to 90%. The concentration of Zn first exceeded the PEC in the early 20th century. The maximum exceedance occurred in the late 1940s when the concentration of Zn was 360% higher than the PEC, although this had dropped to only 10% by 2008. The large exceedances of Ni and Zn reflect the fact that the highest concentrations of these metals were found at this lake. As with Zn, the concentration of Pb has also been higher than the PEC since the early 20th century and was still above it in 2008. The greatest exceedance occurred in the late 1950s when the concentration of Pb was 230% more than the PEC, but this had fallen to 30% by 2008. Copper only exceeded the PEC three times in the lake's history; in the mid-1940s, the early 1960s and the mid-1980s. The exceedance occurred over short periods and the maximum concentration was only 30% higher than the PEC. Similarly, As only exceeded the PEC at one brief point in the past, in the late 19th century, by 10%. The concentration of Hg has never exceeded the PEC, and in 2008 was at approximately the same level as the TEC.

a)



b)

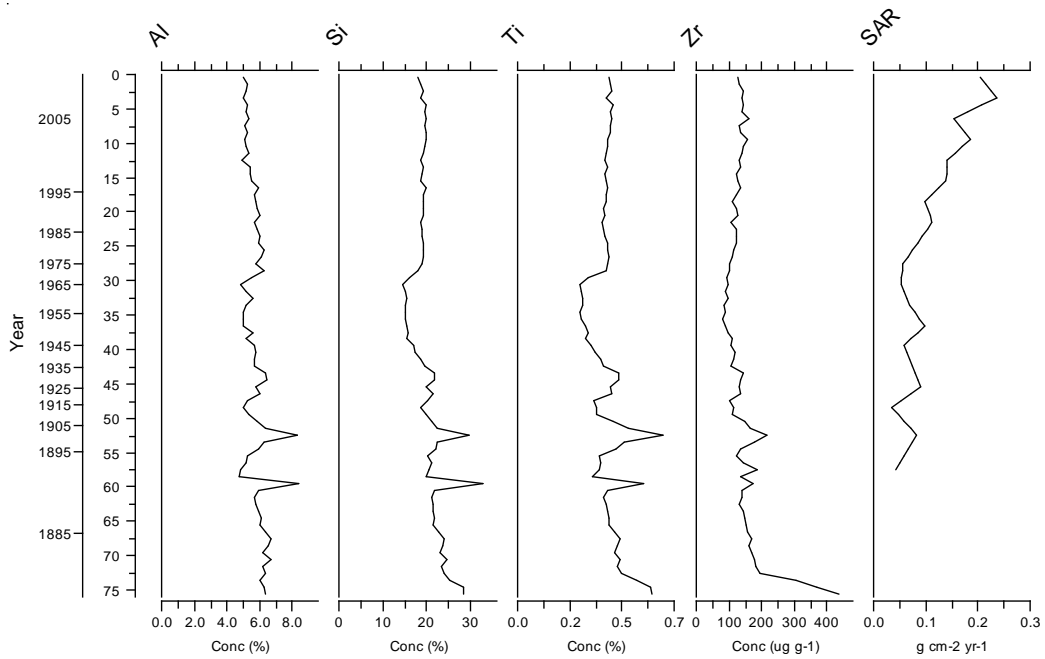
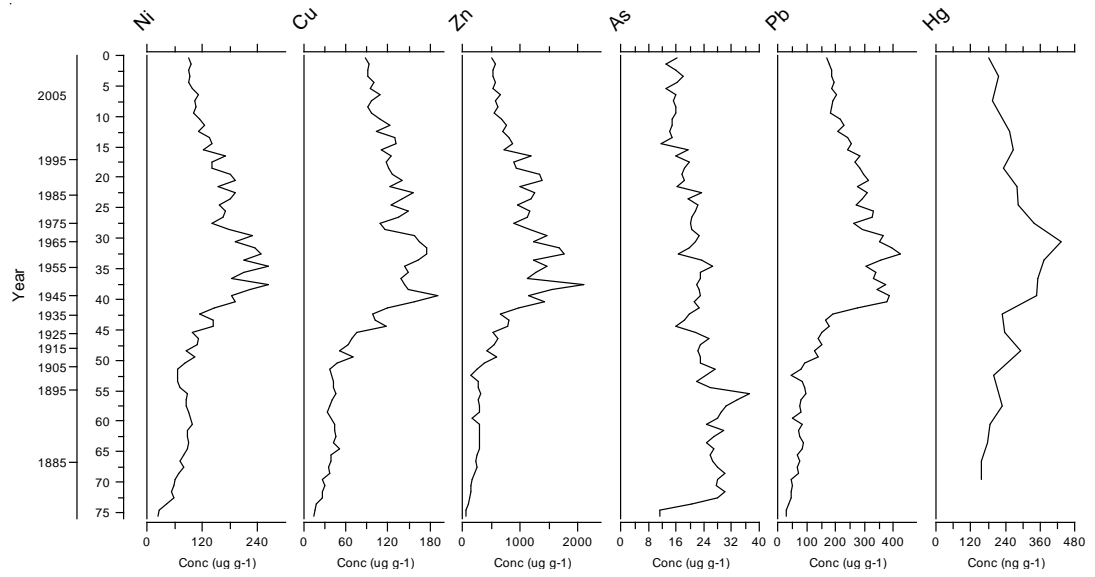


Figure 4.29 – Sediment core profiles from Wake Valley Pond showing a) lithostratigraphic data – wet density, dry weight, organic matter and carbonate content, and b) lithogenic element (Al, Si, Ti and Zr) concentrations and sediment accumulation rate (SAR), all plotted against sediment age (and depth)

a)



b)

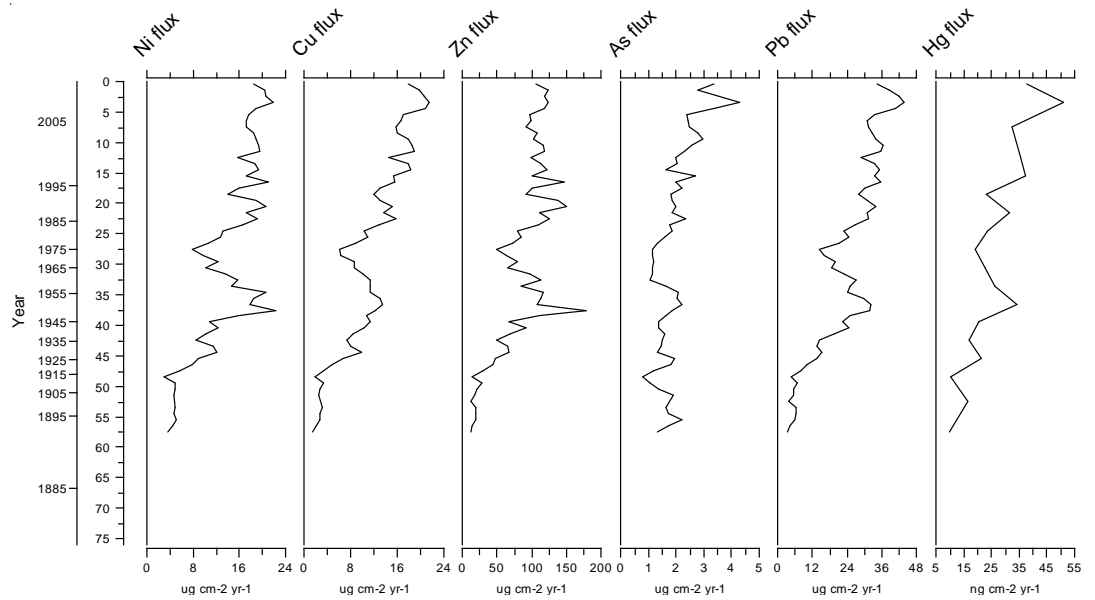
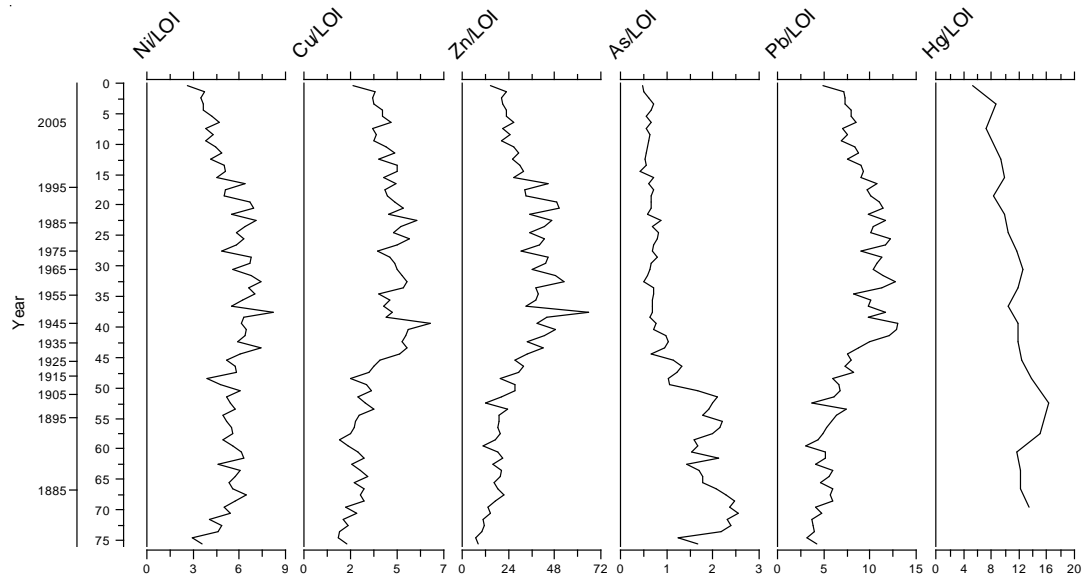


Figure 4.30 – Sediment core profiles from Wake Valley Pond showing a) metal concentrations and b) metal flux profiles, of Ni, Cu, Zn, As, Pb and Hg, each plotted against sediment age (and depth).

a)



b)

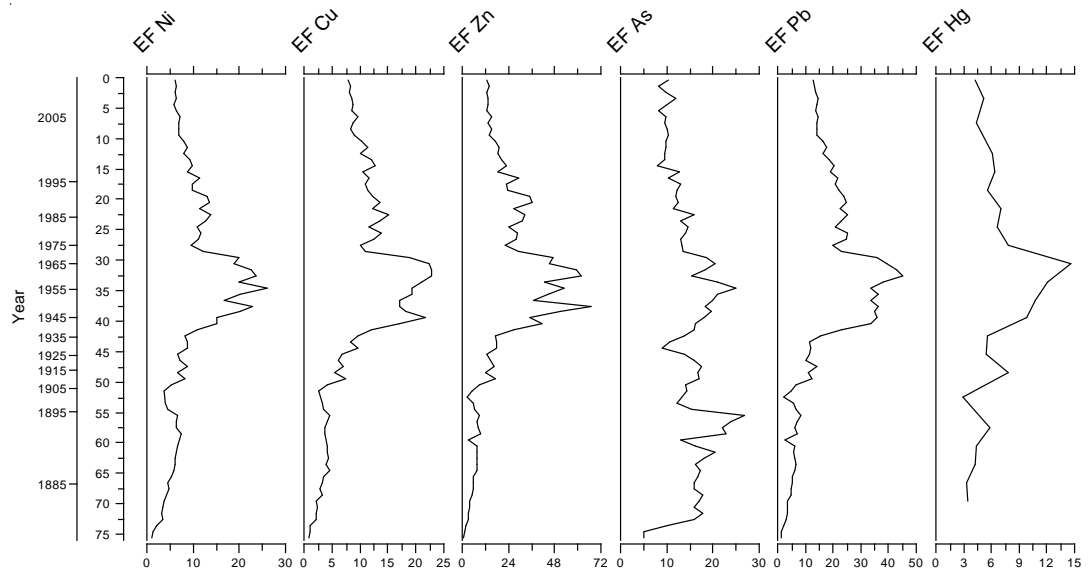
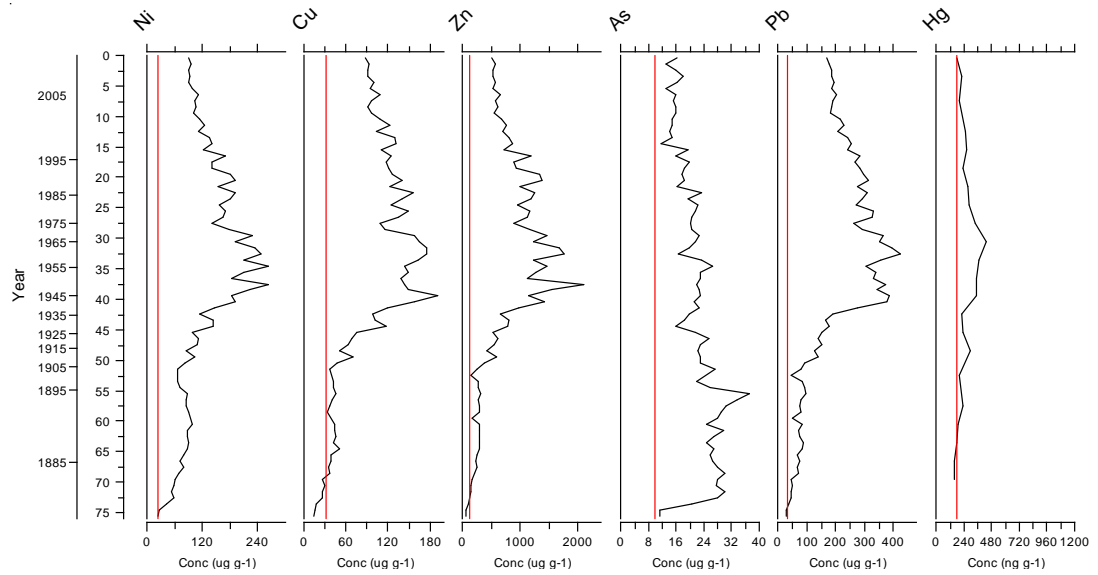


Figure 4.31 – Sediment core profiles from Wake Valley Pond showing a) metal concentrations normalised to organic matter content, and b) metal enrichment factors (EF), for Ni, Cu, Zn, As, Pb and Hg, each plotted against sediment age (and depth)

a)



b)

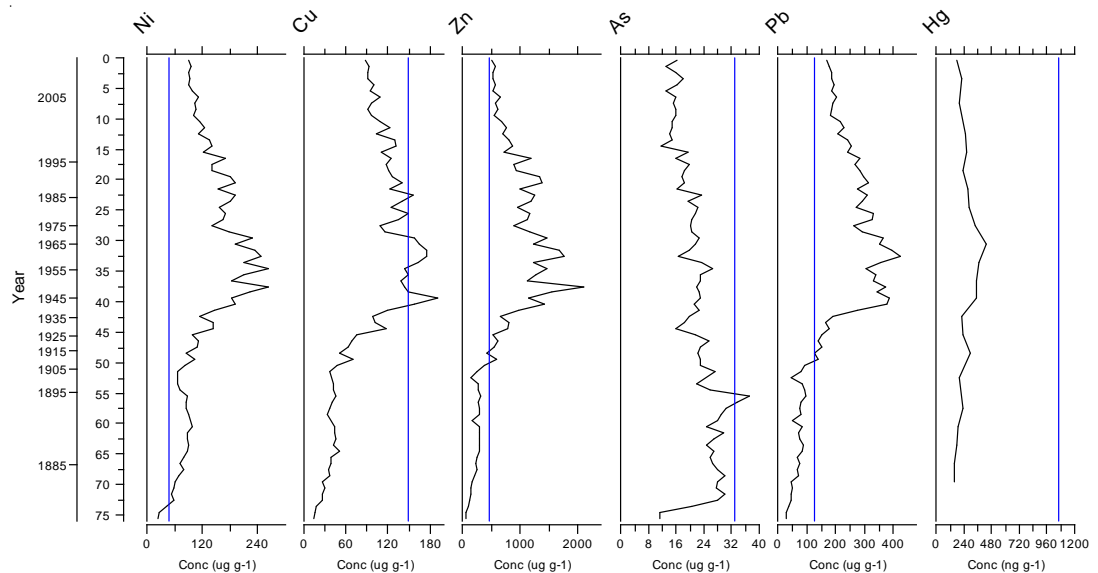


Figure 4.32 – Sediment core profiles from Wake Valley Pond showing a) metal concentrations in relation to TECs (red lines) and b) metal concentrations in relation to PECs (blue lines), for Ni, Cu, Zn, As, Pb and Hg, each plotted against sediment age (and depth)

4.5. Discussion

The results from each of the London lakes (Sections 4.4.1 to 4.4.7) have highlighted a number of different but interlinked themes that will be discussed within three contexts. Firstly, it will be determined if it is possible to establish a pollution pattern particular to London. Secondly, comparisons between metal pollution in London lakes and recent trends

in emissions and deposition will be made, and lastly, sediment quality in these lakes, along with records of contamination from other urban sites will be assessed.

4.5.1. Establishing a London pollution pattern

As outlined in Section 1.5.3, the sources of metals to urban areas are complex. The aim of the first part of the discussion is to establish whether the change in metal concentration at each of the lakes was site specific, or if there was a more general pattern across the London area. The relative importance of the sources of contamination within the urban environment could then be assessed.

There are a number of factors which affect metal concentrations in lake sediments that might explain some of the differences in concentration, both between, and within sites. At the smallest scale, the behaviour of metals in sediments is important. Within a single sediment core, the pattern of As concentration commonly differs to those of other metals, and is often characterised by large variability (e.g. Yang et al, 2004; Lavilla et al, 2006). Although some studies have attributed the difference in behaviour to separate pollution sources (e.g. Yang et al, 2004), more emphasis has been placed on the chemical behaviour of As in comparison with other metals. In contrast to the cationic nature of Ni, Cu, Zn, Pb and Hg, As behaves as an anion in aquatic environments and changes oxidation state as the redox environment changes (Luoma & Rainbow, 2008). Arsenic mobility is also connected to the lacustrine cycling of Fe. In oxidised sediments, Fe is an important scavenger of As, and co-precipitation of As(V) and Fe-oxides can take place. In anoxic sediments, As is found in its reduced form, As(III), and is connected to Fe(II) (Rognerud & Fjeld, 2001). In addition to explaining why As might show different trends to other metals in lake sediment cores, the redox behaviour of As is also important with respect to toxicity, as the reduced form, As(III), is more soluble, more mobile and more toxic than the oxidised form, As (V).

Although no urban studies are available, a number of studies have used principal components analysis (PCA) to show the relationship between As and Fe-oxyhydroxides. Lavilla et al (2006) produced a PCA with data from a lake in the Spanish Pyrenees. Arsenic, Co, Mn and Fe clustered together on the first principal component, and the results were interpreted as confirmation of the preferential binding of As and Co to Fe-Mn oxyhydroxides. This was also supported by the depth profiles of the four elements, with As and Co concentrations increasing alongside the concentrations of Fe and Mn. A separate cluster containing Cu, Ni, Sr, Pb and Zn was identified and it was suggested the separation between the two was due to the different binding behaviour of the metals, as well as to different origins. Rognerud and Fjeld (2001) found that in a PCA of data from Norwegian

lakes, out of a cluster of elements including Hg, Sb, Bi, Pb and As, as well as organic matter, As behaved differently to the rest by also being associated with Fe. Wallstedt et al (2008) found that increased sequestration of As in a number of Swedish lakes was probably at least partly caused by an increased adsorption to Fe oxyhydroxides, in addition to changes in pH.

Principal components analysis was applied to selected data from the London lakes to determine if this could be the reason why the As concentration profiles were so different to those of the other metals in the sediment cores in this study. The plot of principal component axes 1 and 2 (Figure 4.19) showed a clear overlap between the As and Fe vectors, which supported the theory that the redox behaviour of both was closely linked. However, the signal for As was much stronger than that for Fe, which indicated that there was a much larger loading of As to the lakes. Iron is often considered to represent natural sources of elements (Liu et al, 2003; Wu et al, 2007), so the difference could be attributed to anthropogenic loading of As.

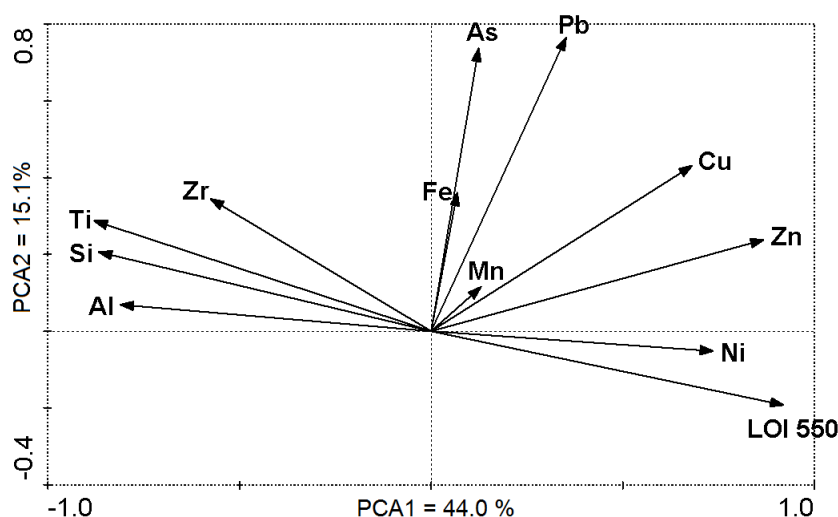


Figure 4.33 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb, lithogenic elements (Ti, Si, Al, Zr), redox-sensitive metals (Fe, Mn) and levels of organic matter (LOI 550), from all sediment core samples from the seven London lakes. The first two principle components are shown, the first accounting for 44% of the variance within the samples, and the second accounting for 15.1%.

Although the behaviour of As in sediments explained why the As profiles at each of the sites were so different from those of the other metals, it did not account for the differences in trends between some of the other metals. The Pearson correlations were generally highest between Ni, Cu, Zn and Pb. This was also found in the study by Lavilla et al (2006), where correlations greater than 0.8 were found between all four metals. The high correlations were

attributed to the metals having both the same binding behaviour and anthropogenic origins. However, these results were obtained from just one lake. There was more variation across the London lakes. In STCK2, Pb correlated better with As than with Ni, Cu or Zn. In WAKE1, Ni, Cu, Zn, Pb and Hg were all highly correlated, but in contrast at VALE1 Hg correlated better with As than any of the other metals. There could be two reasons for this, (1) the sources of metal contamination were different at these sites, or (2) the binding behaviour of the metals had changed.

The PCA (Figure 4.19) corroborated the former to an extent. Arsenic and Pb were more closely related to each other than they were to Cu, Zn and Ni, which were grouped separately. This suggested that the metals came from different sources. There are a number of studies which support this theory. Yang et al (2004) traced the sources of heavy metals to a lake in China and found that the metals could be split into two groups, those of anthropogenic origin (Pb, Hg, As) and those that were associated with lithogenic elements (Ni, Cu and Zn). The study of another lake in China, Taihu Lake (Wang et al, 2004), concluded that the relationship between Ni, Cu and Zn showed that they came from the same kind of pollution source, separate to that of Pb, Cd and Cr. Gerritse et al (1998) showed that in a study of surface sediments in an industrialised estuary in Western Australia, the concentration of Pb was much greater than expected, particularly in comparison with the levels of Zn, Cd and Cu. The difference was assumed to be because there was an additional source of Pb to the estuary, in the form of particulate Pb-oxides from road runoff.

Although different sources of metal contamination at each of the sites may therefore be responsible for some of the differences in concentration trends, the binding behaviour of the metals to different sediment components must also play a part. The redox sensitive relationship between As and Fe-oxides has already been described, and a similar relationship has been found between Pb and Mn-oxides (Liu et al 2003; Soto-Jiménez et al, 2003). However, the amount and type of organic material in the sediments is also very important as it is a major metal-binding substrate that is not sensitive to changes in redox (Luoma & Rainbow, 2008). The results in Section 4.4 showed that normalising the metal concentrations to LOI changed some of the profiles at some of the sites. Nickel was particularly affected at all of the sites except Wake Valley Pond, and Cu showed substantial changes at all of the Hampstead Heath Ponds. The normalised profile of Hg at Wake Valley Pond was also different to the original, but there was little change to the Hg profile at the Vale of Health Pond. Many studies have shown that Cu has a high affinity for organic matter (e.g. Luoma & Bryan, 1981; Ikem et al, 2003; Fytianos & Lourantou, 2004; Li et al, 2007)

and therefore the relationship between the two at the Hampstead Heath Ponds is unsurprising.

Mercury has also been shown to have a great affinity for organic material (e.g. Rognerud & Fjeld, 2001; Bilali et al, 2002; Wällstedt et al, 2008) which would explain the link between the two at Wake Valley Pond. However, it doesn't explain why the same relationship is not seen at the Vale of Health Pond. A study by Sanei & Goodarzi (2006) assessed the relationship between different fractions of organic matter and Hg. The results were mixed, with Hg correlating with some fractions in some lakes, and different fractions in other lakes. A positive association between Hg and algal biomass was confirmed, and it was also noted that the affinity of Hg was lessened for allochthonous refractory organic matter. Therefore, binding of Hg must depend to an extent on the types of material from which the organic matter is composed, and this would vary between lakes.

The relationship between Ni and organic matter is more difficult to explain. The PCA (Figure 4.19) clearly shows that there is a close link between the two. However, most studies investigating the affinity of metals to organic matter have shown that Ni is more likely to be related to the inorganic sediment fraction of sediments, rather than the organic component (e.g. Young & Harvey, 1992; Rognerud & Fjeld, 2001; Bilali et al, 2002; Ikem et al, 2003; Koinig et al, 2003; Borůvka et al, 2005; Tylmann et al, 2011). A few studies have recorded an association between Ni and organic matter. Weisz et al (2000) noted that although Ni compounds were usually found in silicates and phosphates together with Zn, Cu and Cr, in their study of Lake Balaton, Hungary, Ni was found to be most associated with the organic matter/sulphide fraction of the sediments. Soto-Jiménez et al (2003) found that there was a good correlation between organic C and Ni in salt marsh sediments in Mexico, and Wang et al (2004) found that Ni had the highest correlation with total organic carbon apart from Cu in the sediments of Taihu Lake, China. However, within these studies the affinity of Ni for organic material still tends to be lower than for other metals.

Assuming that Ni does have a higher affinity for organic matter than the other metals in London lakes, then the lack of change in the normalised profile at Wake Valley Pond is odd. One factor that seems to explain this is metal concentration, as Ni concentrations were substantially higher at Wake Valley Pond than at any of the other sites. The same is true for Hg at the Vale of Health Pond, where the concentration was much higher than at Wake Valley Pond. Conversely, the concentration of Cu at the Hampstead Heath Ponds was much lower than at the other London sites, which was reflected by the relationship with SQGs. This implies that normalising higher concentrations of metals to organic matter will have less

of an impact than normalising lower concentrations. This could be due to the normalisation method, or related to the fact that the amount of metal available to bind to a site is one factor which determines the distribution of metals amongst sediment substrates (Luoma & Rainbow, 2008).

On a slightly larger scale, metal concentrations in the lake sediments may have been influenced by changes to the catchments. Although these were accounted for through the calculation of enrichment factors and metal flux in Sections 4.4.1 to 4.4.7, comparison of the lithogenic element and sediment accumulation rate profiles and identification of the causes of any major changes would show if the effects are specific to a particular lake, or occur more generally over a wider area. SAR profiles varied between sites, in terms of both profile shape and sedimentation rate (Figure 4.20). Direct comparison between the profiles was made more difficult because of the variable limits of the radiometric dating at each site. Overall, the highest SARs occurred more recently, between 1975 and 2005 (Table 4.20).

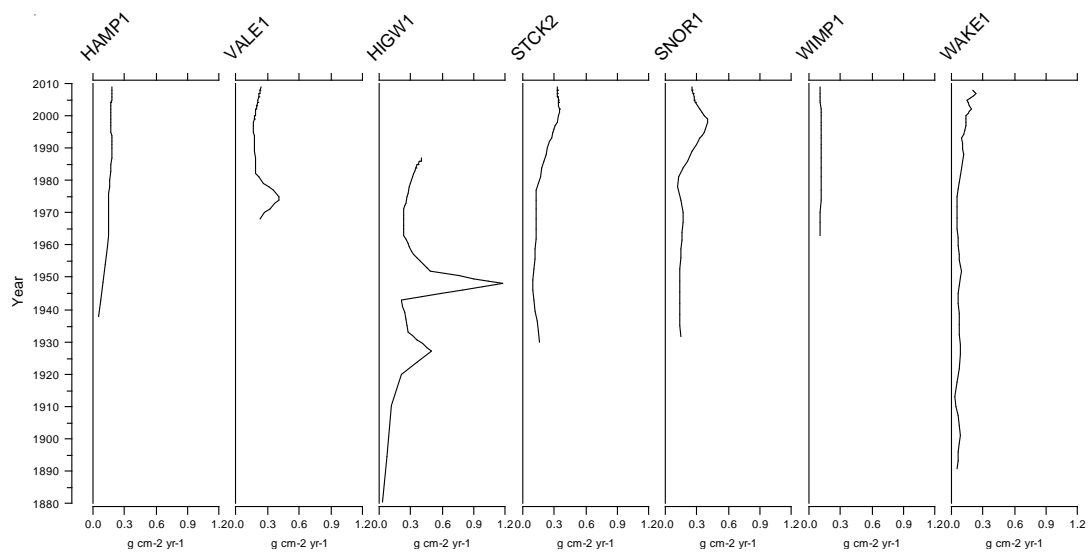


Figure 4.34 – Comparison between SAR at all of the London lake sites. The shorter profiles of HAMP1, VALE1, STCK2, SNOR1 and WIMP1 reflect the radiometric dating records from these cores (see Chapter 3), which were used to calculate SAR. The profile for HIGW1 stops in 1987 as this was the date the core was taken from this pond (see Section 4.2).

	SAR (g cm ⁻² yr ⁻¹)		Year of max SAR
	Minimum	Maximum	
HAMP1	0.05	0.18	1990
VALE1	0.17	0.43	1975
HIGW1	0.23	1.18	1950
STCK1	0.09	0.35	2000
SNOR1	0.11	0.41	2000
WIMP1	0.11	0.12	1980
WAKE1	0.04	0.24	2005

Table 4.20 – Minimum and maximum sediment accumulation rates at the London lakes. The date at which maximum SAR occurs is also recorded.

The exception was the Highgate Ladies Bathing Pond, where the peak in SAR occurred in 1950. However, HIGW1 was taken 20 years earlier than the cores from the other lakes and therefore it is not known if SAR has peaked again since 1987. Certainly, the profile showed that SAR was increasing at the time the core was taken. The maximum accumulation rate in HIGW1 was 1.18 g cm⁻² yr⁻¹, over twice the rate found at any of the other sites. The two large peaks that occurred in the 1920s and 1940s were not reflected in any of the SAR profiles at the other lakes (where the records were long enough), but the 1940s peak was evident in the lithogenic element profiles of HIGW1 (Figure 4.9). Therefore, the peaks must have been caused by changes specific to the catchment. Isolating the particular cause of catchment events such as these is more difficult. The catchments of both the Highgate Ladies Bathing Pond and Stock Pond are very similar, being comprised of a mixture of open heathland and the residential area of Fitzroy Park. Fitzroy Park is an area of low density housing that was first built on in the late 18th century (Elrington, 1989). Given that the catchments of the two ponds are adjacent to one another, the source of the large peaks in SAR must have been very specific to the Highgate catchment otherwise it is likely that a similar increase would have been visible in the record of Stock Pond. There was no record of any building work being carried out in the catchment of the Highgate Ladies Bathing Pond in the 1940s (Elrington, 1989) which would have been a possible source of material, and no new buildings were noted on maps post-1940 (Edina Digimap, 2011). However, the pattern of buildings directly adjacent to the pond changed between 1910 and 1930 and some new houses were also built (Edina Digimap, 2011) which may have contributed to the increase in SAR during this period. The North London Bowling Club is situated on ground just to the north east of the pond. Records from the club show that the bowling green was relaid between 1910 and 1914 and the Pavillion was built at the same time. In the early 1930s, tennis courts and some new buildings were built at the site. In the mid-1930s, the bowling green was extended and relaid again (North London Bowling Club, 1941). It is possible that material produced from these activities may have lead to the increases in SAR recorded in the core profile.

Sediment accumulation rate in HAMP1, STCK2, SNOR1 and WAKE1 was more consistent, and increased from the base of the core to the surface. For HAMP1 and WAKE1, the rise was quite steady, whilst for STCK2 and SNOR1 there was a sharper increase from the 1980s to the late 1990s, followed by a decline. The accumulation rate was also slightly higher at the latter two ponds. Comparison with the lithogenic element profiles at each of these sites showed that there had been little change in silicate inputs over the periods for which SAR had been calculated, although earlier increases in inorganic material from the catchment had occurred at Stock Pond (19th century) and South Norwood Lake (c. 1920). The latter may have been caused by extensive building in the immediate vicinity of the lake between 1910 and 1930 (Edina Digimap, 2011), but the provenance of the material in Stock Pond is unknown. SAR in the Vale of Health Pond peaked in the 1970s, which was different to the patterns of accumulation in the other lakes. Records from the Vale of Health Society show that new sewers were laid in the Vale of Health housing estate in 1973, and that the track past the edge of the pond became a temporary access road for the purpose (Harrison, 2011, pers. comm.). Both of these factors could have contributed to the sudden increase in SAR in the lake at this time. The rate of accumulation in VALE1 was of a similar magnitude to that in HAMP1, STCK2, SNOR1 and WAKE1 (Table 4.20), and SAR also increased up to the surface of the core, the same as in HAMP1 and WAKE1. The distinct change in the lithogenic element profiles of VALE1 from the 1940s occurred prior to the start of the SAR record. In contrast to all of the other sites, SAR in WIMP1 showed no change between the 1960s and the top of the core.

The results have shown that at some of the sites, such as the Vale of Health and Highgate Ladies Bathing Ponds, changes to the catchment over short periods of time are important drivers of SAR and are reflected as sedimentary 'events' in the profiles. However, at most of the other sites SAR has consistently increased over the 20th century. This links in with a worldwide increase in SAR that has occurred in many lakes over the last c. 100 years (e.g. Guilizzoni et al, 2001; Dearing & Jones, 2003). The increase has been attributed to changes in land use and agricultural practices causing accelerated catchment soil erosion, and nutrient enrichment causing an increase in the production of organic matter (Rose et al, 2011). Within an urban context, historically there would have been considerable disturbance to lake catchments as the land became more built up. However, little large scale building has taken place in any of the catchments of the London lakes since the mid-20th century. Urbanised catchments have often been associated with low sediment yields after the initial construction and catchment disturbance phase is complete (Wolman, 1967; Douglas, 1985). Charlesworth & Foster (1999) compared the SAR of two lakes, Swanswell Pool and Wyken Pool in Coventry, with those in rural catchments and concluded that SAR was lower in urban areas because land use was no longer changing and had been covered by concrete and tarmac. If land use change is not the main cause of the increase in SAR in the London lakes,

then eutrophication must be an important factor. The organic matter profiles of HAMP1, STCK2 and VALE1 (Figures 4.6, 4.7 and 4.11) support this theory as they all increased over the same period as SAR, although the same was not true for WAKE1 and SNOR1 (Figures 4.14 and 4.17). Whatever the cause of the increase in SAR, the effect that it has is very important. The results in Sections 4.4.1 to 4.4.7 showed that it was the key driver behind metal flux at all of the London lakes except Wimbledon Park. This has further implications for sediment quality and will be discussed in Section 4.5.2.

In addition to metal behaviour and catchment influences, the different metal concentration profiles found at each of the sites could simply have been caused by different pollution sources. As outlined in Section 1.5.3, metals are produced anthropogenically from a wide variety of sources. Studies of individual industrial sources have shown that the highest concentrations of metals are found closest to the source in question. For example, both Bradley & Morris (1986), and Pyle et al (2005) found that concentrations of Ni, Cu and Zn in sediments were greater in lakes closest to the Ni and Cu smelter in Sudbury, Ontario, than in those further away. Therefore, if some of the lakes in this study were located nearer to areas of industry than others (either in the past or at present), the extent of metal contamination in the sediments is likely to be greater and have a different profile to those further away. In addition, if each of the lakes were located near a different type of industrial source, the degree of contamination by certain metals might differ between sites. This could also help to explain the differences in metal profiles within a site, as some metals may have come from the same source and therefore have a similar profile, whilst others may have had slightly different origins.

Metal concentrations have also been found to decline on a gradient from the urban environment to the rural. Azimi et al (2003) showed that atmospheric deposition fluxes of Al, Cr, Cu, Fe and Pb were greater in a suburb of Paris than in a rural park 250 km away, and a similar pattern was found for soils in Torino, Italy in a study by Biasioli et al (2006). Spatial distributions of Pb, Cu and Zn presented an abrupt division between urban and rural samples. This is of importance to this study, because before the expansion of London out into the surrounding countryside lakes such as Wimbledon Park and South Norwood were ostensibly situated in rural areas. Development of the Wimbledon Park area began in the mid- to late 19th century, but the area was not built up as it is today until the early 20th century (Wimbledon Park Heritage Group, 2010). Similarly, the area around South Norwood Lake was undeveloped until the late 19th century (Edina Digimap, 2011). Therefore, the metal concentration of sediments deposited prior this period might have been lower than those of the Hampstead Heath Ponds which were already within the built up area of London.

Wake Valley Pond has always been situated in an undeveloped area, and therefore concentrations would be expected to be lower at this site than at any of the others. However, this was not the case, as the highest concentrations of Ni and Zn were found there. This indicated that there was a local source of pollution to the site. One possible source of contamination particular to Wake Valley Pond was the road to which it lies directly adjacent. As with the studies that have shown that metal concentrations tend to be higher closer to industry, the same is true of metal concentrations and proximity to roads. Localised atmospheric deposition, wind dispersion and runoff are all pathways by which metals can be transported from roads into the surrounding environment (Leggett & Pagotto, 2006). Many studies have been carried out to assess the impact of traffic on soils adjacent to roads e.g. Lagerwerff & Specht, 1970; Warren & Birch, 1987; Garcia et al, 1996; Pagotto et al, 2001; Akbar et al, 2006. In all cases, metal enrichment was evident in the soils. The study by Garcia et al (1996) found that the concentrations of Cu, Pb and Zn were high enough to exceed the critical soil concentrations of 400 mg kg⁻¹ for Zn and Pb, and 125 mg kg⁻¹ for Cu. All of the studies cited showed that concentration decreased with distance away from the roads, irrespective of the type of road/volume of traffic. These results suggest that road traffic pollution will have been an important source of metal contamination to Wake Valley Pond, whether through atmospheric deposition, runoff or secondary erosion of soils. However, the literature also suggests that the high levels of Ni at the site are unlikely to have come from traffic pollution. Pagotto et al (2001) showed that although most enrichment of Pb, Cu and Zn occurred in the immediate vicinity of a major highway in a rural location near Paris, Ni related to traffic did not result in any major enrichment of the roadside soil. Garcia et al (1996) found that the potential availability of Ni in roadside soils was much lower than for Pb, Cu and Zn, and that factor analysis of the four metals grouped Pb, Cu and Zn together, implying that Ni came from a different source. This contrasts with the highly correlated profiles of Ni, Cu, Zn and Pb at Wake Valley Pond which suggested that the metals came from the same source. However, if this is the case and the high concentration of Ni is not due to the proximity of the road, another source of unknown origin must be responsible.

Collating the locations and type of industrial metal sources in London over the last 200 years and assessing the likely impact on each lake, as well as the effect of the growth of roads and motor vehicles in the 20th century, would be a massive undertaking. Some attempts have been made to catalogue certain types of industry in the city over that time period, for example all power stations used for public power supply (Horne, 2009). Approximately 130 power stations were identified that existed at different times between 1883 and the mid-1980s, of varying size and output and in locations all across the city, both central and farther out. However, public power supply would only have been responsible for part of the metal pollution produced within the city. In addition, historically, inputs of metals into the

environment would have occurred not only through atmospheric emissions, but directly into water courses, before legislation was put in place to restrict both practices (see Section 1.6). This widens the possible sources of contamination to the lakes even further. As stated in Section 1.6, legislation was introduced in the mid-20th century to reduce levels of air and water pollution. In the case of air pollution, the Clean Air Act resulted in the creation of smokeless zones and the relocation of power stations to the outside of the city over the latter half of the 20th century. In terms of the lake sediment metal profiles, the control and removal of localised sources of contamination would explain the decline in concentration that was seen in all of the cores from the 1980s. Collecting information about past transport and industry in London is complicated by the fact records are not always available in the detail that is required. For example, with particular reference to the Vale of Health Pond, records show that a building directly adjacent to the lake called the Athenaeum Hall was used as a factory on three occasions, firstly in the 1870s, then during the First World War, and again for the duration of the Second World War (Bentwich, 1977). However, the records do not state what the factory was for, and hence it is unknown whether an industry so close to the lake would have had any impact upon it.

In light of the complexity brought about by all of the factors cited above, another method to draw out patterns from the metal concentration data was required. Principal components analysis (PCA) was used, which is an indirect ordination method that is performed on species or environmental datasets where the controlling factors are unknown, and is useful for revealing major patterns and outliers in the data (Jolliffe, 1986). The aim of PCA is to reduce many correlated variables to a few uncorrelated components. PCA has been widely applied to determine the sources of metal inputs to sediments and to distinguish between those of anthropogenic or natural origin (e.g. Soto-Jiménez et al, 2003; Yang et al, 2004; Borůvka et al, 2005; Wu et al, 2007; Augustsson et al, 2010), and has also been used to identify regional patterns of pollution (Tylmann et al, 2011). The general hypothesis for PCA in this study was that if there was a regional pattern of metal deposition across London, then the degree of contamination across the sites should be similar. However, if there are or have been local sources of pollution within each lake catchment, the relationship between sediment samples and metals would vary between sites. The PCA was carried out using Canoco 4.5 and the data was centred and standardised.

If regional contamination was dominant, the four lakes situated on Hampstead Heath might be expected to show similar patterns of metal contamination because of their close proximity. Therefore, PCA was initially carried out on the Hampstead Heath core data and is shown in Figure 4.21. Mercury was not included in the analysis because concentration data for this metal was only available from the Vale of Health Pond. PCA1 explains 53.9% of the

variance in the data and PCA2 accounts for a further 26.9%. Broken stick analysis is a tool that is used to assess the likely statistical significance of the PCA axes by comparing them with the sizes expected under a random model, such as the broken-stick model. If the PCA axes eigenvalues are higher than the variance values calculated with broken-stick, then the axis is significant (Jolliffe, 1986). For the PCA of the Hampstead Heath data, broken-stick analysis showed that both axes were significant.

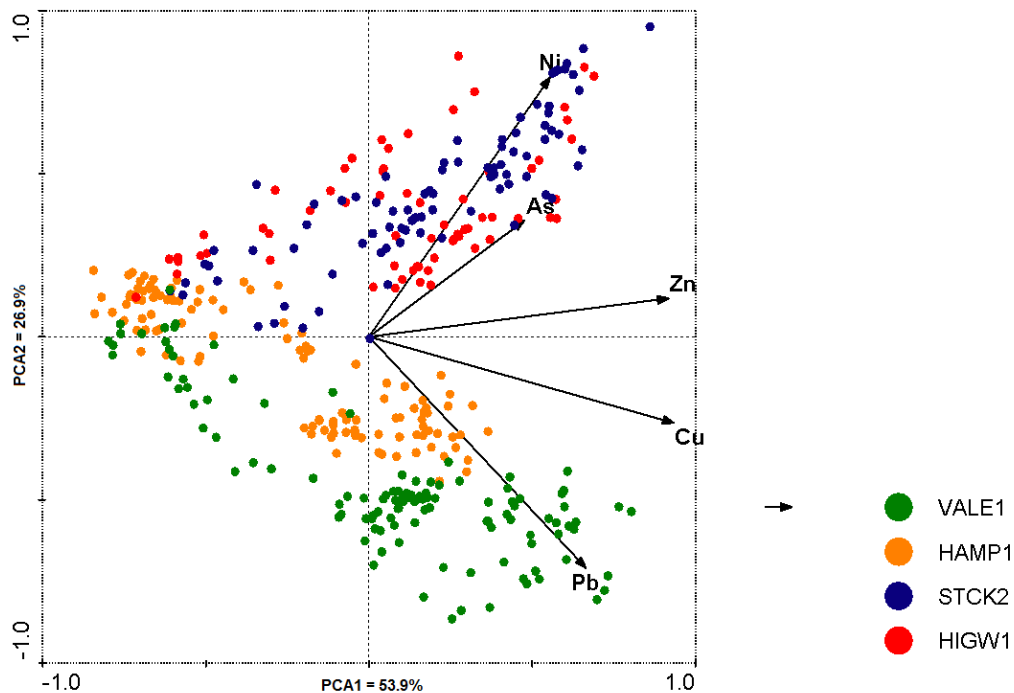


Figure 4.35 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb from all of the sediment core samples from the Hampstead Heath Ponds – Hampstead No. 1 Pond (HAMP1), Vale of Health Pond (VALE1), Highgate Ladies Bathing Pond (HIGW1) and Stock Pond (STCK2). The first two principle components are shown, the first accounting for 53.9% of the variance within the samples, and the second accounting for 26.9%.

Cu and Zn are the most important variables, explaining 93.4% and 91.8% of the variance of axis 1 respectively. The even spacing and length of all the vectors (except As) shows that each metal has a similar influence across the sites, with correlations highest between adjacent metals e.g. Pb/Cu or Cu/Zn. Arsenic is less influential in terms of concentration change than the other four metals, and is closely related to Ni, which contradicts the low Pearson correlations found between the two elements. In terms of the samples from each site, those from STCK2 and HIGW1 overlap considerably, and have a particular relationship with Ni and As. This reflects the high enrichment of Ni that has been shown to be present at the two lakes. VALE1 and HAMP1, although showing less overlap, are situated adjacent to one another and linked to Pb. There is a distinct separation between them and the other two sites. The results suggest that there is a spatial difference between pollution at the different

lakes, implying that local sources of contamination are important at these sites. The overlap between HIGW1 and STCK2 suggests that sources of contamination to these ponds are the same, which would be expected as the two ponds are located next to one another and are joined by a stream. VALE1 and HAMP1 are found on the other side of the Heath. They are further apart and do not directly adjoin one another, which explains why the samples from both sites are less similar.

