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THE POLLUTION HISTORY OF TWO URBAN LAKES IN COVENTRY, UK

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Abstract

Human society has influenced the environment for at least the last 15000 years but, since the Industrial Revolution, the resultant environmental impacts have become more widespread. Lake and reservoir bottom-sediments have been widely used in many studies for reconstructing this impact over medium timescales (tens to hundreds of years). Few long-term studies of hydrological change exist and sediments are useful as surrogates for direct monitoring since they are sensitive to change within the catchment. This study uses the properties of urban lake sediments in order to reconstruct environmental pollution history.

The two principal objectives of this study were the reconstruction of historical atmospheric, point source and diffuse heavy metal pollution in an urban environment and the evaluation of the lake-sediment record as a source of proxy hydrological data over the last 100-150 years.

A paired lake-catchment study was undertaken by comparing the records contained in a closed and an open lake. The closed lake (Swanswell Pool) is situated in the centre of the city of Coventry where the main source of pollution is atmospheric. This site provides a contrast to an open basin (Wyken Pool) with a multi-source catchment in addition to an atmospheric influx.

Trends in urban lake sediment cores indicate increasing heavy metal concentrations upcore, with cultural enrichment factors for individual heavy metals of between 55.4 and 2.6. Storage of heavy metals in the catchment of the closed basin
were significant, although it was found that up to 85% of the Zn and 90% of the Pb were actually stored in the lake sediments. Catchment sources contributed up to 5 times more than the atmosphere in the Wyken Slough catchment. Heavy metals budgets were calculated, and these showed that loadings of metals have increased by up to 7.5 times between 1850 and the present day. Sequential digestion of the lake sediments at both sites showed that the important fractions containing heavy metals were Fe and Mn oxides and organic matter. The heavy metals associated with these fractions could be remobilised with changing environmental conditions, but an analysis of contemporary water quality indicated that, at present, suitable Eh and pH conditions for remobilisation did not occur.

It was concluded that these urban lakes do preserve the heavy metals record and can provide surrogate data on medium-term environmental change. However, the complex mixture of materials associated with urban sedimentation resulted in a lack of correlation between heavy metals and mineral magnetic properties in either lake, and in the catchment of Wyken Slough. Hence mineral magnetic properties of sediments in urban catchments do not appear to be a suitable surrogate for heavy metals analysis.

Urban lakes appear to provide a much-neglected opportunity for palaeolimnological reconstruction over a period when little directly monitored data exists.
# THE POLLUTION HISTORY OF TWO URBAN LAKES IN COVENTRY, UK.

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Chapter 1

1.1 Introduction

"...human activity has been and will continue to be a major extrinsic force of change."

Starkel et al. (1991) p 521

This study is concerned with the detection of change in the environment. The observation by Starkel et al. (1991) above, highlights an important force of change in the natural environment; that of the activities of mankind. The importance of the role of human beings in environmental change has taken time to assume its present significance. Until the 1950s and 60s Physical Geographers tended to focus on changes to the environment before human activity or

"...at best to include man as an afterthought or an appendage."


However, the impact of human activities has now

"...come prominently into focus and (is) a major concern of scientific endeavour."


This scientific endeavour has profited from the drive in the 1980s to understand the impact of climate change brought about by anthropogenic activity (Gregory, 1991). Associated with
this has perhaps come the realization that the whole field of human influence needs to be assessed, enabling suggestions to be made as to how this influence may best be controlled.

1.2 Timescales

Humans have influenced the environment for at least the last 15000 years and there have been many palaeohydrological studies concerned with the late glacial and Holocene in which the human impact has been identified. The International Geological Correlation Programme (IGCP) Project 158 is an example of a long to medium timescale study of the magnitude of human impact over the last 15000 years on fluvial systems and the environmental changes recorded in lakes, mires and their contributing catchments (IGCP Subprojects A and B; Berglund, 1983). Chapter 2 of this thesis outlines many other such long to medium timescale projects in which attempts have been made to reconstruct Quaternary events and environments.