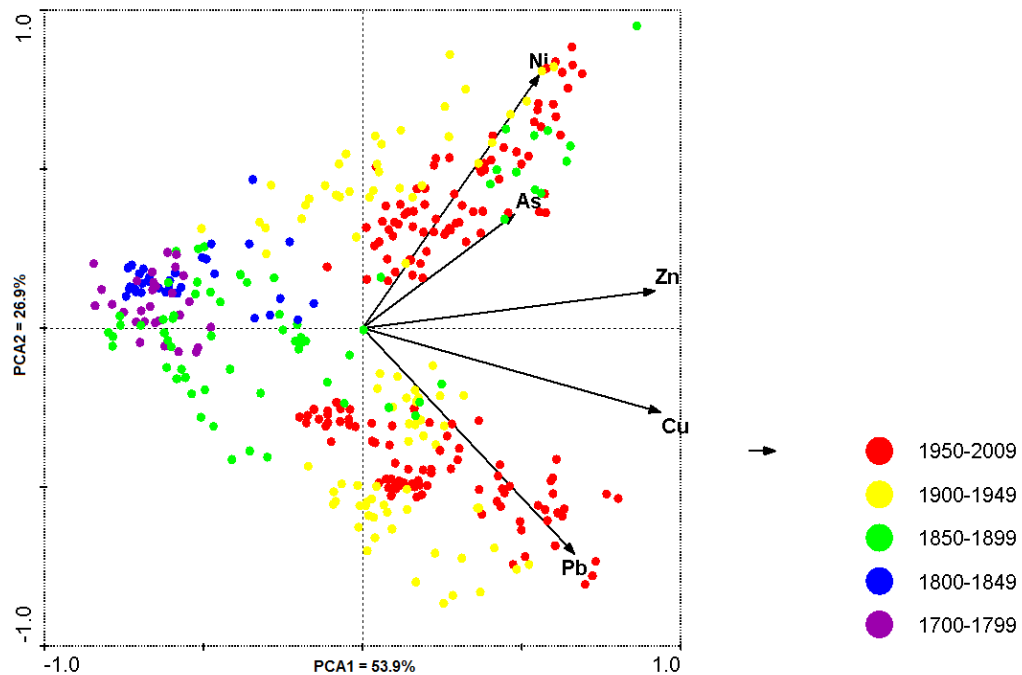


Figure 4.36 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb from all of the sediment core samples from the Hampstead Heath Ponds – Hampstead No. 1 Pond, Vale of Health Pond, Highgate Ladies Bathing Pond and Stock Pond. In this biplot the samples are grouped by date range across the four sites. The first two principle components are shown, the first accounting for 53.9% of the variance within the samples, and the second accounting for 26.9%.

There are a large number of samples in the top and bottom left hand quadrants which have values less than the mean of each of the metals in the PCA. Plotting the PCA up with the samples bracketed into periods of time rather than by lake (Figure 4.22), shows that these samples are older and have been dated to between 1700 and 1899. The samples with the most positive relationships to the metals were deposited in the sediments between 1900 and the present day. Replotting the PCA to include the lithogenic elements Ti, Si, Al and Zr (Figure 4.23) shows that these older sediment samples are linked to catchment material. The separation between the metals and lithogenic elements show that they come from different sources, corroborating the interpretation that most of the metal contamination that has occurred over the 20th century has been anthropogenic in origin. The split between metals and lithogenic elements is commonly seen in other studies. Lavilla et al (2006) found

that a PCA of trace elements from a sediment core of a lake in the Spanish Pyrenees produced two distinct clusters, the first containing Cu, Ni, Pb and Zn, and the second Al, Ti, Mg and Si. The former was attributed to anthropogenic contamination, and the latter to natural sources. Similarly, PCA was used by Wu et al (2007) to distinguish between those elements deposited anthropogenically and those which came from natural sources in sediments from Dongjiu Lake, China, and the plot showed a clear split with Ti, Al, K and Fe explaining the first principal component, and Zn, Cu, Pb and Cd explaining the second.

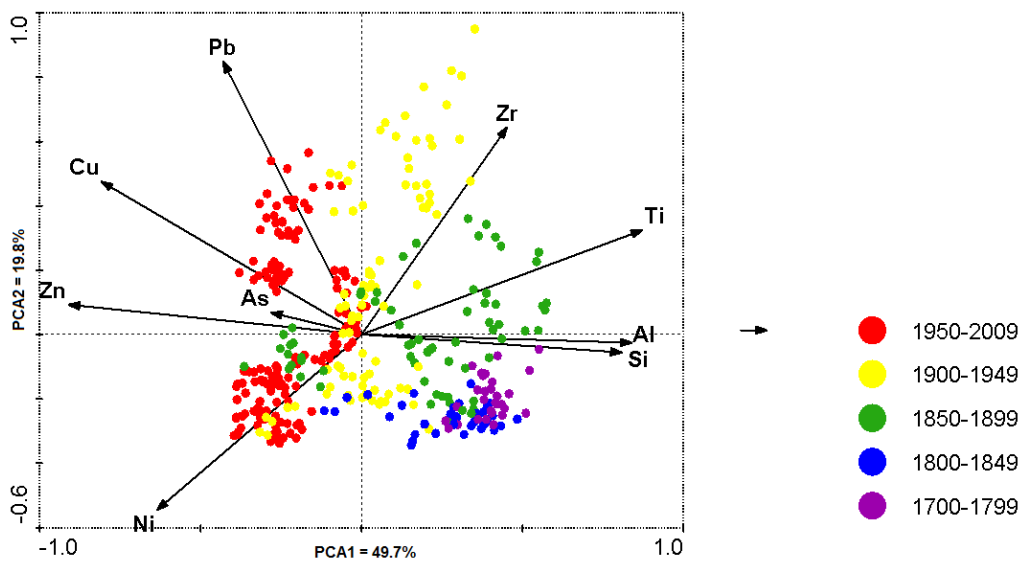
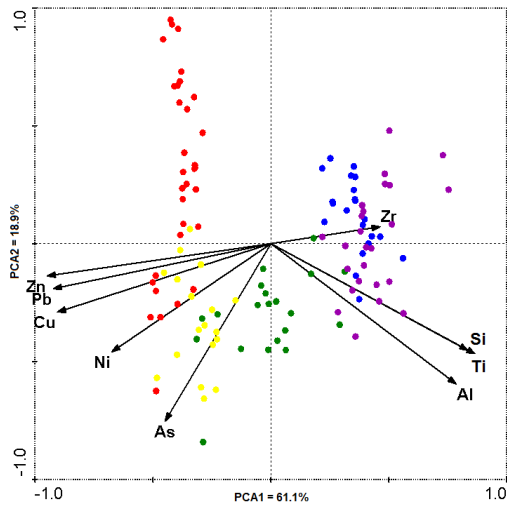


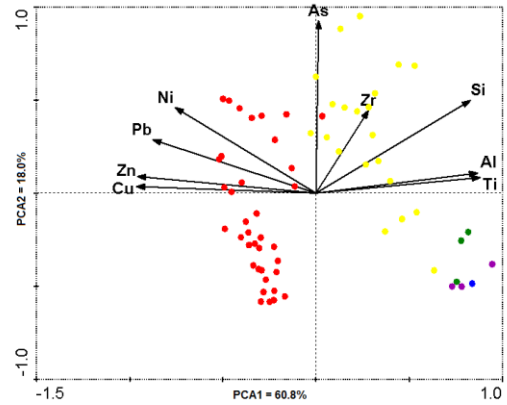
Figure 4.37 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb, together with the lithogenic elements Ti, Si, Al and Zr from all of the sediment core samples from the Hampstead Heath Ponds – Hampstead No. 1 Pond, Vale of Health Pond, Highgate Ladies Bathing Pond and Stock Pond. In this biplot the samples are grouped by date range across the four sites. The first two principle components are shown, the first accounting for 49.7% of the variance within the samples, and the second accounting for 19.8%.

PCA was also carried out on the individual Hampstead Heath ponds (see Figure 4.24). The samples were split by date, and as with the PCA in Figure 4.24, show a progression over time with respect to the elements that they are related to. The PCAs for all of the sites show the same general pattern. The oldest samples from each core tend to be isolated with no specific relationship to any of the elements included in the PCA. Moving up the cores, a relationship between the samples and the lithogenic elements becomes apparent. Newer samples (from the 20th century) are related to the metals, which is a reflection of the more recent anthropogenic nature of the contamination.

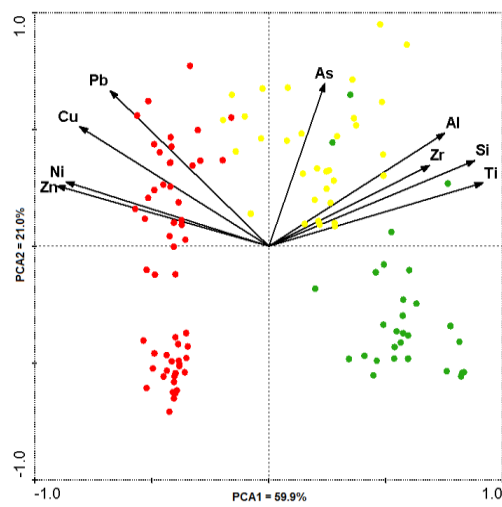
HAMP1



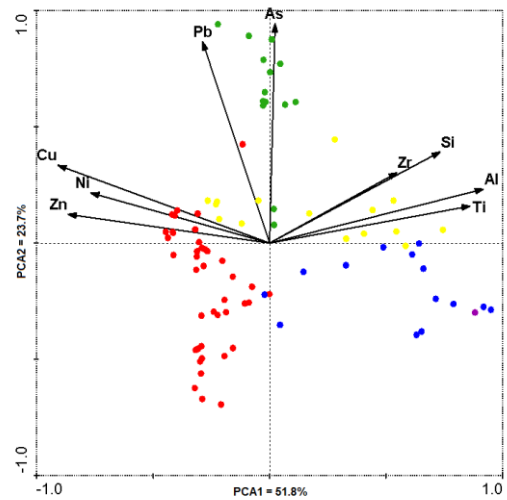
HIGW1



VALE1



STCK2



KEY

- 1950-2009
- 1900-1949
- 1850-1899
- 1800-1849
- 1700-1799

Figure 4.38 – PCA biplots produced using concentrations of Ni, Cu, Zn, As and Pb, together with the lithogenic elements Ti, Si, Al and Zr, from the samples from each of the individual Hampstead Heath cores, HAMP1, VALE1, HIGW1 and STCK2. The samples are grouped by date range within these biplots.

Of the metals, in every case As is the first to appear in the time track, although it emerges at slightly different times – the earliest in STCK2, followed by HAMP1, VALE1 and lastly HIGW1. The most recent sediments, like the oldest, show no particular relationship with any of the elements. This could be interpreted as a sign that the sediments are recovering, with a reduced impact from metal contamination. However, there are also a number of differences between the PCAs from each site. Even though the oldest sediments are unrelated to any of the elements included, the date of these sediments varies between sites, from the 18th century at HAMP1, HIGW1 and STCK2 to the mid-19th century at VALE1. This variation in date continues with respect to the relationships with the lithogenic elements and the metals, with each occurring at slightly different times depending on the lake in question. If there was a common history of contamination across all of the sites, the relationships between the dates and the metals would be similar at every lake. Although As always appears first and is quite separate to the other vectors, the sequence in which the rest of the metals appear varies. VALE1 and STCK2 show the same order of Pb, Cu, Ni and Zn, but HAMP1 and HIGW1 are both different. This variation between sites suggests that local sources of contamination have impacted upon each lake slightly differently, and therefore have more influence on the sediment core record than atmospheric sources of metal pollution.

The initial hypothesis of the PCA was that the proximity of the Hampstead Heath Ponds would mean any regional signal would be best recorded in these four lakes. However, the results showed the opposite, that the sources of metals differed between sites and that local inputs were very important. This meant that either there was no regional pattern of metal pollution or that the level of focus was too narrow to show it. Expanding the data set outwards to include the other London lakes and assessing patterns on a larger scale would help to establish if there was a regional pattern. The PCA of all the London lake data is shown in Figure 4.25. Axis 1 explains 52.3% of the variance in the data, with axis 2 accounting for an additional 23.4%, although only axis 1 was found to be significant using the broken-stick model. As with the Hampstead Heath ponds PCA, Cu and Zn are still the most important explanatory variables for PCA1, explaining 84.5% and 91.2% of the variance of the axis respectively. The angle between As and Pb is smaller than between any of the other vectors, which shows that there is a relationship between the two. Yang et al (2004) found a similar pattern in sediments from a lake in China, although they interpreted the grouping of Pb and As to be anthropogenic in origin, whilst Ni, Cu and Zn were associated with lithogenic elements and therefore came from different sources. As discussed earlier in this section, As and Pb are more redox-sensitive than the other metals which would also explain their close relationship. The vectors are all the same length, apart from As which is shorter. This shows that the change in concentrations over the course of the last 200 years has occurred to the same degree for all of the metals, except for As where the concentration change has been less.

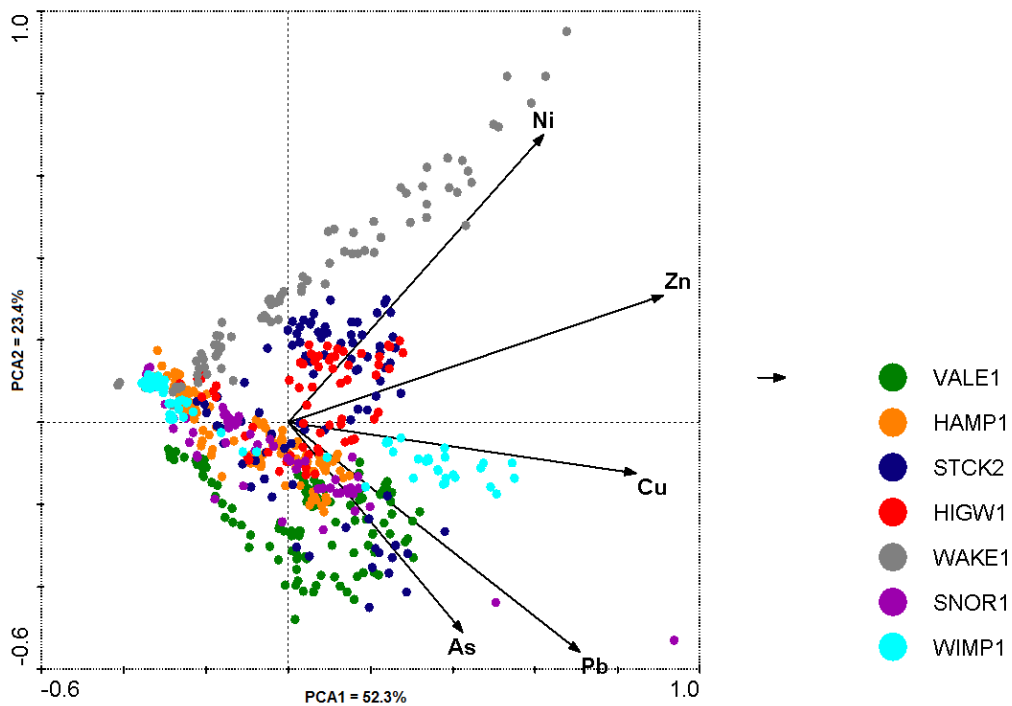


Figure 4.39 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb from all of the sediment core samples from the seven London lakes – Hampstead No. 1 Pond (HAMP1), Vale of Health Pond (VALE1), Highgate Ladies Bathing Pond (HIGW1), Stock Pond (STCK2), South Norwood Lake (SNOR1), Wimbledon Park Lake (WIMP1) and Wake Valley Pond (WAKE1). The first two principle components are shown, the first accounting for 52.3% of the variance within the samples, and the second accounting for 23.4%.

At this scale, there is a visible overlap between all of the sites around the centre of the axes, with the exception of WAKE1. This suggests that the sources of contamination are common across the area, and could be attributed to a widespread pattern of atmospheric deposition. However, the overlap could also be caused by older, uncontaminated sediments which have come from the same geology and hence have a similar chemical signature. Therefore the dates of the samples need to be considered, and these are shown in Figure 4.26. Adding dates to each of the samples highlights the same distinction as found with the Hampstead Heath cores, with samples from 1900 to the present day showing an association with metal contamination, and sediments deposited prior to 1900 showing little connection to the metals. As with the Hampstead ponds, these older samples are positively correlated with lithogenic elements, the PCA of which is shown in Figure 4.27. Changes in the relationship of lake sediments with elements over time has been found in other studies, albeit over much longer periods of time. A sediment core covering the last 9,000 years of a Swiss alpine lake was analysed by Koinig et al (2003). They produced a PCA that showed a distinct change in composition between samples dated to 9050-6440 cal. BP and those dated to 6440 cal. BP-present. The older samples related to elements associated with a carbonate fraction, whilst the more recent sediments corresponded to elements associated with a silicate fraction.

Augustsson et al (2010) studied a core covering 5,500 years from Lake Lehmilampi, Finland. The second and third principal components showed a clear depth-dependency – the variance in the elements was most probably related to the development of the catchment soil, a process that proceeded over a long period of time. Although some of the overlapping samples to the left of PCA2 in Figure 4.27 are older, the cluster of samples at the centre of the axes are from the 20th century. The fact that these samples are from different sites but show similar relationships with the metals suggests that the PCA does reflect a common pollution source. The particular affiliation of WAKE1 to Ni suggests that there is a local source of contamination to Wake Valley Pond as none of the other sites show the same relationship.

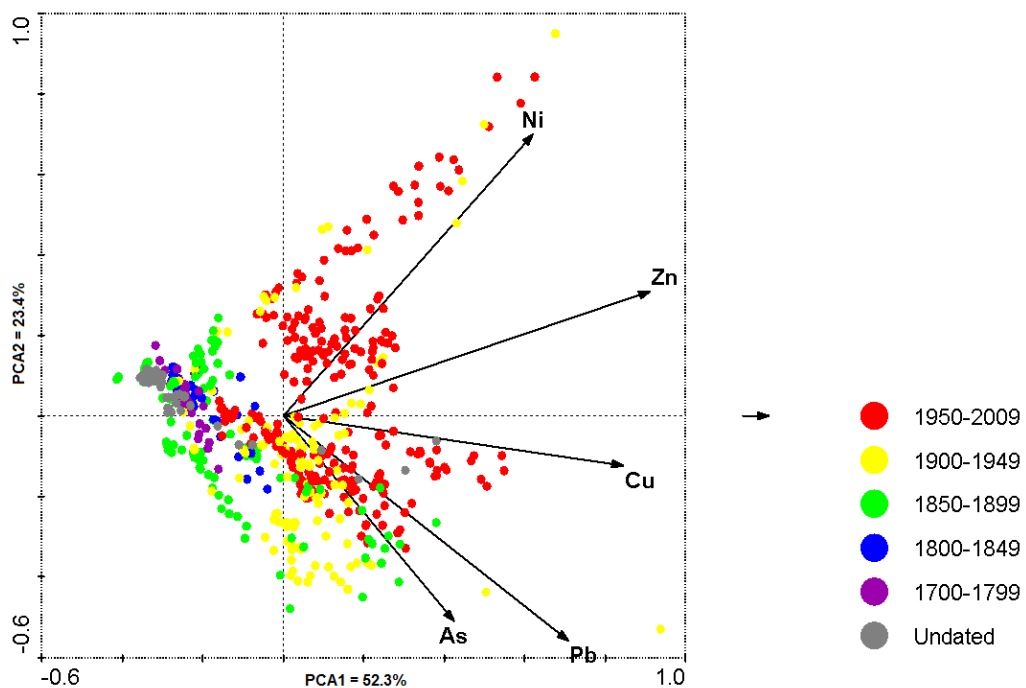


Figure 4.40 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb from all of the sediment core samples from the seven London lakes – Hampstead No. 1 Pond, Vale of Health Pond, Highgate Ladies Bathing Pond, Stock Pond, South Norwood Lake, Wimbledon Park Lake and Wake Valley Pond. In this biplot the samples are grouped by date range across the seven sites. The first two principle components are shown, the first accounting for 52.3% of the variance within the samples, and the second accounting for 23.4%.

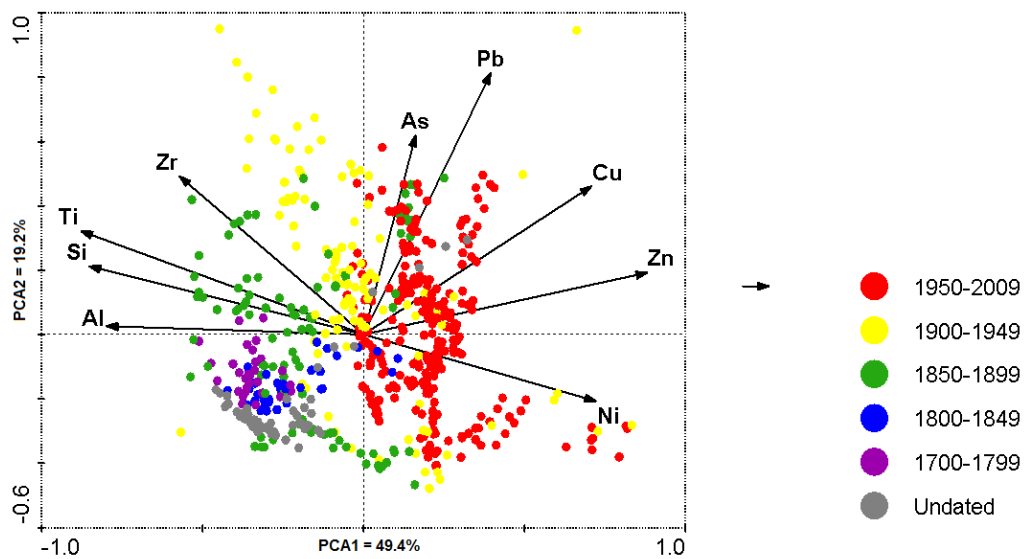


Figure 4.41 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb, together with the lithogenic elements Ti, Si, Al and Zr from all of the sediment core samples from the seven London lakes – Hampstead No. 1 Pond, Vale of Health Pond, Highgate Ladies Bathing Pond, Stock Pond, South Norwood Lake, Wimbledon Park Lake and Wake Valley Pond. In this biplot the samples are grouped by date range across the seven sites. The first two principle components are shown, the first accounting for 49.4% of the variance within the samples, and the second accounting for 19.2%.

The data from South Norwood Lake and Wimbledon Park Lake was analysed to assess whether a common pollution source was still visible in the PCA when comparing sites from the south of the city. The result of the PCA is shown in Figure 4.28, with PCA1 explaining 75.1% of the variance in the data, and PCA2 explaining a further 13.4%, although broken stick analysis found only axis 1 to be significant. Overall, Zn and Pb are the most important variables explaining axis 1, with values of 95.3% and 94.8% respectively. The sediments from SNOR1 are more closely related to As and Cu, whilst those from WIMP1 are linked to Ni, Zn and Pb. There are a number of samples from both sites which overlap, but these are the older sediments rather than those particularly related to anthropogenic contamination (see Figure 4.29).

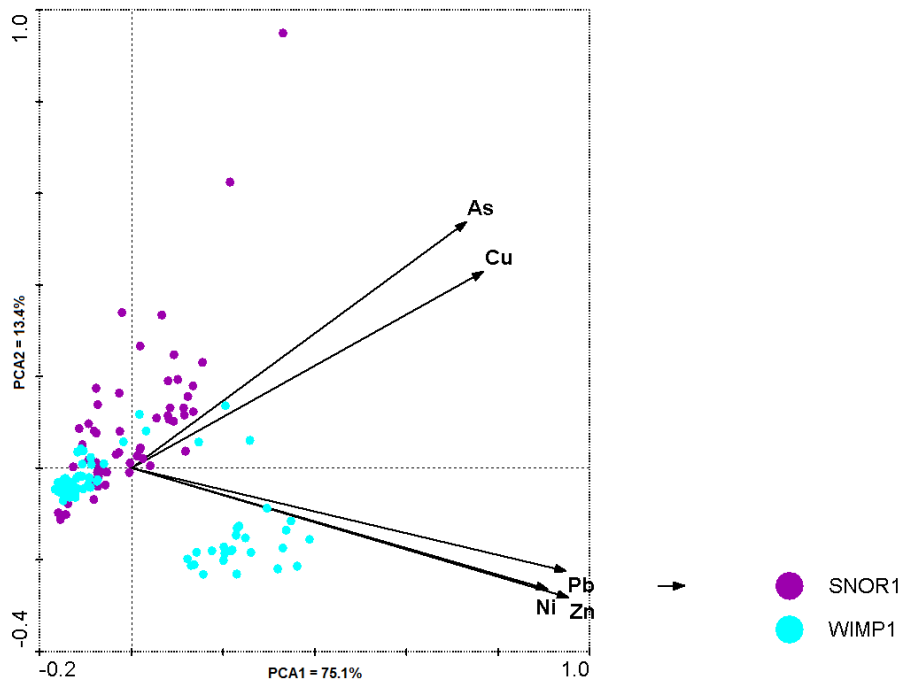


Figure 4.42 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb from all of the sediment core samples from South Norwood Lake (SNOR1) and Wimbledon Park Lake (WIMP1). The first two principle components are shown, the first accounting for 75.1% of the variance within the samples, and the second accounting for 13.4%.

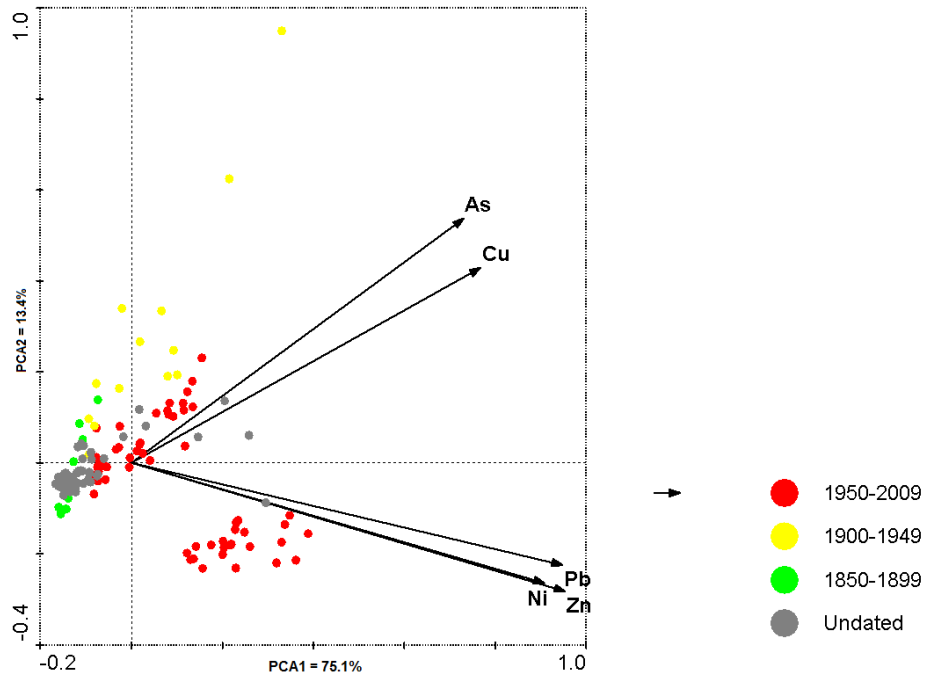


Figure 4.43 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb from all of the sediment core samples from South Norwood Lake and Wimbledon Park Lake. In this biplot the samples are grouped by date range across the two sites. The first two principle components are shown, the first accounting for 75.1% of the variance within the samples, and the second accounting for 13.4%.

The individual PCA of SNOR1 and WIMP1 were also plotted to see how the sediments related to different elements at each lake (Figures 4.30 and 4.31). The oldest samples from SNOR1 were related to the lithogenic elements, with the 20th century samples being more closely linked to the metals. However, there are also some sediments from the early 20th century which are not related to any elements in particular. The profile of WIMP1 shows a clear split between the older, undated sediments and the sediments deposited after dredging, with the former being associated with the lithogenic elements and the latter with the metals. The most recent samples in the top right quadrant show little relationship to any of the elements and indicate that metal concentrations in the lake are recovering. The order in which the elements appear in the PCA differs between the two southern lakes. Despite the samples from the southern sites overlapping in the PCA of all the London data (Figure 4.25), the results from the PCAs of SNOR1 and WIMP1 show little similarity. This suggests that the sources of metals to each site are different, and corroborates the interpretation from the Hampstead Heath ponds that on a smaller scale local sources of contamination are important.

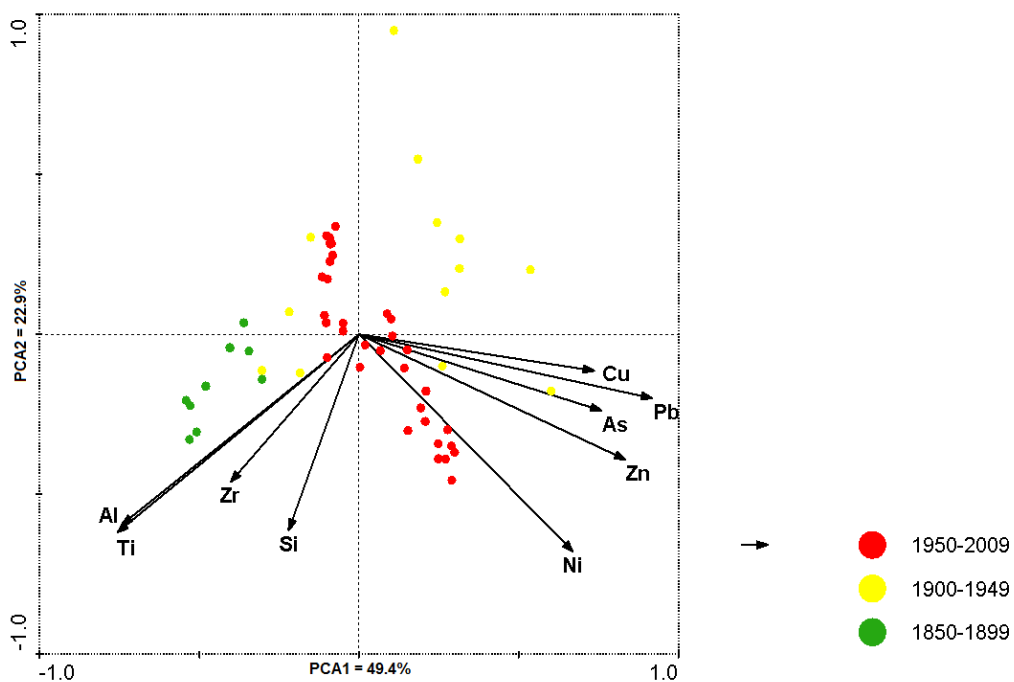


Figure 4.44 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb, together with the lithogenic elements Ti, Si, Al and Zr from the sediment core samples from South Norwood Lake. In this biplot the samples are grouped by date range. The first two principle components are shown, the first accounting for 49.4% of the variance within the samples, and the second accounting for 22.9%.

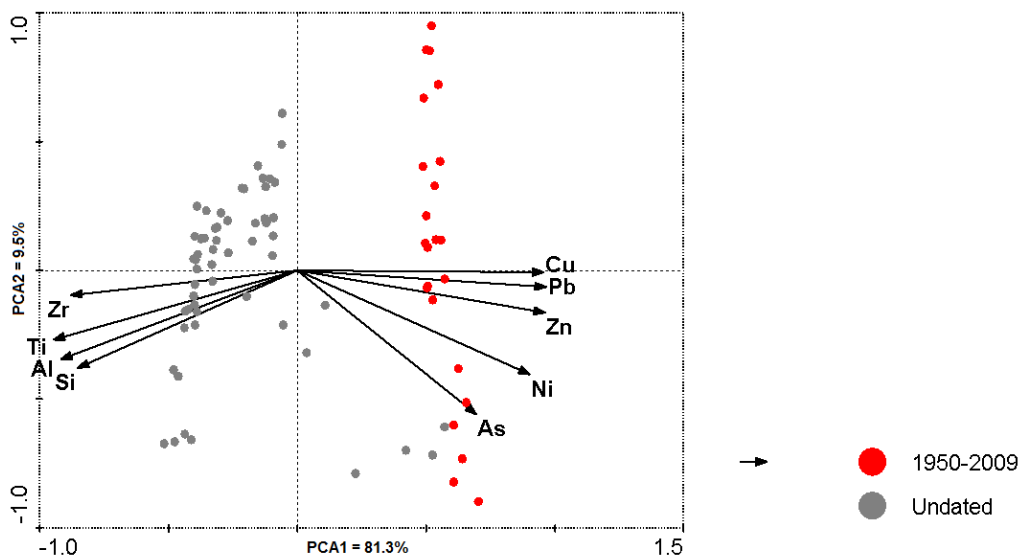


Figure 4.45 – PCA biplot produced using concentrations of Ni, Cu, Zn, As and Pb, together with the lithogenic elements Ti, Si, Al and Zr from the sediment core samples from Wimbledon Park Lake. In this biplot the samples are grouped by date range. The first two principle components are shown, the first accounting for 81.3% of the variance within the samples, and the second accounting for 9.5%.

The main conclusion drawn from the PCAs carried out on the London cores is that the scale of the analysis is important when it comes to trying to determine a London pollution signal. The results from the Hampstead Heath ponds highlighted the differences in contamination of the sites at a small scale, emphasising the effects of local inputs. This was also evident in the PCAs carried out at the southern sites. However, exploring the data from London as a whole, on a larger scale, did produce a pattern of contamination that was similar for most of the lakes, which may be indicative of a London atmospheric contamination signal. There are two possible reasons why the results from Wake Valley Pond differ to the rest of London on a large scale, either that there is/has been a local source of contamination to the site which has had a much greater effect than deposition from the atmosphere, such as the nearby road (which was discussed in Section 4.5.1), or that the site is simply too far from the city to be subject to the same regional pattern. Further examination of data would be necessary to confirm if a London pollution signal can be defined for certain. One way of doing this would be to create a PCA of sediment core data from 'reference' lakes across the UK to see if the London pollution signal becomes more distinct when related to lakes from other areas of the country.

The key aim of this section was to determine whether a regional pattern of metal pollution could be identified from London lake sediments, or if local inputs were more influential. Few common patterns were visible in the raw concentration data. Metal behaviour, catchment influences and the complexity of pollution sources in an urban area such as London were cited as reasons why the trends in metal concentration differed between and within sites. Statistical analysis of the data was used to try to draw out any patterns, and showed that on a broad scale there was some indication of a regional pollution signal. However, on a smaller scale the sources of metals to the lakes differed, which showed that local influences were more important and that patterns of metal concentration were site specific. In an urban context it is difficult to separate regional and more localised contributions of metals to lake sediments. The next section of the discussion will focus on more recent metal contamination in the London lakes.

4.5.2. Recent trends in metal contamination

The previous section (4.5.1) focused upon the patterns in metal concentration across London, but no distinction was made between the anthropogenic and natural components. The enrichment factors calculated for the sediment cores at each lake were all greater than 1 (Sections 4.4.1 to 4.4.7), which showed that human activity had impacted upon all of the lakes over the timescales covered by each core. The oldest core sediments were found in Hampstead No. 1 and the Highgate Ladies Bathing Ponds, both showing that anthropogenic contamination of metals had occurred in this area of London at least as early as the mid-18th century. In some palaeolimnological studies, sediments dated to AD 1800 have been assumed to contain 'pre-industrial' concentrations of metals (e.g. Verta et al, 1989; Klein & Jacobs, 1995; Engstrom & Swain, 1997). However, this is clearly not the case for the London lakes, and the longer anthropogenic record is unsurprising given the industrial history of the city and the numerous complaints about air quality that have been recorded since the 13th century (Brimblecombe, 1988; see Section 1.6). 'Pre-industrial' enrichment is not uncommon, even in sites remote from industry. For example at Loch Dee in Galloway, Scotland, enhanced signals of Pb and Cu were found as early as AD 1500 (Williams, 1991), and in peat cores from the Jura Mountains in Switzerland anthropogenic enrichment has been found as early as 3000 ¹⁴C yr BP (Shotyk et al, 2001).

Of particular interest are the more recent patterns in enrichment and flux. Figures 4.32 to 4.37 show the profiles of Ni, Cu, Zn, As, Pb and Hg enrichment and flux calculated for each of the London lakes (Hg only for VALE1 and WAKE1) between 1970 and 2009. They are plotted in comparison to metal emissions and deposition in the UK and London respectively over the same period. Metal emissions in the UK have been recorded annually since the 1970s (Murrells et al, 2010). Emissions of Ni, Cu, Zn, As, Pb and Hg have all declined over

the last 40 years, as shown in Figures 4.32 to 4.37. Metal deposition has been recorded in urban areas since 1980. In London, deposition has been monitored at three sites in London (Brent, Central London and Cromwell Road) (DEFRA, 2010) over this period. Deposition of Ni, Cu, Zn, As, Pb and Hg at each of the three sites is plotted in Figures 4.32 to 4.37. The amount of Ni, Zn and Pb deposition at all three London sites has declined, the profiles being very similar to the pattern in emissions. Arsenic deposition has only been recorded since 2003, but has declined since that date. Records of Hg deposition have also only been recorded since 2003. The profiles from Brent and Cromwell Road show that deposition increased between 2003 and 2005, and then decreased sharply in the years 2006 to 2009. The data from Central London showed the same trend, although there was an initial decrease between 2003 and 2004. This variation between sites suggested that local sources of Hg contamination were important in London, particularly given the overall decline in emissions across the UK. Copper deposition has not shown the same decrease that is seen in the metal profiles. Although the data from Cromwell Road mirrors the decline in emissions, deposition at the other two sites has remained fairly consistent, and was at the same level in 2009 as in 2003.

Figures 4.32 to 4.37 show clearly that despite a decline in emissions and deposition of the last 40 years, there has not always been a corresponding decrease in enrichment or metal flux. As discussed in Sections 4.4.1 to 4.4.7, sediment accumulation rate was the main driver of metal fluxes at all of the sites, apart from Wimbledon Park Lake. However, sediment accumulation rates can vary considerably between lakes or within a lake (Fitzgerald et al, 1998; Anderson, 1990). Studies have shown that sediment accumulation rate can change with water depth as a result of sediment focusing processes (Davis & Ford, 1982; Blais & Kalff, 1995). Sediment focusing is the process whereby water turbulence moves sedimented material from shallower to deeper zones of a lake. Yang et al (2002c) took 17 sediment cores from Lochnagar, an upland lake in Scotland, to investigate the distribution of sediment across the whole lake basin. The study showed that sediment accumulation varied across the lake, with more focusing occurring in the shallower areas, and lower rates of accumulation in the deepest part. This contrasted to the traditional model of sediment focusing where higher accumulation is expected in deeper water (Likens & Davis, 1975). Consequently, trace metals inventories varied between different areas of the lake, and it was concluded that sediments from the deepest area may not have been representative of the whole lake (Yang et al, 2002c). Therefore, the use of a single sediment core to reconstruct SAR for a whole lake basin may not provide entirely accurate results.

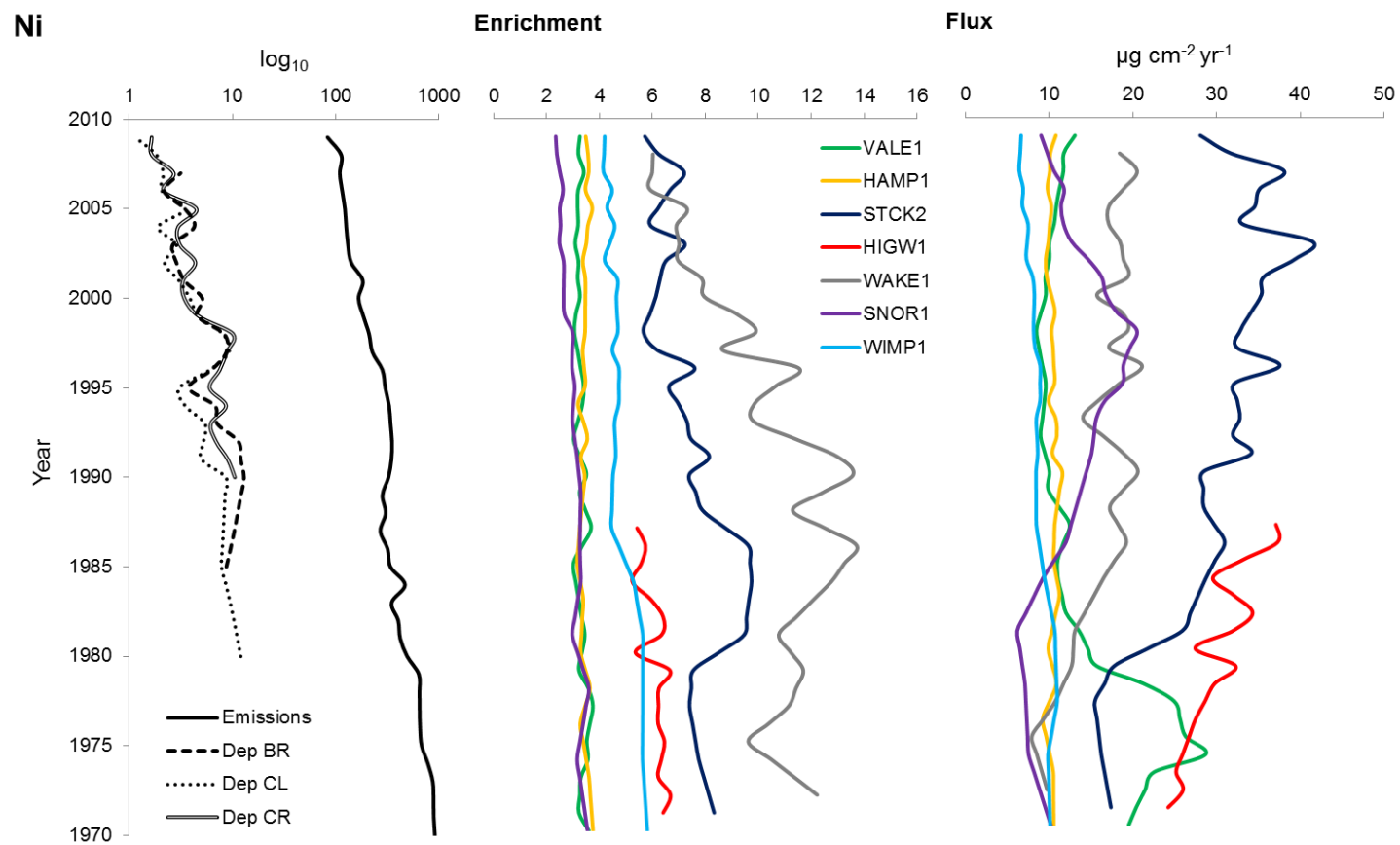


Figure 4.46 – Left: Emissions of Ni in the UK between 1970 and 2009 (from Murrells et al, 2010) and deposition of Ni in London when recorded during the same period (at three different locations: BR – Brent; CL – Central; CR – Cromwell Road) (DEFRA, 2010); Middle: Ni enrichment; Right: Ni flux; both calculated for each London lake between 1970 and 2009 (1970 and 1987 for HIGW1).

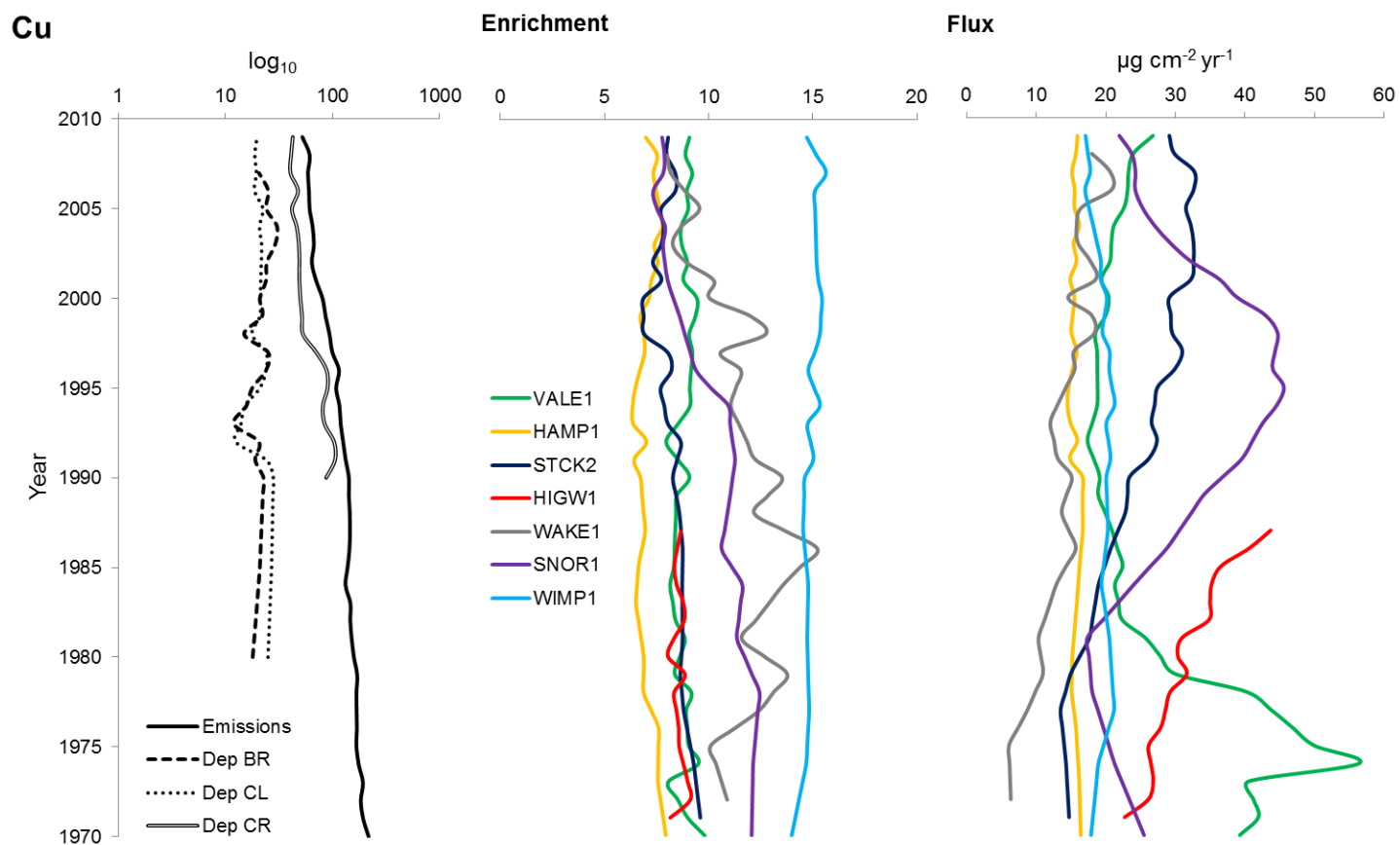


Figure 4.47 – Left: Emissions of Cu in the UK between 1970 and 2009 (from Murrells et al, 2010) and deposition of Cu in London when recorded during the same period (at three different locations: BR – Brent; CL – Central; CR – Cromwell Road) (DEFRA, 2010); Middle: Cu enrichment; Right: Cu flux; both calculated for each London lake between 1970 and 2009 (1970 and 1987 for HIGW1).

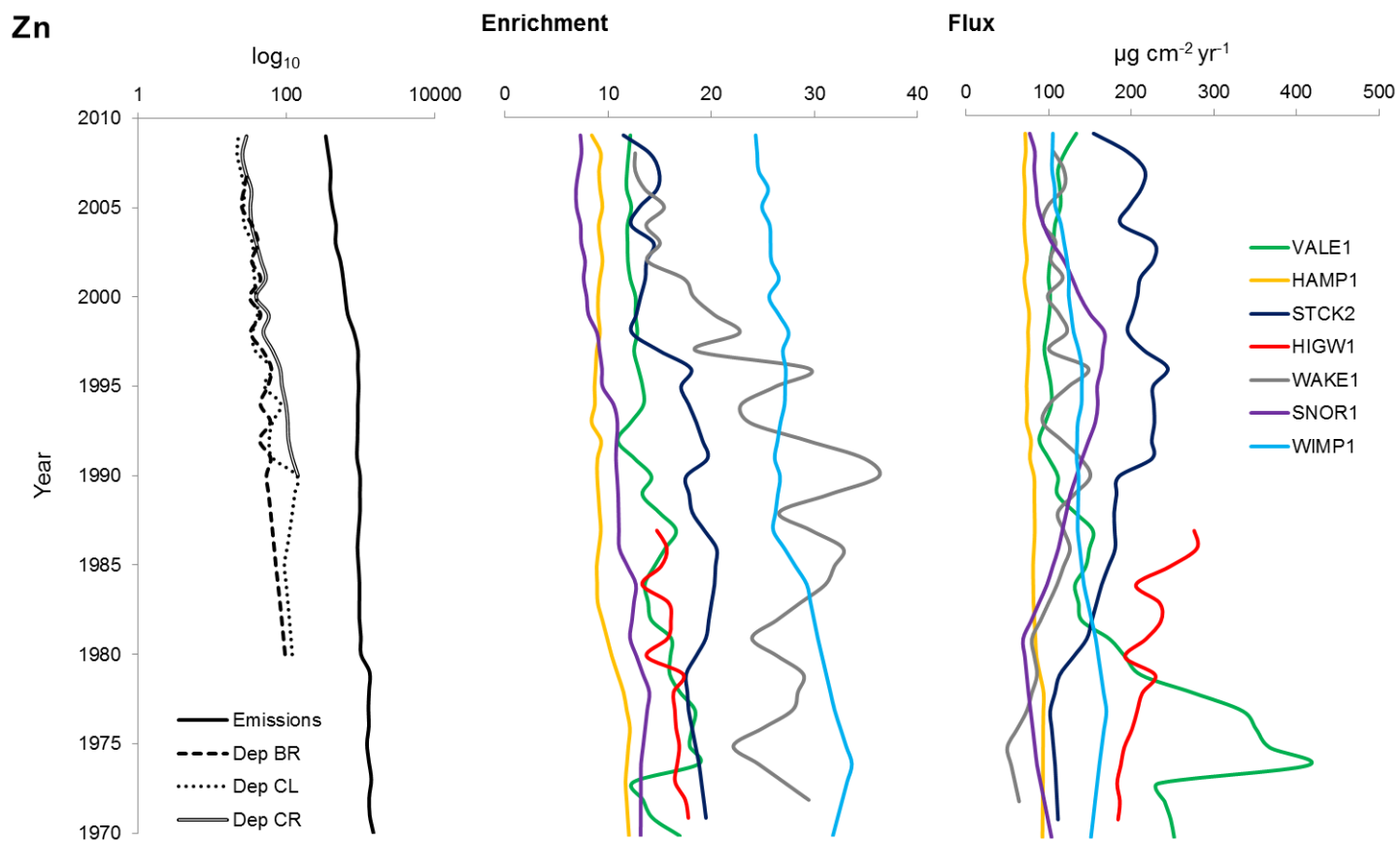


Figure 4.48 – Left: Emissions of Zn in the UK between 1970 and 2009 (from Murrells et al, 2010) and deposition of Zn in London when recorded during the same period (at three different locations: BR – Brent; CL – Central; CR – Cromwell Road) (DEFRA, 2010); Middle: Zn enrichment; Right: Zn flux; both calculated for each London lake between 1970 and 2009 (1970 and 1987 for HIGW1).

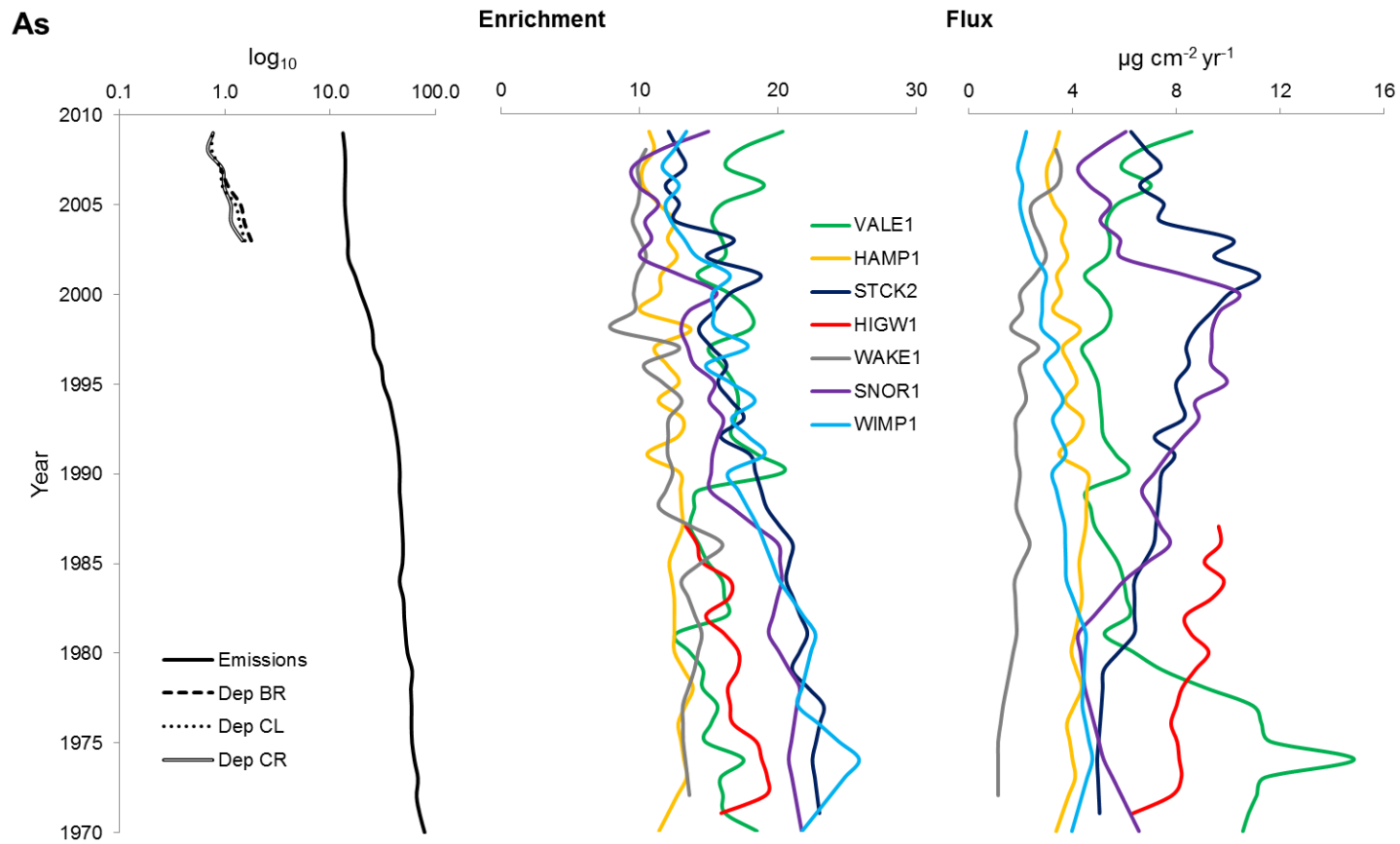


Figure 4.49 – Left: Emissions of As in the UK between 1970 and 2009 (from Murrells et al, 2010) and deposition of As in London when recorded during the same period (at three different locations: BR – Brent; CL – Central; CR – Cromwell Road) (DEFRA, 2010); Middle: As enrichment; Right: As flux; both calculated for each London lake between 1970 and 2009 (1970 and 1987 for HIGW1).

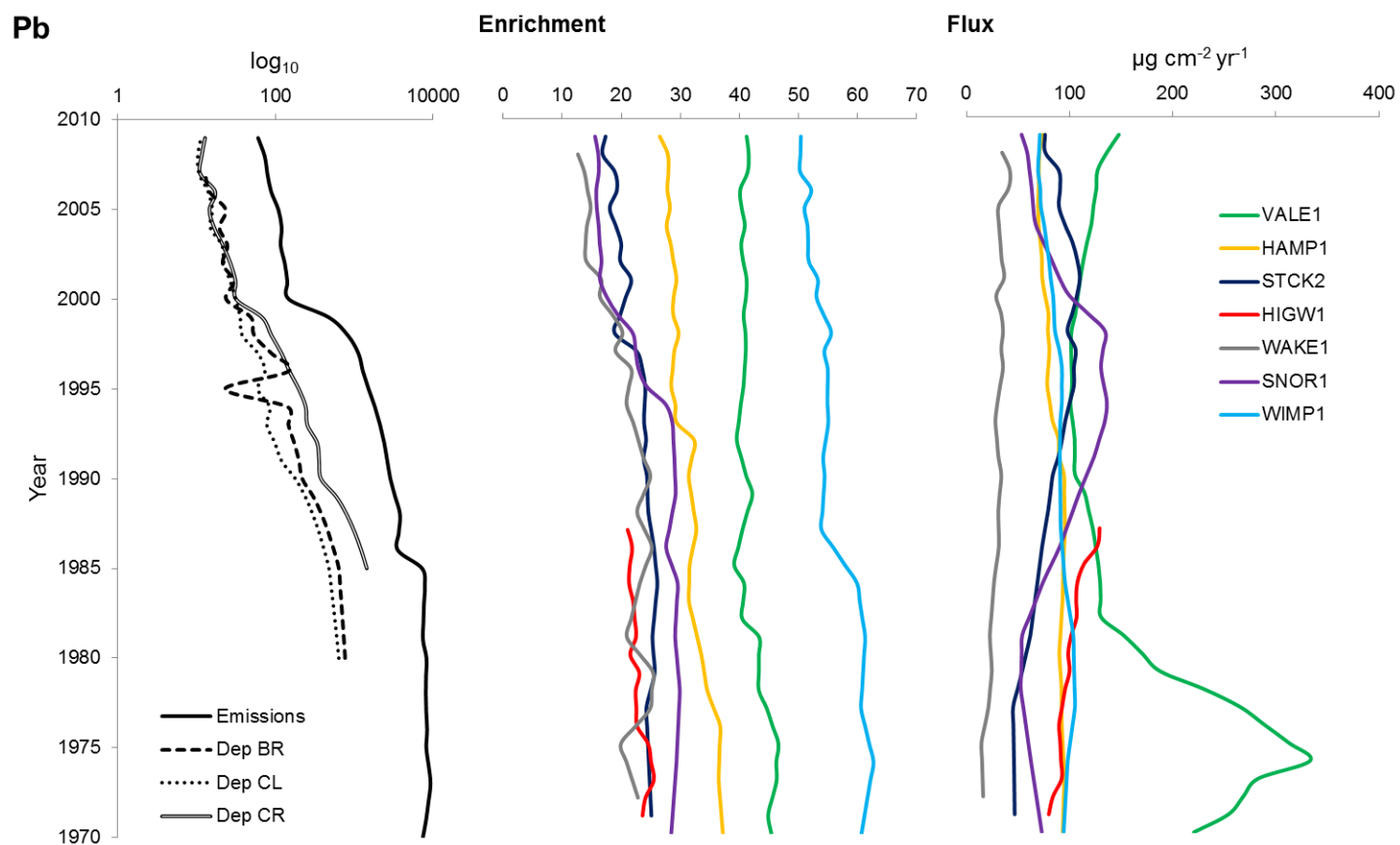


Figure 4.50 – Left: Emissions of Pb in the UK between 1970 and 2009 (from Murrells et al, 2010) and deposition of Pb in London when recorded during the same period (at three different locations: BR – Brent; CL – Central; CR – Cromwell Road) (DEFRA, 2010); Middle: Pb enrichment; Right: Pb flux; both calculated for each London lake between 1970 and 2009 (1970 and 1987 for HIGW1).

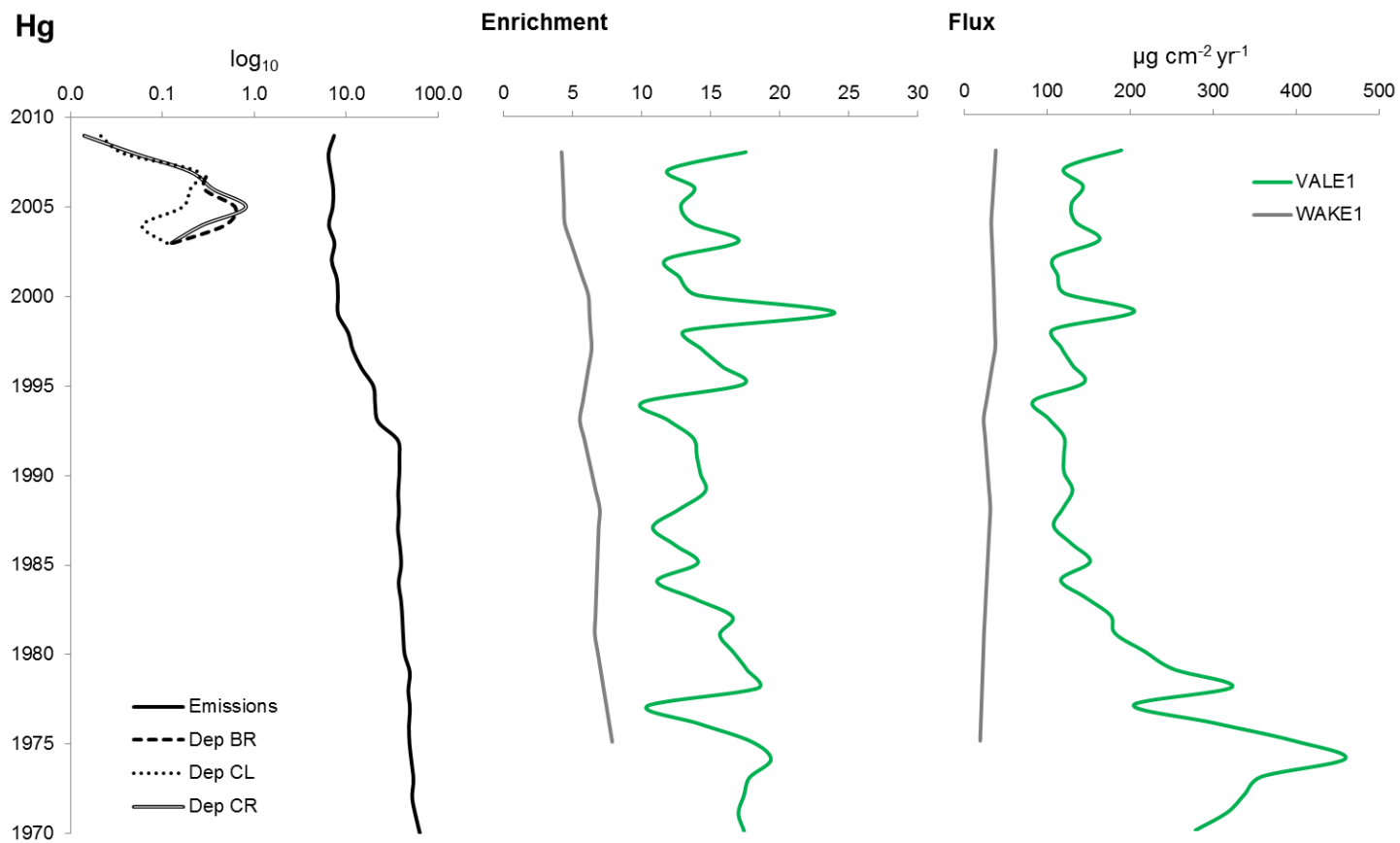


Figure 4.51 – Left: Emissions of Hg in the UK between 1970 and 2009 (from Murrells et al, 2010) and deposition of Hg in London when recorded during the same period (at three different locations: BR – Brent; CL – Central; CR – Cromwell Road) (DEFRA, 2010); Middle: Hg enrichment; Right: Hg flux; both calculated for each VALE1 and WAKE1 between 1970 and 2009.

However, if sediment focusing is not driving the increase in metal flux in the lake sediments, then there must be another reason. The fact that neither flux nor enrichment have declined over recent years in many of the cores suggests that despite declining emissions and deposition, metals are entering the lakes from another source. Erosion of contaminated catchments is now thought to be an important source of metal contamination to fluvial systems. Yang et al (2002b) studied the inputs of Hg and Pb to Lochnagar, a mountain lake in Scotland, UK. Hg and Pb budgets for the whole catchment for 1998 indicated that 78% of the Hg and 91% of the Pb input to the lake were transported from the catchment, and the expected decline resulting from the decrease in atmospheric deposition of Pb was obscured in the sediment record. Similarly, Rothwell et al (2005) studied peat erosion in the southern Pennines, UK and showed that erosion of the upper peat layer was releasing high concentrations of industrially derived Pb (and by inference, other metals associated with industrial particulates) into the fluvial systems of the southern Pennines. More recently, Rose et al (2012) carried out a study to identify whether a simple time-lag, catchment soil erosion, or leaching with dissolved organic carbon was causing increased trace metal input to upland Scottish lakes. Catchment soil erosion was found to be the main transfer mechanism for trace metals at these sites. Although, these studies were carried out in remote locations, catchment soil erosion as a source of trace metals will be of particular importance in an urban environment where there will be a large legacy of contaminants within the soils. In addition, urban lake catchments are likely to be more disturbed which means that erosion of contaminated soils would be greater in urban areas.

4.5.3. Sediment quality and other urban studies

The comparison of the concentrations of metals in the London lakes with probable effect concentrations (PECs) and threshold effect concentrations (TECs) reflected the high levels of contamination in the London area, both historically and in the present day. At all of the sites, concentrations exceeded PECs for all of the metals at some point in the past. The only exception was at the Hampstead Heath sites, where at no point did Cu concentrations exceed the PEC. At the other three sites, Cu concentrations fell below the PEC towards the top of the cores. This spatial difference suggested the Hampstead Heath area had fewer local sources of Cu than the locations in the north and the south of the city. Arsenic concentrations at all sites decreased below the level of the PEC in the last 20 years, although contamination at Wake Valley Pond was consistently much lower than the PEC throughout the core. Mercury concentrations at the Vale of Health Pond also declined over the last 20 years to levels below that of the PEC. The behaviour of Zn in London was a lot more mixed than for the other elements. The concentrations in the surface sediments at Wake Valley Pond were still much higher than the PEC, whilst those at South Norwood and Hampstead No. 1 had declined to less than the PEC from the mid-1980s. Concentrations at the remaining sites were greater but almost equivalent to the PEC at the top of the cores. Ni

and Pb concentrations were both greater than their respective PECs for all sites, apart from South Norwood where Ni concentrations declined from the 1990s. Pb concentrations are of particular note, as apart from at the very base of some of the cores, they have always been greater than the PEC. Although sediment concentrations have fallen below PECs in many cases, at present all concentrations of all metals are still higher than their respective TECs in every lake. Sediments storing such high levels of contamination could pose problems in the future by being potentially toxic if they are disturbed. The impacts of high metal concentrations on the rest of the lake ecosystem will be investigated in Chapter 5, and the potential toxicity of the sediments will be discussed in greater depth in Chapter 6.

Three other studies have been carried out using sediments from London lakes. Yang et al (2001) assessed the spatial pattern of contamination in surface sediments taken from 29 lakes across London in 1998. A paper by Rippey et al (2008) included analysis of a surface sediment sample from Tooting Common Lake in south London, taken in 2002. A core was taken from Banbury Reservoir in north east London in 1998 (Yang et al, 2001; Yang & Rose, 2003; Yang & Rose, 2005). The range of metal concentrations found at each site have been plotted alongside the range of concentrations found at the lakes from this study (Figure 4.38).

The graphs in Figure 4.38 show that the metal concentrations found in previous studies of lake sediments in London are similar to those found in this study. Of the previous investigations, the samples taken from the study by Yang et al (2001) have a much larger range of metal concentrations than those from the other two. However, this is to be expected as it takes into account the results from 29 lakes, rather than just a single site. Only one result is available from Tooting Common Lake, with metal concentrations tending to be equivalent to the minimum values found at the other sites. This is due to the fact that the sample was a surface sediment taken recently, rather than a core, when concentrations have generally declined. Although the results from the previous studies give similar concentrations to those found in this one, they are still lower than the maximum concentrations that have been recorded in this project.

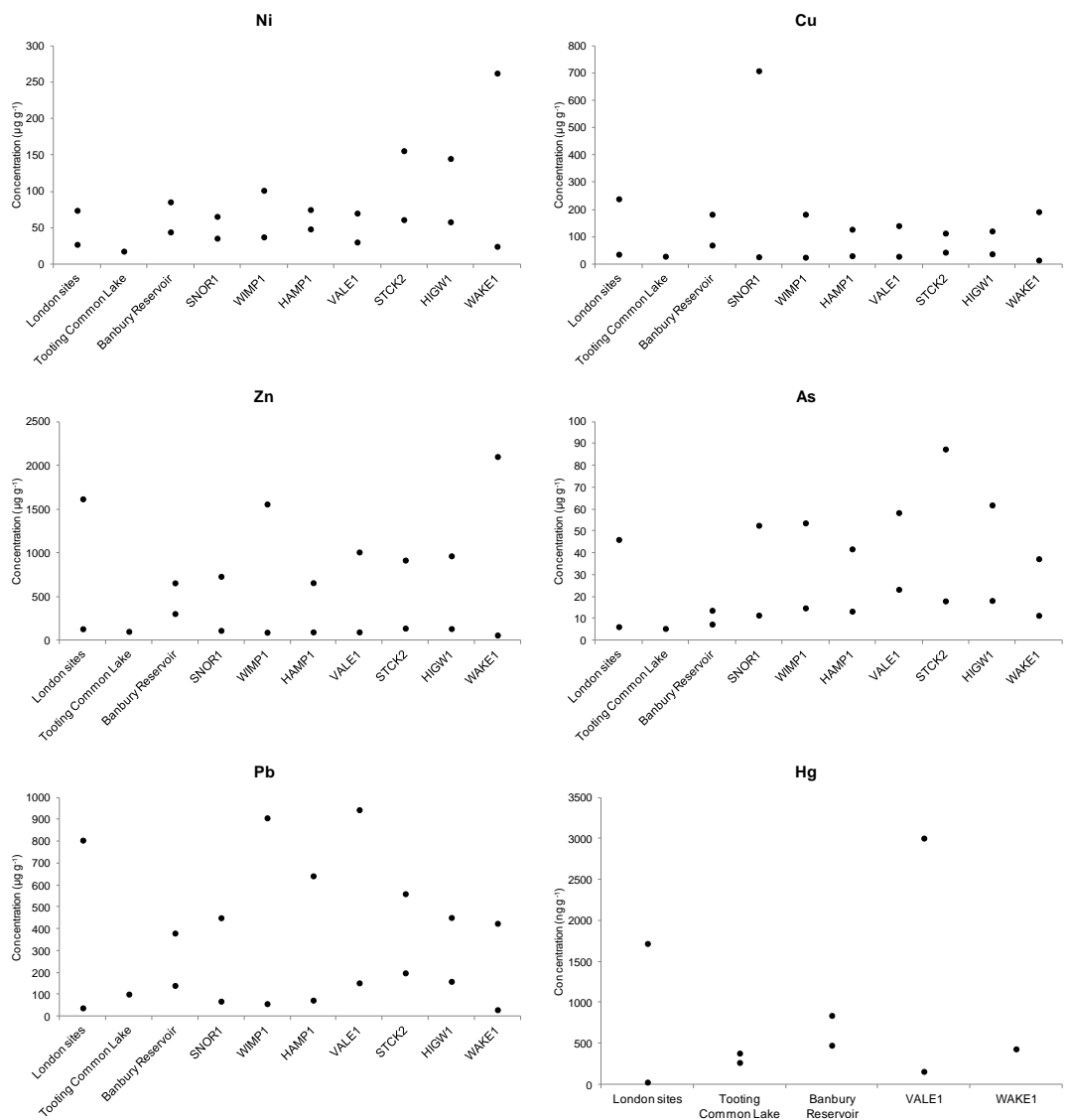


Figure 4.52 – Graphs comparing the range of concentration values of Ni, Cu, Zn, As, Pb and Hg found at each site in this study with the results from previous studies by Yang et al, 2001; Yang & Rose, 2003; Yang & Rose, 2005 and Rippey et al, 2008

Two studies have explored the levels of metal contamination in the sediments of the Thames estuary (Attrill & Thomes, 1995; Pope & Langston, 2011). Both of these accounts have included sampling locations in the inner estuary, within the boundaries of London as defined in Section 2.1 in this project. Neither study has investigated the history of metal pollution in the Thames, but rather has focussed levels of contemporary contamination. Table 4.21 shows the concentrations of metals found in these studies, compared to the range found in the lakes.

Study	Ni ($\mu\text{g g}^{-1}$)	Cu ($\mu\text{g g}^{-1}$)	Zn ($\mu\text{g g}^{-1}$)	As ($\mu\text{g g}^{-1}$)	Pb ($\mu\text{g g}^{-1}$)	Hg (ng g^{-1})
Attrill & Thomes, 1995 Data from Upper estuary sampling point	55	123	401	17	465	1300
Pope & Langston, 2011 Mean concentrations	46.89	68.58	223.36	8.33	133.54	
This study (mean range)	42.17-124.94	29.67-226.54	101.37-1132.04	15.69-56.07	104.43-624.84	316.58-1717.58

Table 4.21 – Metal concentrations in sediments from studies by Attrill & Thomes (1995) and Pope and Langston (2011), compared to the average range of metal concentrations found across the seven lakes studied in this project

The results show that the metal concentrations found in the sediments of the Thames estuary are comparable to those found in the sediments of London lakes. A key finding of the study by Attrill & Thomes (1995) was that the majority of maximum values were recorded in the part of the estuary running through central London, between Hammersmith and London Bridges. This is the most developed part of the Thames, and it was inferred that road run off and sewerage discharge from storm drains were responsible for the higher levels of contaminants in the area. The concentrations from the study by Pope & Langston (2011) were ranged against threshold effect levels (TEs) and probable effect levels (PEs), taken from sediment quality guidelines produced by the Canadian Council of Ministers for Environment. The results showed that all the metals exceeded the TEs in the Inner and Middle estuary, whilst Cu, Pb and Zn also exceeded PEs at all of the Inner estuarine sites.

A limited amount of data is available regarding metal contamination of soils in the London area. A study by Kelly et al (1996) investigated topsoil pollution in the London Borough of Richmond. Pb ranged from 20-1840 $\mu\text{g g}^{-1}$, Zn between 11.4 and 1810 $\mu\text{g g}^{-1}$, and Cu from 3.8 to 1130 $\mu\text{g g}^{-1}$. The concentration range of each element is large, much greater than the mean range found in the lakes (Table 4.21). Local sources of contamination are likely to be important explanatory factors for this, as the highest concentrations were found in samples taken adjacent to busy roads and major road junctions.

Data from lake sediments in other urban areas of the UK is similarly sparse to that in London. Two sites have been studied as part of OPAL which were also in cities, Edgbaston Pond in Birmingham and Chapman's Pond in York. The metal profiles for these are shown in Figures 4.39 and 4.40 respectively. The results from Edgbaston Pond show metal concentrations started to increase at a depth of about 80 cm, prior to 1875. Concentrations in Chapman's Pond increased from the base of the core, which has been dated to pre-1920. However, as with the London cores, it is difficult to ascertain exactly when anthropogenic contamination of the sediments began due to issues with high accumulation rates and interruptions to the sediment record (see Chapter 3).

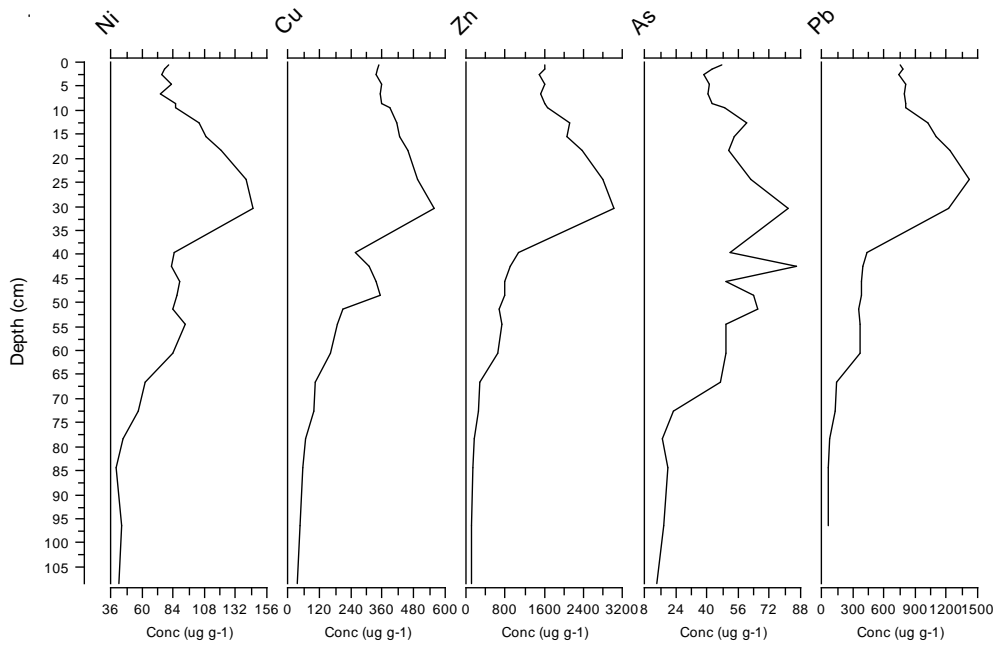


Figure 4.53 – Sediment core profiles from Edgbaston Pond, Birmingham, showing concentrations of Ni, Cu, Zn, As and Pb, each plotted against sediment depth

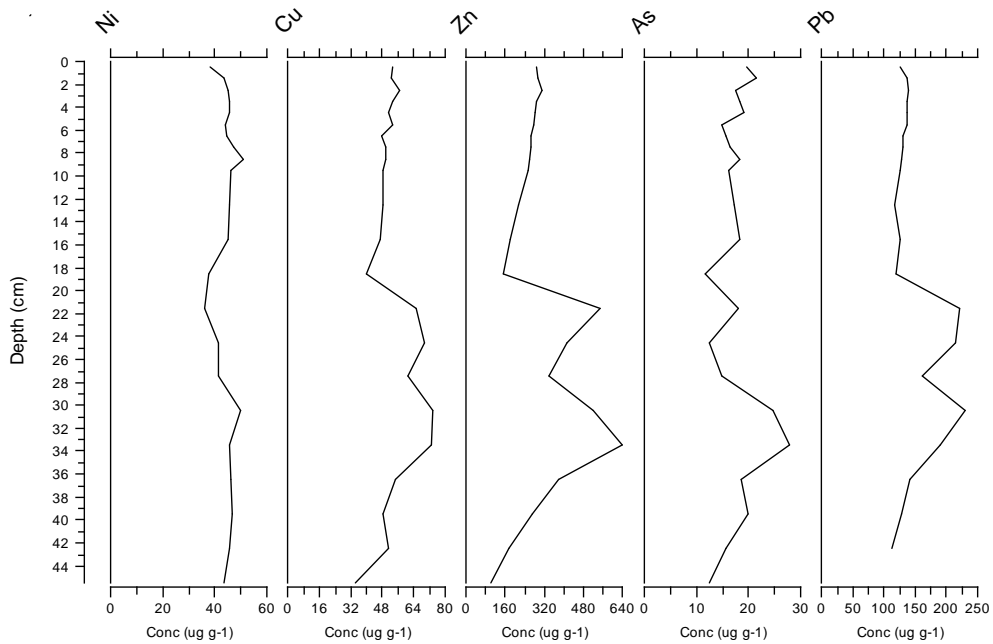


Figure 4.54 – Sediment core profiles from Chapman's Pond, York, showing concentrations of Ni, Cu, Zn, As and Pb, each plotted against sediment depth

In terms of concentrations, the highest found at Edgbaston and Chapman's are listed in Table 4.22 alongside those found in the sites from London. Concentrations of all metals at Chapman's are much lower than those in London and Birmingham. Edgbaston contains

much higher concentrations of Zn and Pb than London, which may be linked to specific types of industry that occurred in Birmingham.

	London	OPAL		Foster et al, 1991	
		Edgbaston Pond, Birmingham	Chapman's Pond, York	Wyken Slough Coventry	Swanswell Pool, Coventry
Ni $\mu\text{g g}^{-1}$	262.2	145.4	50.8	163.4	165.3
Cu $\mu\text{g g}^{-1}$	707.8*	558.5	74	490.1	292.2
Zn $\mu\text{g g}^{-1}$	2099	3023	638.4	1000	1800
As $\mu\text{g g}^{-1}$	87.4	85.7	28		
Pb $\mu\text{g g}^{-1}$	943.6	1420	230.8	475.9	311.5

Table 4.22 – Maximum concentrations of metals found other UK urban lakes, in relation to those found in London

Few other studies of metal contamination of urban lakes have been carried out in the UK. Foster et al (1991) compared metal contents of sediment cores from two rural lakes in the Midlands with two urban lakes in Coventry. Enriched concentrations of metals were found in the urban lakes, the maximum values of which can be seen in Table 4.22. These concentrations vary, but are still generally within the realms of the concentrations found at the other urban sites. Sediment cores from urban ponds in the Liverpool area were used by Power & Worsley (2009) to reconstruct a history of air pollution in northwest England. Zn was used as a proxy for combustion and industrial emissions. Four phases of pollution were identified, showing low values before the 1900s, increased levels of from the start of the 19th century peaking in the mid-20th century, a subsequent decline in the 1960s before a further increase in the 1980s, a pattern not unlike that found in some of the London sediment cores. The changes in the Liverpool ponds were attributed to the development and intensification of industry, followed by the impact of the Clean Air Acts, and the subsequent increase in the use of road and air traffic. Although data from other urban ponds has been provided for comparison, it is difficult to directly compare the results from different cities. In a further study of the Coventry lakes, Charlesworth & Foster (1999) conclude that “sources, transport and accumulation of heavy metals in urban lake sediments may be ecosystem-specific, reflecting the type of industry in the catchment and the spatial and temporal patterns of transport. The data from such studies may therefore not be transferable to other urban sites.”

Study	Location	Metals	Concentrations ($\mu\text{g g}^{-1}$)	Key findings
Chillrud et al, 1999	Central Park Lake, New York City	Zn Pb	1000 (max) 1200 (max)	Increase from 1870 (base of core), peak 1940, second peak 1960, decline to surface Main source of contamination is from the atmosphere
Durant et al, 2004	Spy Pond, Arlington, MA	As	2900 (max)	Low concentrations followed by steep rise and peak occurring ~ 1960 Due to application of arsenical herbicide around 1960
Mahler et al, 2006	Urban lakes across USA (13 lakes in dense urban areas)	Ni Cu Zn Pb	1970s/1990s (median) 37/33 86/83 350/343 483/214	Overall decrease in contamination between 1970s and 1990s
Thapalia et al, 2010	Lake Ballinger, Seattle, WA	Cu Zn As Pb	140 (max) 800 (max) 60 (max) 1000 (max)	Concentrations begin to increase c. 1900 Cu peaks in the 1960s, Zn increases continually between 1900 and 2005 As peaks 1939, Pb peaks in 1972 Records urbanisation of the watershed and emissions from nearby smelter
This study	London	Ni Cu Zn As Pb	262.2 707.8* 2099 87.4 943.6	

Table 4.23 – Key information from the literature of urban lake sediment studies in America (with metal concentrations from this study with which to provide a comparison)

As highlighted in Section 4.5.1, urban sites may not be directly comparable to one another because they contain many localised sources of contamination. It is only at remote sites contaminated by deposition from the atmosphere that more widespread, regional patterns of pollution are discernible in lake sediments. In light of this, comparisons between metal concentrations in London lakes and those in urban areas elsewhere in the world may be difficult. However, it would be interesting to examine how the temporal history of metal contamination in London lakes differs from those in cities in other countries with alternative histories of industrialisation and also to explore how concentrations vary between geographical area (for example, do 'newer' urban areas have lower levels of contamination than those with a long history?). The lack of research into urban lake sediments is not just confined to the UK. Few studies have been published worldwide, and the majority of these are from the USA (Chillrud et al, 1999; Durant et al, 2004; Mahler et al, 2006; Thapalia et al, 2010), or increasingly, from China (e.g. Hu et al, 2011).

The studies from the USA are ranged over a wide geographical area. The main results and findings from the investigations are shown in Table 4.23. The results vary widely which is unsurprising given the range over which the studies have been carried out. In the two studies where maximum metal concentrations are available (Chillrud et al, 1999; Thapalia et al, 2010), Pb and As concentrations are roughly equal to those in London, whilst Zn and Cu concentrations are lower. The As concentration in the study by Durant et al (2004) is extremely high, but this is due to a local source of contamination. The median concentrations supplied in the study by Mahler et al (2006) are hard to compare, but the overall decrease that is recorded between 1970 and 1990 is also reflected in the studies by Chillrud et al (1999) and Durant et al (2004). Where the start of anthropogenic contamination has been recorded in the cores (Chillrud et al, 1999; Thapalia et al, 2010), it occurs from the late 19th century, which is equivalent to the results from London. In the study by Hu et al (2011) of urban shallow lakes in Nanjing, China, short cores were taken from two lakes. The cores were undated and therefore a comparison of metal profiles is not possible. Maximum concentrations of metals found in the cores were 57.8-62.6 $\mu\text{g g}^{-1}$ for Cu, 47.6-47.8 $\mu\text{g g}^{-1}$ for Ni, 169-198 $\mu\text{g g}^{-1}$ for Zn and 31.9-49.9 $\mu\text{g g}^{-1}$ for Pb. These are much lower than the concentrations found in both London and US lakes and is likely to be due to the more recent industrialisation of China.

Examination of other studies of urban lakes has highlighted a few key points. The results obtained from the sediment cores in this study were comparable to those that have been acquired in previous investigations of London. However, there is only a limited amount of research available from which to draw such comparisons. Study of urban lakes at other sites in the UK reveals differences in concentration, suggesting that contamination patterns may

be site or area specific, and therefore that the results from different urban areas are not really comparable. Worldwide, only a few investigations have been carried out into metal contamination of urban sediments. More studies of urban lake sediments in newly industrialised countries would be of interest to see how they compare.

4.6. Conclusion

The first aim of this chapter was to identify metal concentrations in the sediments of London lakes and describe the temporal changes that occurred. The concentrations of Ni, Cu, Zn, As and Pb were determined in Hampstead No. 1 Pond, Highgate Ladies Bathing Pond, Stock Pond, South Norwood Lake and Wimbledon Park Lake using X-ray fluorescence. Mercury concentrations were also determined in addition to the other metals in the Vale of Health Pond and Wake Valley Pond using atomic fluorescence. The concentrations ranged between 24 and 262 $\mu\text{g g}^{-1}$ for Ni, 15 and 708 $\mu\text{g g}^{-1}$ for Cu, 57 and 2099 $\mu\text{g g}^{-1}$ for Zn, 11 and 87 $\mu\text{g g}^{-1}$ for As, 29 and 944 $\mu\text{g g}^{-1}$ for Pb and 160 and 3003 ng g^{-1} for Hg. The concentrations of the lithogenic elements Al, Si, Ti and Zr were also determined for each of the cores, together with organic matter, carbonate content, wet density and dry weight. Sediment accumulation rate at each site was calculated from the radiometric chronologies in Chapter 3 and then used to calculate metal flux. The anthropogenic fraction of the metal concentrations was calculated using enrichment factors, with Ti as a tracer element. Enrichment factors were found to exceed 1 for all metals in all cores, which showed that anthropogenic pollution had occurred at every site for at least as long as the lakes had existed – as far back as the mid-18th century in the case of the Hampstead Heath Ponds. Comparison of the metal concentrations with sediment quality guidelines showed that they had exceeded TECs at all times in the past, and that PECs had been exceeded at all sites for at least some period of time. The concentration of Pb in the sediments was particularly noteworthy as it exceeded the PEC at all sites throughout the 20th century, and in most cases for the whole period the cores covered. Temporal changes in metal contamination varied both between metals within the sediment cores, as well as between the different sites.

The second aim of this chapter was to explain the variation in metal concentrations within and between sediment cores and identify whether the changes in metal pollution across the city reflected a regional pattern or if they were more localised, to ascertain the importance of different pollution sources within the city. One of the key findings of this chapter was that the sedimentary archives of metal contamination in urban lakes are complex. The temporal variation in metal concentration both within and between sites was the result of a combination of different influences. Pearson correlations revealed that the patterns of As concentration differed to those of the other metals. This was supported by previous studies into metal behaviour which have shown that As behaves differently in sediments to other

elements. The amount of organic matter - which is a major metal-binding substrate – influenced the retention of metals within the sediments at some sites. Changes or disturbance to individual lake catchment areas were found to be important drivers of SAR and were reflected as sedimentary ‘events’ in some sediment core profiles. Sediment accumulation rate was found to be a key driver of metal flux at all sites except Wimbledon Park Lake. Metals coming from different sources and via different means (run off, the atmosphere, point sources etc) will also have influenced the contamination patterns in the sedimentary record. A PCA of the data from all the lake cores showed that the sources of As and Pb were similar, but were different to sources of Ni, Cu and Zn. However, in an urban setting such as London which has an extensive industrial past it is difficult to identify and separate specific sources of pollution.

Another key finding from this chapter was that on a broad scale there was some indication of a regional pollution pattern across the Greater London area, but that overall local influences were more important in determining patterns of metal pollution in urban lake sediments. Principal components analysis of all the core samples resulted in some overlap between all the sites (see Figure 4.25), which suggested that the amounts and patterns of contamination were not dissimilar. However, at a larger scale it was noticeable that local influences were actually more important and that patterns of metal contamination were site specific. The results of a PCA of the Hampstead Heath Ponds (Figure 4.21) showed that the core samples from Highgate Ladies Bathing Pond and Stock Pond overlapped, suggesting that the sources of contamination to these ponds were the same, which would be expected as the two ponds were located next to one another and were joined by a stream. However, the core samples from the Vale of Health Pond and Hampstead No. 1 Pond, which were further apart and did not directly adjoin one another, did not overlap. The PCA also showed a distinct separation between the core samples from the two pairs of ponds, which reflected the fact they were located on opposite sides of the Heath. These results highlighted the importance of local, catchment specific, influences on the pollution record in urban lake sediments.

The third aim of this chapter was to identify and explain the trends and levels of metal contamination in the most recent core sediments. The key finding was that although in general the concentrations of metals in the sediments have declined since the 1970s, there has not been a corresponding decrease in enrichment or metal flux. Comparison to records of metal emissions and deposition in the UK and London accentuated the difference, as both emissions and deposition have also decreased since the 1970s. This suggested that there was a secondary source of metals to the lake sediments, most likely from the erosion of soils from contaminated catchments. The levels of contamination found in the lakes in this study

were comparable with those found in previous investigations of London, although only a limited amount of research was available from which to draw such comparisons. Studies of urban lakes at other sites globally revealed differences in concentration.

CHAPTER 5: CONTEMPORARY TRACE METAL CONTAMINATION IN A LONDON LAKE

5.1. Introduction

Historic concentrations of metals in London lakes, reconstructed from sediment cores in Chapter 4, were shown to have exceeded sediment quality guidelines in the past, and in some cases were still exceeding guideline values in recent sediments. However, high metal concentrations in the sediments do not necessarily indicate that metal concentrations will also be high in other parts of the lake ecosystem, as sediments act as storage for metals. The aim of this chapter is to identify metal concentrations in other parts of the lake ecosystem and explore the relationships between the sediments and the rest of the ecosystem. Metal concentrations will be determined in recent sediments, deposition, water, macrophytes, benthic algae, zooplankton and fish at the Vale of Health Pond to provide a snapshot of the degree of contamination in an urban lake. The variability in concentrations both within and between the different components of the ecosystem will be discussed with reference to previous studies and the concentrations of metals in sediments, water and fish will be compared to guideline values.

5.2. Field methodology

Fieldwork was carried out at the Vale of Health Pond (for site information and history see Chapter 2) on a monthly basis between the 26th January 2010 and the 25th January 2011. Additional visits were made on the 3rd/4th May 2011. Table 5.1 shows the type and frequency of sampling carried out at the pond.

Year	Date	Bulk deposition	Physical measurements	Lake water	Sediment traps	Zooplankton	Benthic algae	Macrophytes	Fish
2010	26 Jan		x	x	x				
	23 Feb	x	x	x	x				
	24 Mar	x	x	x	x	x			
	27 Apr	x	x	x	x	x	x		
	25 May	x	x	x	x	x			
	29 Jun	x	x	x	x	x			
	27 Jul	x	x	x	x	x	x		
	31 Aug	x	x	x	x	x			
	27 Sep	x	x	x	x				
	26 Oct	x	x	x	x	x	x		
	29 Nov	x	x	x		x		x	
20 Dec	x	x							
2011	25 Jan	x	x	x	x	x	x	x	
	04 May								x

Table 5.1 – Type and frequency of sampling carried out at the Vale of Health Pond

5.2.1. Bulk deposition

Two deposition collectors were installed at Kenwood Staff Yard (TQ 27506 87550), 1.4 km from the Vale of Health Pond. This site was chosen because it had no public access which meant that it was likely to be the most secure place on the Heath. Its proximity to the lake monitoring site was also advantageous. Meteorological data to be used in conjunction with the deposition results was also collected close by. The Hampstead weather station is located 2 km to the south west of the deposition collectors, at grid reference TQ 263862. It is run by Philip Eden on behalf of the Hampstead Scientific Society.



Figure 5.1 – Bulk deposition collectors installed at Kenwood Staff Yard

One deposition collector was for mercury and the other was for Ni, Cu, Zn, As and Pb (Figure 5.1). Each collector consisted of a borosilicate glass funnel (200 mm top diameter) running down into a 500 ml polytetrafluoroethylene (PTFE) bottle. An inverted plastic funnel acted as a seal between the glass funnel and the bottle, only allowing water to reach the collecting bottle through the glass funnel stem, as well as limiting any splash back from the ground. A bird guard was attached to the top of the glass funnel to prevent the collector from being used as a perch and a small piece of stainless steel mesh was placed inside the neck of each funnel to prevent debris from falling in and blocking the stem. The components were secured in place using a combination of electrical tape and cable ties. Each deposition

collector was attached to the top of a 2.0 m metal stake driven 0.5 m into the ground, so that the collectors were located 1.5 m above ground level. Both collectors were stabilised using guy ropes.

The funnels and collection bottles were cleaned prior to installation by soaking in a 5% Decon 90 solution for 24 hours, followed by multiple rinses with deionised water and a further 24 hour soak in a 4% HCl solution bath. They were then rinsed extensively again in deionised water and left in a static air drying cabinet. Once dry, the bottles were acidified before they were used, to keep the collected metals in solution. 5 ml (1% vol) Aristar ® grade nitric acid was added to the collector for Ni, Cu, Zn, As and Pb, and 5 ml (1% vol) Aristar ® grade hydrochloric acid was added to the mercury collector. The collectors were installed on the 26th January 2010. The bottles were collected and exchanged for new ones on a monthly basis. The funnels were changed every three months to ensure that the equipment was clean and in working order.