A second approach to the study of the impact of human activity on environmental systems, working in parallel with long-term reconstruction, is the measurement of contemporary hydrological processes in experimental catchments. Lewin (1980) defined this as the "eclectic" phase of geomorphology in which the two factions studied past and present in isolation from one another and is exemplified by the work of Gregory & Walling (1973), Burt & Walling (1984) Hadley (1985) and Roberts (1989). The observation of contemporary events is necessarily curtailed by the length of the research project from as little as a field season to "the few years of 'PhD
Problems associated with the investigation of contemporary processes include the lack of knowledge of antecedent catchment conditions. Monitoring of a pollution problem after the event makes it difficult to assess the seriousness of the impact on the environment as the conditions prior to the event are not known:

"...extensive monitoring of various aspects of environmental pollution was generally not carried out until after the major problems were identified."

Foster and Dearing (1987) p 173

There is, therefore, a need for an approach which evaluates human impacts at intermediate timescales, lying between that covered by palaeohydrological reconstruction and the data generated by contemporary monitoring. Petts (1989) characterised the period between 100 and 500 years ago and the present day as being the time of increasing human impact on rivers and hence on the lakes within their drainage basins. This present study covers part of the timescale of greatest human influence on the environment by focusing on the past 150 years. The importance of this period is shown by the Industrial Revolution; the industrial and technological advances of which touched every aspect of the biosphere and hydrosphere.

Whilst there are many studies of lakes and the effects of human intervention in the natural environment (Elner & Happey-Wood, 1980; Hamilton-Taylor, 1979, 1983; Batterbee et al., 1988) there are few which have investigated any sites at the
focal point of industrialisation and urbanisation; the urban lake. Many studies have examined the temporal distribution of atmospheric pollutants by examining the heavy metal content of lake sediment cores taken from remote sites, such as those undertaken by Verta et al. (1989), in sparsely populated areas of Finland and polar ice cores in the Northern Hemisphere (Nriagu et al., 1979). There are also studies of the atmospheric contribution of pollutants to lowland rural and semi-rural lake sediments, such as those undertaken in North Warwickshire (Foster and Dearing, 1987) and in south central Wales, (Jones, 1984; Jones et al., 1978, 1985). This present study concentrates on lakes proximal to the industrial and urbanised areas responsible for the production of atmospheric pollutants.

1.3 Aims and Objectives

This research project was designed in order to meet two basic aims:

1. To reconstruct the history of pollution in an urban environment

2. To evaluate the lake sediment-record as a source of proxy hydrological data over the last 100-150 years.

In relation to the above aims, the following specific objectives were identified:
1.1 To quantify the historical changes in atmospheric pollution as recorded in urban lakes

1.2 To quantify the historical changes in the heavy metal content of lake sediment derived from a slowly industrialising catchment over the last 150 years and to identify the role of the drainage basin in the sediment delivery process.

1.3 To quantify the relative contribution of atmospheric and catchment derived contaminants.

2.1 To evaluate the use of paired lake-catchments in reconstructing change over short to medium timescales

2.2 To identify the practical limitations of utilising a range of environmental tracers (heavy metals, environmental magnetism and radioisotopes) for reconstructing pollution histories and identifying contaminant sources.

1.4 Structure of the thesis

The first section of Chapter 2 justifies the use of lake catchments and, specifically, the paired lake-catchment approach adopted in this study. Sections 2.2 to 2.4 address the use of a lake-sediment based approach to reconstruct the history of a lake basin over a time period of around 150 years. Section 2.5 gives the justification for the selection of sites, particularly in terms of the value of using closed and open basins for comparative purposes. Sections 2.5 to 2.9
explain the methodological framework applied to this study of urban lake pollution.

Chapter 3 describes the two sites in detail, using historical documents to reconstruct site histories. The results of sediment sampling and laboratory analysis are presented in Chapters 4 to 6. Chapter 7 attempts to construct heavy metal budgets for both sites and then to set them in a framework in which a gradient of atmospheric pollution from urban to rural sites is quantified. The discussion, presented in Chapter 8, summarises the degree to which the foregoing aims and objectives have been achieved.
Chapter 2

The Conceptual and Methodological framework

2.1 Introduction

This chapter explains the rationale behind the present study by examining previous work carried out in the broad fields of catchment hydrology, limnology and palaeolimnology. It explains the use of heavy metals, in terms of the properties which make them suitable for such a study, and also explores the methodology and techniques chosen in terms of their suitability and past application. The chapter considers the following:

1. The use of lake sediments in the reconstruction of past environments.

2. The use of lake sediments in reconstructing the history of anthropogenic pollution.

3. The chemical properties of heavy metals in the context of their suitability for reconstructing pollution history.

4. The sites selected for this research project.
5. A critique of the methodology employed in sampling and analysis of lake and other sediments.