5.2.2. Physical measurements

Physical measurements were necessary to ascertain general limnological conditions at the site that would be required for interpretation of the metal concentration data. Physical measurements were taken once a month at the deepest point of the lake (in order to obtain the longest depth profile). This was located at TQ 26605 86437 (Figure 5.3). The water depth at this point varied between 2.8 m and 3.1 m over the year. The only exception was in December 2010 when the lake was frozen and the sampling point was not accessible. Dissolved oxygen, conductivity, temperature and pH measurements were taken from the edge of the lake during that month.

5.2.2.1. Light penetration

The absorption and attenuation of light by the water column are major factors controlling temperature and potential photosynthesis within a lake, and determine the maximum depth at which algae and macrophytes can grow. Light penetration was assessed by the measurement of light levels using a submergible LI-COR LI-250 Light Meter (values expressed in μmol). The sensor was lowered through the water column and averaged readings were taken at 0.5 m intervals to the bottom of the lake. Above water measurements of ambient and reflected light were also recorded. A Secchi disc was used to measure turbidity, which is related to light penetration. A quartered black and white metal disc attached to a tape measure was lowered into the water until it could no longer be seen and the depth at which this occurred was recorded.

5.2.2.2. Conductivity

Conductivity is a measure of the resistance of a solution to electrical flow. Resistance is affected by the amount of dissolved ions in the water and will decline as the ion content increases. Catchment properties such as geology and size will influence conductivity. It is commonly used to assess changes in water quality, often due to seasonal variations. Conductivity was measured using a Hach HQ 30D conductivity probe on a cable (values are expressed in $\mu\text{S cm}^{-1}$) at 0.5 m depth intervals from the surface to the lake bed.

5.2.2.3. Dissolved oxygen

Oxygen dissolved in lake water is important for the metabolic processes of aerobic aquatic organisms. It comes directly from the atmosphere, but also from aquatic macrophytes as a product of photosynthesis. Measurements of dissolved oxygen help to evaluate the biological processes occurring in the lake. Dissolved oxygen concentrations were measured using a Hach HQ 30D DO probe on a cable (values are expressed in mg L^{-1}) at 0.5 m depth intervals from the surface to the lake bed.

5.2.2.4. pH

pH is a measure of the acidity or alkalinity of water, expressed in terms of its concentration of hydrogen ions. The pH of water determines the solubility and biological availability of chemical constituents such as nutrients (P, N, C) and heavy metals (Pb, Cu, Cd etc), which can in turn have an effect on the aquatic organisms found in lakes. pH was measured using a Hach HQ 30D pH probe on a cable at 0.5 m depth intervals from the surface to the lake bed.

5.2.2.5. Temperature

Temperature was measured at 0.5 m depth intervals from the surface to the lake bed. Temperature was recorded simultaneously by the same probes that were used for conductivity and dissolved oxygen. A Gemini Tinytag Plus 2 TGP-4017 temperature data logger was also installed at the Vale of Health for the duration of the monitoring programme. This was located just beneath the surface of the water at TQ 26574 86414 (see Figure 5.3). It recorded the temperature of the lake at 15 minute intervals for 12 months. The device was changed every 2 months to ensure that there was always enough battery power and to download and secure the data.

5.2.3. Lake water

Water samples were taken once a month from the same location as the physical measurements (See Section 5.2.2 and Figure 5.3), apart from in December 2010 when the lake was frozen. Four water samples were taken on each visit. Water was collected for analysis of Ni, Cu, Zn, As and Pb in a 250 ml HDPE (NALGENE ®) bottle which had been pre-cleaned. This involved rinsing in distilled water, followed by soaking for 24 hours in a 5% Decon 90 solution. The bottle was then rinsed successively with deionised water, soaked for a further 24 hours in a 4% HCl solution bath, rinsed again in deionised water and dried in a static air drying cabinet. Once dry, 2.5 ml (1% vol) Aristar ® grade nitric acid was added to the bottle to preserve the samples. Water was collected for analysis of Hg in a 125 ml Teflon bottle that had been rigorously acid washed and which contained 1.25 ml (1% vol) Aristar ® grade hydrochloric acid. Bottles were provided by, cleaned and acidified by NILU (Norwegian Institute of Air Research) in Norway. Water was collected for analysis of major chemistry in clean bottles provided by the National Laboratory Service (Environment Agency). Water was collected for analysis of suspended solids in a 2 litre plastic bottle, which had been pre-cleaned in 5% Decon 90 solution, rinsed in distilled water and dried. All samples were taken from 0.5 m water depth using a manually operated pump with a hose lowered to the correct depth. The bottles for major chemistry and suspended solids were rinsed twice with lake water before being filled, whilst the bottles for metal analysis were filled without rinsing to ensure they remained acidified.

5.2.4. Sediment traps

Sediment traps provide a tool for monitoring sediment deposition in lacustrine environments. Sedimenting material can be collected from a lake over a discrete time interval, providing a valuable method for physical, chemical and biological monitoring. Two cylindrical sediment traps (Figure 5.2) were installed close to the deepest point in the pond. Trap # 1 was located at TQ 26606 86428 and trap # 2 at TQ 26598 86442 (Figure 5.3). Each sediment trap was suspended at about 2.5 m depth about 40 cm above the bed of the pond, and secured with an anchor and a subsurface buoy. Every month (with the exception of November and December 2010 when the lake was frozen and the traps were not accessible) the sediment traps were pulled (carefully to reduce sediment resuspension) to the surface and the excess water siphoned off. The remaining water and sediment was poured into pre-weighed Whirlpak bags. The traps were then returned to the water. On return to the laboratory, the sample bags were placed in beakers and left to settle in the cold store for two days. The water was then siphoned off and the remaining sediment was freeze dried and re-weighed to give a total sediment mass prior to analysis.



Figure 5.2 – one of the two sediment traps installed at the Vale of Health Pond

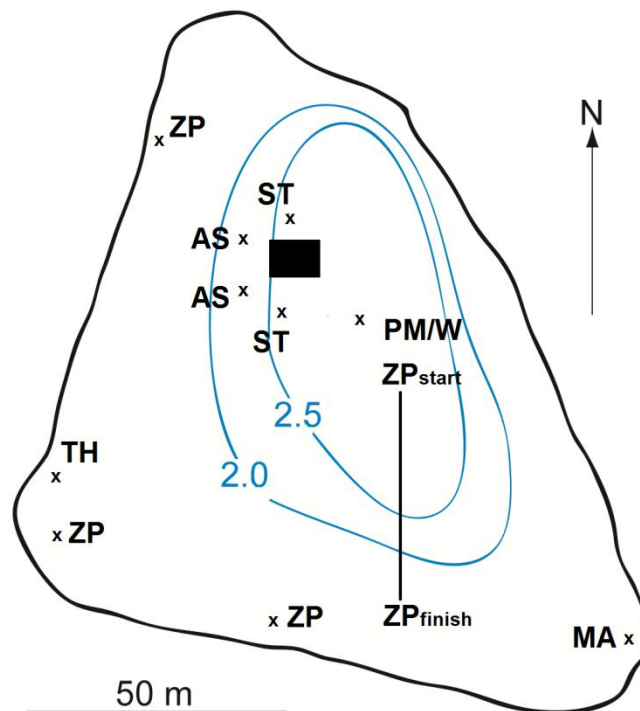


Figure 5.3 – Map of the Vale of Health Pond, showing the location at which physical measurements and water samples were taken (PM/W); the locations of sediment traps (ST), artificial substrates (AS), and the thermistor (TH); littoral zooplankton sampling locations (ZP) and the open water zooplankton sampling transect (ZP_{start}/finish); macrophyte sampling location (MA). The black rectangle represents an artificial island anchored near the deepest point.

5.2.5. Zooplankton

Zooplankton samples were collected monthly from the lake, from both littoral and open water zones (with the exception of November and December 2010 when the lake was frozen). In order to obtain a quantitative estimate of abundance, a 2 m long plastic tube (internal diameter 7.5 cm) was used to take an integrated sample of the top 2 m of the water column. In the open water, tube samples were taken at five locations along a visual transect across the deeper, most central part of the lake (Figure 5.3). The volume of water taken was recorded each time and the samples were pooled and filtered through a 50 µm net. The start and end points of each transect were recorded so that sampling could be carried out across a similar area each time. The littoral samples were taken in three locations, each with a slightly different shoreline habitat (Figure 5.3). Because the water was much shallower, the tube was put in at an angle to try to cover the entire water column and to collect the greatest possible volume. The volumes of water taken were once again recorded, and the samples were pooled and passed through a 50 µm net. All samples were preserved with Industrial Methylated Spirits (IMS). In addition to abundance, the lake was also trawled for zooplankton in order to obtain a sufficient quantity for metals analysis. A 50 µm net was placed in the water behind the boat and towed around the lake. A number of trawls were made in order to cover as wide an area of the lake as possible. The collected zooplankton were poured into clean, pre-weighed Whirlpak bags. The bags were placed in beakers and left to settle in the cold store for two days. The water was then siphoned off and the remaining zooplankton were frozen, freeze dried and re-weighed.

5.2.6. Benthic algae

Initially, three different types of artificial substrate were designed and constructed. These were tested to see how effective each one was before a final solution was chosen. The mass of benthic algae that could be obtained was a chief concern as a minimum of 0.5 g was required for analysis. Based on research by Goldsmith (2000) and Tyler (2007), it was decided that polypropylene sheeting, roughened using coarse sandpaper, would be the most practical material to use. Three different types of substrate were created from this material (Figure 5.4).

- 1) The first was essentially a copy of the substrate used by Tyler (2007). This consisted of a 1 mm thick flat polypropylene sheet of dimension 400 mm x 300 mm (1200 cm²) clipped to ropes with stainless steel carabiners, which was designed to be suspended vertically within the top of the water column between two subsurface buoys and anchors (Figure 5.4a).
- 2) The second was also a 400 mm x 300 mm x 1 mm flat sheet of polypropylene, but this time it was designed to lie horizontally beneath the surface of the water, in order to maximise the surface area visible to the light. As with the first substrate, the sheet

was attached to ropes using stainless steel carabiners, with one subsurface buoy and one anchor to hold it in position (Figure 5.4b).

- 3) The final design used polypropylene with the same surface area as the other two, but in this case it was wrapped around and tied so it was cylindrical in shape (Figure 5.4c). The tube was attached to a rope with stainless steel carabiners and suspended in the water just beneath the surface, with the open ends top and bottom. One subsurface buoy and one anchor were required to moor the substrate in place.

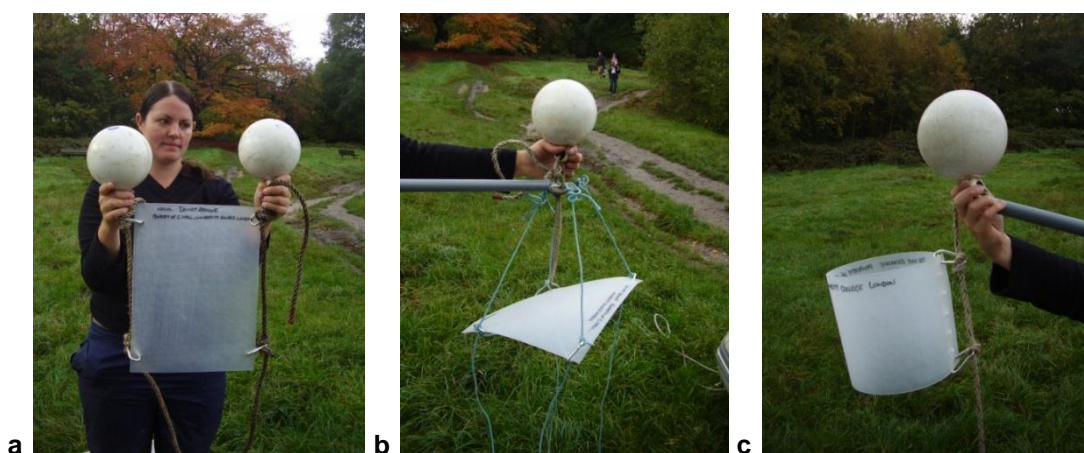


Figure 5.4 – The three different types of artificial substrate that were tested prior to commencement of the monitoring programme at the Vale of Health Pond, designed to be suspended a) vertically and b) horizontally beneath the water surface, and c) a cylindrical substrate also designed to be suspended vertically just below the surface

The size of the substrates was kept constant so that the effect that shape had on algal colonisation could be compared more easily. All the substrates were deployed from an inflatable boat, the vertical artificial substrate being located approximately 40 cm below the surface of the water at TQ 26602 86434 and the horizontal and round substrates being anchored together close by, also at a depth of approximately 40 cm at TQ 26603 86434. The location on the southern side of the artificial floating island that is anchored towards the centre of the pond was chosen in order to get the most sun and because it was inaccessible unless by boat. After approximately one month, each of the artificial substrates was removed from the water in turn and placed in separate acid washed plastic trays. In the laboratory, the algae on each substrate were removed by scrubbing the substrate with a clean toothbrush under running deionised water. The resultant algae/water mix was poured from the tray into a clean, pre-weighed Whirlpak bag (one bag for each style of substrate). The bags were placed in beakers and left to settle in the cold store in the dark (to prevent further growth) for one week. The water was then siphoned off and the algae were freeze dried and re-weighed.

The total amount of benthic algae obtained from each type of substrate varied considerably. The greatest mass of material was obtained from the horizontal substrate (2.04 g). However, much of this was sediment which was deposited on the surface of the substrate. Of the other two substrate designs, a larger mass of algae was obtained from the vertical substrate (0.88 g) than from the round substrate (0.69 g). Both types of substrate were relatively easy to make and install, and therefore it was decided that the vertical substrate would be the chosen design. The prototypes were tested in the autumn when algal growth would be minimal in comparison to that of the summer months (when longer daylight hours and warmer temperatures would encourage growth) and therefore the size of the substrate was sufficient to obtain enough material for analysis. However, to ensure that this was the case, two substrates were used and their dimensions were increased to 500 mm x 400 mm, with an area of 2000 cm² each.

The chosen artificial substrates were installed at the Vale of Health on the 26th January 2010. They were located approximately 40 cm below the surface of the water; substrate # 1 at TQ 26596 86430 and substrate # 2 at TQ 26600 86437 (Figure 5.3). The substrates were unclipped and replaced every three months. The used substrates were removed and cleaned in the laboratory. Once the benthic algae had been removed the substrates were thoroughly cleaned, acid washed and repeatedly rinsed in deionised water to enable them to be used again.

5.2.7. Macrophytes

Macrophyte samples were taken twice, in November 2010 and January 2011. There were only three species present at the pond; *Ceratophyllum demersum*, *Iris pseudacorus* and *Nymphaea alba*. The intention was to take a sample of each at the end of the growing season, so that the metal concentrations reflected the total uptake of metals over the year. However, the lake was frozen in November and December 2010. *Ceratophyllum demersum* and *Nymphaea alba*, which had both still been in growth in October were killed by the ice cover, and therefore could not be sampled. A sample of *Iris pseudacorus* was taken in November 2011 as the extent of ice cover did not reach the edge of the lake where the macrophyte grew (Figure 5.3) although by December the macrophyte was inaccessible. However, a second sample was also taken in January 2011 when the ice had melted. The samples were removed by carefully cutting a number of submerged leaves near the root. The tops of the leaves were discarded leaving sections about 10 cm in length. These were placed in clean Whirlpak bags and taken back to the laboratory, where they were washed with deionised water and freeze dried.

5.2.8. Fish

A 2002 study into fish stocks at the Vale of Health Pond (CB Fisheries) showed that the most dominant fish in the lake by weight was carp, which reflected the ponds status as a designated carp fishery. Perch and roach were the most common fish by number, but tended to be much smaller in size. Common bream, pike and tench were also present in smaller numbers. The pond had not been restocked since 2002 and the exact composition at the time of the present study was unknown. A number of restrictions were in place regarding removal of fish from the pond. The Corporation of London had requested that no carp be taken, and that the smaller the size of fish and numbers removed the better. For the purposes of this study, the fish needed to be at least one year old to ensure that the tissues incorporated metals from the same period over which the rest of the sampling had taken place. The addition of older fish would be beneficial but was not crucial to the study. Given these restrictions, it was decided that perch would be the most suitable species to sample. Choosing only one species to sample meant that a larger number of one type could be removed rather than smaller numbers of more types, which had implications for the robustness of the data. Perch was one of the most common species present in the pond, and their position in the food chain was important. The main source of food for perch was algae and zooplankton. Therefore a direct link could be drawn between metal concentrations in their tissues and concentrations in the algae and zooplankton which had also been collected. In addition, perch are themselves a source of food for piscivorous species of fish such as pike, which has implications for biomagnification.

The Corporation of London requested that fishing be carried out during the coarse fishing close season (15 March to 15 June), in order to cause minimal disruption to anglers. Authorisation was obtained from the Environment Agency to fish using fyke nets fitted with otter guards (Licence no. B/NE/28012011/LH2). Fyke nets were deployed before dusk on the 3rd May 2011 and left overnight. The nets were laid following prior consultation with a number of regular anglers at the site about the best locations to set them. The nets were collected the following morning of the 4th May 2011. Fishing was concentrated over this period as fish are most active around dusk and dawn. Ten small perch were collected and taken directly back to the laboratory.

5.2.9. Other biota considered for sampling

Ideally, all types of biota present at the Vale of Health Pond needed to be collected for this study, to ensure that the results were representative of the whole ecosystem. Therefore, a number of biota were considered in addition to those described in Sections 5.2.5 to 5.2.8. Benthic macroinvertebrates were collected monthly throughout the sampling year. However,

only a small number of species were present and only a very limited number were retrieved at any given time – not enough to be able to analyse for metal concentrations. The same applied to chironomids and phytoplankton – both were present in the pond but it was not possible to obtain the quantities required for analysis. Baited traps were set to determine if any crayfish were present in the pond and searches were made for swan mussels. However, neither met with any success and the conclusion was drawn that no populations of either were present in the pond. This was corroborated by anecdotal evidence given by regular anglers at the site.

5.3. Laboratory methodology

5.3.1. Trace metal (Ni, Cu, Zn, As and Pb) analysis

5.3.1.1. Bulk deposition and lake water

Both bulk deposition and lake water were analysed for trace metal content at Imperial College London using inductively coupled plasma mass spectrometry (ICP-MS). Standard reference samples such as Standard Reference Material ® 1640, and acidified blanks were analysed frequently (typically every fifth sample) for the purposes of QA/QC. Typical detection limits for these analyses were, in $\mu\text{g L}^{-1}$; Cd = 0.02, Pb = 0.01, Zn = 0.20, Cu = 0.18 and Ni = 0.11.

5.3.1.2. Sediment traps

Sediment trap samples were analysed for trace metals using XRF. The method was the same that was used for the sediment core samples and is described in Section 4.3.

5.3.1.3. Biota

Concentrations of Ni, Cu, Zn, As and Pb were determined in zooplankton, benthic algae, macrophytes and fish using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Inductively coupled plasma (ICP) is the ionization source that is used in both techniques. When Ar gas passes through a quartz torch placed in an induction coil (or load coil) to which a radio frequency power between 750 and 1700 W is applied, an alternating current oscillates within the field. The frequency of oscillation is usually 27.1 MHz or 40.6 MHz. Oscillations set up electrical and magnetic fields at the top of the torch. If a spark is then applied to the Ar gas via a Tesla coil, electrons are stripped from some of the Ar atoms. These electrons are trapped in the magnetic field and accelerated in closed circular paths. This is known as inductive coupling

and therefore the plasma formed is IC plasma. A chain reaction is established when electrons collide with neutral Ar atoms. The plasma consists of e^- , Ar^+ and Ar^0 . It needs radio frequency power in the induction coil to exist and its function is to transform a liquid sample into ions. The temperature of the plasma is between 6000 and 10000 K (Montaser, 1998; Nelms, 2005). In ICP-AES, the sample is vaporized and excited in the IC plasma and the atomic emission spectra are observed.

ICP-MS is a type of mass spectrometry. Mass spectrometry is used in identification, to determine molecular weight and to investigate break down. This is done by ionizing molecules and accelerating the ions, which are then separated according to their mass/charge (m/e) ratio. The relative abundance of isotopes or other ionized species is determined by measuring the positive or negative ion currents arriving at a fixed focus, using various controlled magnetic fields and accelerating potentials. The results obtained are called mass spectra. They consist of ions of varying intensity at different m/e ratios. For elements, the individual lines correspond to different isotopes. For compounds, individual lines may be due to the presence of isotopic species, fragmentation of the molecule or ionisation of the parent species in the mass spectrometer (Sharp, 1990). Once the IC plasma has been generated, a sample is introduced and mass separation is achieved by passing ions through a magnetic field. The magnetic field can be static (magnetic field steady) or dynamic (electric field varied). Once the ions have been separated the signals are detected and amplified in order to determine intensities (Montaser, 1998; Nelms, 2005).

ICP-MS is often used for the analysis of trace metals in environmental samples, including sediments (e.g. Nguyen et al, 2005; Pyle et al, 2005; Yang & Rose, 2005) and biological matrices such as fish (e.g. Chandra Sekhar et al, 2003; Pyle et al, 2005; Yang et al, 2007), macrophytes (e.g. Buchmann et al, 2000; Ravera et al, 2003) and plankton (e.g. Chen et al, 2000; Nguyen et al, 2005). The technique is useful because it offers simultaneous multi-element analysis of a large number of elements, with rapid sample throughput. The method operates within a wide, linear concentration range of five orders of magnitude and is very sensitive. Detection limits are very low, which allows both the analysis of small samples and also those of low concentration (Ridout et al, 1988; Friel et al, 1990). However, there are difficulties associated with ICP-MS which include matrix effects, instrumental drift and molecular ion interference. Both matrix effects and drift are compounded by the total dissolved solids of the analytical solutions, which can cause a loss of sensitivity. However, this problem can be resolved to some extent by dilution of the samples before analysis. The low limits of detection of the technique mean that the metal concentrations can still be determined, and dilution helps to minimise interferences from the sample matrix (Ridout et al, 1988).

Metal concentrations were determined in biological samples using both methods. All samples were first analysed by ICP-AES. Those which were below the detection limit of the method were subsequently analysed by ICP-MS. All laboratory equipment used in the preparation of the samples was cleaned prior to installation by soaking in a 5% Decon 90 solution for 24 hours, followed by multiple rinses with deionised water and a further 24 hour soak in a 2 % HNO₃ solution bath. HNO₃ was chosen rather than HCl because chloride ions from HCl can interfere with ICP-MS. The equipment was then rinsed extensively with deionised water again and left in a static air drying cabinet. Samples have to be in solution in order to be analysed by ICP. The general procedure involves the digestion of a sample in an acid to break down the solid components and release the metals into solution.

The acid digestion method follows that described by Yang & Rose (2005), which is the extraction method for the fraction of trace elements that is loosely bound for assessing biological availability. Freeze dried samples were disaggregated and homogenised with a pestle and mortar until finely powdered. 0.2 g of each sample was weighed into Teflon beakers and 8 ml of concentrated HNO₃ (Normaton for trace metals) was added. The beakers were then heated on a hotplate at 100°C for 1 hour until the samples reached near dryness. The samples were removed from the hotplate, topped up with deionised water and left to cool. The samples were filtered through pre-cleaned 2.5 cm GF/C filter papers directly into sterile polystyrene containers. This was done to remove any suspended solids which could block the nebuliser in the ICP. After filtering, the samples were made up to 20 ml with deionised water. Samples that were below the limits of detection on the ICP-AES were diluted a further 10 times to reduce the levels of total dissolved solids and then analysed on the ICP-MS. The same digestion method was applied to certified reference materials of known concentration (BCR-060 Aquatic plant (*Lagarosiphon major*); BCR-414 Plankton; NRC DORM-3 Fish protein). Sample blanks made from deionised water were also digested in the same way to determine if there was any contamination from the acid and filter blanks were prepared with deionised water to ascertain if there was any contamination from the filter papers.

Samples were analysed on a Horoba JY Ultima 2C ICP-AES and a Bruker M90 ICP-MS. Standard solutions were run every ten samples to monitor measurement stability. Reference materials, sample blanks and filter blanks were analysed regularly during sample analyses. Metal concentrations in the sample blanks were below the limits of detection for both ICP methods. Concentrations in the filter blanks were also below the limits of detection for all metals except Zn, which was present in measurable concentrations on the ICP-MS. The mean concentration calculated from the filter blanks was deducted from the Zn

concentrations of the biological samples. The measured values of each reference material are shown in comparison to the certified values in Table 5.2. Percent recovery varied depending on the type of material and metal in question. The lowest recoveries were for Pb in fish tissue (30%) and Ni in plankton (49%).

	Ni	Cu	Zn	As	Pb
BCR-060					
Certified value	40	51.2	313	8	64
Measured value	27	42.5	251	7.7	52
SD	4.11	7.27	35.83	0.88	7.99
Recovery (%)	68.39	82.98	80.24	95.64	80.58
BCR-414					
Certified value	18.8	29.5	111.6	6.82	3.97
Measured value	9.3	23.4	83.7	7.67	3.34
SD	1.47	3.40	5.87	0.94	0.25
Recovery (%)	49.39	79.47	74.96	112.52	84.08
NRCDORM-3					
Certified value	1.28	15.5	51.3	6.88	0.395
Measured value	1.06	13.4	52.0	8.51	0.119
SD	0.07	0.73	1.67	1.05	0.02
Recovery (%)	83	86	101	124	30

Table 5.2 – Recovery of standard reference materials (n = 6)

5.3.2. Mercury analysis

5.3.2.1. Bulk deposition and lake water

Bulk deposition and lake water were both analysed for Hg at the Norwegian Institute of Air Research (NILU) in Norway using cold vapour atomic fluorescence spectrometry (CV-AFS). Samples were stored at +5°C in the dark for a maximum of 3 months prior to analysis. Stable mercury forms were converted to water soluble species using BrCl, which were then reduced to Hg⁰ by adding SnCl₂. Hg analysis was performed using a Tekran 2600 CV-AFS, which concentrates the Hg⁰ on a gold trap before it is detected in the AFS detector. The detection limits were 0.5 ng Hg L⁻¹. The procedure (NILU-U-60) for sampling of precipitation followed by determination of total mercury using CV-AFS is accredited by Norwegian Accreditation in accordance with ISO IEC-17025.

5.3.2.2. Sediment traps and biota

Concentrations of Hg were determined in sediment, zooplankton, benthic algae, macrophytes and fish using cold vapour atomic fluorescence spectroscopy (CV-AFS). All laboratory equipment used in the preparation of the samples was cleaned prior to installation

by soaking in a 5% Decon 90 solution for 24 hours, followed by multiple rinses with deionised water and a further 24 hour soak in a 2 % HNO₃ solution bath. The equipment was then rinsed extensively with deionised water again and left in a static air drying cabinet.

The digestion method for the sediment was slightly different to that of the biological materials. Total Hg was extracted from the sediment trap samples (as with the sediment core samples, see Section 4.3.3). A number of test digestions were carried out on sediment reference material NCS DC 73374 Stream Sediment. Replicate digestions were made using only nitric acid, and a combination of nitric and hydrochloric acids. The samples were also heated for different lengths of time. The method which gave the greatest recovery was chosen as the most effective extraction technique. Freeze dried sediment samples were disaggregated and homogenised with a pestle and mortar until finely powdered. Approximately 0.2 g of each sample was weighed into Teflon beakers and 8 ml of an *aqua regia* solution (1:3 HNO₃:HCl (Normaton for trace metals:Aristar grade) was added. The beakers were then heated on a hotplate at 100°C for 2-3 hours until the samples reached near dryness. The samples were removed from the hotplate and topped up with deionised water. Then they were left to cool and any undigested material was able to settle out. The digested sediment solutions were decanted directly into sterile polystyrene containers and topped up to 40 ml with deionised water and any remaining undissolved sample was discarded. The same digestion method was applied to a certified reference material of known concentration (Stream sediment NCS DC73374). Sample blanks made from deionised water were also digested in the same way to determine if there was any contamination from the acid.

The acid digestion method for the biological materials follows that described by Yang & Rose (2005), which is the extraction method for the fraction of trace elements that is loosely bound for assessing biological availability (and was the same method used for trace metals in Section 5.3.1). Freeze dried samples were disaggregated and homogenised with a pestle and mortar until finely powdered. Approximately 0.2 g of each sample was weighed into Teflon beakers and 8 ml of concentrated HNO₃ (Normaton for trace metals) was added. The beakers were then heated on a hotplate at 100°C for 1 hour. The samples were removed from the hotplate and topped up with deionised water. Then they were left to cool and any undigested material was able to settle out. The samples were filtered through 2.5 cm GF/C filter papers directly into sterile polystyrene containers. This was done to remove any suspended solids which could block the valve in the Hg analyser. After filtering, the samples were made up to 40 ml with deionised water. Fish samples were diluted a further 10 times to reduce the organic content of the samples which could interfere with the measurements. The same digestion method was applied to certified reference materials of known concentration

(BCR-060 Aquatic plant (*Lagarosiphon major*); BCR-414 Plankton; NRC DORM-3 Fish protein). Sample blanks made from deionised water were also digested in the same way to determine if there was any contamination from the acid and filter blanks were prepared with deionised water to ascertain if there was any contamination from the filter papers.

The samples were analysed using a PS Analytical Millennium Merlin 1631 atomic fluorescence spectrometer. Internally, extracts were first diluted and subjected to a tin (II) chloride reduction, which converted Hg (II) into Hg (0) vapour, before the Hg concentrations were detected. The linear dynamic range of the method is approximately 1 ng L⁻¹ to 100 µg L⁻¹. The instrumental detection limit varies depending on the selected operating conditions and calibration range. Standard solutions were run every five samples to monitor measurement stability. Reference materials, sample blanks and filter blanks were analysed regularly during sample analyses. Hg concentrations in the sample blanks were low, but the Hg concentrations in the sample were adjusted by them to ensure the greatest accuracy was obtained. Concentrations in the filter blanks were also low, but again the concentrations were adjusted. The measured values of each reference material are shown in comparison to the certified values in Table 5.3. Percent recovery was high for sediment (105%), but was much lower for the biological materials. The standard deviations for the latter samples were also high, although this may be partly due to the small sample size (n=5).

	Hg
NCS DC73374	
Certified value	37
Measured value	39
SD	4
Recovery (%)	105
BCR-060	
Certified value	340
Measured value	167
SD	39
Recovery (%)	49
BCR-414	
Certified value	276
Measured value	31
SD	15
Recovery (%)	11
NRC DORM-3	
Certified value	382
Measured value	49
SD	20
Recovery (%)	13

Table 5.3 – Recovery of standard reference materials (n = 5)

5.3.3. Other analyses

5.3.3.1. Major chemistry and suspended solids

All major water chemistry analysis was undertaken by the National Laboratory Service (Environment Agency) in Nottingham. The type and method of analysis and minimum reporting values (MRV) are listed in Table 5.4.

Analyte	Method	MRV	Units
Alkalinity to pH 4.5 as CaCO ₃	Automated colourimetric	5	mg/l
Aluminium	Inductively coupled plasma mass spectrometry	10	ug/l
Aluminium : Active	Colourimetry	4	ug/l
Ammoniacal Nitrogen as N	Automated colourimetric	0.002	mg/l
Calcium	Optical emission spectroscopy	1	mg/l
Carbon, Organic, Dissolved as C :- {DOC}	Automated colourimetric	0.2	mg/l
Chloride	Automated colourimetric	1	mg/l
Chlorophyll, Acetone Extract	Acetone extract / UV spectrophotometry	0.5	ug/l
Conductivity at 20C	Electrometric	10	uS/cm
Magnesium	Optical emission spectroscopy	0.3	mg/l
Nitrate as N	Calculation	0.005	mg/l
Nitrite as N	Automated colourimetric	0.001	mg/l
Nitrogen : Total as N	Automated colourimetric	0.1	mg/l
Nitrogen, Total Oxidised as N	Automated colourimetric	0.005	mg/l
Nitrogen, Kjeldahl as N	Calculation	0	mg/l
Nitrogen, Organic as N	Calculation	0	mg/l
Orthophosphate, reactive as P	Automated colourimetric	0.001	mg/l
pH	Electrometric	0.05	pH Units
Phosphorus : Total as P	Automated colourimetric	0.001	mg/l
Potassium	Optical emission spectroscopy	0.1	mg/l
Sodium	Optical emission spectroscopy	2	mg/l
Sulphate as SO ₄	Optical emission spectroscopy	10	mg/l

Table 5.4 – Type and method of analyses carried out by the National Laboratory Service on lake water samples from the Vale of Health Pond

Suspended solids were analysed by filtering a known volume (usually 500 mL) of lake water through a pre-weighed Whatman GF/C filter. The filter was then dried to constant weight at 40°C and re-weighed. The difference in mass was then used to calculate the mass of suspended solid per litre of lake water.

5.3.3.2. Stable isotope analysis

Stable isotope analysis of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ was carried out at the UC Davis Stable Isotope Facility in California, USA using EA-IRMS using the following method. Sediments were analysed for ^{13}C and ^{15}N isotopes using an Elementar Vario EL Cube or Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Samples were combusted at 1000°C in a reactor packed with copper oxide and lead chromate.

Following combustion, oxides were removed in a reduction reactor (reduced copper at 650°C). The helium carrier then flowed through a water trap (magnesium perchlorate). N₂ and CO₂ were separated using a molecular sieve adsorption trap before entering the IRMS.

During analysis, samples were interspersed with several replicates of at least two different laboratory standards. These laboratory standards, which were selected to be compositionally similar to the samples being analysed, had been previously calibrated against NIST Standard Reference Materials (IAEA-N1, IAEA-N2, IAEA-N3, USGS-40, and USGS-41). A sample's preliminary isotope ratio was measured relative to reference gases analyzed with each sample. These preliminary values were finalised by correcting the values for the entire batch based on the known values of the included laboratory standards. The long term standard deviation was 0.2 ‰ for ¹³C and 0.3 ‰ for ¹⁵N. The final delta values were expressed relative to international standards V-PDB (Vienna PeeDee Belemnite) and Air for carbon and nitrogen, respectively.

5.4. Results

5.4.1. Monthly variability

5.4.1.1. Deposition

Highest monthly concentrations of Ni, Cu, As and Hg were deposited during February (Figure 5.5). The concentration of Ni in February (195 µg L⁻¹) was over 20 times greater than that deposited at any other point in the year. Contamination of samples was considered, however, this interpretation was negated by the fact that Pb and Zn did not show the same pattern (Figure 5.5). In addition, a separate collector was used for Hg and yet high concentrations were also found in February. Therefore there must have been another reason for the high concentrations deposited during that month, which is discussed further in Section 5.5.1.

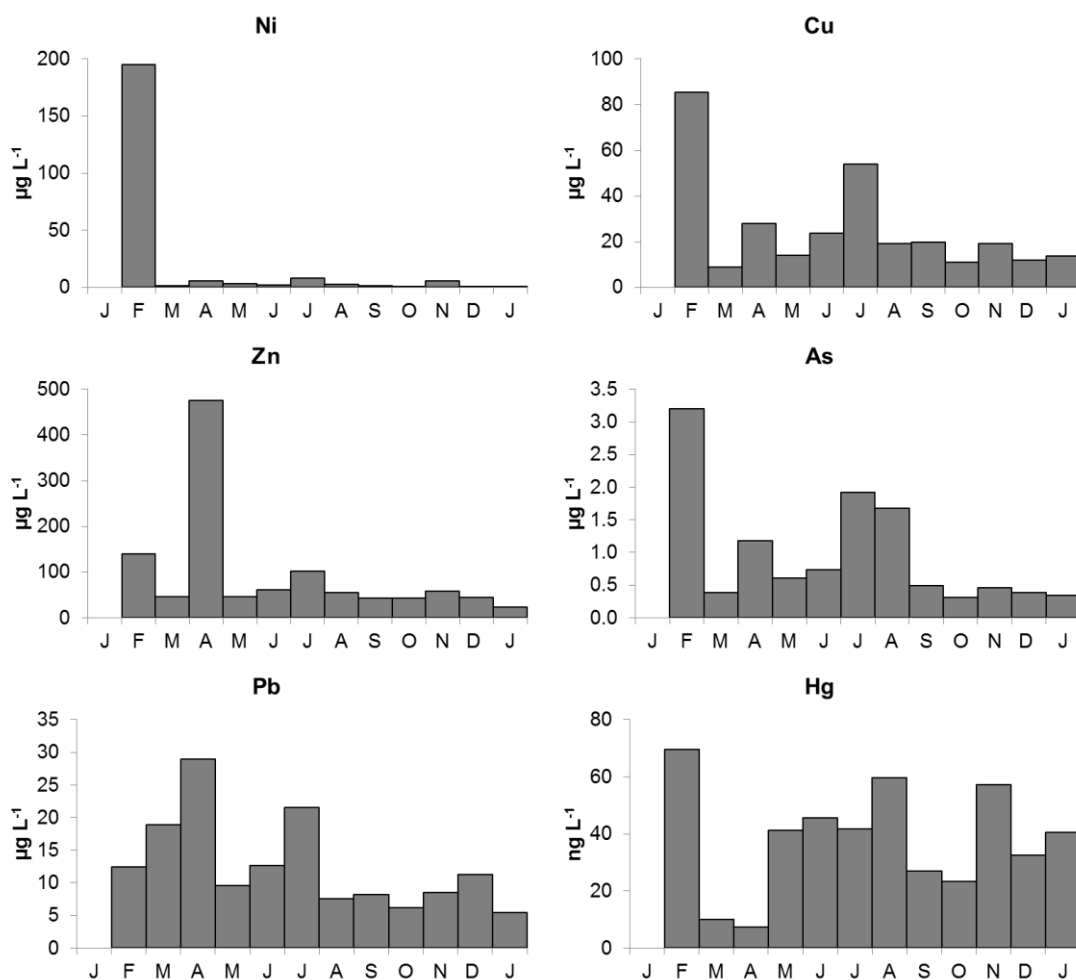


Figure 5.5 – Concentrations of Ni, Cu, Zn, As, Pb and Hg in deposition at the Vale of Health Pond between January 2010 and January 2011

DEPOSITION	Ni	Cu	Zn	As	Pb	Hg
Minimum	0.6485	8.9562	22.562	0.3070	5.4813	7.4500
Maximum	8.1573	53.880	475.31	1.9195	28.918	59.600
Mean	2.8645	20.318	90.636	0.7716	12.625	35.093
Median	2.0173	19.090	46.669	0.4921	9.5753	40.460

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g L}^{-1}$
 Measurements of Hg in ng L^{-1}

Table 5.5 – Summary statistics for metal concentrations in deposition at the Vale of Health Pond, between January 2010 and January 2011

Table 5.5 summarises metal concentrations in deposition at the Vale of Health Pond. With the exception of the high February data, the concentration of Ni ranged between $0.7 \mu\text{g L}^{-1}$ and $8.2 \mu\text{g L}^{-1}$. Inclusion of error on each of the data points showed that there was little change in concentration, apart from during July and November when the concentration increased. Inclusion of error on the Cu and As data showed that there was little change in the concentration of either over the year. The concentration of Cu varied between $9 \mu\text{g L}^{-1}$ and $53.9 \mu\text{g L}^{-1}$, and As between $0.3 \mu\text{g L}^{-1}$ and $1.9 \mu\text{g L}^{-1}$. Zinc concentration showed an

increase in April, reaching 475 $\mu\text{g L}^{-1}$, although the concentration over the rest of the year was fairly consistent, with a median of 51 $\mu\text{g L}^{-1}$. Lead concentration was greater in April than May and June, and higher in July than the following six months. The maximum concentration recorded was 29 $\mu\text{g L}^{-1}$ and the minimum was 5.5 $\mu\text{g L}^{-1}$. The concentration of Hg increased between March and August. There were no other changes over the rest of the year. The concentration ranged between 60 ng L^{-1} and 7.5 ng L^{-1} . Pearson product-moment analysis of log-transformed data found some significant correlations between the metals (Table 5.6). The most positive correlations occurred between Ni, Cu and As, and all were significant at the 0.01 level (2-tailed; $n=12$). The correlation between Zn and Pb was also significant at the 0.01 level (2-tailed; $n=12$). In contrast, no significant correlations were found between Hg and any of the other metals.

Deposition	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.876	1				
Zn	<i>.614</i>	<i>.612</i>	1			
As	.834	.885	<i>.646</i>	1		
Pb	<i>.383</i>	<i>.384</i>	.773	<i>.443</i>	1	
Hg	<i>.325</i>	<i>.371</i>	<i>-.364</i>	<i>.307</i>	<i>-.535</i>	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.6 – Pearson product-moment correlations between the metal concentrations in deposition at the Vale of Health Pond

5.4.1.2. Deposition flux

The rainfall for Hampstead Heath between February 2010 and January 2011 is shown in Figure 5.6. Rainfall data was obtained from the Hampstead weather station (see Section 5.2).

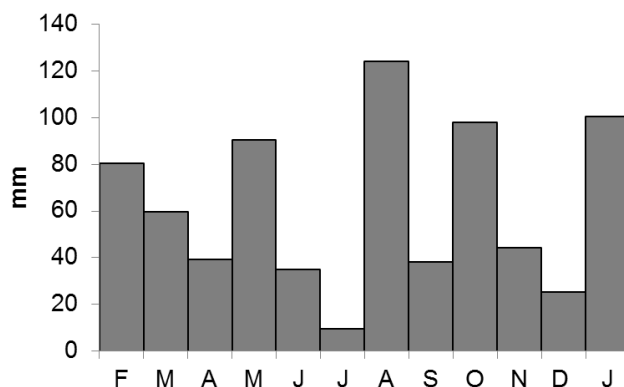


Figure 5.6 – Rainfall at the Vale of Health between February 2010 and January 2011

Deposition flux graphs for each of the metals are shown in Figure 5.7 and summary statistical details are listed in Table 5.7. High rainfall led to increased flux, whilst low rainfall resulted in decreased flux. The effect that variations in rainfall had on metal deposition was particularly noticeable for the months of May, July and August. The highest rainfall recorded for the year was 125 mm in August. Rainfall in May was also high, reaching 90 mm. In contrast only 10 mm of rainfall fell in July. Consequently, for all metals flux was greater relative to concentration in May, much lower in July and then higher again in August. High rainfall also occurred in October and January, which lead to increased flux during those months. The changes in concentration that occurred in July and November for Ni were no longer evident, instead flux declined between May and June and also between August and September. Flux in August of both Cu and As was greater than the adjacent months, and for As for the rest of the year as a whole. The peak in Zn in April was also still much higher than the flux in any of the other months. The changes in Pb concentration were not evident in the flux graphs. However, there was a fall in flux between March and July. As with Cu and As, there was a peak in Hg flux in August.

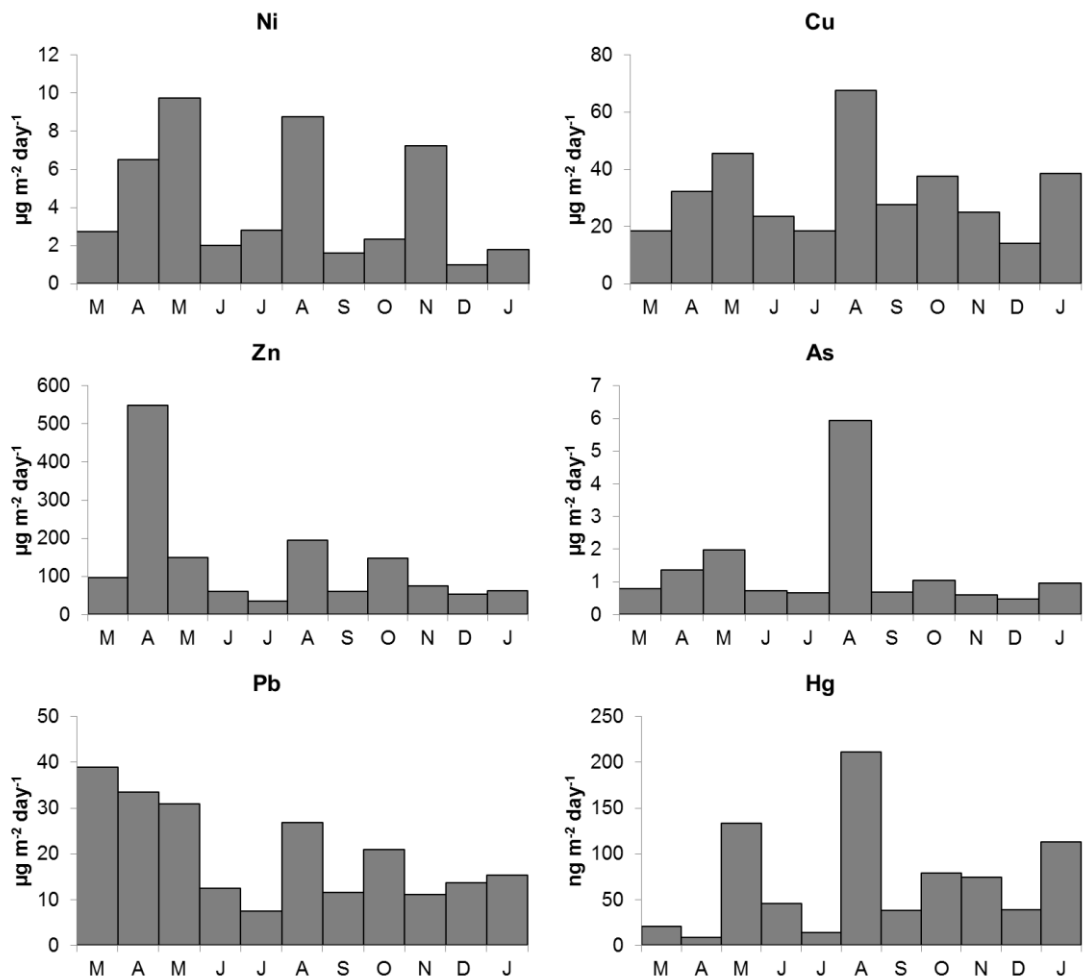


Figure 5.7 – Deposition flux of Ni, Cu, Zn, As, Pb and Hg at the Vale of Health Pond between March 2010 and January 2011, calculated from metal concentrations in deposition and rainfall volume per month

DEPOSITION FLUX	Ni	Cu	Zn	As	Pb	Hg
Minimum	0.9817	14.229	34.770	0.4676	7.3985	8.6113
Maximum	560.55	245.25	549.40	9.1782	38.961	211.15
Mean	50.593	49.549	157.07	2.0308	21.525	81.353
Median	2.7660	30.026	85.410	0.8709	18.120	59.908
Total	17168	17869	58623	746	7851	30320

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g m}^{-2} \text{day}^{-1}$, apart from total flux $\mu\text{g m}^{-2} \text{yr}^{-1}$
Measurements of Hg in $\text{ng m}^{-2} \text{day}^{-1}$, except for total flux $\text{ng m}^{-2} \text{yr}^{-1}$

Table 5.7 – Summary statistics of deposition flux at the Vale of Health Pond, between January 2010 and January 2011

There were more significant Pearson correlations between the metal fluxes than there had been between metal concentrations (Table 5.8). In particular, As became more highly correlated and all Hg correlations became positive, which suggested that rainfall had a strong influence on these elements. In general, the correlations showed that the amount of rain which fell each month was important in determining the rate of metal deposition to the Vale of Health. However, the fact that some metals were still not significantly correlated, as changes in flux occurred at different times for different metals, showed that rainfall was not the only driver of flux. The concentration of each metal (and therefore the source) was also important.

Deposition flux	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.891	1				
Zn	.676	<i>.684</i>	1			
As	.835	.929	.734	1		
Pb	.514	.529	.821	.643	1	
Hg	.459	.675	.167	.611	.213	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.8 – Pearson product-moment correlations between the metal fluxes of deposition at the Vale of Health Pond

5.4.1.3. Lake water

The monthly concentration data for each of the metals are shown in Figure 5.8 and summary statistical data in Table 5.9. The Ni concentration of water at the Vale of Health was greatest in January and February, at approximately $3 \mu\text{g L}^{-1}$. The concentration declined from March, with no changes occurring over the rest of the year. The concentration ranged from 2.0 to $2.3 \mu\text{g L}^{-1}$ between April to January 2011. The highest concentration of Cu occurred in June, peaking at over $10 \mu\text{g L}^{-1}$. There were no other changes over the course of the year. The Zn profile was dominated by a large peak of over $50 \mu\text{g L}^{-1}$ which occurred in September. Throughout the rest of the year the concentration fluctuated from month to month, but did

not change unduly. The concentration of As was higher in the summer months (June, July, August) than in the winter months (November, December, January). The highest concentration was $2.4 \mu\text{g L}^{-1}$ which occurred in July, whilst the lowest was $1.0 \mu\text{g L}^{-1}$, found in January 2011. There was no change in the concentration of Pb over the course of the year. The concentration ranged between 2.3 and $5.7 \mu\text{g L}^{-1}$, with a median of $4.6 \mu\text{g L}^{-1}$. The concentration of Hg did not change between January and August. Between September and November the concentration increased and peaked at 25.6 ng L^{-1} , before falling to 7.5 ng L^{-1} by January 2011. The Pearson product-moment correlations that were calculated for the water data only produced one significant relationship (Table 5.10). This was between Ni and Hg at the 0.05 level (2-tailed; $n=12$) and was negative.

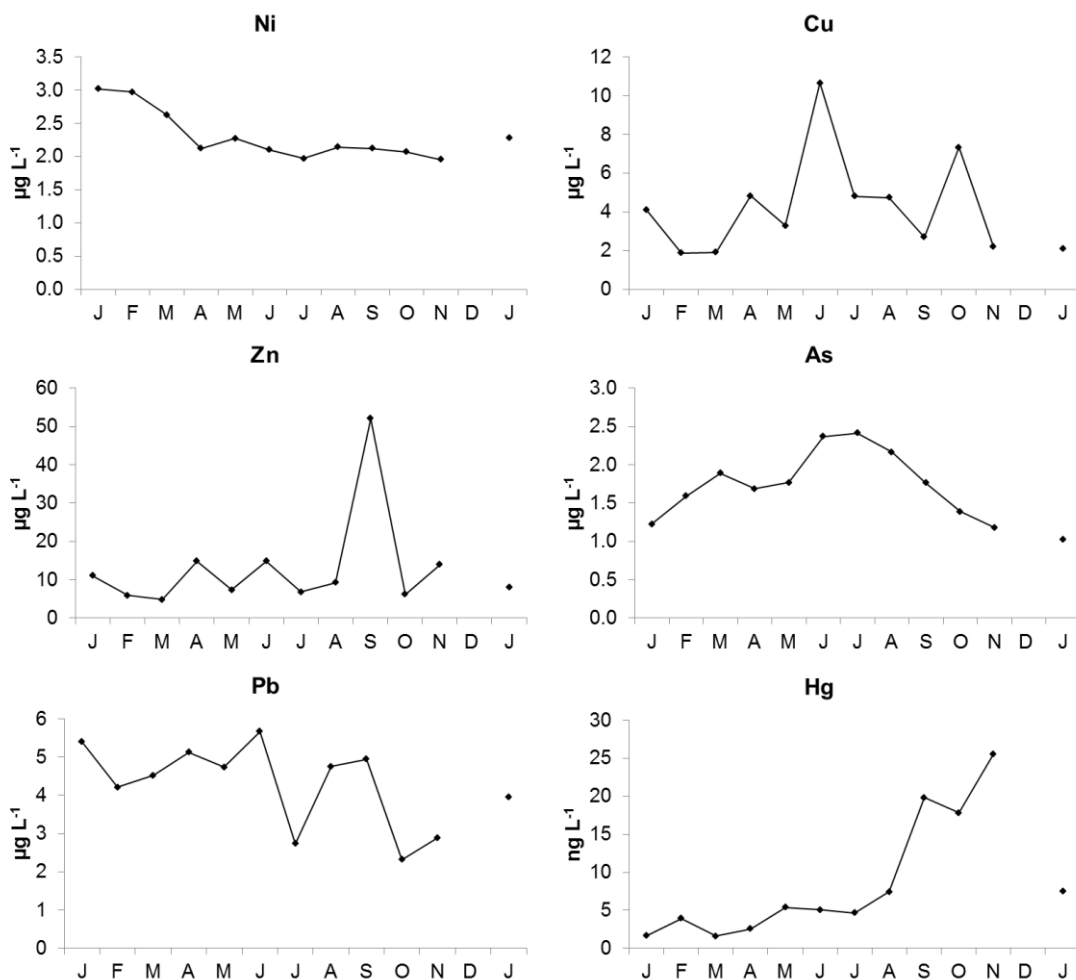


Figure 5.8 – Ni, Cu, Zn, As, Pb and Hg concentrations in water at the Vale of Health Pond between January 2010 and January 2011

WATER	Ni	Cu	Zn	As	Pb	Hg
Minimum	1.9531	1.8646	4.8065	1.0289	2.3175	1.62
Maximum	3.0220	10.666	52.053	2.4121	5.6721	25.59
Mean	2.3049	4.2090	12.926	1.7054	4.2735	8.59
Median	2.1324	3.6966	8.6158	1.7245	4.6301	5.22

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g L}^{-1}$
Measurements of Hg in ng L^{-1}

Table 5.9 – Summary statistics for metal concentrations in water at the Vale of Health Pond, between January 2010 and January 2011

Water	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	-.404	1				
Zn	-.322	.101	1			
As	-.251	.449	.021	1		
Pb	.420	.010	.359	.220	1	
Hg	-.651	.016	.411	-.220	-.525	1

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.10 – Pearson product-moment correlations between the metal concentrations in water at the Vale of Health Pond

5.4.1.4. Sediment traps

Concentrations of Ni, Cu, Zn and Pb over the year were fairly similar to one another (Figure 5.9). For Ni, the concentration ranged between 33 and 47 $\mu\text{g g}^{-1}$ during this period, for Cu 74 to 98 $\mu\text{g g}^{-1}$, for Zn 313 to 409 $\mu\text{g g}^{-1}$ and for Pb 316 to 460 $\mu\text{g g}^{-1}$ (see Table 5.11 for summary statistical data). The concentration of As averaged at 33 $\mu\text{g g}^{-1}$ over the year. The concentration decreased in March to 20 $\mu\text{g g}^{-1}$, but the error associated with each value showed that there were no other changes in concentration between January and October. The mean concentration of Hg between January 2010 and January 2011 was 505 ng g^{-1} . There was one fall between May and June when the concentration decreased from 590 to 430 ng g^{-1} .

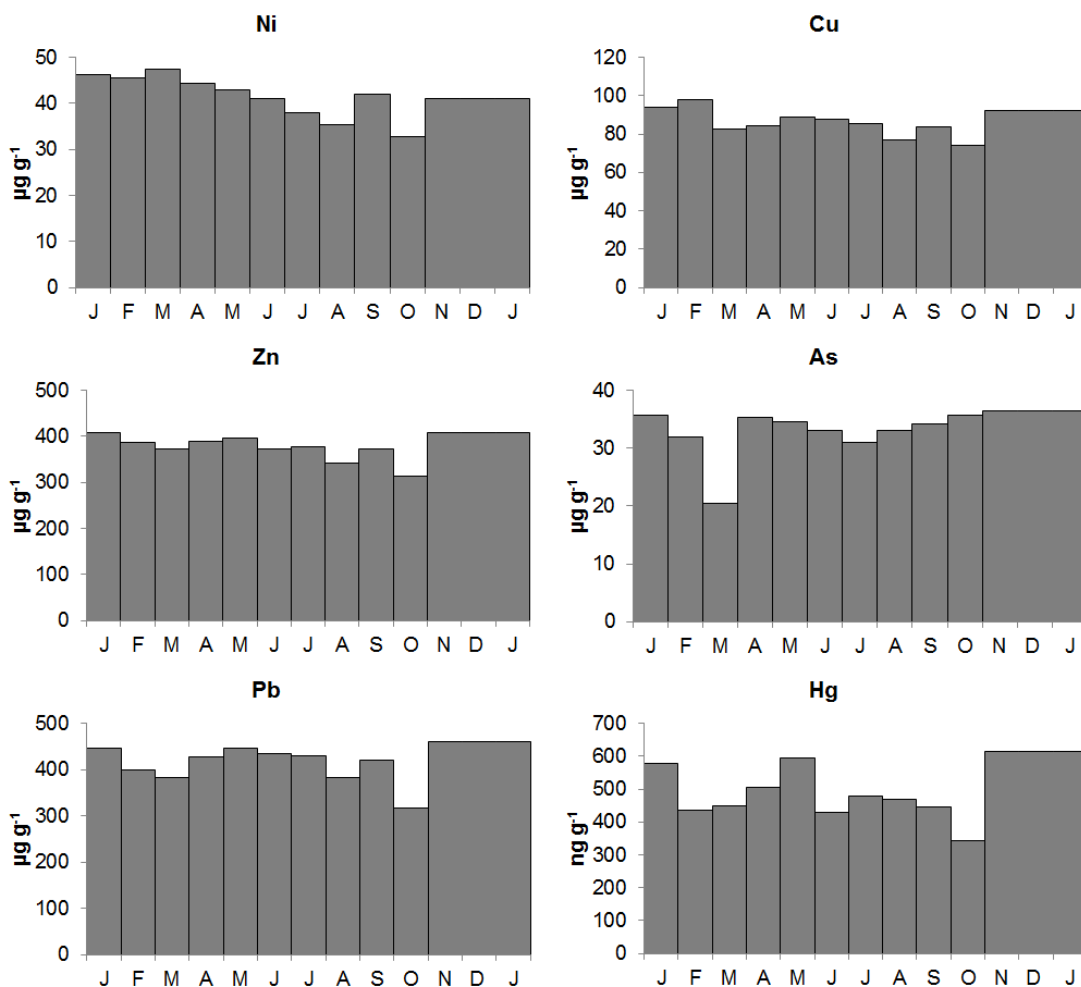


Figure 5.9 – Concentrations of Ni, Cu, Zn, As, Pb and Hg in sediment traps at the Vale of Health Pond between January 2010 and January 2011. November, December and January 2011 are grouped together as the lake was ice covered during those months which prevented the sediment from being collected monthly. The concentration was calculated from the total sediment collected from the trap in January 2011.

SEDIMENT TRAP	Ni	Cu	Zn	As	Pb	Hg
Minimum	32.750	74.150	312.55	20.467	315.80	344.01
Maximum	47.400	97.733	408.60	36.450	459.90	613.28
Mean	41.424	87.172	381.16	33.403	420.26	505.43
Median	41.033	87.800	387.97	34.567	429.00	477.83

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g g}^{-1}$
 Measurements of Hg in ng g^{-1}

Table 5.11 – Summary statistics for metal concentrations in sediment traps at the Vale of Health Pond, between January 2010 and January 2011

The results of the Pearson product-moment correlations that were calculated for the data are shown in Table 5.12. The most positive correlations were found between Ni, Cu, Zn, Pb and Hg, although not all were found to be significant. Arsenic correlated poorly with all of the other metals which emphasised the difference in profile pattern.

Sediment trap	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.724	1				
Zn	.801	.876	1			
As	-.365	.122	.055	1		
Pb	.573	.721	.908	.208	1	
Hg	.483	.590	.834	.207	.839	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.12 – Pearson product-moment correlations between the metal concentrations in sediment at the Vale of Health Pond

5.4.1.5. Sediment trap flux

Sediment accumulation rate (SAR) at the Vale of Health between January 2010 and January 2011 is shown in Figure 5.10. The accumulation rate increased between February and August, and then declined. Sediment accumulation rate was much lower throughout the months of November, December, and January 2011. This was due to the fact that the Vale of Health Pond was covered in ice during that period which provided a barrier to sediment accumulation.

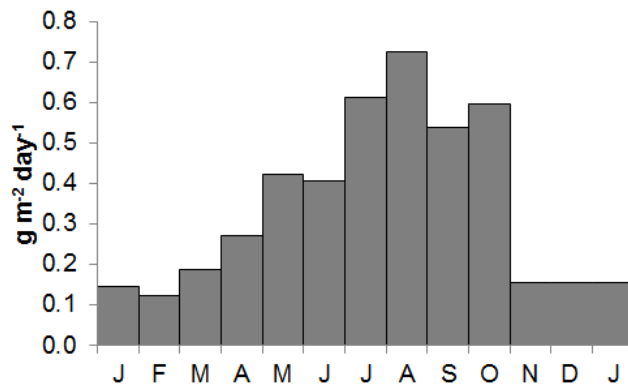


Figure 5.10 – Sediment accumulation rate at the Vale of Health between January 2010 and January 2011. November, December and January 2011 are grouped together as the lake was ice covered during those months, and SAR was calculated as an average over the three months from the total sediment collected from the trap in January 2011.

Sediment metal flux was calculated to take into account the varying sediment deposition throughout the year. The rate of flux for all metals increased between February and August, and then declined over the latter half of the year (Figure 5.11). Metal flux was also much lower throughout the months of November, December, and January 2011. The similarity of the metal flux profiles to SAR, and the contrast with concentration, showed that sediment

accumulation rate in the lake was the driver of metal flux. The same conclusion was drawn from the sediment core data in Chapter 4. The metal fluxes appeared to show a seasonal pattern, with metal flux being much greater during the summer months than in the winter. However, it was not possible to confirm a seasonal pattern due to the relatively short period over which the data was collected. Minimum and maximum fluxes are recorded in Table 5.13.

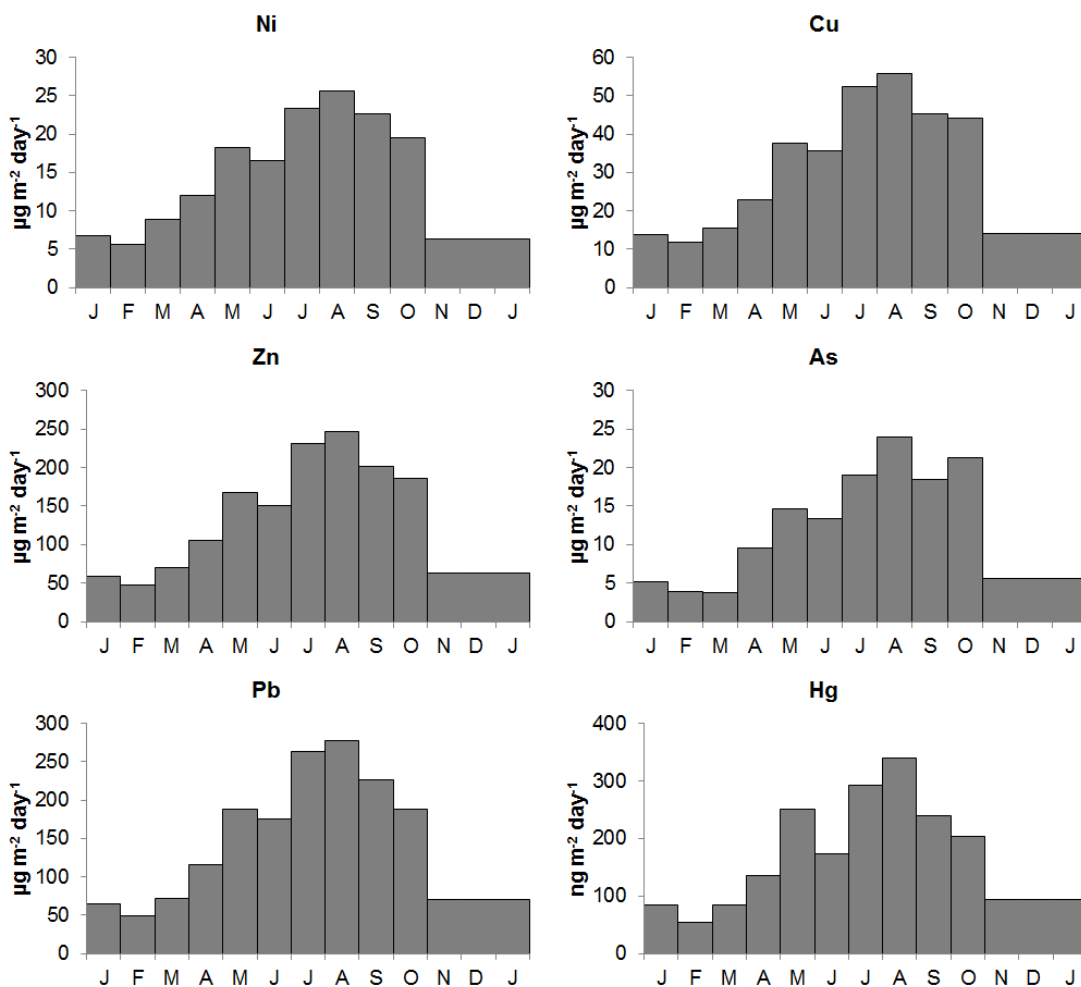


Figure 5.11 – Sediment flux of Ni, Cu, Zn, As, Pb and Hg at the Vale of Health Pond between January 2010 and January 2011, calculated from metal concentrations in sediment trap material and sediment accumulation rate per month

SEDIMENT FLUX	Ni	Cu	Zn	As	Pb	Hg
Minimum	5.5676	11.942	47.404	3.8289	48.720	53.357
Maximum	25.688	55.725	246.99	23.913	277.75	339.76
Mean	13.681	28.992	127.17	11.526	140.90	164.85
Median	11.975	22.852	105.18	9.5264	115.64	136.43
Total	5586	11826	51862	4704	57499	67482

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g m}^{-2} \text{day}^{-1}$, apart from total flux $\mu\text{g m}^{-2} \text{yr}^{-1}$
 Measurements of Hg in $\text{ng m}^{-2} \text{day}^{-1}$, except for total flux $\text{ng m}^{-2} \text{yr}^{-1}$

Table 5.13 – Summary statistics for sediment flux at the Vale of Health Pond, between January 2010 and January 2011

The Pearson product-moment correlations between metal fluxes also differed to those of concentration, as would be expected (Table 5.14). Positive correlations were observed between all of the metals, and all were significant at the 0.01 level (2-tailed; n=11). All correlations had r values of over 0.9, which reflected the great similarity between the different metal fluxes and the role of SAR in driving the metal flux data.

Sediment flux	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.991	1				
Zn	.994	.998	1			
As	.955	.978	.974	1		
Pb	.989	.994	.998	.972	1	
Hg	.968	.974	.983	.959	.988	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Table 5.14 – Pearson product-moment correlations between the metal fluxes of sediment at the Vale of Health Pond

5.4.1.6. Zooplankton

The metal concentrations of zooplankton sampled over the year are shown in Figure 5.12 and statistical data for each metal are shown in Table 5.15. Nickel concentration showed an increase in June, peaking at $3.8 \mu\text{g g}^{-1}$. For the rest of the year, the concentration ranged between 0.25 and $2.24 \mu\text{g g}^{-1}$. Lead concentration showed the same pattern, increasing in June to $60 \mu\text{g g}^{-1}$, and ranging from 4.9 to $34.5 \mu\text{g g}^{-1}$ over the rest of the year. There were no changes in the concentration of Cu over the whole year. The concentration ranged between 1.2 and $13.4 \mu\text{g g}^{-1}$, with a median value of $9.3 \mu\text{g g}^{-1}$. The concentration of Zn increased between May and June to a maximum of $119 \mu\text{g g}^{-1}$. The concentration then declined through July and August, after which no more changes occurred. Arsenic concentration in August was greater than that which was observed in March ($7.2 \mu\text{g g}^{-1}$ in comparison to $3.9 \mu\text{g g}^{-1}$). The concentration was lower again by October. All of the monthly concentrations apart from August were within the margin of error of one other and had a median value of $4.4 \mu\text{g g}^{-1}$. The concentration of Hg in March was 207ng g^{-1} , which was over four times greater than any other concentration recorded during the year. There were no changes in concentration between April and January 2011. The median value of Hg concentration was 9.8ng g^{-1} .

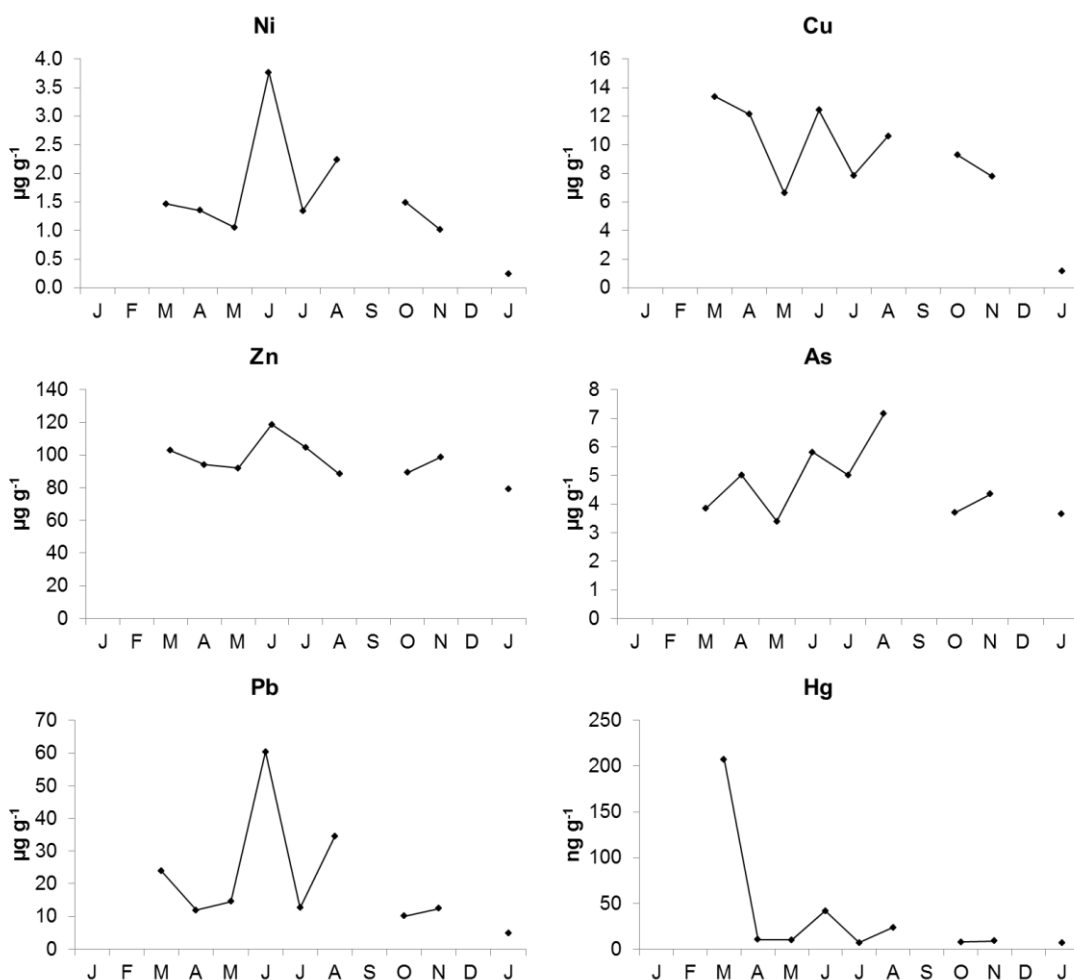


Figure 5.12 – Ni, Cu, Zn, As, Pb and Hg concentrations in zooplankton at the Vale of Health Pond between January 2010 and January 2011. Gaps indicate months when no samples were taken (see Section 5.2.5).

ZOOPLANKTON	Ni	Cu	Zn	As	Pb	Hg
Minimum	0.2457	1.1750	79.104	3.3910	4.8945	6.86
Maximum	3.7661	13.356	118.63	7.1597	60.371	207.20
Mean	1.5534	9.0194	96.360	4.6584	20.573	35.87
Median	1.3538	9.2628	94.041	4.3518	12.640	9.76

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g g}^{-1}$
 Measurements of Hg in ng g^{-1}

Table 5.15 – Summary statistics for metal concentrations in zooplankton at the Vale of Health Pond, between January 2010 and January 2011

The results of the Pearson product-moment correlations are shown in Table 5.16. Significant correlations were found between Ni and Cu, and Ni and Pb at the 0.01 level (2-tailed; $n=9$), and Ni and Zn, Cu and Pb and Zn and Pb at the 0.05 level (2-tailed; $n=9$) (Table 5.16). However, no significant correlations were found between As and Hg and any of the other metals.

Zooplankton	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.902	1				
Zn	<i>.731</i>	<i>.662</i>	1			
As	<i>.621</i>	<i>.434</i>	<i>.338</i>	1		
Pb	.886	<i>.710</i>	<i>.710</i>	<i>.652</i>	1	
Hg	<i>.455</i>	<i>.486</i>	<i>.473</i>	<i>.165</i>	<i>.666</i>	1

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.16 – Pearson product-moment correlations between the metal concentrations in zooplankton at the Vale of Health Pond

5.4.1.7. Benthic algae

The graphs of metal concentration in benthic algae are shown in Figure 5.13 and statistical data are listed in Table 5.17. The concentration of Ni between spring and autumn did not change, ranging between 6.1 and 7.0 $\mu\text{g g}^{-1}$. However, the concentration over winter, 8.9 $\mu\text{g g}^{-1}$, was higher. The concentration of Cu increased from 9.8 $\mu\text{g g}^{-1}$ in summer to 15.9 $\mu\text{g g}^{-1}$ in winter. The pattern was the same for Pb, with the concentration increasing from 13.8 to 57.4 $\mu\text{g g}^{-1}$. Although the concentration of Zn appeared to be much higher during the winter months than during the summer, taking into account the error associated with each value meant that there was actually no change over the course of the year, with the concentration averaging at 126 $\mu\text{g g}^{-1}$. The concentration of As increased over the course of the year, from 3.9 $\mu\text{g g}^{-1}$ in spring to 12 $\mu\text{g g}^{-1}$ in autumn and winter. The Hg concentration was approximately 14 ng g^{-1} in spring and summer, but then increased over the latter half of the year to 54 ng g^{-1} in winter. The Pearson product-moment correlations for the benthic algae data only produced one significant relationship (Table 5.18). This was between Cu and Pb at the 0.05 level (2-tailed; n=4).

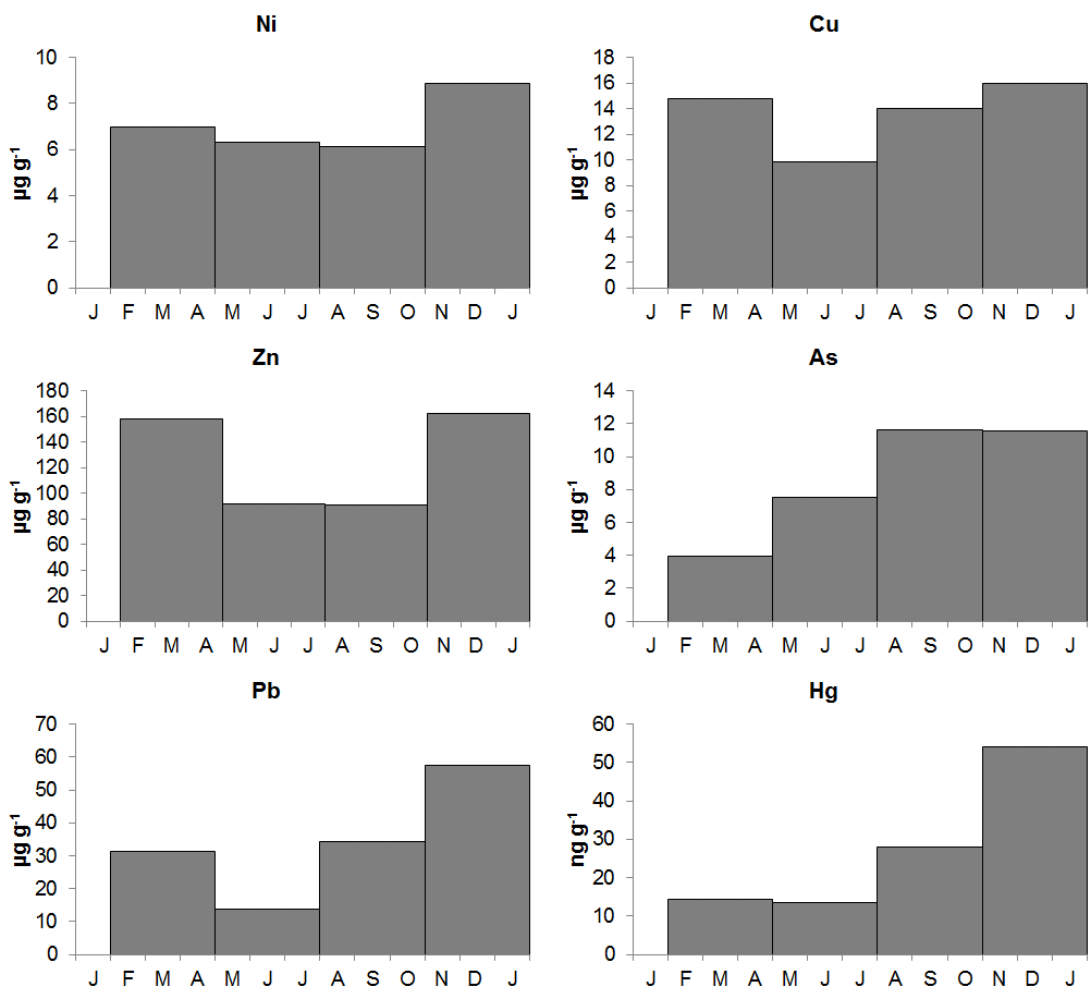


Figure 5.13 – Ni, Cu, Zn, As, Pb and Hg concentrations in benthic algae at the Vale of Health Pond between January 2010 and January 2011. Four samples of algae were obtained, in April, July, October, and January 2011. Each bar represents the quarterly period that each of the four samples covered (classed as spring, summer, autumn and winter). The total concentration determined in each of the four samples is reflected in the height of the bar for each quarter.

BENTHIC ALGAE	Ni	Cu	Zn	As	Pb	Hg
Minimum	6.1192	9.8460	90.703	3.9256	13.774	13.64
Maximum	8.8637	15.941	162.53	11.651	57.354	54.19
Mean	7.0723	13.630	125.65	8.6571	34.132	27.60
Median	6.6532	14.367	124.69	9.5259	32.699	21.29

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g g}^{-1}$
 Measurements of Hg in ng g^{-1}

Table 5.17 – Summary statistics for metal concentrations in benthic algae at the Vale of Health Pond, between January 2010 and January 2011

Benthic algae	Ni	Cu	Zn	As	Pb	Hg
Ni	1					
Cu	.626	1				
Zn	.837	.720	1			
As	.164	.094	-.345	1		
Pb	.728	.960	.661	.338	1	
Hg	.704	.662	.344	.755	.845	1

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.18 – Pearson product-moment correlations between the metal concentrations in benthic algae at the Vale of Health Pond

5.4.1.8. Relationships between deposition, lake water and sediment traps

Pearson product-moment correlations were calculated to investigate the relationship between metal concentrations in deposition, lake water and sediment trap material (Table 5.19). Only one significant relationship was identified, which was between Ni in water and sediment ($P < 0.05$, 2-tailed, $n = 11$).

	Ni dep	Ni sed	Ni wat		Cu dep	Cu sed	Cu wat		Zn dep	Zn sed	Zn wat
Ni dep	1			Cu dep	1			Zn dep	1		
Ni sed	.371	1		Cu sed	.527	1		Zn sed	.155	1	
Ni wat	.493	.678	1	Cu wat	-.011	-.440	1	Zn wat	.050	.112	1
	As dep	As sed	As wat		Pb dep	Pb sed	Pb wat		Hg dep	Hg sed	Hg wat
As dep	1			Pb dep	1			Hg dep	1		
As sed	.072	1		Pb sed	.220	1		Hg sed	.081	1	
As wat	.507	-.367	1	Pb wat	.230	.588	1	Hg wat	.443	-.405	1

Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.19 – Pearson product-moment correlations between deposition, water and sediment metal concentrations at the Vale of Health Pond

Pearson correlations were also carried out between the deposition flux and sediment flux data (Table 5.20). No significant correlations were found. The difference between flux patterns was clearly seen when the two were plotted together on the same axes (Figure 5.14). The graphs also show that Pb sediment flux was particularly high and consistently greater than deposition flux over the course of the year. The same was the case for Ni, As, and Hg (apart from in November, December and January 2011 when Hg deposition flux was higher). Zinc deposition flux was greater than sediment flux in March and April, and November, December and January 2011, but less than sediment flux for the remainder of the year. The levels of deposition and sediment flux were much closer for Cu, and the former exceeded the latter for the majority of months over the course of the year, between March and May, and again in August, November, December and January 2011.

	Ni dep	Ni sed		Cu dep	Cu sed		Zn dep	Zn sed
Ni dep	1		Cu dep	1		Zn dep	1	
Ni sed	-0.462	1	Cu sed	-0.358	1	Zn sed	-0.340	1
	As dep	As sed		Pb dep	Pb sed		Hg dep	Hg sed
As dep	1		Pb dep	1		Hg dep	1	
As sed	-0.165	1	Pb sed	-0.518	1	Hg sed	-0.057	1

Table 5.20 – Pearson product-moment correlations between deposition flux and sediment flux at the Vale of Health Pond

These results showed that from month to month, the concentration and flux of metals in deposition, water and sediment were not related. The processes by which metals move through the lake system (see Chapter 1) are complex and mean that relationships between abiotic matrices are not straightforward. There was also no evidence of seasonal patterns within the data. However, finding the latter was unlikely due to the short timescale that the dataset covered.

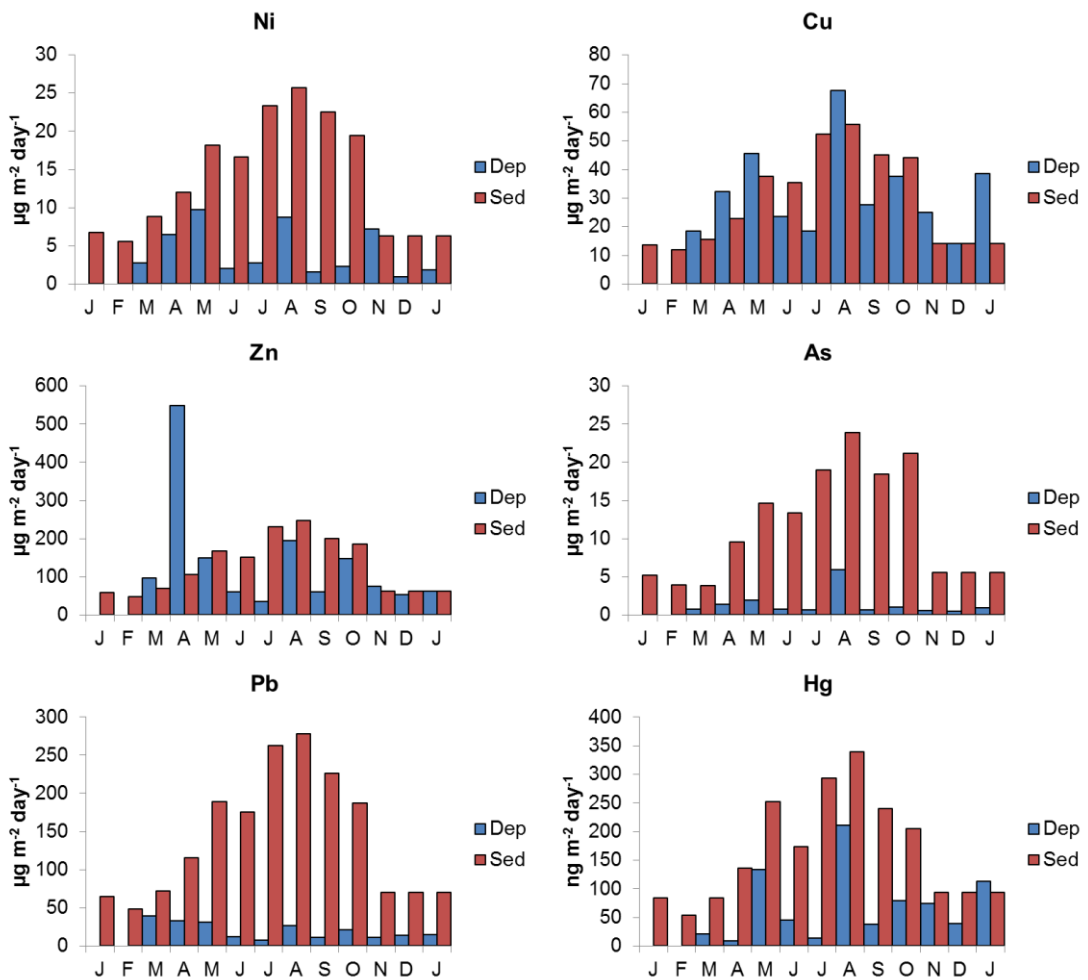


Figure 5.14 – Comparison of Ni, Cu, Zn, As, Pb and Hg deposition and sediment fluxes at the Vale of Health Pond between January 2010 and January 2011

5.4.2. Annual patterns

Exploring the annual concentrations of metals within parts of the lake system enabled the inclusion of data from macrophytes and fish, in addition to the other parameters recorded. Table 5.21 shows the annual (January 2010 to January 2011) concentrations (mean and median) of metals in both macrophyte and fish samples, as well as the range of values encountered.

	Ni	Cu	Zn	As	Pb	Hg
MACROPHYTES				BDL		
Minimum	0.4461	1.2250	24.285		0.8994	2.34
Maximum	0.6003	2.1938	31.747		1.6180	4.93
Mean	0.5340	1.8184	28.230		1.2634	3.65
Median	0.5449	1.9274	28.444		1.2681	3.67
FISH (1 YEAR)	BDL					
		0.9170	25.598	0.1428	0.0254	8.76
FISH (2 YEARS)						
Minimum	0.0000	0.6869	19.897	0.0580	0.0000	5.08
Maximum	0.1379	1.2852	36.517	0.2400	0.0848	30.32
Mean	0.0260	1.0612	28.130	0.1385	0.0237	14.35
Median	0.0015	1.0764	26.830	0.1225	0.0125	11.47
FISH (3 YEARS)						
	0.3033	2.2932	23.952	0.0432	0.4244	13.49
FISH LIVER	BDL					
		6.0703	90.049	0.7102	0.3411	23.97
FISH GILL						No sample
	0.1895	1.9718	77.863	0.1762	1.3721	

All measurements of Ni, Cu, Zn, As and Pb in $\mu\text{g g}^{-1}$

Measurements of Hg in ng g^{-1}

BDL = below detection limit

Fish (1 year), Fish (3 years), Fish liver and Fish gill contained only 1 sample each

Table 5.21 – Summary statistics for metal concentrations in macrophytes and fish from the Vale of Health Pond, between January 2010 and January 2011

Comparing the annual data for deposition, water, sediment, zooplankton and benthic algae over the year as a whole using box and whisker diagrams (Figure 5.15) clearly showed that the highest concentration of metals were found in the sediment. The large range on the deposition boxplots for Ni, Cu and Zn represent the much higher values found in some of the deposition samples.

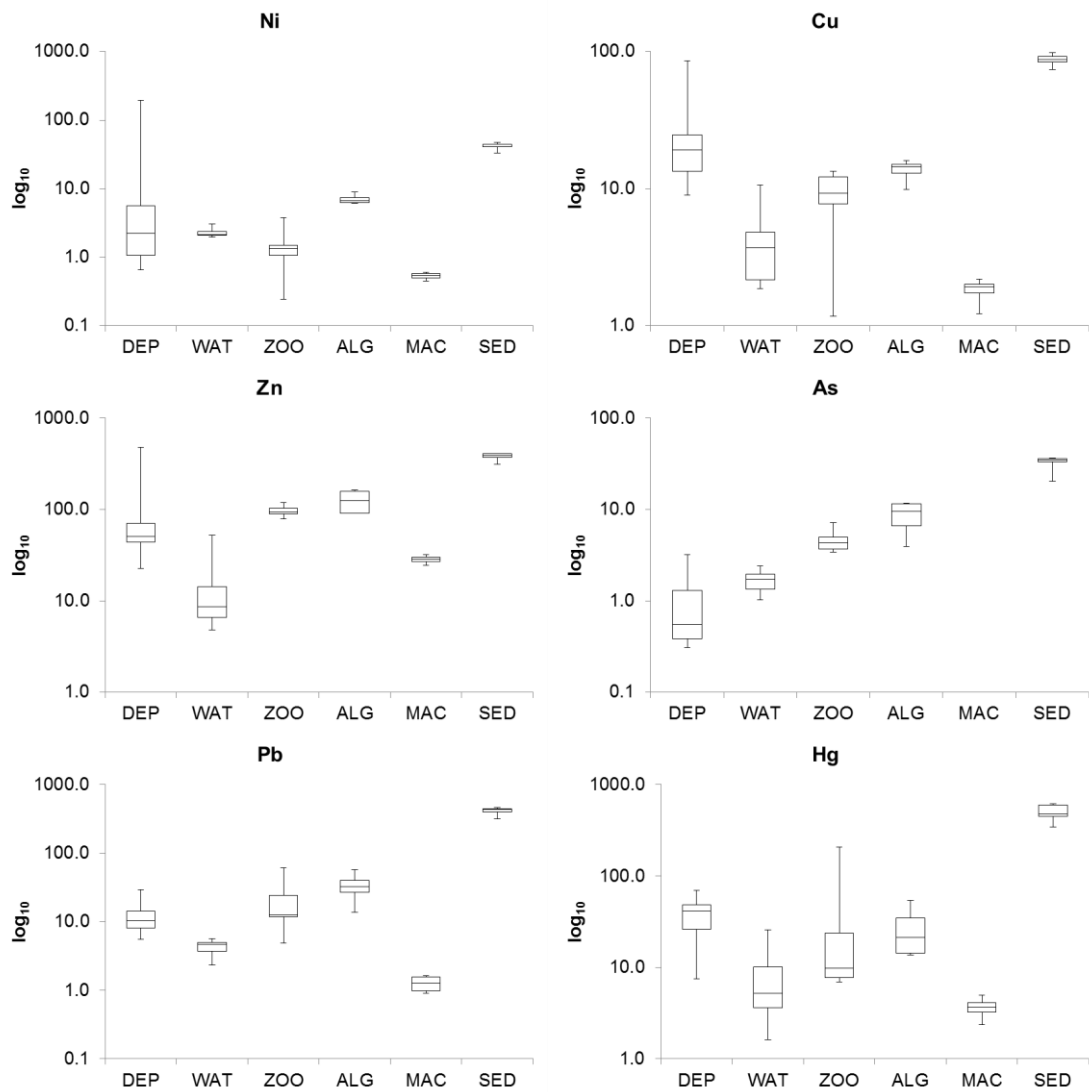


Figure 5.15 – Box and whisker plots showing the median, 1st and 3rd quartiles and range of the metal concentration data from deposition (DEP), water (WAT), zooplankton (ZOO), benthic algae (ALG), macrophytes (MAC) and sediment traps (SED) at the Vale of Health Pond. Values have been converted to a logarithmic scale in order to make them comparable.

After sediment, the highest concentrations of Ni, Cu, Zn, As, Pb and Hg were found in benthic algae, followed by zooplankton (Figures 5.16 and 5.17), although fish liver contained a higher concentration of Hg than benthic algae.

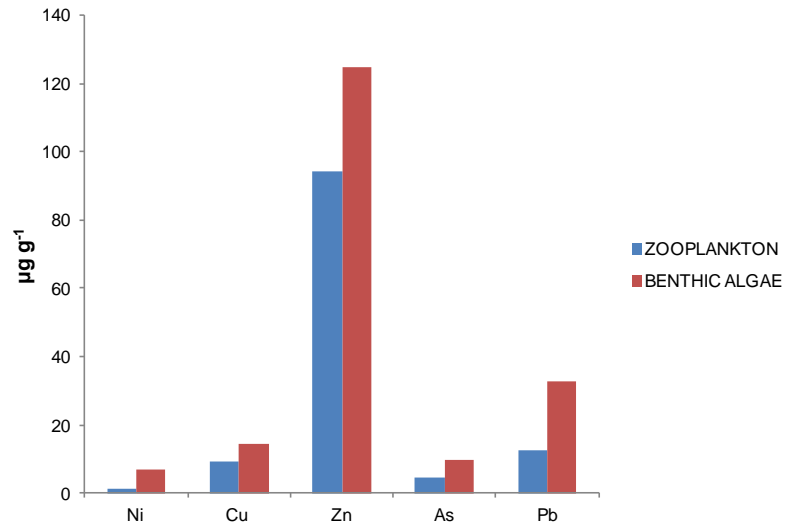


Figure 5.16 – Median annual concentrations of Ni, Cu, Zn, As and Pb present in zooplankton and benthic algae

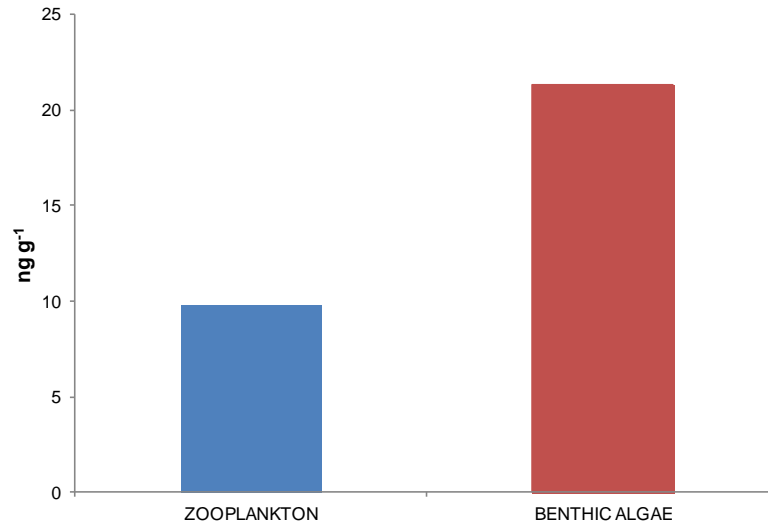


Figure 5.17 – Median annual concentrations of Hg present in zooplankton and benthic algae

The lowest concentrations were found in the water and deposition samples. For all of the metals, the concentrations were lower in water than in deposition, apart from As for which the concentration of deposition was the lowest. This is shown for Ni, Cu, Zn, As and Pb in Figure 5.18 and for Hg in Figure 5.19.