2.2 Lake-catchment based studies.

The study of lakes and their drainage basins can provide two types of important information: firstly, contemporary process-based monitoring of change in the short term (years to decades) and, secondly, the study of longer term change (decades to centuries) by analysis of deposited sediment. Direct observation of an active system enables modelling of several aspects of environmental behaviour (eg. Hadley, 1985; Roberts, 1989). Reconstruction of past events permits an assessment of the impact of change within the catchment, but cannot provide a resolution high enough for the data to be used as a substitute for monitoring. The advantages and disadvantages of various monitoring and reconstruction strategies employed to quantify change in catchment systems are briefly considered in the following sections.

The Hubbard Brook study (Bormann & Likens, 1969) originated the idea of the ecosystem-watershed concept in which a study of the integration of various ecological, meteorological and hydrological processes was attempted within a single drainage basin, water being the linking factor. O'Sullivan (1979a), in his review of the ecosystem-watershed concept, emphasised the importance of the interdisciplinary nature of this study:
"The ecosystem-watershed concept is thus capable of providing a conceptual framework for interdisciplinary studies of the dynamics and processes of contemporary environments."

O'Sullivan (1979a) p 273

However, even though contemporary process monitoring of this kind can take account of the impact of society on the catchment, these data are only available for a relatively short time span (discussed further in section 2.3). Since atmospheric pollution, for example, has been affecting the environment for at least the past 130 years (Norton, 1986), longer term data are needed to reconstruct catchment pollution history. Sediment accumulating within the catchment in rivers, lakes and on floodplains will incorporate heavy metals and will potentially contain evidence of such pollution through time. The following section considers the relative merits of fluvial, limnic and alluvial deposits in retaining this evidence.

Lewin (1987), assessed the patterns of change within the course of the River Severn and found that the channels exhibited marked changes spatially over time. Hence sediment deposited in the channel will also change spatially with time. Förstner’s (1983), critique of the use of river water samples to establish trends in aquatic pollution, highlights problems which also might be associated with the use of river sediments, principally those of fluctuations in daily and seasonal flows which will directly impact on the depositional
or transportational regime of the river. River sediments thus represent a means of monitoring pollution on a timescale of hours to decades (Fig 2.1) rather than a means of reconstructing pollution history.

Alluvial deposits represent inundation of the floodplain and deposition of fine sediment (Macklin, 1992). They therefore do not represent a continuous sedimentary sequence necessary for the reconstruction of pollution history of a catchment. There are few studies dedicated to long term monitoring of river sediments and alluvial deposits. A review of these studies is beyond the scope of this thesis, but is presented in Foster & Charlesworth (1995).

Atmospheric deposition of pollutants onto land can contaminate soils, but their heavy metals record is a transient one (Foster & Charlesworth, 1995). The soil profile is dominated by pedogenic processes and interactions with plants (Mattigod & Page, 1983). It is therefore dynamic and the distribution of heavy metals in the profile reflects these processes rather than historical accumulation of pollutants sequentially. Soils, however, are subject to erosion and, if they are contaminated with heavy metals, may provide secondary, non-point sources of pollution in the hydrological cycle. The analysis of soils, therefore, does not provide a means of pollution history reconstruction, although soils are an important sink and, ultimately, source of heavy metals in the fluvial system.
Fig 2.1 Comparison of the timescales of environmental monitoring and palaeoenvironmental reconstruction (after Smol, 1992)
Lake sediments on the other hand

"...potentially contain a tremendous 'library' of information."

Smol (1992) p 50

The use of lake sediments as proxy hydrological data are the subject of detailed review in section 2.3.

Most studies or "experiments" (Deevey, 1969; Church, 1984) of this kind use historical reconstruction as a proxy means of monitoring the effect of catchment disturbance on the system. They do not involve the intentional interference with the landscape which would produce inarguable results. Most catchment studies, therefore, show little evidence of experimental control. They are, however

"...an essential part of the complete enquiry that develops conceptual understanding."