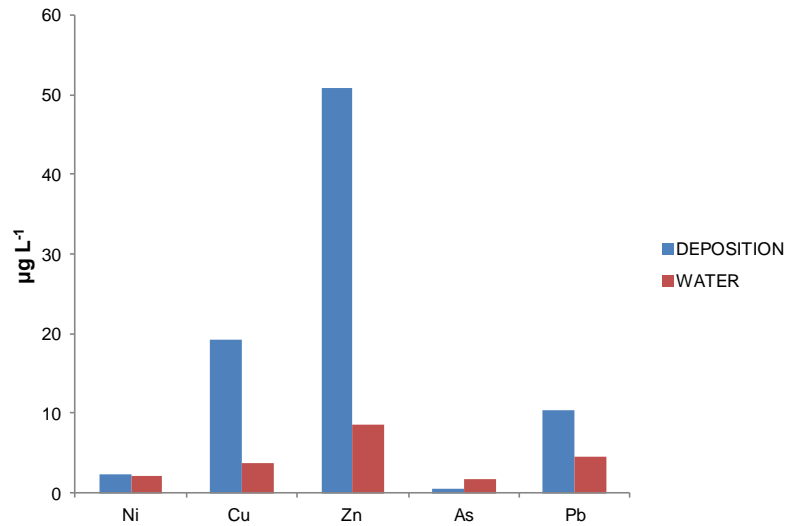


Figure 5.18 – Median annual concentrations of Ni, Cu, Zn, As and Pb present in deposition and water

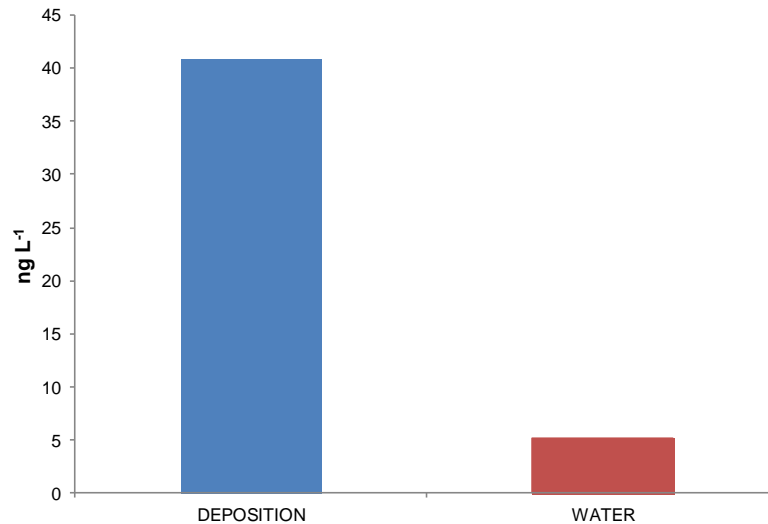


Figure 5.19 – Median annual concentrations of Hg present in deposition and water

The concentrations found in the fish and macrophytes varied between each metal (Figure 5.20). For Ni, the macrophytes contained higher concentrations than the fish. Concentrations in the different categories of fish followed in the order muscle tissue (aged 3 years) > fish gill > muscle tissue (aged 2 years). The concentration of Ni was below the limit of detection in muscle tissue (aged 1 year) and fish liver. The concentration of Cu was highest in fish liver, followed by muscle tissue (aged 3 years), fish gill, macrophytes, muscle tissue (aged 2 years) and muscle tissue (aged 1 year). The concentration of Zn was highest in fish liver, followed by fish gill, macrophytes, muscle tissue (aged 2 years), muscle tissue (aged 1 year) and muscle tissue (aged 3 years). The concentration of As was highest in fish liver, followed by fish gill, muscle tissue (aged 1 year), muscle tissue (aged 2 years) and muscle tissue

(aged 3 years). The concentration of As was below the limit of detection for the macrophyte samples. The concentration of Pb was highest in the fish gill sample, followed by macrophytes. These were followed by muscle tissue (aged 3 years), fish liver, muscle tissue (aged 1 year) and muscle tissue (aged 2 years). The concentration of Hg was highest in fish liver (Figure 5.21). This was followed by muscle tissue (aged 3 years), muscle tissue (aged 2 years), muscle tissue (aged 1 year) and macrophytes.

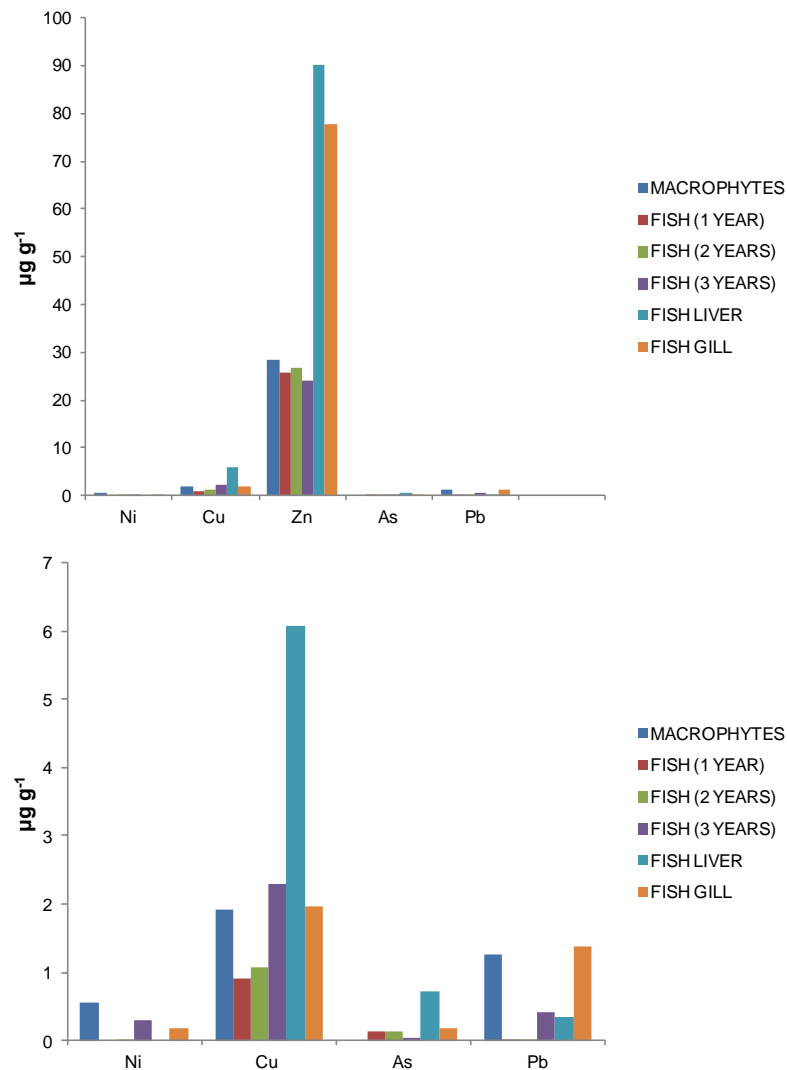


Figure 5.20 – Top graph: Median annual concentrations of Ni, Cu, Zn, As and Pb present in macrophytes and fish. The graph highlights the much higher concentrations of Zn. Bottom graph: Zinc has been removed to show median annual concentrations of Ni, Cu, As and Pb more clearly.

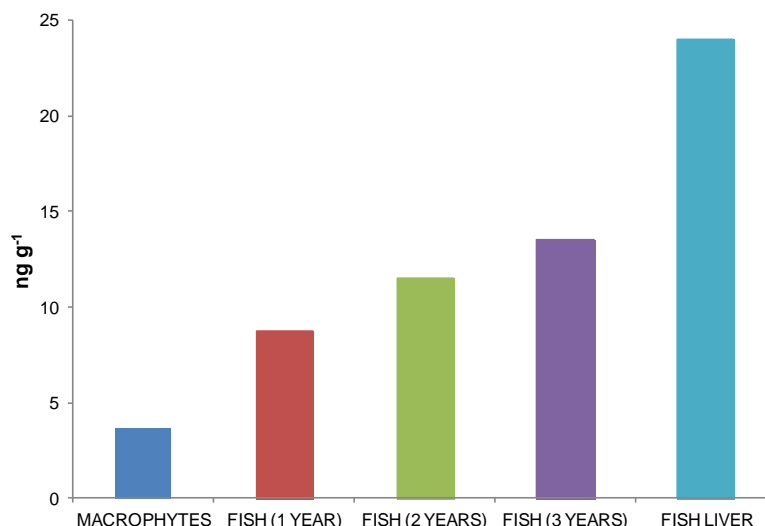


Figure 5.21 – Median annual concentration of Hg in macrophytes and fish

For each parameter therefore, metal concentration followed the order:

Water Zn > Pb > Cu > Ni > As

Sediment Pb > Zn > Cu > Ni > As

Zooplankton and benthic algae Zn > Pb > Cu > As > Ni

Deposition, macrophytes, fish (3 years) and fish gill Zn > Cu > Pb > Ni > As

Fish (1 year), fish (2 years) and fish liver Zn > Cu > As > Pb > Ni

Mercury was not included because concentration is always an order of magnitude lower – ng c.f. µg.

In addition to assessing the relationship between the sediments and the other components of the ecosystem, the sediment concentrations and fluxes from 2010 (January to December mean) were also compared to the data from the Vale of Health sediment core. Figure 5.22 shows the mean concentrations of metals for 2010 in comparison with the concentrations found in the cores since 2000. In all cases excluding As, the 2010 concentrations were considerably lower than those found in previous years. Although the concentration of As was lower in 2010 than in 2009, it was still within the range of values found since 2000.

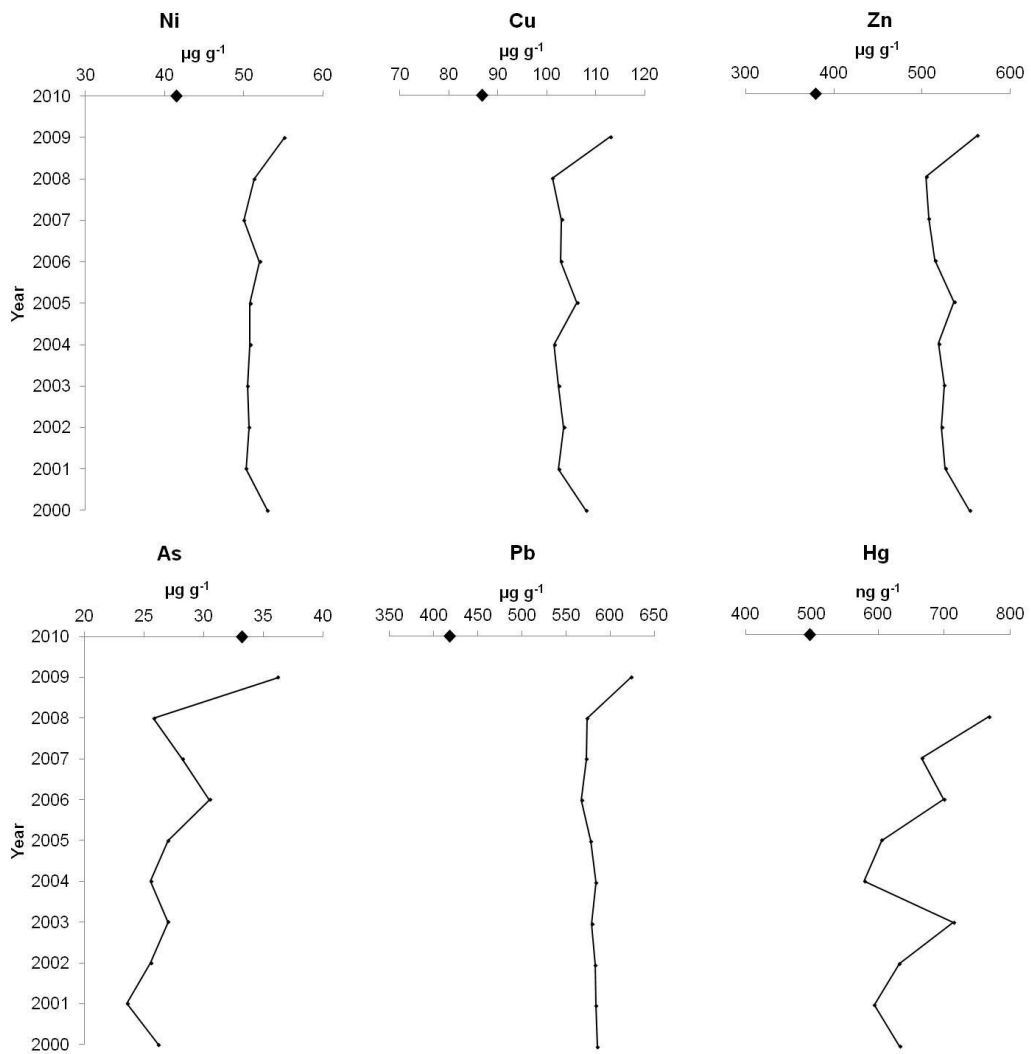


Figure 5.22 – Metal concentrations in the sediments of the Vale of Health Pond between 2000 and 2010. Concentrations between 2000 and 2009 were obtained from the analysis of the sediment core, whilst the mean concentration for 2010 was determined from the sediment trap samples (January to December 2010)

Figure 5.23 shows the mean metal fluxes from 2010 in comparison with the fluxes from the core since 2000. As with concentration, the 2010 fluxes were much lower than those from the preceding ten years. This was also the case for As. The difference in metal flux between 2009 and 2010 is proportionately much greater than the difference in concentration. Such a large fall in concentration and flux over such a short timescale is unlikely to be due to a reduction in metal pollution. The reasons for the decrease will be discussed further in Section 5.5.2.

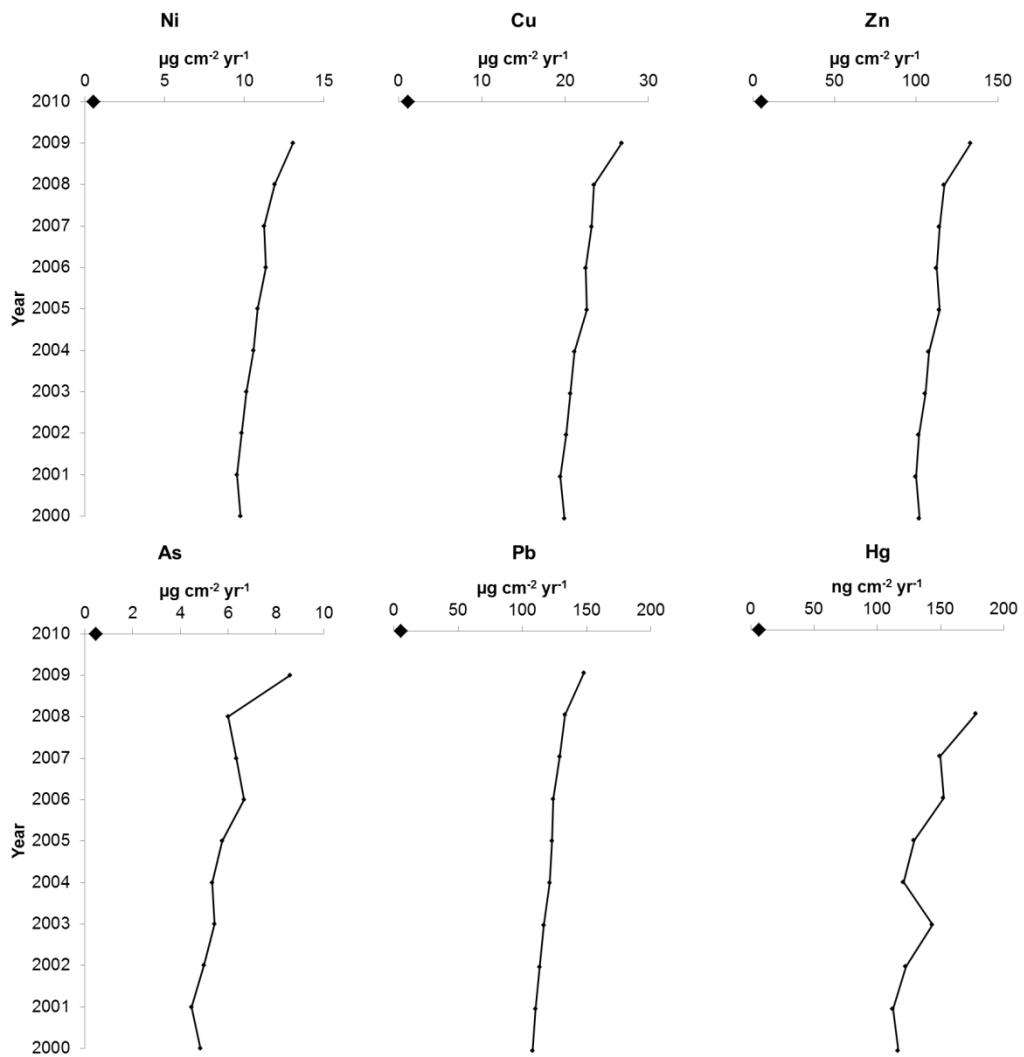


Figure 5.23 – Metal fluxes to the sediments of the Vale of Health Pond between 2000 and 2010. Fluxes between 2000 and 2009 were obtained from the analysis of the sediment core, whilst the mean flux for 2010 was determined from the sediment trap samples (January to December 2010)

5.5. Discussion

The results from the Vale of Health Pond (Section 5.4) have highlighted two main themes for discussion. The first is the monthly variability that occurred for some of the metals in deposition, water, benthic algae and zooplankton. These will be put into the context of other studies in order to explain the reasons for the variance. Secondly, the relationship between the sedimentary record and the rest of the ecosystem will be discussed, explaining the reasons for the differences in metal concentrations between parameters. The possible implications that metal contamination may have at the site will be assessed.

5.5.1. Monthly variability

There are a number of factors which affect metal concentrations in deposition, water, zooplankton and benthic algae that might explain some of the variability in monthly concentrations recorded between January 2010 and January 2011 at the Vale of Health Pond. Factors affecting metal concentrations in sediments have already been discussed in some detail in Chapter 4.

Previous studies of atmospheric deposition in urban areas in some parts of the world have shown clear seasonal trends related to changes in rainfall and wind direction. In a study of the Pearl River Delta, China, Wong et al (2003) found that atmospheric deposition of Cu, Cr and Zn was higher in the summer than in the winter, caused by the washout effect of the rainy season (summer) in the subtropical region. In Mexico City, Garcia et al (2009) showed that the differences in concentration of trace metals in deposition between winter, spring, summer and autumn was a product of changes in wind direction in the different seasons. However, in more temperate climates, seasonality in atmospheric deposition is not so evident. Kaya & Tuncel (1997) studied deposition in Ankara, Turkey. Although the concentration of Ni was slightly higher in the summer, the concentrations of Cu, Zn and Pb varied from month to month and did not show clear seasonal differences. The results were interpreted as the consequence of changes in pollutant sources (increases and decreases in emissions from road traffic and fossil fuel burning industries) over different months. Analysis of heavy metals in deposition in Paris (Azimi et al, 2005) didn't show any seasonal patterns either. However, there was also no significant variation in flux between months, in contrast to the results from Kaya & Tuncel (1997). The lack of change was attributed to the consistent impact of anthropogenic activities (non-ferrous metal refining, waste incineration and road traffic) in urban areas, which rather conflicts with the interpretation from the Turkish study. However, in the Paris study, information for separate metals wasn't available as the results were based on 'total' metal flux (the sum of flux for 13 different elements). Monthly variability may have been distinguishable between each of the different metals.

These studies highlight the various factors that can influence metal deposition from the atmosphere. The different metal concentrations deposited during some months at the Vale of Health have already been partially explained by the variation in precipitation at the site over the course of the year. High rainfall led to increased flux, whilst low rainfall resulted in decreased flux. However, this did not explain all of the variation at the site. Wind direction and speed may also have contributed to the differences in monthly deposition. Change in metal source is likely to be an important factor at the Vale of Health. The significant correlations between Ni, Cu and As might suggest a common pollution source, whilst the other metals may have different origins. This supports the evidence from Chapter 4 (Section 4.5.1), which showed that the different patterns of metals found in the sediments was partly due to different pollution sources.

Variations in the metal concentrations of water at the Vale of Health Pond (higher concentration of As in summer and of Hg in the autumn) might be connected to meteorological changes, but are more likely to be related to water chemistry and biological activity. In a study of Manchar Lake, Pakistan, Arain et al (2008) attributed the high concentrations of As, Ni, Pb and Zn in the summer months to a reduction in precipitation and surface run-off into the lake, and increased evaporation. Although there was no seasonal trend in rainfall at the Vale of Health, the higher temperatures over the summer (Figure 5.24) may have contributed to an increase in evaporation which would have resulted in a slight concentration of the metals.



Figure 5.24 – Temperature changes at the Vale of Health Pond between January 2010 and January 2011

Water chemistry is more likely to have affected the concentrations metals in the water at the Vale of Health Pond. This is supported by the fact that only As and Hg showed any significant changes in concentration, and both of these elements behave slightly differently in aquatic environments to Ni, Cu, Zn and Pb. A study of Hg in Lake Champlain in North America by Chen et al (2012) has shown that increases in lake water pH and alkalinity may reduce the amount of methylmercury (MeHg) in the water column. In an earlier study of Baiyangdian Lake, China, Chen et al (2008) also showed that dissolved concentrations of both Hg and As decreased with increasing chlorophyll concentrations, suggesting that there was a significant uptake of metal from water by algae. Therefore in eutrophic lakes, and in periods where there is more algal growth, metal concentrations in the water may decrease. Similarly, dissolved organic carbon (DOC) plays an important role in controlling bioavailability because MeHg and Hg(II) form strong 'complexes' with DOC, thereby influencing their speciation in natural waters. Concentrations of Hg(II) and MeHg in water generally increase with increasing DOC concentrations (Gorski et al, 2008).

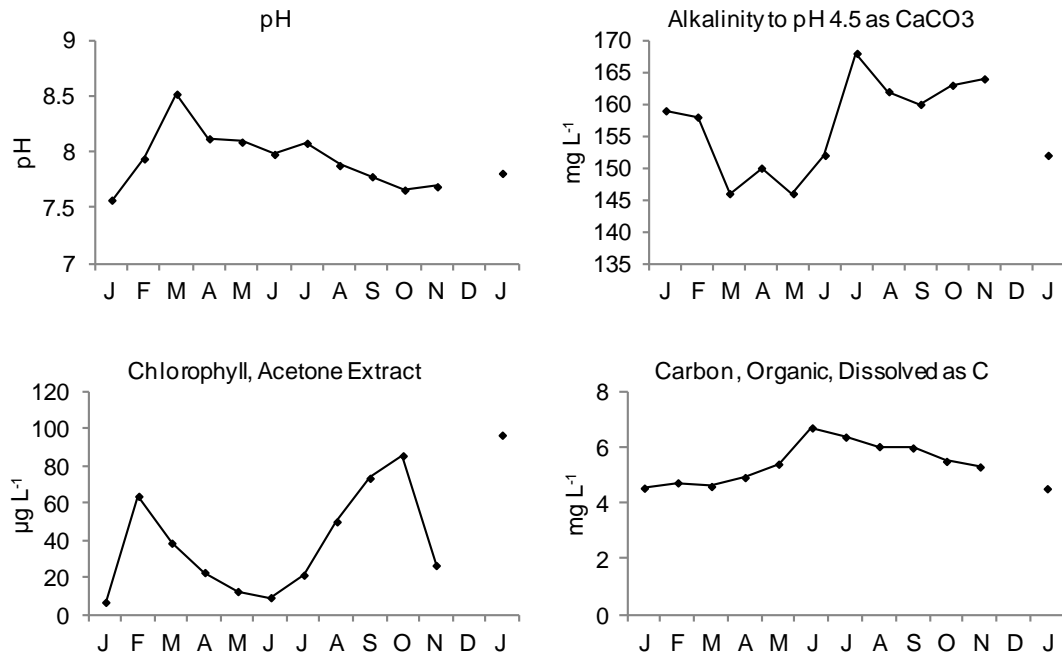


Figure 5.25 – Changes in pH, alkalinity, chlorophyll and DOC at the Vale of Health Pond between January 2010 and January 2011

However, as the graphs in Figure 5.25 show, it is difficult to discern a relationship between these four factors and metal concentrations at the Vale of Health Pond. This may be partly to do with the fact that the metal concentrations determined in the water samples from the Vale of Health Pond were for total metals rather than just the dissolved fraction, and total Hg was analysed rather than MeHg, which does not make these results directly comparable to the studies cited. However, there is a visible similarity between As and DOC. Pearson correlations between all the water chemistry data collected at the lake and metal concentrations support this link, showing a significant positive correlation between the two (Table 5.22). Dissolved organic carbon also showed a positive correlation with Cu, and was negatively correlated with Ni.

	Ni	Cu	Zn	As	Pb	Hg
DOC	<i>-.684</i>	<i>.642</i>		<i>.713</i>	<i>-.595</i>	<i>.725</i>
Ca	<i>-.596</i>			<i>-.710</i>	<i>-.593</i>	<i>-.802</i>
Na	<i>-.582</i>			<i>-.762</i>		
				<i>.840</i>		

Correlations in **BOLD** are significant at the 0.01 level (2-tailed)
 Correlations in *ITALIC* are significant at the 0.05 level (2-tailed)

Table 5.22 – Significant Pearson product-moment correlations between water chemistry data and metal concentrations at the Vale of Health Pond

Water chemistry also affects metal concentrations in benthic algae and zooplankton (Yan et al, 1989a). Changes in metal concentrations of benthic algae at the Vale of Health Pond during the year were likely to have been connected to the amount of algal growth, which is also related to water chemistry. Figure 5.26 shows the higher levels of algal growth that occurred at the Vale of Health over the spring and summer months (May to October). Pickhardt et al (2002) tested the effects of increasing algal biomass on Hg levels in freshwater food webs. Increasing algal biomass resulted in the dilution of Hg, as the same concentration of metal was split between a greater number of algal cells. Chen et al (2008) also showed that algal density is an important factor in accounting for changes in metal concentration in algae. Therefore, higher concentrations of metals in the winter months at the Vale of Health Pond are likely to have been caused by the concentration of metals in a smaller algal mass. The lower concentrations in the summer months will have been due to dilution of metal concentrations caused by an increase in algal biomass.

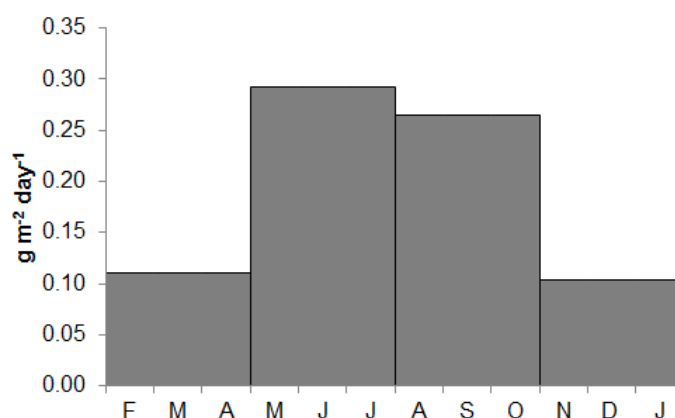


Figure 5.26 – Algal growth on artificial substrates at the Vale of Health Pond between February 2010 and January 2011

Similarly, changes in the biomass of zooplankton over the course of the year at the Vale of Health Pond may have affected the concentration of metals. Figure 5.27 shows how the zooplankton biomass varied between March 2010 and January 2011. There was no significant change in the biomass of open water zooplankton, but there was a large peak in the biomass of littoral zooplankton in June. The biomass of littoral zooplankton was also greater than that of open water over the year as a whole. Rather than an increase in biomass resulting in the dilution of metal concentrations however (as with benthic algae), the increase in zooplankton biomass in June resulted in a rise in the concentrations of Ni, Zn and Pb, and to an extent, As. Therefore the zooplankton in the littoral zone during this month must have contained higher concentrations of metals. Yan et al showed in their 1989 (a) study of Canadian lakes that patterns in the seasonal changes of various elements in zooplankton could be explained by changes in taxonomic composition over the growing season. Different species were found to accumulate metals differently. Therefore, if a

species which contained high concentrations of metals dominated during a particular period, overall metal concentrations would also be greater. The increase in concentration in June at the Vale of Health Pond may therefore have been related to the domination by a species which accumulated particularly high concentrations of metals. The metal concentration was related to taxonomic composition as the increase only occurred in the littoral species and not the open water. Identification of the zooplankton showed that some of the species differed between the two zones during that month (Table 5.23). Yan et al (1989a) found that metal levels in zooplankton were also related to changes in water chemistry, such as lake water pH and dissolved organic content, although to a lesser degree. An additional study by the same authors (1989b) also showed that metal concentrations in the water influenced the concentration of metals in zooplankton. A study by Altındağ & Yiğit (2005) of Lake Beyşehir, Turkey largely supported these findings, suggesting that the accumulation of heavy metals in zooplankton at the site depended upon the productivity of the water body, the physio-chemical properties of the water, and both quantitative and qualitative species composition.

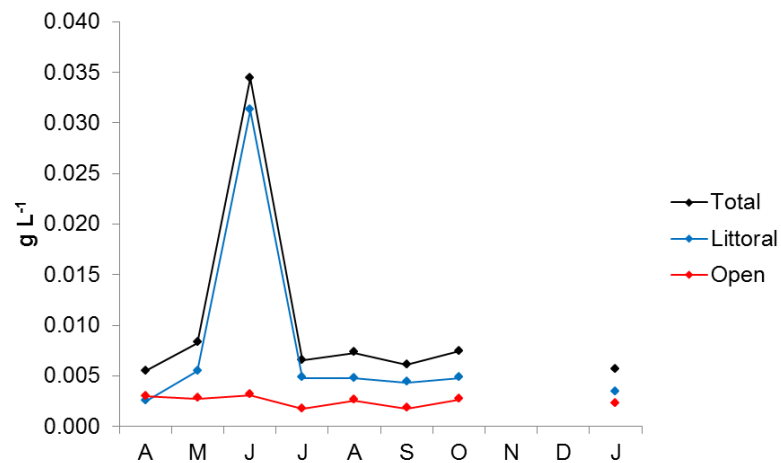


Figure 5.27 – Zooplankton biomass (total, littoral and open water) at the Vale of Health Pond between April 2010 and January 2011

Species	Jun-10	
	LITTORAL	OPEN
<i>Acroperus harpae</i>		
<i>Alona (quadrangularis/affinis)</i>	x	
<i>Bosmina sp</i>		
<i>Bosmina coregoni</i>		
<i>Bosmina longirostris</i>		x
<i>Bosmina sp</i>	x	
<i>Ceriodaphnia sp</i>	x	x
<i>Chydorus sphaericus</i>	x	
<i>Cyclops sp</i>	x	x
<i>Daphnia hyalina agg c.f. Cucullata</i>		
<i>Daphnia sp c.f. cucullata</i>		x
<i>Daphnia sp c.f. longispina</i>		x
<i>Diaptomus sp</i>		x
<i>Eurycercus lamellatus</i>	x	
<i>Leydigia sp</i>	x	
<i>Pleuroxus sp</i>	x	
<i>Scapholeberis sp</i>		
<i>Simocephalus sp</i>	x	x

Table 5.23 – species composition of littoral and open water zooplankton at the Vale of Health in June 2010

5.5.2. Metal concentrations in different parts of the ecosystem

The aim of this part of the discussion is to explain the reasons for the differences in metal concentrations between matrices at the Vale of Health Pond, and to assess the effects that metal pollution is having and may continue to have at the lake.

5.5.2.1. Metal concentrations in abiotic matrices

The high concentrations of metals found in the sediments in comparison to any other constituent of the ecosystem is consistent with previous studies (e.g. Ashraf et al, 1991; Arain et al, 2008; Lillebø et al, 2011). As explained in Chapter 1 (Section 1.7.3), lake sediments act as a sink for trace metals. Metals are scavenged by particulates in the water column which then sink to the bottom of the lake. Metals are concentrated by this process, resulting in higher concentrations of metals in the sediments and lower concentrations in the water column, as was the case at the Vale of Health Pond. The same process means that metal concentrations in deposition will also be lower than those in the sediments.

The rate of deposition to the Vale of Health Pond from the atmosphere was also lower than the rate of deposition to the sediment for Ni, Zn, As, Pb and Hg. In particular, sediment flux of Pb was much greater than the deposition flux. In contrast, deposition flux of Cu exceeded sediment flux for 6 of the 11 months that data was available for both. The concentration of Pb in the sediment core from the Vale of Health exceeded the PEC significantly over the whole history of the core, whilst the concentration of Cu never exceeded the PEC at any point (see Section 4.4.2).

Although the concentration of metals in the sediment trap material was much greater than that in the deposition and water, it was still less than the concentration of metals in the sediment core. The same was true for the sediment flux rates, with those in the sediment trap being lower than in the core. This disparity has also been found in other studies where both sediment traps and cores have been analysed. Although not freshwater, a study of trace metal pollution in the canals of Venice by Argese et al (1997) found that concentrations of Cd, Pb, Zn, Ni and Cu in surface core samples were greater than those found in trap samples. However, there was no difference in the concentrations of Fe, Mn and V. The difference was attributed to two factors, both connected to the resuspension of sediments. Firstly, the metals that did show a difference were mostly of anthropogenic origin and were bound to the most labile geochemical phases of the sediments, whilst Fe, Mn and V prevalently bound to the more resistant phases. This indicated that the difference between core and trap samples was due to metal exchange at the water/sediment interface. During resuspension, the most labile phases (such as sulphides and organic matter) were partially solubilised, releasing the associated metals into the water. The second factor was related to grain size distribution. It was proposed that the sediments collected by trap were mostly of finer particles, whilst larger particles prevailed in the core. Finer sediment particles would be kept in suspension in the overlying oxygenated water column for a longer period, favouring the release of metals bound to the oxidisable components of the sediment into the water. Although sediment traps are primarily used to collect sinking particles in the water column, the problems associated with the additional collection of resuspended material are known (Flower, 1991). A more recent study of Cu in a mining impacted lake in the USA (McDonald et al, 2010) showed a similar pattern. The concentration of Cu in material collected from sediment traps was lower than that in the core taken from the same area of the lake. Sedimentation rates measured with the traps and sediment accumulation rates established for the core agreed well, which suggested that significant local resuspension was not occurring at the coring site. If resuspension was occurring, sedimentation fluxes would be higher than accumulation rates. Instead, the difference was attributed to the effects of sediment focusing in the lake (see Section 4.5.2) and also to diffusive transport of dissolved copper from underlying mine tailings providing Cu to the surface sediments. Although the latter is unlikely at the Vale of Health Pond, both resuspension of sediments and sediment focusing may explain the disparity between concentrations and flux in the sediment traps and sediment core.

Despite the slightly lower concentrations of the sediment trap material, median annual concentrations still exceeded TECs (MacDonald et al, 2000) for all metals, and the PEC for Pb (see Figure 5.28). Comparison of metal concentrations in the water with a range of Environmental Quality Standards (Table 5.24) showed that whilst Ni, Cu, Zn, As and Hg do not exceed recommended values, the concentration of Pb did exceed the Criterion

Continuous Concentration (CCC) recommended by the US Environmental Protection Agency. The CCC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (USEPA, 2012). The exceedance of Pb above this value shows that aquatic biota at the Vale of Health may be at risk. The high concentration of Pb in both the sediments and water of the Vale of Health Pond and the exceedance of US EPA CCC and PEC guidelines show that contamination of the lake by Pb is of great concern.

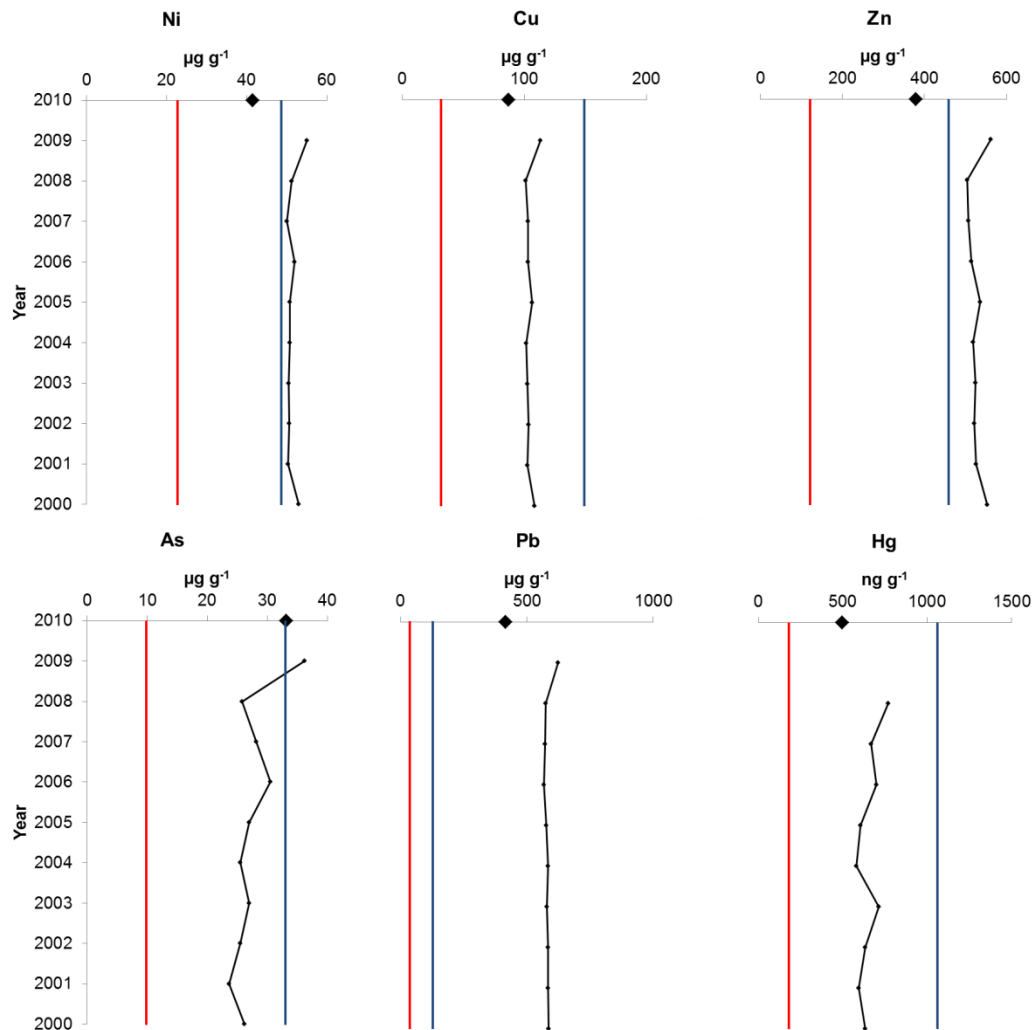


Figure 5.28 – Metal concentrations in the sediments of the Vale of Health Pond between 2000 and 2010 in comparison to SQGs (MacDonald et al, 2000). TECs are shown by the red lines and PECs are shown by the blue lines.

Ni	Cu	Zn	As	Pb	Hg	
2.13	3.70	8.62	1.72	4.63	5.22	Median metal concentration
						EQS reference
20				7.2	50	EC directive 2008 (Annual average)
					70	EC directive 2008 (Maximum allowable concentration)
	10	75	50			WFD 2010 (Good status)
470		120	340	65	1400	US EPA (Criteria Maximum Concentration)
52		120	150	2.5	770	US EPA (Criterion Continuous Concentration)

Concentrations measured in $\mu\text{g L}^{-1}$, apart from Hg measured in ng L^{-1}

Table 5.24 - Comparison of median metal concentrations in the water from the Vale of Health Pond with a range of Environmental Quality Standards

5.5.2.2. Metal concentrations in biotic matrices

In order to be able to explain why metal concentrations differed between biota at the Vale of Health, it was important to be able to identify the structure of the food web at the site. The results of the stable isotope analyses ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) carried out on the samples from the Vale of Health are shown in Table 5.25. $\delta^{15}\text{N}$ values of benthic algae and the macrophyte, *Iris pseudacorus*, were both approximately 7 ‰. There was an increase of 3 ‰ between them and zooplankton, which showed that the latter was in a higher trophic level (Mao et al, 2012). There was another increase of 3-4 ‰ between zooplankton and fish, *Perca fluviatilis*, again reflecting the higher trophic level of fish.

Biota	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
Benthic algae	-23.16	7.34
Zooplankton	-37.85	10.27
Fish muscle tissue (2 years)	-34.76	13.46
Fish muscle tissue (3 years)	-32.64	14.33
Macrophyte	-29.88	7.71

Table 5.25 – Mean $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for biota from the Vale of Health Pond

The distinction between the trophic levels of biota at the Vale of Health Pond is shown more clearly in Figure 5.29, with benthic algae and macrophytes at the bottom, zooplankton in the middle and fish at the top. Analysis of the fish stomach contents had shown that the diet of *Perca fluviatilis* at the pond was primarily composed of zooplankton. The largest proportion consisted of *Daphnia* sp., but there was also evidence of *Chidoriid* sp, *Alona* sp and *Bosmina* sp. Chironomid larvae, phantom midge larvae, oligochaetes and small green algae were also present in very small amounts. The latter may have been the source of food for the zooplankton and larvae, rather than for the fish. The combination of the stable isotope and fish gut data showed that the biota sampled from the lake contained one small food chain – algae-zooplankton-fish.

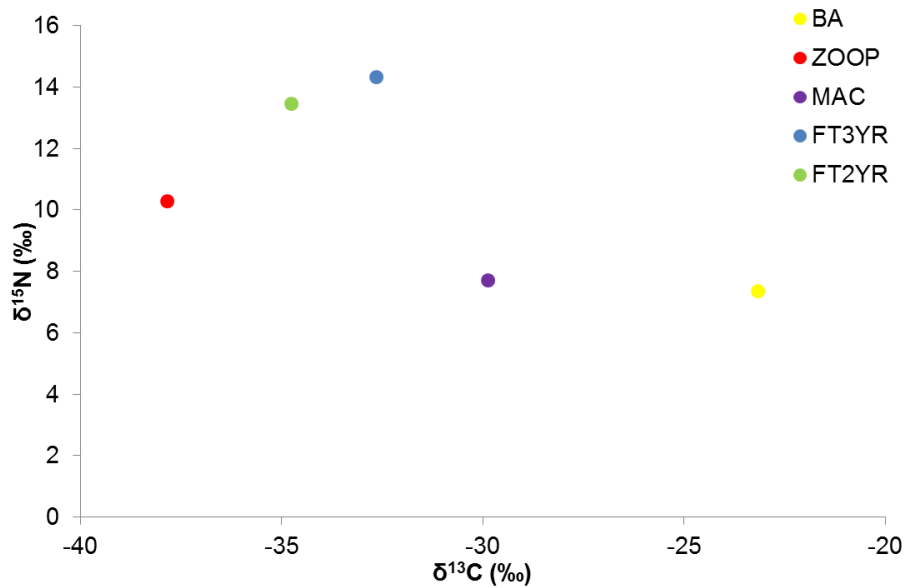


Figure 5.29 – biplot of mean $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for biota (benthic alge (BA), zooplankton (ZOOP), macrophytes (MAC), fish aged 3 years (FT3YR) and fish aged 2 years (FT2YR)) from the Vale of Health Pond. There is a clear distinction between trophic levels, the highest level consisting of fish, the lowest level incorporating both benthic algae and macrophytes, and zooplankton situated in between.

For all metals, concentrations were found in the order benthic algae > zooplankton > fish, showing that there was no biomagnification of metals at the Vale of Health Pond. That the highest concentrations occurred in benthic algae, a primary producer (as shown by the stable isotope analysis), is not uncommon. The accumulation of a variety of trace metals in the food web components of Flix Reservoir in north east Spain was studied by Soto et al (2011). Concentrations tended to be one order of magnitude larger in biofilms (primarily comprised of diatoms and filamentous cyanobacteria) than in any other component for Pb and Hg. The concentrations of Cu and As were also greatest in biofilms. Such high concentrations were explained by a number of different factors. Firstly, biofilms grow on the top of surfaces such as sediment, rocks and plant debris and therefore they are likely to suffer higher exposures to trace metals that accumulate on these surfaces. Secondly, the fact that biofilms are constituted by simple unicellular or cell colonial organisms means they accumulate metals from dissolved contaminant forms. For example, they have been found to accumulate large amounts of Hg due to passive adsorption from their surroundings. Lastly, natural aquatic biofilms can also accumulate metals in a second way, by binding metals to their surfaces by adsorption processes (Soto et al, 2011). An older study of trace metals in lake water and biota from Little Rock Lake, Wisconsin, USA (King et al, 1992) showed that concentrations of Cu, Pb and Zn decreased from periphyton (algae) to higher trophic levels. As with Soto et al (2011), the reasons for the higher concentrations related to the method of uptake by the algae. However, only one method was cited – the diffusion of surface-bound metals through cell membranes (King et al, 1992).

In contrast, the other primary producer identified at the Vale of Health Pond, the aquatic macrophyte *Iris pseudacorus*, contained much lower concentrations of metals. The same macrophyte was used in a study of the effects of acidification on water and plants in manmade lakes in Poland (Samecka-Cymerman & Kempers, 2001). The concentrations of metals in *Iris pseudacorus* were much higher in the Polish lakes than they were in the Vale of Health Pond. However, the concentrations of metals in the water were also much higher in the Polish sites than in the Vale of Health. The high concentrations in the plants in the lakes in Poland were attributed to the high concentrations in the water, as aquatic macrophytes concentrate elements from the water column. The paper by Soto et al (2011) expands on this explanation, stating that 'macrophytes take up metals only from solution, either from the water column or sediment pore water. The main pathway of trace metal uptake occurs through roots from sediment pore water in rooted aquatic plants.' Therefore, the low concentrations found in *Iris pseudacorus* at the Vale of Health Pond were directly related to the low concentrations found in the water.

The accumulation of trace metals in zooplankton depends on factors such as the metal content of water and absorption properties of the zooplankton species (Adhikari et al, 2009). In addition, diet will also contribute to the uptake of metals. At the Vale of Health, diet is likely to be the key factor which determined metal concentrations in zooplankton, given the high concentrations found in the benthic algae, upon which the zooplankton feeds, and the low concentrations which occurred in the water. The slightly lower concentrations that were found in zooplankton in comparison to benthic algae at the Vale of Health Pond, and the even lower concentrations found in fish is termed biopurification (King et al, 1992).

A variety of factors such as sex, age, season, spawning periods, choice of food by younger and older fish and variations in pollutant exposures across fish species may influence uptake, retention and bioaccumulation of contaminants in fish tissues (Ikem et al, 2003). Within the fish samples from the Vale of Health Pond, the highest concentrations of Cu, Zn, As and Hg were found in the composite liver sample. High concentrations, particularly of Pb, Zn and As were also present in the gill. The lowest concentrations of all metals tended to occur in the muscle tissue. The same has been found in a large number of other studies, irrespective of species or location (e.g. Bradley & Morris, 1986; Ashraf et al, 1991; Rashed, 2001a,b; Chandra Sekhar et al, 2003; Wagner & Boman, 2003; Swaibuhl Lwanga et al, 2003; Farkas et al, 2003; Papagiannis et al, 2004; Pyle et al, 2005; Evans et al, 2005; Yang et al, 2007; Türkmen & Ciminili, 2007; Chi et al, 2007; Arain et al, 2008). The liver stores metals for detoxification, which occurs through the production of metallothioneins (Karadede & Ünlü, 2000). Therefore metal concentration in liver tends to be higher than in other parts of

the fish. High concentrations are also found in the gills. Large volumes of water pass through the gill surface. The large surface area caused by the highly branched structural organisation of the gill, combined with the greatly vascular physiological state and the relatively small biomass make the gill a prime site for metal accumulation (Adhikari et al, 2009). Put more simply, the concentrations of metals in the gill reflect the concentrations of metals in the water, whereas the concentration in the liver represents storage of metals (Karadede et al, 2004). Concentrations of metals in muscle tissue are much lower because muscle does not come into direct contact with trace metals as it is covered externally by the skin which acts as a barrier. It is also not an active site for detoxification and therefore transport of metals from other tissues to muscle does not occur (Adhikari et al, 2009).

Trace metal concentrations frequently increase in relation to fish age or length, known as bioaccumulation (Section 1.5.2). This is particularly the case for Hg. It is thought that excretion of Hg is very slow and therefore it accumulates at a rate greater than the rate of tissue growth during much of the lifetime of the animal. The same is true for other non-essential metals such as Pb. Essential elements such as Zn and Cu do not usually increase in concentration with age or size because they are thought to be under homeostatic control (Evans et al, 1993). The fish from the Vale of Health Pond showed evidence of bioaccumulation not only in Hg and Ni, but also in Cu, increasing in concentration between the samples aged 1 year, 2 years and 3 years. There was no bioaccumulation of Pb. However, the sample sizes of each of the different fish age groups were small (Fish 1 year (n=1); Fish 2 years (n=8); Fish 3 years (n=1). Much larger sample sizes of each age group would be required to get a more accurate idea of metal concentrations in *Perca fluviatilis* at the lake. In addition, it would also be beneficial to analyse older fish to confirm the presence of bioaccumulation.

It is difficult to compare metal concentrations in fish from different lakes as numerous factors can influence the results. In addition to those already mentioned, watershed size, lake size, DOC concentration and metal concentrations in the water can all affect metal levels in fish (Evans et al, 2005). There have been few studies of metal concentrations carried out in the UK, particularly of *Perca fluviatilis*. However, the metal concentrations in the fish from the Vale of Health can be compared with EC and USEPA guidelines for maximum levels of Pb and Hg in fish muscle tissue (Table 5.26). Guidelines tend to be for muscle tissue concentrations as that is the edible part of the organism and the guidelines refer to maximum levels for consumption. The concentrations of Hg were all below the guidelines set by the EC and USEPA. However, although the concentrations of Pb in fish aged 1 and 2 years were below the EC guideline, the concentration in fish aged 3 years exceeded the value by $0.12 \mu\text{g g}^{-1}$. This confirms that there is a problem with Pb contamination at the site,

as concentrations exceed guidelines and quality standards in all parameters for which they exist (sediment, water and fish).

Pb	Hg	
0.03	8.76	Median metal concentration (1 year)
0.01	11.47	Median metal concentration (2 years)
0.42	13.49	Median metal concentration (3 years)
		Guideline reference
0.3	500	EC directive 2006
	300	US EPA

Concentrations measured in $\mu\text{g g}^{-1}$, apart from Hg measured in ng g^{-1}

Table 5.26 - Comparison of median metal concentrations in fish aged 1, 2 and 3 years from the Vale of Health Pond with EC and USEPA guidelines for maximum levels of Pb and Hg in fish muscle tissue

Contamination by Pb may be even greater in the other species of fish present in the lake. There are many different types of fish at the Vale of Health in addition to perch, including both carp and pike. The size of individuals from both of these species have been recorded in fish surveys as being much larger than perch. Clearly if metal concentrations can increase with fish size (and age) larger and older species such as these may contain much higher concentrations of metals. In addition, both of these species have different feeding habits to perch. Carp are bottom feeders, scavenging the bottom of lakes for insects, benthic worms and other detritus found amongst the sediments. This means that they are also likely to consume the much higher concentrations of metals that are found in the sediments of the Vale of Health Pond. Pike are piscivorous and will therefore consume metal concentrations from other small fish, such as the perch. Lead concentrations in other fish at the Vale of Health Pond are therefore likely to be much greater than those found in the perch in this study. Concentrations of Ni, Cu, Zn, As and Hg may also be higher than guideline values in other fish species at the site.

5.6. Conclusion

The aim of this chapter was to identify metal concentrations in other parts of the lake ecosystem at the Vale of Health Pond and explore the relationships between the sediments and the rest of the ecosystem. Metal concentrations were determined in sediments collected from traps, bulk deposition, water, macrophytes, benthic algae, zooplankton and fish at the lake, providing a snapshot of the degree of contamination in an urban lake. The study highlighted a number of important points. Firstly, of all the parts of the ecosystem the highest concentrations of metals occurred in the sediment trap material. Box and whisker plots of the data (Figure 5.15) highlighted the clear difference in concentration for all of the metals. This was consistent with previous studies, and reflected the capacity of particulates to scavenge and then store metals. The study also showed that both metal concentration and flux in the sediment trap material was much lower than that in the sediment cores analysed in Chapter

4, possibly due to a combination of resuspension processes, grain size distribution and sediment focusing. Secondly, deposition flux was low in comparison to sediment flux for all metals. This suggested that even though deposition from the atmosphere was a source of some metals to the Vale of Health Pond, it was not the only source and that run off from the catchment may be as, if not more, important. This corroborated the evidence from Chapter 4 which showed that erosion of soils from the lake catchments were contributing to metal flux and enrichment.

The third key finding was that the metal concentrations in biota, which were in the order benthic algae > zooplankton > fish, reflected the trophic levels at the Vale of Health Pond. Stable isotope analysis ($\delta^{15}\text{N}$) showed clear differences of 3-4 ‰ between macrophytes and algae, zooplankton, and fish, which, together with fish gut contents, confirmed the presence of a food chain algae-zooplankton-fish. The results showed that there was no evidence of biomagnification of Hg up the food chain, although the low recovery rate of Hg and the limited number of fish samples may have affected the data. Lastly, and most importantly, the level of Pb pollution within the ecosystem was found to be high. Guideline values were available for Pb in sediment, water and fish. Median annual concentrations of Pb in the sediment trap samples exceeded both TECs and PECs, despite the concentrations being lower in the trap material than in the cores. This emphasised the degree to which Pb pollution is a problem within the lake sediments of London. However, the concentration of Pb also exceeded USEPA Criterion Continuous Concentration (CCC) guidelines for water, which is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (USEPA, 2012), showing that aquatic biota at the Vale of Health may be at risk. This was confirmed by comparison of fish muscle tissue concentrations with EC guidelines, which showed that the concentration of Pb in some fish exceeded the recommended amount. These results showed that Pb pollution is pervasive throughout the lake ecosystem at the Vale of Health Pond, and is not just confined to the sediments where most particulates are stored. This may also be reflective of other lake ecosystems in the London area with similarly high concentrations of Pb in their sediments, and has implications for future management of lake sediments, which will be discussed more in Chapter 7.

CHAPTER 6: CONTEMPORARY AND HISTORICAL TOXICITY IN LAKE SEDIMENTS

6.1. Introduction

Analysis of the cores in Chapter 4 showed that on an individual basis metals stored in London lake sediments may pose a potential risk to ecosystem health. Although concentrations of most metals within water and fish at the Vale of Health Pond studied in Chapter 5 were below guideline values, this was not the case for Pb, which suggested that some of the potential risk was being realised. However, the concentration of a single metal, whether above or below guideline amounts, does not necessarily reflect whether that metal is actually toxic to the ecosystem, nor does it give any indication of the potential toxicity which the combination of all the metals in the sediments may have. The aim of this chapter is to reconstruct the potential toxicity of the sediments from each of the London lakes. The potential toxicity of surface sediments from the OPAL lakes will be calculated and compared with the results from toxicity tests carried out on the same sediments. The potential toxicity of both historic and contemporary sediments in cores from the OPAL lakes and the lakes in London will be calculated. These will then be related to guideline thresholds for toxicity to gauge the potential impact future disturbance of the sediments could cause.

6.2. Methods

Following the method from Rippey et al (2008), a Tier I Sediment Ecological Risk Assessment was carried out on sediments from the nine OPAL lakes. The concentrations of a range of metals were determined and compared with sediment quality guidelines and complete laboratory sediment toxicity tests. The concentrations of persistent organic pollutants (POPs) and spheroidal carbonaceous particles (SCPs) were also determined. The OPAL toxicity data was used to help interpret potential toxicity calculated for the London lakes as no laboratory toxicity test data was available for these sites.

Collection of the sediment cores from the OPAL lakes was carried out by the OPAL Water Centre in November 2008 (see Table 6.1 for basic characteristics of each of the sites). Seven sediment cores were taken from the profundal area of each lake using a gravity corer with a polycarbonate tube of internal diameter 8.5 cm. The top 5 cm of each of the seven cores was extruded vertically in the field, amalgamated and homogenised in a hexane washed glass container. All sampling equipment and utensils in contact with samples were precleaned rigorously, and hexane washed and stored in hexane washed foil before use. Approximately 10 g of the homogenised wet sediment was stored in sealable plastic bags, freeze dried and analysed for trace metals. A second, larger subsample of approximately

100 g wet sediment was transferred into hexane washed amber jars, then frozen and freeze dried prior to analysis for POPs. A third subsample of approximately 2 g wet sediment was also stored in sealable plastic bags and air dried prior to the analysis of SCPs. The remainder of the sediment sample was used for the sediment toxicity tests. A Livingstone-type piston core was also taken from the deepest point of each lake.

Lake	Location	Altitude (m.a.s.l.)	Lake area (ha)	Max. Depth (m)	Sediment collection date
Edgbaston Pool	SP 054841	127	7.2	2.0	13/11/2008
Chapman's Pond	SE 578490	16	0.6	4.5	16/11/2008
Marton Mere	SD 343352	7	10.8	4.2	14/11/2008
Fleet Pond	SU 820550	68	26.4	0.9	06/11/2008
Slapton Ley	SX 823432	3	65.9	2.5	02/11/2008
Holt Hall Lake	TG 076398	47	0.7	1.0	11/11/2008
Wake Valley Pond	TQ 420987	96	1.0	3.7	10/11/2008
Thoresby Lake	SK 630704	37	30.4	3.1	12/11/2008
Crag Lough	NY 766679	244	10.1	2.0	15/11/2008

Table 6.1 – Site locations, basic characteristics (lake altitude, lake area, maximum water depth) and dates when sediment cores were taken

The sediment cores were radiometrically dated (as per the methods outlined in Section 3.2) and analysed using X-ray fluorescence (as per Section 4.3.2). The concentrations of Ni, Cu, Zn, Cd, Pb and Hg were determined in the surface sediments by Handong Yang at UCL using the following methodology. Sediment samples were treated with 8 ml concentrated Aristar HNO₃ and heated at 100°C for 1 hour in rigorously acid leached 50 ml Teflon beakers. For measurement of Hg, the supernates were carefully transferred into polyethylene tubes after digestion. The residue in the beakers was then washed with deionised water and the supernates transferred into the same tubes. Nickel, Cu, Zn, Cd and Pb were measured using atomic absorption spectroscopy (AAS) whilst Hg was measured using cold vapour atomic absorption spectrometry (CV-AAS) following reduction of Hg in the digested sample to its elemental state by 2 ml SnCl₂ (10% in 20% (v/v) HCl). Certified standard reference materials were included in all digestion and analytical procedures. For AAS, reference materials and sample blanks were analysed every 20 samples. The procedure for extraction and enumeration of SCPs was carried out by Neil Rose at UCL, following his method (Rose, 1994), outlined in Section 3.3.

Analysis of POPs was carried out by Stuart Harrad and Mohamed Abou-Elwafa Abdallah of the Division of Environmental Health and Risk Management at the University of Birmingham, who measured the concentrations of selected chemicals from three groups of POPs. These included seven polychlorinated biphenyl congeners (PCBs), 28, 52, 101, 118, 138, 153 and 180; fifteen polycyclic aromatic hydrocarbons (PAHs), acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j+k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene,

dibenz[*ah+ac*]anthracene, benzo[*ghi*]perylene; and ten polybrominated diphenyl ether congeners (PBDEs), 17, 28, 47, 49, 66, 85, 99, 100, 153 and 154. The extraction and purification methods employed by the University of Birmingham for the determination of PCBs, PAHs and PBDEs in sediments are described in the following paragraphs. Briefly, accurately weighed 10 g aliquots of freeze dried sediment were treated with known quantities of internal standards (PCB congeners 34, 62, 119, 131, and 173, deuterated PAHs (acenaphthylene, phenanthrene, fluoranthene, benzo[*a*]pyrene, and benzo[*ghi*]perylene) and $^{13}\text{C}_{12}$ -PBDEs congeners 47, 99, and 153) and extracted with hexane in an accelerated solvent extractor (ASE, Dionex, UK). After cooling, the crude extract was concentrated to approximately 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 fractions were 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 concentrated 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 in nonane containing the recovery determination standards PCB 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 between 200 μL to 2 mL CH_2Cl_2 containing *p*-terphenyl as a recovery determination standard (the exact volume depended on the anticipated concentrations in a given sample). 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. The limit of detection for individual PCBs, PBDEs and PAHs was 0.1-0.2, 0.2-0.4, and 1 $\mu\text{g kg}^{-1}$ dry weight, respectively. Method accuracy and reproducibility was evaluated by ongoing replicate analyses of appropriate certified or standard reference materials.

Sediment toxicity tests and analyses were carried out at ABC Laboratories Inc., in Columbia, Missouri, USA. Two sediment toxicity tests were completed, a 10-day chironomid survival and growth test and a 7-day cladoceran survival and reproduction test, according to ASTM (2000) and US EPA (2002). For the chironomid test, five replicates of a reference sediment and five for each lake sediment sample were used, all with 10 organisms per replicate chamber. All sediment and control samples were observed for the number of adults emerging from the sediment. The number of live and dead animals in each test chamber was enumerated at test termination day (day 10) by sieving through a 425 or 500 μm sieve. The criterion for test acceptability was mean survival in the reference sediment of $\geq 70\%$. For the cladoceran test, the reference sediment sample and the lake sediment samples were each replicated ten times and one *Daphnia magna* juvenile was added to each replicate beaker. All beakers were monitored daily for the survival of *Daphnia* and for

production of young. The criteria for test acceptability were mean survival of $\geq 80\%$, an average of 20 or more young surviving per female in the reference sediment and production of at least three broods in 60% of the surviving organisms.

In the chironomid test, the hardness of the water used was 130 to 160 mg L⁻¹ as CaCO₃, whilst in the cladoceran test it was 160 to 180 mg L⁻¹ as CaCO₃. The reference sediment was formulated by mixing the following ratio of constituents: 75% fine industrial sand, 20% kaolin clay and 5% sphagnum peat. The sediment constituents were mixed based on dry weight equivalents. The peat moss was sieved to a finely ground consistency and did not contain any visible plant remains. Calcium carbonate was added to the artificial sediment to adjust the pH to 7.0 ± 0.5 units. The mixed sediment was stored dry until it was hydrated to approximately 39% of its dry weight just prior to its use in the studies. The water was monitored for temperature, dissolved oxygen, pH, conductivity, total ammonia, alkalinity and hardness. The test chambers were maintained in a temperature-controlled water bath adjusted to maintain a sediment temperature of 20 ± 1 °C for chironomids and 25 ± 1 °C for cladocerans, each under a 16 hour light: 8 hour dark photoperiod. The statistical significance of animal survival was determined by hypothesis testing ($P=0.05$). Analysis of each endpoint between samples was evaluated by first analysing the data for normality and homogeneity of variance with Shapiro-Wilk's Test or Levene's Test, before comparison of means. Analysis of variance was utilised for the survival and weight data in the chironomid test, and for the survival and reproduction data in the cladoceran test, along with Dunnett's procedure for comparing the means. Survival data were also analysed using Fisher's Exact test.

6.3. Results

The concentrations of the six metals and SCPs in the surficial (0-5 cm) sediment of the nine OPAL lakes are presented in Table 6.2. The highest concentration of Zn, Pb and Hg was found in Edgbaston Pool and the highest concentration of Ni, Cu and Cd was found in Wake Valley Pond. The lowest concentration of metals was found in Marton Mere (Cd), Slapton Ley (Zn, Cd), Holt Hall Lake (Ni) and Crag Lough (Cu, Pb, Hg). The highest concentration of SCPs was found in Wake Valley Pond, Edgbaston Pool and Fleet Pond, and the lowest in Crag Lough. The differences in metal concentration between sites can be explained by the locations of the lakes. Edgbaston Pool and Wake Valley Pond are both situated close to large urban centres (Birmingham and London respectively), whilst Marton Mere, Slapton Ley, Holt Hall Lake and Crag Lough are located in more rural areas. Although these latter lakes are subject to atmospheric deposition of contaminants (supported by the occurrence of SCPs in the lake sediments), the close proximity of Edgbaston Pool and Wake Valley Pond to concentrations of industry and transport results in greater levels of localised contamination in the sediments of these sites. The high concentration of SCPs found at

Fleet Pond might also be explained by its proximity to London, although the lower metal concentrations found at the site reflect the smaller number of pollution sources within the immediate area.

Lake	SCPs no./g	Ni µg/g	Cu µg/g	Zn µg/g	Cd µg/g	Pb µg/g	Hg ng/g
Edgbaston Pool	2852	59	267	536	5.5	541	863
Chapman's Pond	1318	25	43	214	1	107	171
Marton Mere	600	36	39	177	0.6	81	198
Fleet Pond	3945	30	69	448	3.2	155	508
Slapton Ley	1113	20	24	118	0.6	48	164
Holt Hall Lake	1005	15	67	225	3.6	264	316
Wake Valley Pond	7991	83	763	326	7.2	144	289
Thoresby Lake	923	24	77	382	3.6	104	363
Crag Lough	366	22	15	157	1.1	37	153

Table 6.2 – The concentration of Ni, Cu, Zn, Cd, Pb and Hg, along with SCPs in the surficial (0-5 cm) sediment of the nine OPAL lakes

Toxicity quotients (concentration/PEC) were calculated for each of the metals (Table 6.3). Toxicity quotients can give an indication of whether a metal could possibly be toxic to biota in the sediment (Long et al, 1998). The higher the value, the stronger the possibility that the concentration of the metal is toxic and therefore cause for concern. The highest values were calculated for the samples from Edgbaston Pool and Wake Valley Pond, which reflected the high concentrations of metals found at those sites. Toxicity quotients were also greater overall for Pb than for the other metals. This showed that Pb was an important contaminant within the sediments, as the concentrations tended to be much higher than the PEC in comparison to the other metals.

Lake	Toxicity quotient (concentration/PEC)					
	Ni	Cu	Zn	Cd	Pb	Hg
Edgbaston Pool	1.21	1.79	1.17	1.10	4.23	0.81
Chapman's Pond	0.51	0.29	0.47	0.20	0.84	0.16
Marton Mere	0.74	0.26	0.39	0.12	0.63	0.19
Fleet Pond	0.62	0.46	0.98	0.64	1.21	0.48
Slapton Ley	0.41	0.16	0.26	0.12	0.38	0.15
Holt Hall Lake	0.31	0.45	0.49	0.72	2.06	0.30
Wake Valley Pond	1.71	5.12	0.71	1.45	1.13	0.27
Thoresby Lake	0.49	0.52	0.83	0.72	0.81	0.34
Crag Lough	0.45	0.10	0.34	0.22	0.29	0.14

Table 6.3 – Toxicity quotients calculated using Long et al (1998) method for Ni, Cu, Zn, Cd, Pb and Hg at all nine OPAL sites

The combined action of a group of chemicals can be assessed by calculating the Probable Effect Concentration Quotient (PEC-Q) (Ingersoll et al, 2001). This is used to evaluate possible toxicity from groups of chemicals determined in the sediment. Two types of PEC-Q were calculated for the data (Table 6.4):

PEC-Q Mean-metals – the average of the toxicity quotients for a number of metals

PEC-Q Mean-MPP (or) – the average of the PEC-Q Mean-metals and (total PAHs/PEC) or (total PCBs/PEC)

Toxicity quotients calculated for PCBs were all less than 0.02 (Table 6.4) and therefore their contribution to toxicity was likely to be very small. Consequently, they were not included in the calculation of PEC-Q Mean-MPP (or) and instead the toxicity quotients of PAHs were used.

Lake	PEC-Q Mean-metals	Total PAHs ng/g	Total PAHs/PEC	Total PCBs ng/g	Total PCBs/PEC	PEC-Q Mean-MPP (or)
Edgbaston Pool	1.72	4373	0.19	2.93	0.004	0.96
Chapman's Pond	0.41	1077	0.05	2.76	0.004	0.23
Marton Mere	0.39	3941	0.17	6.53	0.010	0.28
Fleet Pond	0.73	8198	0.36	3.00	0.004	0.55
Slapton Ley	0.25	997	0.04	5.67	0.008	0.15
Holt Hall Lake	0.72	703	0.03	2.14	0.003	0.38
Wake Valley Pond	1.73	1503	0.07	6.20	0.009	0.90
Thoresby Lake	0.62	1341	0.06	8.85	0.013	0.34
Crag Lough	0.26	438	0.02	1.42	0.002	0.14

Table 6.4 – PEC-Q Mean-metals and PEC-Q Mean-MPP (or) for the nine OPAL lakes. Total concentrations of PAHs and PCBs are also presented, together with toxicity quotients for each at every site.

Comparison of PEC-Q Mean-metals and total PAHs/PEC showed that the former was the main contributor to PEC-Q Mean-MPP (or). This meant that although both metals and PAHs were of concern, metals were the most important. The PAHs that contributed most to the value of total PAHs/PEC were fluoranthene, pyrene, chrysene, benzo[b]fluoranthene and benzo[a]pyrene. MacDonald et al (2000) stated that a mean PEC quotient of 0.5 could be used as a useful threshold to accurately classify sediment samples as both toxic and not toxic. In this study, the lakes with PEC-Q Mean-metals values greater than 0.5 were Edgbaston Pool, Fleet Pond, Holt Hall Pond, Wake Valley Pond and Thoresby Lake. The same five lakes also had the highest PEC-Q Mean-MPP (or) values (all > 0.34). The PEC-Q values indicated that these five lakes had the potential for toxicity in the sediment.

Site	Replicate 1	2	3	4	5	Survival (%)	Growth AFDW (mg)
REFERENCE SEDIMENT	9N, 1NF	8N, 2NF	6N, 4NF	11N	7N, 3NF	80	1.120
Edgbaston Pool	7N, 3NF	10N	11N	12N	8N, 2NF	91	0.696 ***
Chapman's Pond	9N, 1NF	8N, 2P	10N	10N	10N	98	1.310
Marton Mere	11N	8N, 2NF	10N	12N	11N	96	0.893 ***
Fleet Pond	9N, 1NF	8N, 2NF	8N, 2NF	10N	10N	90	1.010
Slapton Ley	10N	8N, 2NF	9N 1NF	9N, 1NF	7N, 3NF	86	0.624 ***
Holt Hall Lake	11N	6N, 4NF	8N, 2NF	10NF	8N, 2NF	65	0.501 ***
Wake Valley Pond	7N, 3NF	11N	8N, 2NF	7N, 3NF	10N	84	1.220
Thoresby Lake	9N, 1NF	10NF	10NF	9N, 1NF	10N	56**	0.924 ***
Crag Lough	10NF	10NF	10NF	10N	5N, 5NF	30 *	0.700 ***

P = Pupae; N = Normal Larvae; NF = Not Found

* A statistically significant reduction in percent survival as compared to the control mean percent survival (Dunnett's and Fisher's Exact test; $p < 0.05$)

** A statistically significant reduction in percent survival as compared to the control mean percent survival (Fisher's Exact test only; $p < 0.05$)

*** A statistically significant reduction in ash-free dry weight as compared to the control mean ash-free dry weight (Dunnett's test; $p < 0.05$)

Table 6.5 – Survival and growth of *Chironomus riparius* in a 10-day sediment toxicity test in the surficial (0-5 cm) sediment of the nine OPAL lakes

Site	Survival (%)	Mean reproduction (no. young/adult)
REFERENCE SEDIMENT	100	19.5
Edgbaston Pool	90	11.0 **
Chapman's Pond	100	14.5
Marton Mere	90	11.3 **
Fleet Pond	100	14.4 **
Slapton Ley	100	10.8 **
Holt Hall Lake	80	8.6 **
Wake Valley Pond	90	8.8 **
Thoresby Lake	80	9.6 **
Crag Lough	40 *	6.1 **

* A statistically significant reduction in percent survival as compared to the control mean percent survival (Dunnett's and Fisher's Exact test; $p < 0.05$)

** A statistically significant reduction in young per adult as compared to the control mean young per adult (Dunnett's test; $p < 0.05$)

Table 6.6 – Survival and reproduction of *Daphnia magna* in a 7-day sediment toxicity test in the surficial (0-5 cm) sediment of the nine OPAL lakes

In the sediment toxicity tests that were completed on the nine lake sediment samples, the survival in the reference sediment was 80% in the chironomid toxicity test and 100% in the cladoceran toxicity test (Tables 6.5 and 6.6). In the chironomid toxicity test, survival was significantly different ($p < 0.05$) to the reference sediment in Crag Lough and Thoresby Lake (Table 6.5) which suggested that there was toxicity in the sediments of those two lakes. The chironomid growth results supported this, but in addition showed evidence for toxicity in a number of the other lakes. Growth was statistically different ($p < 0.05$) to the reference sediment at Edgbaston Pool, Marton Mere, Slapton Ley and Holt Hall Lake, as well as at Crag Lough and Thoresby Lake (Table 6.5).

However, the sediments were not sieved as a precaution against changing the sediment characteristics. Therefore, organisms other than *C. riparius* were found in several of the site sediment test chambers at test termination. In replicates 1-3 of the Crag Lough site sample, chironomidae larvae of a predatory species (*Ablabesymia* sp.) were present. These larvae may have adversely affected the overall survival of the *C. riparius* larvae in these test chambers. Oligochaete worms were found in replicates 2-4 of the Thoresby Lake sediments. Although unlikely to be predatory, they may have adversely affected *C. riparius* survival if they competed for space in the test chambers. The presence of other organisms in the sediments of Crag Lough and Thoresby Lake may therefore have contributed to the lower rates of survival of *C. riparius* in those sediments in comparison to the reference sediment. This will be taken into account when interpreting the survival data.

Temperature was maintained between 19.2 and 20.9 °C during the test, which was within the acceptable limits. Dissolved oxygen ranged from 2.6 to 8.6 mg/L. Whenever the dissolved oxygen values fell below 4.2 mg/L, the water delivery cycle rates were increased and the system was checked to make sure each test chamber received the renewal water. Although the dissolved oxygen in some instances was below 4.2 mg/L for the Chapman's Pond, Edgbaston Pool and Thoresby Lake sediment replicates, survival did not appear to be impacted by the low dissolved oxygen values. Sample pH values ranged from 7.7 to 8.2 and total ammonia values ranged from 0.25 to 1.0 ppm. Conductivity, total alkalinity and total hardness values ranged from 358 to 438 μS , 122 to 196 mg CaCO_3/L and 148 to 200 mg CaCO_3/L respectively. All other water quality parameters were within acceptable limits for maintenance of healthy *C. riparius* populations.

In the cladoceran test, survival was significantly different ($p < 0.05$) to the reference sediment in Crag Lough (Table 6.6), which suggested that there was toxicity in the sediments at this site. Reproduction was significantly different ($p < 0.05$) at all sites except

Chapman's Pond (Table 6.6), suggesting that toxicity was present in the sediments at the majority of the lakes. The temperature was maintained between 24.1 and 25.1 °C during the test which was within the acceptable limits. Dissolved oxygen concentration ranged from 6.1 to 8.0 mg/L and pH between 7.8 and 8.7. All water quality parameters were within the acceptable limits for maintenance of healthy *Daphnia magna* populations.

	<i>C. riparius</i>		<i>D. magna</i>	
	Survival	Growth	Survival	Reproduction
Edgbaston Pool		*		*
Chapman's Pond				
Marton Mere		*		*
Fleet Pond				*
Slapton Ley		*		*
Holt Hall Lake		*		*
Wake Valley Pond				*
Thoresby Lake	*	*		*
Crag Lough	*	*	*	*

* Test where there was evidence for toxicity in the lake sediment

Table 6.7 – Summary of sediment toxicity test results showing the lakes at which evidence for toxicity was found

Evidence for toxicity in the nine OPAL lake sediments from the chironomid and cladoceran sediment toxicity tests is summarised in Table 6.7. The results from the chironomid sediment toxicity test provided evidence for toxicity in all of the sites excluding Chapman's Pond, Fleet Pond and Wake Valley Pond. The results from the cladoceran test supported this for all sites, and in addition found evidence for toxicity at Fleet Pond and Wake Valley Pond. The possibility of adverse affects on the survival and growth of *C. riparius* due to competing organisms in the sediments of Crag Lough and Thoresby Lake was discounted as toxicity was also found in both lakes in the cladoceran test. In summary, all of the OPAL sites showed evidence for toxicity with the exception of Chapman's Pond.

6.4. Discussion

6.4.1. Mean PEC quotients and toxicity

The proposal that a mean PEC quotient of 0.5 could be used as a useful threshold to accurately classify sediment samples as both toxic and not toxic (MacDonald et al, 2000) was supported by a study which analysed sediment toxicity data from 92 published reports from North America. It was found that three different types of freshwater sediment toxicity test (10- to 14-day *Hyalella azteca*; 28- to 42-day *Hyalella azteca*; 10- to 14-day *Chironomus tentans* or *C. riparius*) all showed a consistent increase in toxicity at a PEC-Q value above 0.5, for any form of the quotient (Ingersoll et al, 2001). The study showed that for the 10- to 14- day chironomid tests, the incidence of toxicity increased from 23% to 25% to 39% at

PEC-Q Mean-metals values of between 0.1 - < 0.5, 0.5 - < 1.0 and 1.0 – 5.0 respectively (Table 6.8). The incidence of toxicity for PEC-Q Mean-MPP (or) increased from 17% to 43% at values of between 0.1 - < 0.5 and 0.5 - < 1.0 respectively (Table 6.8). Rippey et al (2008) compared the data from UK lakes with that provided by Ingersoll et al (2001) (Table 6.8). Agreement between the two studies was found to be good, although the smaller sample sizes used in the Rippey et al (2008) paper may have contributed to some of the differences in value.

	PEC-Q Mean-metals			PEC-Q Mean-MPP (or)	
	0.1 - < 0.5	0.5 - < 1.0	1.0 - 5.0	0.1 - < 0.5	0.5 - < 1.0
Ingersoll et al, 2001	23%	25%	39%	17%	43%
Rippey et al, 2008	33%	50%		28.60%	100%
This study	75%	66%	50%	83%	33%

Table 6.8 – Incidence of toxicity in 10- to 14- day chironomid toxicity tests from studies by Ingersoll et al (2001) and Rippey et al (2008), in comparison with incidences of toxicity found in this study

The OPAL sites with PEC-Q's of greater than 0.5 were Edgbaston Pool, Fleet Pond, Holt Hall Lake, Wake Valley Pond and Thoresby Lake for Mean-metals, and Edgbaston Pool, Fleet Pond and Wake Valley Pond for Mean-MPP (or). However, all of the sites with the exception of Chapman's Pond showed evidence for toxicity in the toxicity tests. In addition, the incidences of toxicity for PEC-Q Mean-metals and PEC-Q Mean-MPP (or) for the OPAL sites did not increase with PEC-Q value (Table 6.4), instead the highest incidences of toxicity occurred when the mean PEC-Q was between 0.1 - < 0.5. The incidence of toxicity for PEC-Qs of both types was higher for the OPAL lakes than for the two previous studies, with the exception of PEC-Q Mean-MPP (or) 0.5 - < 1.0 which was lower. Incidence percentages were closer in value to those from Rippey et al (2008) than those from Ingersoll et al (2001).

The results from the OPAL sites highlight the complex relationship between the concentration of chemicals in lake sediment samples and laboratory toxicity. Dave (1992a) studied the sediment toxicity of a number of lakes along the river Kolbäckån in central Sweden. One of these, Lake Haggan, was not heavily contaminated with metals, but its whole sediment toxicity was high and the bottom fauna was extremely poor. Two lakes situated adjacently to one another, Lake Väsman and Lake Övre Hillen, both showed similar levels of metal pollution and similar bottom fauna. Whole sediment toxicity, however, was much higher at the latter site than the former. A high incidence of toxicity at low PEC-Q levels could be caused by other contaminants not included in the study (Ingersoll et al, 2001). SQG quotients only take into account the substances included in the calculations. Often sediment quality guidelines are not available for many substances that are measured

in the samples, even though some substances may have occurred at concentrations above toxicological thresholds (Long et al, 1998). The presence of unmeasured substances may also contribute to toxicity (Long & MacDonald, 1998). A recent study by Di Veroli et al (2012) examined the effect of metal mixtures on mouthpart deformities of *C. riparius*. The results showed that a higher incidence of deformities occurred than had been predicted by the measured metal concentrations. It was proposed that the natural sediments contained other toxic compounds which contributed to the deformities incidence. Analysis of only a select number of chemicals led to an underestimation of the potential toxicity of the sediments.

The toxicity of sediments is also a function of many factors in addition to the concentration of chemicals. These include the bioavailability of sediment associated chemicals, chemical form or speciation (Long & MacDonald, 1998) and differences in sediment characteristics (Dave, 1992b). Changes in water chemistry (pH, major ions and organic matter) can also affect both metal accumulation and toxicity (Borgmann et al, 2001). Empirical SQGs such as those used in this study are based on total sediment concentrations and therefore do not address the issue of bioavailability. The bioavailability of sediment contaminants is influenced by a wide variety of factors that are not considered in empirical SQGs, such as particle surface area and size, hardness, type of organic matter, pH, redox gradients, chemical time-of-contact (spatial and temporal dynamics), pore water convection, resuspension and deposition (flux), organism acclimation, ingestion, and bioturbation (Burton Jr., 2002). Consequently, although the guidelines provide a basis with which to assess the potential toxicity of sediments, they do not take into account other factors that will also affect toxicity. Therefore high metal concentrations do not necessarily lead to high toxicity or negative effects on biota (Dave, 1992a).

In addition to the limitations of mean sediment quality guideline quotients outlined above, the type and number of toxicity tests that are used to assess toxicity are important. Longer-term tests that measure growth are more sensitive than shorter term tests. The study by Ingersoll et al (2001) which compared the results of 10- to 14-day *Hyalella azteca*; 28- to 42-day *Hyalella azteca* and 10- to 14-day *Chironomus tentans* or *C. riparius* tests showed that the duration of exposure influenced the sensitivity of the tests. In the 10- to 14- day *Hyalella azteca* test a mean quotient of 3.4 resulted in a 50% incidence of toxicity when survival and growth were used to classify a sample as toxic. Similarly, in the 10- to 14- day *C. tentans* or *C. riparius* test a mean quotient of 3.5 resulted in a 50% incidence of toxicity when survival or growth were used to classify a sample as toxic. In contrast, a 50% incidence of toxicity in the 28- to 42- day *Hyalella azteca* test corresponded to a mean quotient of 0.63 when survival or growth were used to classify a sample as toxic. Therefore, the same incidence of toxicity occurred at a much lower mean toxicity quotient in the longer term test, which means

that higher incidences of toxicity may occur at lower mean toxicity quotients if the tests that are used are carried out over a long enough period of time. In addition, pore water assays have been found to overestimate the toxicity of the more soluble compounds in sediments like metals and ammonia compared to the relatively less soluble organic compounds (Lahr et al, 2003).

The number of tests used to identify toxicity is also important. Lahr et al (2003) carried out standard bioassays on a wide range of organisms, including the bacterium *Vibrio fischeri*, the rotifer *Brachionus calyciflorus*, the anostracan *Thamnocephalus platyurus*, the water flea *Daphnia magna* and the midge larvae *Chironomus riparius*, in addition to some novel bioassays. The intention of the study was to identify the cause of toxicity in sediments taken from various locations in the Netherlands. Routine chemical analyses of priority substances classed the sediments into different pollution classes. None of the results from single bioassay tests seem to correlate in a general way with the pollution classes. However, when the whole test battery was regarded, it was found that the most heavily polluted sediments caused moderate-to-strong effects in one or more bioassays. Lahr et al (2003) concluded that the simultaneous execution of several bioassays increased the chance to demonstrate toxic effects of polluted sediments or their pore water. Based upon the studies of Burton Jr. et al (1996), and subsequently utilised by Rippey et al (2008), it has been recommended that sediment toxicity tests that cover two assays and endpoints from two of the four major toxic response patterns will capture any toxicity in freshwater sediments. Two sediment toxicity tests were completed in the present study and four endpoints were involved (chironomid growth and survival, daphnid reproduction and survival). Therefore the criteria for toxicity were met.

Sediments with high mean PEC-Qs which show evidence for toxicity in laboratory bioassays may indicate the potential for biological effects at a site, but in reality this may not be the case. Toxicity testing can demonstrate whether sediments are toxic, but laboratory conditions are rarely identical to exposure conditions in the field (Borgmann et al, 2001). The status of benthic communities may also reflect other factors, such as habitat alteration, in addition to the effects of contaminants (Ingersoll et al, 2001). Rippey et al (2008) compared their data with biological results from the literature in order to evaluate the significance of the chemical and laboratory toxicity results. Their findings indicated that there were likely to be biological effects in freshwater sediment if PEC-Q Mean-metals was greater than 2. None of the PEC-Q Mean-metals for the OPAL lake sediments exceeded this number (the highest was 1.73 at Wake Valley Pond) which suggested that the risk of biological effects in the surface sediments of the lakes from deposition of trace metals may not be high, despite the prevalence of laboratory toxicity in the samples. A similar conclusion was made about the

other UK lake sediments studied by Rippey et al (2008), for which the highest PEC-Q Mean-metals was 1.08.

6.4.2. Metal number and mean PEC quotients

In a study of chemical and laboratory bioassay data from estuaries along the Atlantic, Pacific and Gulf of Mexico coasts, Long et al (1998) found that the probability of observing toxicity was a function of both the number of sediment quality guidelines exceeded and the degree to which they were exceeded. This meant that the more chemicals that were incorporated into the calculations the more likely that a greater number of thresholds would be exceeded and consequently the likelihood a sample would be found to be toxic. Sediment quality guidelines were not available for many substances that were measured in the samples, which meant that they could not be included in the calculations. In addition, other substances that were not measured probably occurred in many or all of the samples. The suggestion is that the greater the number of chemicals which could be included in the calculation of mean toxicity quotients, the more likely the potential toxicity of the sediment will be captured.

However, such a wide range of data is not commonly available. Therefore, the number and type of chemicals incorporated into the calculations of mean PEC-Qs has varied widely between studies, depending on what information is available. For example, Ingersoll et al (2001) used seven metals (As, Cd, Cr, Cu, Pb, Ni and Zn), as many of up to 13 PAH compounds for which data was reported, and between 21 and 87 PCB congeners to calculate mean PEC-Qs. Rippey et al (2008) also used seven metals, although the combination was slightly different, with Hg replacing Cr, 15 PAHs and only seven PCBs. Other studies have included different chemicals, such as Crane et al (2002) who used eight metals (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn), 13 PAHs and 10 organochlorine pesticides, or Lahr et al (2003) who used eight metals (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn), 16 PAHs, 'various' organochlorine pesticides, two chlorobenzenes, seven PCBs, mineral oil content and extractable organic halogenated hydrocarbons.

The normalisation step in the calculation of mean PEC-Qs (dividing the summed toxicity quotients of each substance by the number of substances) is conducted to provide comparable indices of contamination among samples for which different numbers of chemical substances were analysed (MacDonald et al, 2000). The process gives equal weighting to all PECs. However, Ingersoll et al (2001) suggested that the different patterns of toxicity observed from calculating quotients by different methods (e.g. PEC-Qs Mean-metals; PEC-Q Mean-MPP (and); PEC-Q Mean-MPP (or)) might be due to the number and

type of samples used to make the comparisons. To determine the influence of sample number and type on the observed incidence of toxicity, quotients were calculated for a subset of samples: (1) using up to 10 PECs, (2) using up to 9 PECs and (3) using metals alone, PAHs alone, or PCBs alone. The results indicated that the incidence of toxicity was similar for all subsets, and that therefore different patterns in toxicity were the result of unique chemical signals associated with individual contaminants in samples, rather than the type and number of samples used to make these comparisons.

The focus of this study is on the contribution of metals to toxicity in sediments. The range of metals used in the calculation of PEC-Qs varies widely, and has included combinations of the following metals and other elements: Ni, Cu, Zn, As, Cd, Pb, Hg, Cr, Fe, Se, Co and Mn (MacDonald et al, 2000; Ingersoll et al, 2001; Crane et al, 2002; Lahr et al, 2003; Ingersoll et al, 2009; Yu et al, 2011; McNett & Hunt, 2011; Costa et al, 2012). Although studies like that of Ingersoll et al (2001) have addressed the issue of the effects of including different types of chemicals in mean PEC-Qs, little specific attention has been paid to the effect of using different types and numbers of metals in the calculation of PEC-Q Mean-metals.

The OPAL surface sediments were only analysed for Ni, Cu, Zn, Cd, Pb and Hg. Figure 6.1 shows the PEC-Q Mean-metals value at each of the OPAL sites with each metal excluded in turn. Changes to the mean PEC-Q at each site on the exclusion of different metals were generally within the boundaries of standard error (Figure 6.1). However, at each site the exclusion of one or two metals in particular resulted in a larger change in value. At Edgbaston Pond, the removal of Pb resulted in a fall in value from 1.72 to 1.22. The same decline on the exclusion of Pb occurred at Chapman's Pond (0.41 to 0.33) and Holt Hall Lake (0.72 to 0.45). At Marton Mere, there was a fall in PEC-Q Mean-metals on the exclusion of both Pb and Ni (0.39 to 0.34 and 0.32 respectively), and a similar pattern occurred at Slapton Ley (0.25 to 0.22 and 0.21 respectively). At Fleet Pond, the exclusion of Pb and Zn resulted in a decline in PEC-Q Mean-metals (0.73 to 0.64 and 0.68 respectively). At Wake Valley Pond there was a large drop in PEC-Q Mean-metals when Cu was excluded from the calculation (from 1.73 to 1.05) and at Crag Lough there was a decline when Ni was removed from the equation (from 0.26 to 0.22). There was no distinguishable change on the exclusion of any metals at Thoresby Lake.

The largest changes in PEC-Q Mean-metals occurred when the metals with large individual toxicity quotients were excluded. This reflected the fact that some metals exceeded the PEC to a greater extent at some sites than others, and therefore had a particularly big influence on toxicity. As Long et al (2006) state, "the mean SQGQ approach allows the analyst to

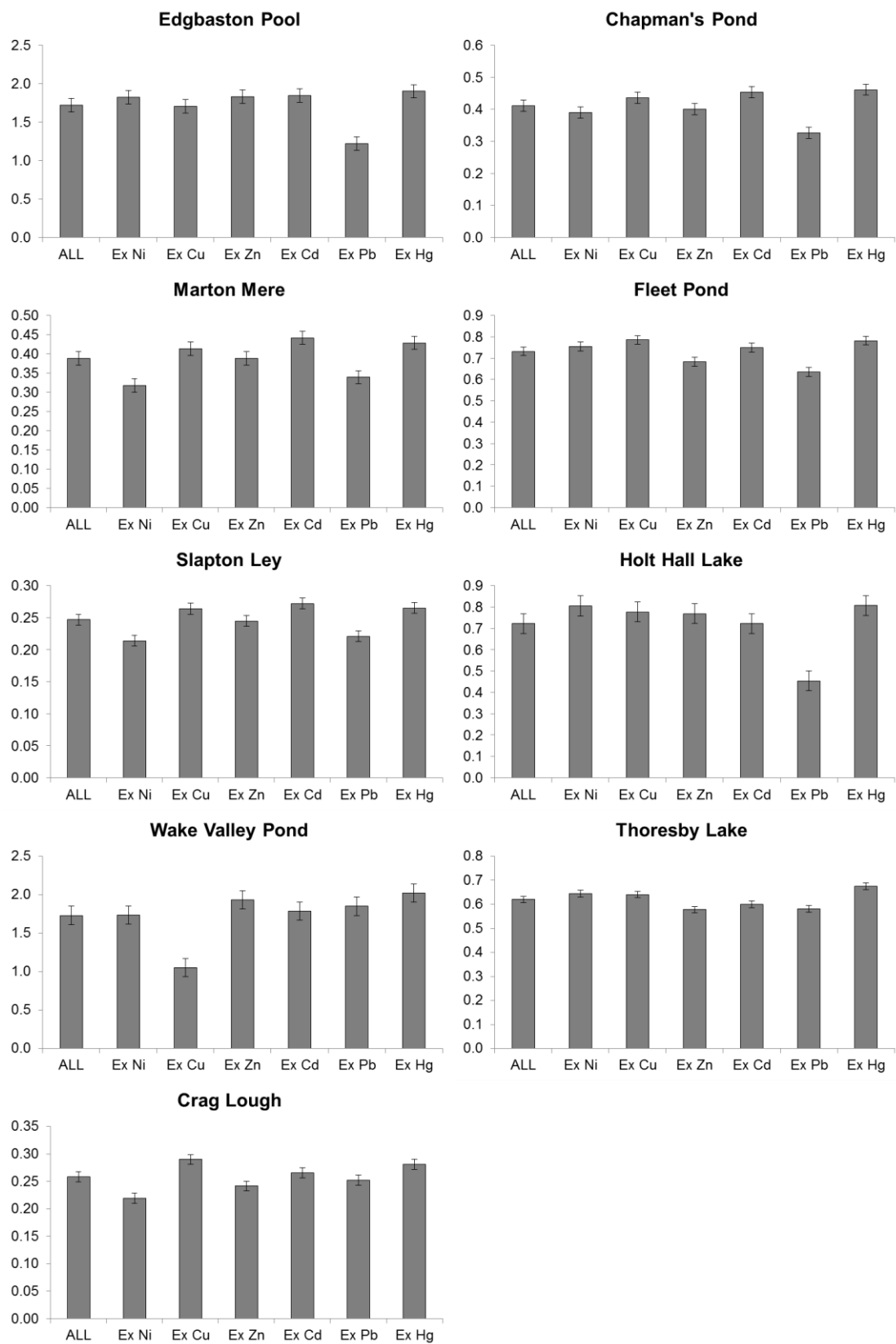


Figure 6.1 – PEC-Q Mean-metals for each of the nine OPAL sites for all metals (Ni, Cu, Zn, Cd, Pb and Hg) analysed (ALL), and then with each metal excluded from the calculation in turn (Ex Ni, Ex Cu, Ex Zn, Ex Cd, Ex Pb, Ex Hg). Standard error bars are also shown.

account for not just the presence of the chemical at a concentration greater than the SQG, but also, the magnitude by which the SQG is exceeded in the sample” i.e. metals with higher exceedances of PECs will contribute more to mean SQGQ. The main implication of this is that if the key drivers of toxicity at each of the sites had been left out of the PEC-Q Mean-metals calculation, an underestimation of the potential toxicity of the sediments would have occurred. Therefore, at each site it is important that a range of metals are included to ensure that the fullest interpretation of potential toxicity can be made. MacDonald et al (2000) showed that As, Cd, Cr, Cu, Pb, Ni and Zn were ‘reliable’ predictors of TEC and PEC, whilst insufficient data were available to evaluate the PECs for Hg. Consequently, Hg was excluded from subsequent calculations of mean toxicity quotients. However, other studies have included Hg in calculations regardless of its reliability (e.g. Rippey et al, 2008; Costa et al, 2012). With regard to the OPAL sites, the influence of Hg upon the toxicity quotients is small in comparison with that of Pb, Ni, Zn and Cu. Therefore, whether it is included or not should make little difference, which is important for the next part of the discussion.