A means of exerting some experimental control in lake-sediment based studies is in the use of a paired lake-catchment approach. This can introduce background control and, hence, improve scientific understanding (Foster et al., 1987). Many studies have been carried out using paired catchment studies, for example in the English Midlands (Foster et al., 1987) and elsewhere (Hewlett, 1967, in Coweeta, USA; Fuehrer, 1993, in Hesse, Germany). A paired lake-catchment study,
coupled with a multiple coring exercise, can provide data which allow long term responses of the environment to pollution from different sources to be quantified. Antecedent catchment conditions can be obtained from an analysis of the sediments prior to the period of interest. The lake sediment records can be used to quantify the responses of the catchment to change, the likelihood of recovery without further interference, and the chances of reinstatement if the catchment is actively managed.

The lake is therefore highly sensitive to changes within the catchment and this is reflected in the sediments, the use of which in historical reconstruction is considered in the next section.

2.3 The use of lake sediments in historical reconstruction

Mackereth (1966) was the pioneer in the UK on the use of lake sediments to infer environmental change. This work in the English Lake District was followed by other research, notably by Pennington (1973), who focussed on the environmental changes in the same area recorded in the upper 30 cm of sediment from Lake Windermere. Pennington described the sediment column as
"...the continuously accumulating column of lake sediment as a medium within which environmental changes are recorded in sequence, including recent changes attributable to Man."

Pennington (1973) p 363

In 1977, Oldfield proposed that

"Lake sediments provide an exceptionally full record of the medium to long term effects of modern technology on environmental systems."

Oldfield (1977) p 496

Further research has indicated that lake sediments can be looked upon as a "bank" of environmental information (Hákanson & Jansson, 1983). The record contained within lake sediments can help discriminate between polluted and unpolluted environments, identify spatial and temporal patterns of such impacts and help to identify the nature and relative importance of individual contaminants.

Hákanson & Jansson (1983) identified four factors responsible for sedimentation in lakes. These include internal productivity, trap efficiency, the ability of upstream components of the catchment to hold sediment, and therefore limit supply, and the relative contributions of allochthonous material from direct drainage basin inputs.

Lake sediments are not a sterile medium, but support micro- and macro-organisms which affect the incorporation of contaminants into the sediment, their subsequent stability
and, hence, their concentration and distribution with depth in the sediment column. Cline & Upchurch (1973) suggest that the movement of metals in the biotic zone (the upper 10 cm of the sediment column) occurs as the metals form a film around gas bubbles in the sediment and are moved upwards through the sediment on the bubble of gas. Bacteria may also selectively take up heavy metals and mobilise them in the sediment. However, as Förstner & Wittmann (1981) suggest, there is little quantitatively known about the effects of bioturbation and Håkanson & Jansson (1983) conclude that the processes are too complex to be able to describe mathematically.

Trap efficiency is a reflection of the ability of the lake basin to trap and retain sediment. It is dependent on several factors including the density gradient between the lake water and the inflowing streams, the position of any thermocline or pycnocline and the chemistry of the lake water which may inhibit settling due to flocculation (Foster et al., 1990). There are several models which can predict trap efficiency and these are reviewed by Foster et al. (1990). These include models based on basin area (Brown, 1944), the capacity inflow ratio (Brune, 1953) and the capacity inflow / particle size relationship (Chen, 1975; Heinemann, 1984; Rausch & Heinemann, 1984). A further model is proposed by Moglen & M'Cuen (1988) in which trap efficiency is related to sediment movement and is related to the proportion of the inflowing sediment retained by the basin:
\[
E_t = \frac{q_{s1} - q_{s0}}{q_{s1}} \quad \text{ (Equation 2.1)}
\]

Where \(E_t\) = trap efficiency

\(q_{s0}\) = sediment carried in the outflow

\(q_{s1}\) = sediment carried in the inflow

In the case of urban lakes, three problems of assessing trap efficiency by these methods are apparent:

1. Urban lakes often do not have a contributing catchment from which to estimate either the basin area or the inflow. The lack of direct inflow or outflow information makes estimation of suspended sediment trap efficiency difficult.