6.4.3. Sediment cores and toxicity

Long & MacDonald (1998) described the use of SQGs in the interpretation of historical data. Data from age-dated sediment cores or time-series sampling can be used to identify temporal trends in sediment quality by comparing chemical concentrations with SQGs. However, few studies have actually used metals data from cores for this purpose, with most focusing on the toxicity of surface sediments. Borgmann et al (2001) studied cores from 12 lakes around Sudbury in Ontario, Canada, to assess the temporal changes in metal concentrations at the sites. Surface sediments were also taken to study the toxicity of metals on benthic community composition in the area. However, little was made of the relationship between the two – the core data was primarily used to identify the sources of contamination to the area. In their 2006 review of mean SQGQs, Long et al highlighted the fact that further research was needed to increase understanding of the effects of natural sedimentological factors such as depth versus anthropogenic chemicals in causing or contributing to the impairment of resident benthos.

Following on from this, Ingersoll et al (2009) completed a study of toxicity in sediment cores from the Ashtabula River in Northeastern Ohio, USA. The purpose of the study was to support an assessment of historic contamination to surface sediments and biota associated with discharges of oil or other hazardous substances in the area since the 1940s. PEC-Q Mean-metals was calculated using Cd, Cu, Pb, Ni and Zn, and toxicity of sediment samples was analysed using a 28-day *Hyalella azteca* survival and growth test. Concentrations of metals were found to be correlated with toxicity and may therefore have contributed to the toxicity of the sediments. However, the concentrations weren’t high enough (none of the

samples exceeded the PEC apart from Zn) to have solely caused the reduced survival and growth of the amphipods.

Toxicity quotients were calculated for the sediment core data from the OPAL sites. PEC-Q Mean-metals was also determined for each of the cores (Figure 6.4). Cadmium had not been analysed in the cores. Based on the evidence found in the study of metal combinations in the surface sediments, Cd was replaced in the calculation by As, to ensure as many metals as possible were included. Mercury was removed from the PEC-Q Mean-metal calculation for the surface sediment. The toxicity quotients in the surface sediments (top 5 cm) and the averages from the top 5 cm in each of the cores were compared (Figure 6.2). The relationship between mean PEC-Qs of the surface sediments and the core sediments was examined. This was to determine if PEC-Qs were similar in the different types of sediments. No toxicity tests had been carried out on the core data and therefore it was necessary to find out if the data in the cores and surface sediments might be comparable in order to be able to make certain assumptions about toxicity within the cores.

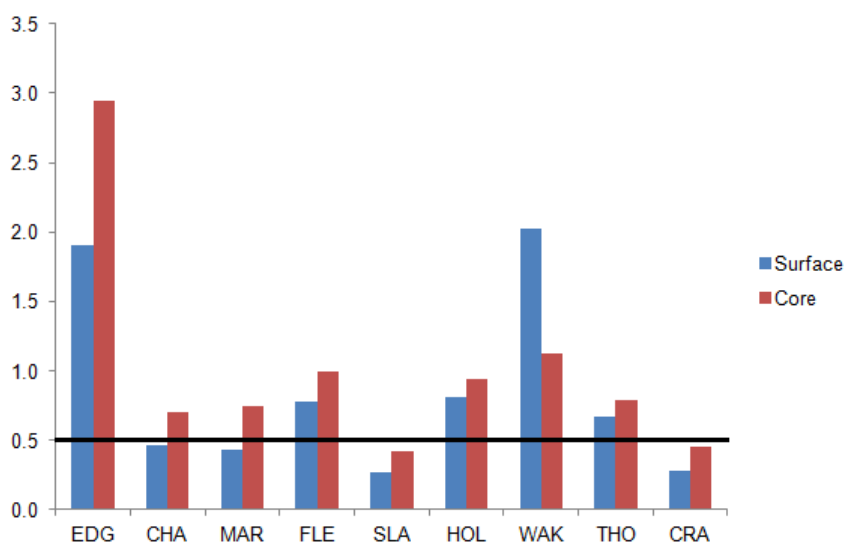


Figure 6.2 – Comparison of PEC-Q Mean-metals of surface sediment samples (0-5 cm) and the top 5 cm of each core at each OPAL site – Edgbaston Pool (EDG), Chapman’s Pond (CHA), Marton Mere (MAR), Fleet Pond (FLE), Slapton Ley (SLA), Holt Hall Lake (HOL), Wake Valley Pond (WAK), Thoresby Lake (THO) and Crag Lough (CRA). The potential toxicity threshold value of 0.5 proposed as the inflection point between toxic and not toxic (MacDonald et al, 2000) is shown as the black line.

The results showed that at all sites, apart from Wake Valley Pond, PEC-Q Mean-metals was greater in the core sediments than in the surface sediment samples. The concentrations recorded in the core sediments were higher than those in the surface sediments and

therefore contributed more to the PEC-Q value. The metal concentrations in the surface sediments of Wake Valley Pond were considerably higher than those in the core, particularly for Cu which had a concentration of $763 \mu\text{g g}^{-1}$. It was conjectured that this may have been an anomalous result. However, on removal of Cu from the PEC-Q calculation, the mean PEC-Q was still greater in the surface sediments (Figure 6.3).

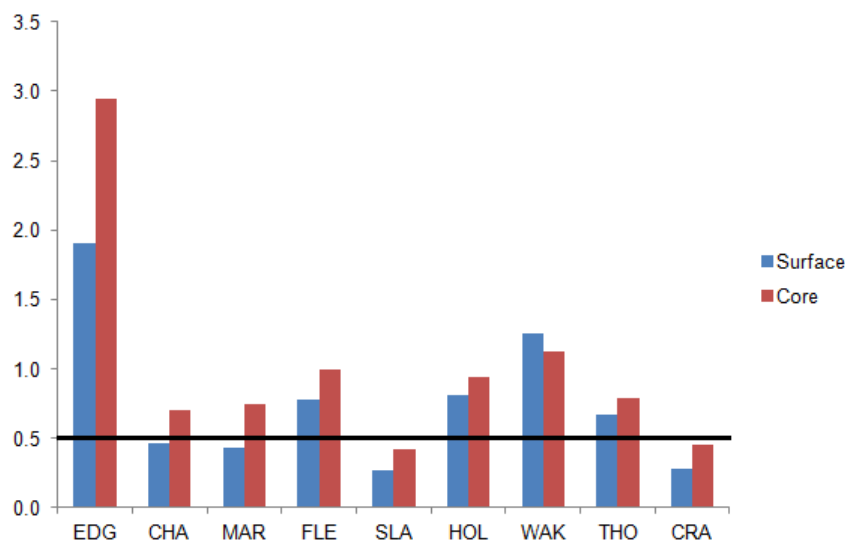


Figure 6.3 – Comparison of PEC-Q Mean-metals of surface sediment samples and the top 5 cm of each core at each OPAL site site – Edgbaston Pool (EDG), Chapman’s Pond (CHA), Marton Mere (MAR), Fleet Pond (FLE), Slapton Ley (SLA), Holt Hall Lake (HOL), Wake Valley Pond (WAK), Thoresby Lake (THO) and Crag Lough (CRA). PEC-Q Mean-metals for Wake Valley Pond was calculated without Cu as the concentration was unexpectedly high. However, the mean PEC-Q was still greater for the surface sediments than the core sediments at this site. The potential toxicity threshold value of 0.5 proposed as the inflection point between toxic and not toxic (MacDonald et al, 2000) is shown as the black line.

The difference in concentration and potential toxicity between surface sediments and the tops of the cores could be explained by a number of factors. The results in Section 5.4 showed that the concentration of metals in sediment cores had been found to be greater than those in sediment trap material. This was attributed to both resuspension of sediments and sediment focusing. The same arguments could be made for the differences in concentration between the surface sediment samples and the core samples. The surface sediments were taken from seven different locations in each lake, which meant that they were sourced from a wider area. They were therefore less likely to have been affected by sediment focusing (unlike the cores). A study by Dave (1992b) showed that the toxicity of sediments from a number of Swedish lakes increased after the sediments had been stored. Although the sediments in the study were taken from the surface of the lakes, the explanations for the change may well also apply to core sediments. One interpretation was that toxicants which had accumulated in the pore water of the sediment were slowly

released over time and that therefore increased toxicity found for some of the sediments upon storage simply reflected the potential toxicity of the actual sediment. Continuous deposition of sediment in the natural environment and bioturbation from sediment dwelling organisms could also affect concentrations in the surficial sediment. Dave (1992b) proposed that sediments having an increased toxicity after storage may have a greater potential toxicity, which has implications for the potential hazards caused by the disturbance of deeper, toxic sediments.

The PEC-Q Mean-metals for the surficial sediments from the OPAL lakes suggested that Chapman's Pond, Marton Mere, Slapton Ley and Crag Lough were unlikely to be toxic. However, all of the surficial sediments from the OPAL lakes were found to have toxicity apart from Chapman's Pond. This showed that the combination of chemicals found in the sediments (in addition to the metals and POPs that were analysed) was toxic and that PEC-Q Mean-metals underestimated the potential toxicity of the sediments. Therefore, sediments with a PEC-Q Mean-metals value of less than 0.5 may still be toxic to benthic organisms. PEC-Q Mean-metals in the cores of Chapman's Pond and Marton Mere were greater than the 0.5 threshold proposed as the inflection point between toxic and not toxic (MacDonald et al, 2000), although Slapton Ley and Crag Lough were still lower (Figure 6.4). Toxicity tests on the core sediments would be required to confirm if the higher PEC-Q values were reflected in the toxicity of the sediments, but the high incidence of toxicity at lower mean PEC-Qs in the surface sediments would suggest that it was likely.

In many cases the PEC-Q Mean-metals calculated for the deeper sediments in the OPAL cores were greater than those in the top 5 cm (Figure 6.4). Mean PEC-Qs for Edgbaston Pool, Chapman's Pond, Marton Mere, Fleet Pond, Holt Hall Lake, Wake Valley Pond and Thoresby Lake were all greater in the past, although the dates at which this occurred varied between each site. Slapton Ley is the only site in which PEC-Q Mean-metals remained lower than 0.5 over the whole core, from the late 19th century to the present day. Potential toxicity at Crag Lough was also below a mean PEC-Q of 0.5 for much of the core, apart from a peak in the 1950/60s.

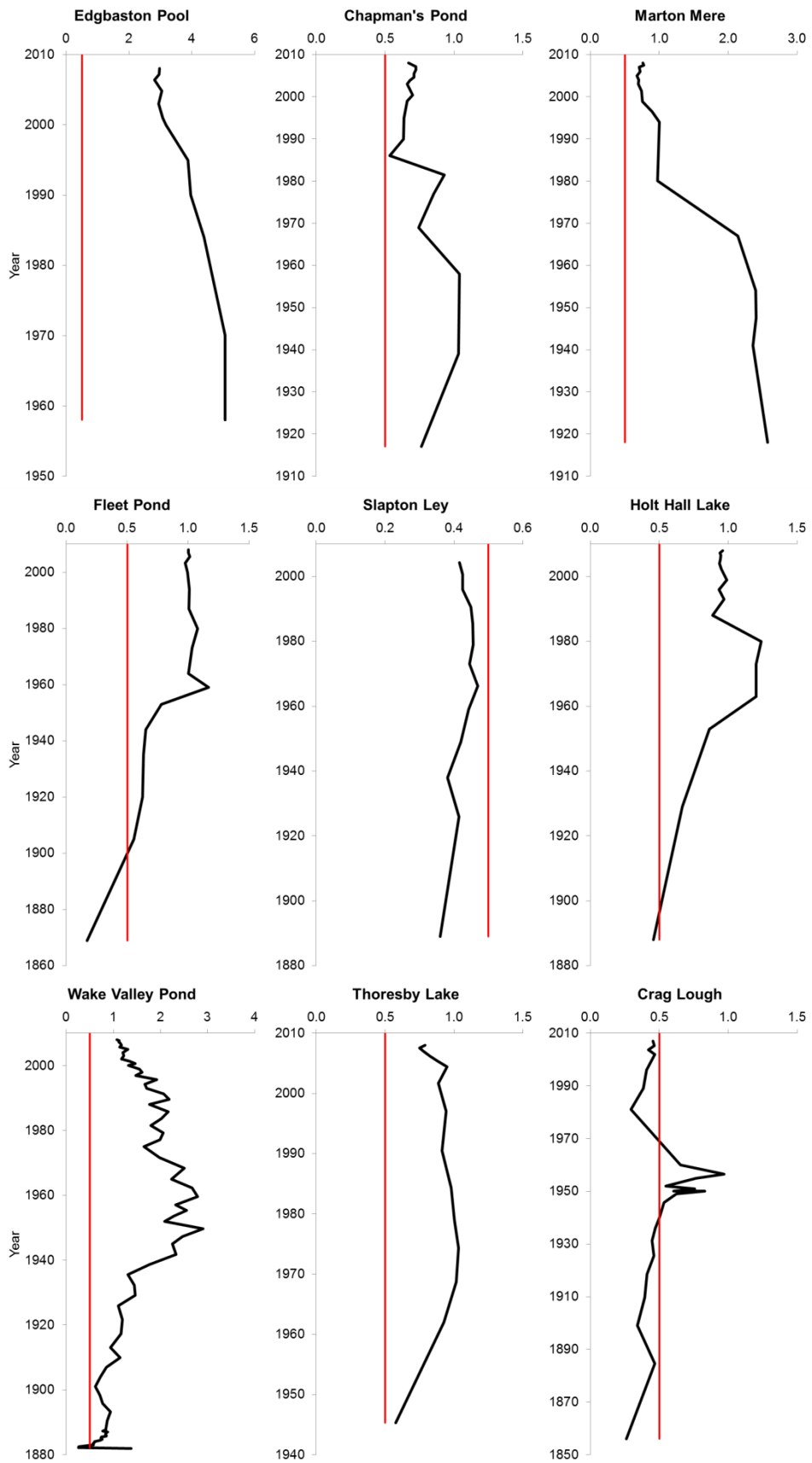


Figure 6.4 – PEC-Q Mean-metals reconstructed for the cores from the OPAL lakes (black lines) plotted against sediment age. The red lines show the mean PEC-Q value of 0.5 proposed by MacDonald et al (2000) to distinguish between not toxic and toxic sediments.

The high PEC-Q Mean-metals values calculated for most of the cores, combined with the knowledge that surface sediments with lower PEC-Q Mean-metals values were found to be toxic at all but one of the sites, suggests that historically the sediments at these lakes have been contaminated to such a high level that toxicity will have occurred. In addition, PEC-Q Mean-metals were above 2 for the whole of the core from Edgbaston Pool, and for part of the cores from Marton Mere and Wake Valley Pond. This indicates that biological effects in the sediments will have occurred at various points in the past at these sites, and are likely to be occurring at present at Edgbaston Pool. It also means that there is a store of contaminated, toxic sediment which could cause further damage if disturbed.

The calculation of toxicity quotients and PEC-Q Mean-metals was also applied to the London lake cores (Figure 6.5). The results of the individual toxicity quotients clearly showed the degree of influence that different metals had on the calculation of mean PEC-Q. At South Norwood Lake, Wimbledon Park Lake, Hampstead No. 1 Pond and Vale of Health Pond, Pb was by far the biggest contributor. The potential toxicity of Pb was also great at Stock Pond and the Highgate Ladies Bathing Pond, although Ni was also important at these sites. The concentration of Ni contributed most to the PEC-Q value at Wake Valley Pond, a consequence of the very high levels of Ni recorded at the site, which was discussed in Chapter 4. The large contribution of Pb to mean PEC-Q reflected the fact that Pb concentrations exceeded the PEC at all sites, apart from at the very base of some cores (see Section 4.4). The toxicity quotients for Pb calculated for the OPAL surface sediments showed that it was also an important contributor to potential toxicity in those lakes. The toxicity quotients calculated for the ten UK lakes in the study by Rippey et al (2008) showed that the metals that contributed most to the value of PEC-Q Mean-metals were Pb, Ni and As, with Pb being the most important. Lead is clearly an important metal pollutant in the UK, and as highlighted in Chapter 5, this has implications for the health of lake ecosystems.

The core profiles of PEC-Q Mean-metals for each of the London lakes are shown in comparison to the 0.5 threshold of toxicity proposed by MacDonald et al (2000) in Figure 6.6. At all of the sites, PEC-Q Mean-metals was greater than 0.5 for the whole period that the cores covered, apart from at the very bottom of the cores from Wake Valley Pond and South Norwood Lake. The average PEC-Q Mean-metals for each of the London lake and OPAL cores as a whole is shown in Table 6.9.

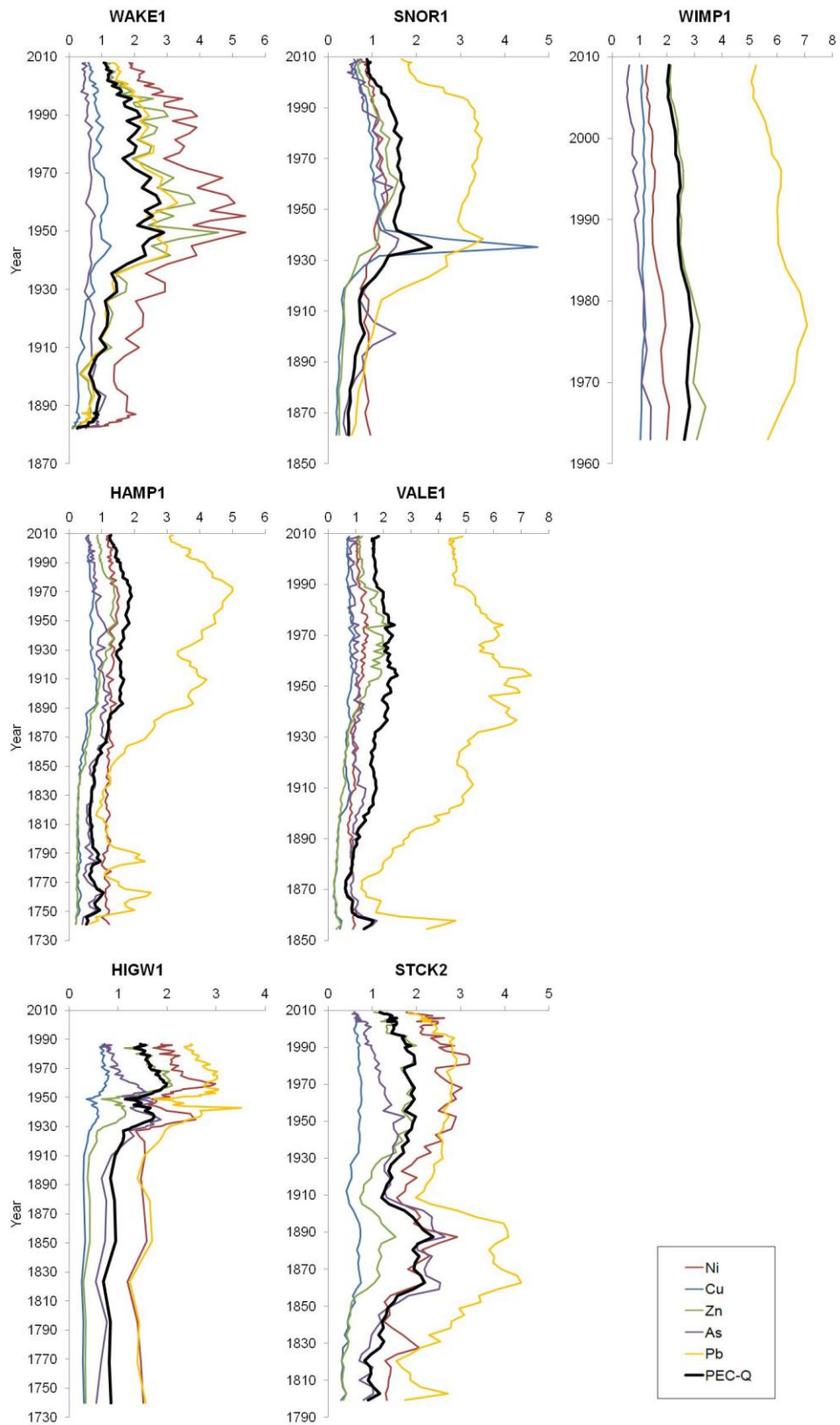


Figure 6.5 – Individual toxicity quotients for Ni, Cu, Zn, As and Pb in the London lake cores plotted against sediment age. PEC-Q Mean-metals for each core is also shown (black line).

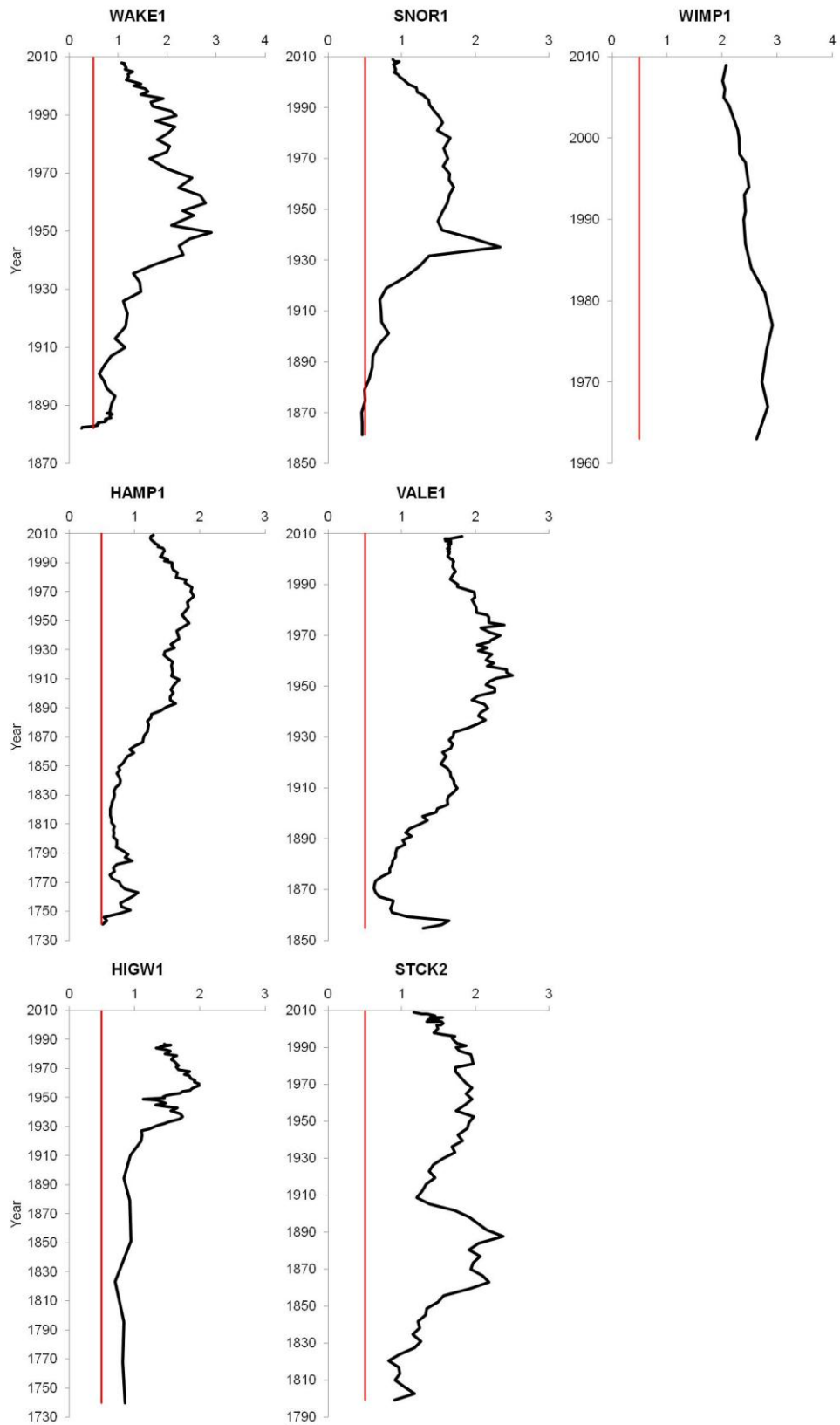


Figure 6.6 – PEC-Q Mean-metals reconstructed for the cores from the London lakes (black lines) plotted against sediment age. The red lines show the mean PEC-Q value of 0.5 proposed by MacDonald et al (2000) to distinguish between not toxic and toxic sediments.

Site	Average PEC-Q Mean-metals
<i>EDG</i>	3.61
WIMP1	2.42
VALE1	1.66
STCK2	1.58
HIGW1	1.47
WAKE1	1.38
<i>MAR</i>	1.25
HAMP1	1.16
SNOR1	1.14
<i>HOL</i>	0.94
<i>THO</i>	0.88
<i>FLE</i>	0.86
<i>CHA</i>	0.74
<i>CRA</i>	0.51
<i>SLA</i>	0.43

Table 6.9 – Average PEC-Q Mean-metals calculated from the OPAL and London lake cores

The extent to which PEC-Q Mean-metals exceeded the threshold was greater in all the London sites than any of the OPAL sites, apart from Edgbaston Pond and Marton Mere. Average PEC-Q Mean-metals for the London lakes, Edgbaston Pool and Marton Mere were all greater than 1.0, whilst the rest of the OPAL sites were all less than 1.0. For the London lakes and Edgbaston Pool this was a reflection of the urban nature of the lake environments, which meant that they were subject to larger amounts of contamination and consequently posed a greater toxicological risk. Marton Mere is located in a more suburban location, but the data from the core suggested that there had been a significant source of metal contamination to the lake prior to the 1970s, possibly from local industry. A comparison of SQGs in a gradient of urban sediments in the Grand Canal, Yangtze River Delta, China (Yu et al, 2011), showed that sediments in the urban sections were found to be more contaminated by heavy metals than those in the agricultural sections, and therefore had higher mean SQG quotients. However, the highest mean SQG quotient was found in a more rural section, which was caused by the outputs from a traditional tannery located nearby. As with Edgbaston Pool, Marton Mere and Wake Valley Pond, Wimbledon Park Lake, Vale of Health Pond and Stock Pond also all exceeded a PEC-Q Mean-metals value of 2 at some period in the past, indicating that biological effects will have occurred at those times.

For the London lakes, PECs were exceeded for all of the metals at all of the sites, at least for some of the period of time the cores covered (except for Cu at the Hampstead Heath Ponds – see Chapter 4). However, there had been times in the past when metal concentrations had not exceeded PECs, and for some metals PECs were no longer exceeded towards the top of the cores. Combining the metals to calculate PEC-Q Mean-metals resulted in a clear exceedance of the toxicity threshold of 0.5 (Figure 6.6) over the

whole time range covered by the cores. The metals stored in the lakes were therefore potentially more toxic in combination with each other than individually. In addition, this study of London lake cores did not take into account the effects of other chemicals (such as POPs) in the lake sediments which could add to the toxicity. The relationship between the OPAL surface sediments and toxicity suggested that the calculation of PEC-Q Mean-metals underestimated the actual toxicity of the sediments. The higher PEC-Q Mean-metals values calculated in the OPAL cores showed that the deeper sediments were likely to be more toxic than those at the surface. PEC-Q Mean-metals in the London lake cores were generally higher than those in the OPAL cores. Therefore, the inference can be made that the sediments stored in the London lakes are potentially toxic.

However, further work would be necessary to confirm this. Mean SQGQs may not be accurate indicators of which chemicals in the sediments are the cause of toxicity or benthic impairment. Additional analyses, such as sediment and pore water toxicity tests, toxicity identification evaluations and laboratory bioassays of clean sediments spiked with known chemicals may be needed to accurately determine causality. Benthic invertebrate community structure could also be assessed to compare with the most recent sediments (Long et al, 2006; MacDonald et al, 2011). However, this study provides an initial reconstruction of the potential toxicity of urban lake sediments, which has so far not been attempted. The results provide a basis for further research, which is important to determine whether sediment quality is improving in urban areas and to assess the potential hazard that could be caused by future disturbance of the sediments.

6.5. Conclusion

The main aim of this chapter was to reconstruct the potential toxicity of the sediments from each of the London lakes. There were a number of key findings from this part of the study. The potential toxicity quotients calculated for the surface sediments of the OPAL lakes were found to underestimate actual toxicity within the sediments. Five of the nine OPAL sites had PEC-Q Mean-metals of greater than 0.5 which is the threshold proposed by MacDonald et al (2000) to accurately classify samples as both toxic and not toxic. However, all of the sites with the exception of Chapman's Pond showed evidence for toxicity in the toxicity tests. The number and type of metals included in the calculation of PEC-Q Mean-metals was found to be important in estimating potential toxicity. If the key drivers of toxicity within the sediments were left out of the calculation then the potential toxicity of the sediments would be underestimated. This was highlighted by excluding each of the metals included in the calculation of potential toxicity of the OPAL surface sediments in turn. The largest change in value occurred on exclusion of Pb from the calculation. Lead exceeded the PEC to the greatest extent out of all the metals and therefore had the largest individual toxicity quotient

and contributed most to the value of PEC-Q Mean-metals. If Pb had been left out of the calculation then the potential toxicity of the sediments would have been underestimated, thereby underestimating actual toxicity to an even greater extent.

The potential toxicity of both historic and contemporary sediments in cores from the OPAL lakes and the lakes in London was calculated. The potential toxicity of the sediments from the OPAL cores was, in general, greater than the potential toxicity of the OPAL surface sediments. This was because the concentrations recorded in the core sediments were higher than those in the surface sediments (similar to the results for the Vale of Health Pond in Chapter 5) and therefore contributed more to the PEC-Q value. Potential toxicity exceeded the threshold of 0.5 at all sites at all times in the past, with the exception of Slapton Ley and Crag Lough. Toxicity tests on the core sediments would be required to confirm if the higher PEC-Q values were reflected in the toxicity of the sediments, but the high incidence of toxicity at lower mean PEC-Qs in the surface sediments would suggest that it was likely. Potential toxicities of the London lake cores were generally higher than those in the OPAL cores, with PEC-Q Mean-metals exceeding the 0.5 threshold to a greater extent at all of the London sites, apart from Edgbaston Pond and Marton Mere.

The metals stored in the lakes were potentially more toxic in combination with each other than individually. Although Chapter 4 showed that metal concentrations in the London lake cores did not always exceed PEC thresholds at all times in the past, combining the metals to calculate PEC-Q Mean-metals resulted in a clear exceedance of the potential toxicity threshold of 0.5 for the whole time period they covered. Wake Valley Pond, Wimbledon Park Lake, Vale of Health Pond and Stock Pond also all exceeded a PEC-Q Mean-metals value of 2 for some period in the past, meaning that biological effects would have occurred at those times. With reference to the relationship that was identified between potential toxicity and actual toxicity within the OPAL surface sediments, it was inferred that the sediments in the London lakes were likely to be toxic. Having toxic metals stored within the lake sediments poses a potential risk as future disturbance could result in the metals becoming available to the ecosystem again. This will be discussed further in Chapter 7.

CHAPTER 7: PROJECT SYNTHESIS

7.1. Summary and key findings of the research

The main aim of the study was to explore the metal pollution history of London lake sediments and find out if there was a relationship between the levels of metal contamination within the sediments and the wider lake ecosystem. The potential toxicity of metal mixtures in the sediments both in the past and at present was assessed in order to ascertain if metal pollution was likely to pose problems to ecosystems in the future. This aim was answered by addressing a number of sub-aims and objectives (Section 1.3). This chapter provides a synthesis of this research project, summarising the key findings in relation to the aims and objectives. Any implications for management highlighted by the study will be addressed, and the chapter concludes by suggesting some areas in which further research would be beneficial.

The onset and expansion of industrialisation over the last 200 years has resulted in a dramatic increase in the impact of human activity on the environment, termed the 'anthropocene' (Crutzen, 2002). This provided the broad context to the current research project. The global population, and in particular the proportion of people living in urban areas has also increased dramatically over the same period, and this growth is only set to continue (WHO, 2013). This growth puts pressure on aquatic ecosystems within urban areas, and in many parts of the world freshwaters are degraded and species are being lost (WWF, 2012). Therefore, the study of pollution levels, patterns and processes in the urban environment is currently of real importance. This research focused on metal pollution in lakes and ponds in London. Metal contamination of aquatic ecosystems in urban areas is understudied globally, and in particular, very little research has been done in London, despite its long urban and industrial history. Therefore, this study aimed to fill a gap in the knowledge of this subject area.

The first sub-aim of the project was to identify metal concentrations in the sediments of London lakes and describe the temporal changes that occurred. In order to do this, sediment cores had to be taken from a number of lakes within the city, and chronologies developed for each. It was difficult to find lakes which contained a sedimentary record long enough to encompass changes in metal concentrations since the Industrial Revolution, as many of the lakes identified as possible sites for investigation were found to have been dredged on a number of occasions. The sedimentation process at each of the London lakes played an important role in the quality of both the radiometric and SCP dating. Variation in the sediment accumulation rate caused by a number of factors including slumping events,

focusing and mixing, and interruptions to the sediment record such as dredging, influenced both the radioisotope and SCP concentrations recorded in the sediment cores. Chronologies were formed using a combination of the two methods, together with the dates the lakes were constructed, which provided a baseline date for each core. Although the chronologies for Wake Valley Pond and Highgate Ladies Bathing Pond were quite robust, those for the Vale of Health Pond, Stock Pond, Hampstead No. 1 Pond, South Norwood Lake and Wimbledon Park Lake were comprised of reliable post-WWII dates and more speculative pre-WWII dates. The difficulty in formulating chronologies in urban lake sediments was not just restricted to the lakes in this study, but was reflected in the wide range of methods that have been used to date sediments in other urban areas.

The temporal trends of metal concentrations in the London lake cores were complex. In general, as might be expected given the effects of industrialisation, metal concentrations increased from the 19th century and then declined up to the present day. However, there were many differences in concentration, both between metals within the sediment cores, as well as between the different sites. Metal concentrations ranged between 24 and 262 $\mu\text{g g}^{-1}$ for Ni, 15 and 708 $\mu\text{g g}^{-1}$ for Cu, 57 and 2099 $\mu\text{g g}^{-1}$ for Zn, 11 and 87 $\mu\text{g g}^{-1}$ for As, 29 and 944 $\mu\text{g g}^{-1}$ for Pb and 160 and 3003 ng g^{-1} for Hg. Enrichment factors were found to exceed 1 for all metals in all cores, which showed that anthropogenic pollution had occurred at every site for at least as long as the lakes had existed – as far back as the mid-18th century in the case of the Hampstead Heath Ponds. Comparison of the metal concentrations with sediment quality guidelines showed that they had exceeded TECs at all times in the past, and that PECs had been exceeded at all sites for at least some period of time. The concentration of Pb in the sediments was particularly noteworthy as it exceeded the PEC at all sites throughout the 20th century, and in most cases for the whole period the cores covered.

The second sub-aim of the project was to explain the variation in metal concentrations within and between sediment cores and identify whether the changes in metal pollution across the city reflected a regional pattern or if they were more localised, to ascertain the importance of different pollution sources within the city. One of the key findings of this chapter was that the sedimentary archives of metal contamination in urban lakes are complex. The temporal variation in metal concentration both within and between sites was the result of a combination of different influences. Firstly, the behaviour of metals in sediments was found to be important. For example, the pattern of As commonly differs to that of other metals and is often characterised by large variability (Lavilla et al, 2006), primarily due to the fact that the chemical behaviour of As is different to that of metals such as Ni, Cu, Zn or Pb (Rognerud & Fjeld, 2001). Secondly, changes that had occurred within the catchments of the different lakes influenced the metal concentrations in the cores. This was particularly

noticeable at the sites on Hampstead Heath. Two lakes, Highgate Ladies Bathing Pond and Stock Pond, which are situated next to one another, showed different temporal metal concentration patterns, despite being close enough to be subject to the same sources of metals. Disturbances that had occurred within the two catchments at different times resulted in changes to the sediment accumulation rates, diluting the metal concentration profiles. Lastly, the complexity of sources of metal contamination in urban areas such as London means that the patterns of contamination in lake sediments will also be complex, with factors such as proximity to the source and the type of source affecting the sedimentary pollution record. Another key finding from this chapter was that on a broad scale there was some indication of a regional pollution pattern across the Greater London area, but that overall local influences were more important in determining patterns of metal pollution in urban lake sediments. Principal components analysis of all the core samples resulted in some overlap between all the sites, which suggested that the amounts and patterns of contamination were not dissimilar. However, at a larger scale it was noticeable that local influences were actually more important and that patterns of metal contamination were site specific.

The third sub-aim of the project was to identify and explain the trends and levels of metal contamination in the most recent core sediments. The key finding was that although in general the concentrations of metals in the sediments have declined since the 1970s, there has not been a corresponding decrease in enrichment or metal flux. Comparison to records of metal emissions and deposition in the UK and London accentuated the difference, as both emissions and deposition have also decreased since the 1970s. Although changes in metal flux may be influenced by sediment focusing, the results suggested that there was a secondary source of metals to the lake sediments, the primary source of which was likely to be from contaminated soils in the catchment. Erosion of contaminated catchments is thought to be an increasingly important source of metals to aquatic systems (Rose et al, 2012). The levels of contamination found in the lakes in this study were comparable with those found in previous investigations of London, although only a limited amount of research was available from which to draw such comparisons. Studies of urban lakes at other sites globally revealed differences in concentration.

The fourth sub-aim of the project was to identify metal concentrations in other parts of the lake ecosystem at the Vale of Health Pond and explore the relationships between the sediments and the rest of the ecosystem. Metal concentrations were determined in sediments collected from traps, bulk deposition, water, macrophytes, benthic algae, zooplankton and fish at the lake, providing a snapshot of the degree of contamination in an urban lake. One of the key findings was that of all the parts of the ecosystem the highest concentrations of metals occurred in the sediment trap material. This was consistent with

previous studies, and reflected the capacity of particulates to scavenge and then store metals. The study also showed that both metal concentration and flux in the sediment trap material was much lower than that in the sediment cores, possibly due to a combination of resuspension processes, grain size distribution and sediment focusing. Another important finding was that deposition flux was low in comparison to sediment flux for all metals, which suggested that even though deposition from the atmosphere was a source of some metals to the Vale of Health Pond, it was not the only source and that run off from the catchment may be as, if not more, important.

A third key finding was that the metal concentrations in biota reflected the trophic levels at the Vale of Health Pond. Stable isotope analysis ($\delta^{15}\text{N}$) showed clear differences of 3-4 ‰ between macrophytes and algae, zooplankton, and fish, which, together with fish gut contents, confirmed the presence of a food chain algae-zooplankton-fish. Metal concentrations were in the order benthic algae > zooplankton > fish, and showed that there was no evidence of biomagnification of Hg up the food chain. Lastly, and most importantly, the level of Pb pollution within the ecosystem was found to be high. Guideline values were available for Pb in sediment, water and fish. Median annual concentrations of Pb in the sediment trap samples exceeded both TECs and PECs, despite the concentrations being lower in the trap material than in the cores. The concentration of Pb also exceeded USEPA Criterion Continuous Concentration guidelines for water, showing that aquatic biota at the Vale of Health may be at risk. This was confirmed by comparison of fish muscle tissue concentrations with EC guidelines, which showed that the concentration of Pb in some fish exceeded the recommended amount. These results showed that Pb pollution is pervasive throughout the lake ecosystem at the Vale of Health Pond, and is not just confined to the sediments where most particulates are stored.

The fifth sub-aim of the project was to reconstruct the potential toxicity of the sediments from each of the London lakes. There were a number of key findings from this part of the study. The potential toxicity quotients calculated for the surface sediments of the OPAL lakes were found to underestimate actual toxicity within the sediments. Five of the nine lakes exceeded the potential toxicity threshold calculated from PEC-Q Mean-metals. However, eight of the nine lakes showed evidence of toxicity in the toxicity tests. This toxicity could have been caused by other chemicals in the sediments that were not included in the calculations. In addition, toxicity is a function of many factors as well as concentration, including bioavailability and chemical form (Long & MacDonald, 1998). The number and type of toxicity tests carried out was also important. In addition, the number and type of metals included in the calculation of PEC-Q Mean-metals was found to be important in estimating

potential toxicity. If the key drivers of toxicity within the sediments were left out of the calculation then the potential toxicity of the sediments would be underestimated.

Toxicity quotients were calculated for the OPAL core sediments and related to the results from the surface sediments. The toxicity quotients calculated for the sediment cores were generally greater than those calculated in the surface sediments, both in the top 5 cm of the cores and historically. Toxicity quotients were also calculated for the London lake cores. Within London, Ni and Pb contributed most to potential toxicity, reflecting the high concentrations of these metals in the sediments. The extent to which PEC-Q Mean-metals exceeded the threshold was greater in all the London sites than any of the OPAL sites, apart from Edgbaston Pond and Marton Mere. The metals stored in the lakes were potentially more toxic in combination with each other than individually. Although Chapter 4 showed that metal concentrations in the London lake cores did not always exceed PEC thresholds at all times in the past, combining the metals to calculate PEC-Q Mean-metals resulted in a clear exceedance of the potential toxicity threshold of 0.5 for the whole time period they covered. Given that the OPAL surface sediment toxicity quotients underestimated the actual toxicity of the sediments, and that the toxicity quotients calculated for the London cores were much higher, it was inferred that the sediments in the London lakes were likely to be toxic. Therefore, there would be implications for lake ecosystems should the sediments be disturbed. The use of sediment archives to reconstruct toxicity is a novel approach, and is one that could be of great importance with respect to the future management of contaminated lake sediments.

This summary has shown that the aims and objectives outlined in Section 1.3 have been achieved. Through the analysis of both palaeolimnological and contemporary records, metal contamination of lakes and ponds in London has been investigated. Although many interesting themes have been highlighted, of particular importance is the degree of Pb contamination found in the sediments at all of the sites and the lake water and fish at the Vale of Health Pond. The implications that disturbance of such contaminated sediments could have on ecosystem health in the future should be of major concern.

7.2. Wider implications of the research

In this study, it was found that the concentrations of Ni, Cu, Zn, As, Pb and Hg in the sediments of London lakes were high enough to exceed both TECs and PECs. It was calculated that at such concentrations, the mixture of these metals in the sediments was potentially toxic. Comparison with toxicity tests also showed that the calculations of potential toxicity appeared to underestimate actual toxicity. The sediments are acting as a store for

toxic metals. However, the study also discovered high concentrations of Pb in water and fish at one London lake. Although this only provided a snapshot of the degree of metal contamination within the wider lake ecosystem, the results suggested that metal pollution was pervasive throughout. A wider scale study would help to understand the link between metal concentrations in the sediments and the rest of the ecosystem, in order to explore more fully whether the sediments act as a source of metals, or if inputs from the catchment are primarily to blame.

Urban lakes are highly managed, particularly because they are visible to a large number of people. This was reflected in the difficulty there was in this study to find suitable sites that hadn't been dredged on a regular basis. Dredging and disturbance of the sediments in general is very likely within urban lakes. Removing sediments from the London lakes would require careful consideration, for two reasons. Firstly, if not all of the polluted sediments were removed there is the potential of leaving disturbed, highly toxic sediments within the lakes, which may result in metals being released back into the ecosystem. Secondly, consideration would need to be given to where any sediment that was removed should be taken, as metals would potentially be released back into the environment wherever they were deposited. The high sedimentation rates found in the London lakes means that if the lakes were dredged completely there would be a lot of sediment that required attention. Enrichment factors calculated in this project showed that it might be impossible to get back to non-polluted levels anyway. In addition, if the purpose of removing the sediments was to eliminate the toxic store of metals within the lakes, the effects might be counteracted through the continuing input of metals from contaminated catchment soils. Also, this study only examined metal pollution and has not included the many other types of contaminant that are also likely to be stored in sediments and which may pose potential problems as well. Careful management of the London lake sediments will be required in the future to avoid and to mitigate the potential impacts of such high levels of metal contamination.

7.3. Directions for further work

Based on the results of the research described above, several directions for further work can be identified:

- 1) It would be useful to set up a new monitoring programme at the Vale of Health Pond which could run for a longer period of time – covering a number of years rather than just one. This would enable seasonal trends in metal concentrations to be determined, and would provide a larger number of samples for analysis. Catching a larger number and variety of fish species would also enable more information to be obtained regarding metal transfer in trophic webs.

2) Contemporary studies of the lake ecosystems at the other sites from which cores were taken could be carried out. Metal concentration data obtained from the studies could be related to the sediment cores from those lakes. This would provide more information about metal concentrations in lake ecosystems in general, and also how site specific the patterns of metal contamination in biota are.

3) Laboratory toxicity testing of the sediment cores from the London sites would be beneficial in order to confirm the interpretation that the sediments are potentially toxic. Potential toxicity could be calculated for sediment cores from other lakes, and laboratory toxicity testing carried out, in order to build further upon the approach used in Chapter 6.

4) The research could be expanded to a number of other lakes and ponds in London, assuming sites with suitable sediment records could be found. Using a larger number of sites over a wider area would result in a much bigger dataset, which could be used to confirm if there is a regional pattern of metal contamination in the London area. It would also provide more experience of urban sediment cores and help to clarify the best way to obtain chronologies for them.

5) The research could also be expanded even further, to other cities in the UK. Although this study has suggested that metal contamination records in urban lake sediments are quite localised, records from other lakes could be used to confirm this. Regional patterns in contamination may be more easily identified by considering lake sediments across a much broader scale. It would also be useful to find out if Pb contamination is a big problem across the UK, or if it is particularly focused upon London.

CHAPTER 8: REFERENCES

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