2. Where the urban lake does have a catchment, the act of urbanisation introduces an artificial drainage network into the system which routes surface runoff from a greater area into the lake (Packman, 1980; Uehara, 1980). This improved drainage changes not only flow volumes but also flow characteristics, so that the storm hydrograph response is quicker with higher peak discharges for even small storm events (Packman, 1980). This impacts on basin area, capacity inflow and particle size relationships, due to increased discharge.
3. Sediment delivery to the lake is not constant. The study by Wolman (1967) showed that suspended sediment yields increased in a catchment subjected to the disturbance associated with urbanisation and industrialisation. In a large urban area, land clearance and construction may be almost continuous as small parts are disturbed each year (Douglas, 1985). In between each period of increased fluvial sediment yield, the levels may fall back to those before urbanisation (Wolman, 1967).

Estimation of trap efficiency of urban lakes is therefore fraught with difficulty which current models cannot address and whilst an important consideration under normal circumstances, the unique conditions of urban lakes with respect particularly to catchment-isolation, canalisation and frequent periods of disturbance means that this problem is not considered in any great detail in this study.

Håkanson & Jansson's (1983) third control on sedimentation was the influence of upstream sediment traps which may prevent some of the suspended load reaching the lake. For the purposes of this study, the influence of marshland is important, this is considered in greater detail in section 2.8ii where the characteristics of the specific research sites are discussed.

Håkanson & Jansson (1983) lastly identify a "load" factor which controls sedimentation in lake basins. This identifies that there are mainly two sources of material from outside the lake; firstly, allochthonous, or catchment-derived material
transported as bed and suspended load, and, secondly, the anthropogenic contribution. Section 2.7 justifies the choice of the research sites in terms of discriminating these, and also in terms of discriminating the atmospheric component of the anthropogenic contribution.

Sediment cores retrieved from a body of lake mud are site specific and can therefore provide data concerning the history of the catchment from which they are derived. This is valuable when formulating management strategies. Once a management problem has been identified, and the threat of the problem with regard to recreation, wildlife or the aesthetics of an environment has been recognised, lake sediment studies can yield results faster than process-based observations and can often be more cost-effective. Oldfield & Clark (1990) designates this a "post-hoc" contribution to scientific methodology. Sediment-based studies can therefore give a more complete picture of the variability, recurrence and trends of pollution events in a far shorter time and over a longer period than process based observations.

Only a fraction of the chemical load transported by a stream are in the dissolved phase. Clays, silts and organic matter all provide large surface areas over which sorbtion of pollutants may occur. Indeed, suspended sediments often provide the transport mechanism for many chemical constituents (Feltz, 1980). The average length of contemporary records for the study of chemical transport processes in fluvial systems are usually no more than 5 years; leaving the data open to
bias by extreme hydrological or pollution events. Lake sediments, in contrast, provide an opportunity to analyse the suspended load not only contemporaneously but also historically.

The longer time scale over which pollution can be assessed using lake sediment records provides a means of establishing the effects of secular variations, of demonstrating the preceding conditions leading to the concerns of the present as well as providing historical data from which to extrapolate trends and rates of change (Oldfield & Clark, 1990).

As in this study, multidisciplinary analysis of lake sediments can yield integrated reconstructions of the history of the catchment in terms of the interactions occurring between ecology, culture and changes in technology. As Oldfield & Clark (1990) point out, the limitation of using lake sediments alone is in the narrowness of disregarding interactions occurring in the rest of the catchment system. The present study attempts to redress this imbalance by examining the sources and sinks of contamination associated with the atmosphere, fluvial systems and the soil and hence to gain some insight into the relative importance of these sources and stores within the whole fluvial system.
2.4 The use of lake sediments to assess anthropogenic heavy metal pollution.

As a result of urbanisation, mining and industrialisation since the Industrial Revolution, the environment has become polluted with the wastes and by-products of the processes involved.

Lake sediments have been widely used as indicators of both contemporary and historical pollution. This is because both natural and manmade lakes are often located in areas of intense development. Often the threat of pollution becomes more serious when the lake is used as a source of potable water. Förstner & Wittmann (1981) illustrate the importance of analytical studies of sediment cores in palaeolimnological reconstruction of pollution:

"During the last 2 decades, sediment analysis has acquired a new dimension by being employed as a tool to trace manmade pollution influences in inland and coastal waters."

Förstner & Wittmann (1981) p 140

The concentration of the contaminant can also reveal trends in catchment history, such as whether pollution of the water courses entering the lake has changed through time.

There have been a great number of sediment-based research projects carried out in North America and Europe in the last 20 years. The majority of the American studies have been based
on an analysis of sediment cores from the Laurentian Great Lakes, and other lakes and ponds in the United States. These studies have been concerned with the enrichment of such elements as Cu, Zn, Pb, Ni, Cd, Sc, Hg, As, Cr, Sb, Co, Ag, V, La and Be where increases in concentration of these elements towards the mud-water interface has been identified; (Shimp et al., 1971; Leland et al., 1973; Walters et al., 1974; Kemp & Thomas, 1976; Kemp et al., 1976, 1978; Kemp & Dell, 1976; Wheeler & Dunning, 1976; Christensen & Chien, 1979; Nriagu et al., 1979; Glooschenko et al., 1981; Goldberg et al., 1981). Workers in Europe, for example Verta et al., (1989), presented a history of heavy metals pollution in Finland from an analysis of lake sediments. In Sweden, Renberg (1986), used sediments dated by their seasonal varves to estimate the effects of industrialisation on six lakes and to assign events in their past histories to fluctuations in the chemistry of their sediments. Förstner, in association with others both in Brazil and Holland, has analysed sediments to assess the catchment history of polluted lakes (Förstner, 1976; Förstner et al., 1979; Förstner & Wittmann, 1981; Förstner & Salomons, 1981a, 1981b).

In the UK, Elner & Happery-Wood (1980) reconstructed the history of two linked Welsh lakes from analyses which included chemical and mineral magnetic stratigraphies. This study indicated that the changes in the catchment due to copper mining in the period between the seventeenth and the end of nineteenth centuries could be identified in the lake sediment
record. Hamilton-Taylor (1979) is one of many working in the English Lake District who attributes the increasing metal content of the lake sediment cores to

"...the atmosphere (which) is clearly a major potential source of the sedimentary flux..."

Hamilton-Taylor (1979) p 696

Similar evidence for the increased concentration of heavy metals incorporated in the lake sediments of the UK are given by Harding & Whitton (1978) from the Derwent Reservoir, northern England, Hilton & Gibbs (1984) from Esthwaite Water, the English Lake District and Jones et al., (1978), from Llangorse Lake, Wales. Hamilton-Taylor (1983) presented the results of analysing sediments from six lakes in north west England demonstrating similar trends in enrichment of Cu, Pb and Zn dating from the mid nineteenth century.

These studies illustrate the trend of increasing heavy metal incorporation in the sediments of lakes in several regions of the world over the last 150 years. Research specific to heavy metal pollution in the urban environment has concentrated on the transport of pollutants and their effect on the biosphere. Few of these have been specific to the urban lake, the sink of a great deal of the anthropogenically derived heavy metals. Studies of the urban environment have therefore concentrated on four main components:
1. The sources of pollution, such as road-side gulley pots (Butler, 1979; Förstner & Wittmann, 1981; Colyer, 1983; Beckwith et al., 1984; Gjessing, 1984; Yousef, 1984; Gibson & Farmer, 1984; Brinkmann, 1985).

2. The transport of anthropogenically derived heavy metal contaminants in urban rivers (Wilber & Hunter, 1979; Samanidou & Fytianos, 1987; Thoms, 1987), and the effects of heavy metal contamination on urban rivers (Keller & Hoffmann, 1977).

3. The effects of heavy metal pollution on biota (Hellawell, 1989; Baudo et al., 1989).

4. Urban lakes (Cherkauer, 1977; Moglen & McCuen, 1988). In both cases the emphasis was on the effect of the lake on the rest of the catchment, rather than the cumulative effects of the upstream catchment on the lake.

Urban lakes are therefore the poor relation in the study of palaeolimnology and historical reconstruction.

The following section outlines the sources of heavy metals in the environment, emphasising the role of industry and urbanisation in their production, transport and redistribution in the environment.
2.5 Heavy metals in the environment

This section outlines the rationale behind the use of heavy metals analysis in the reconstruction of pollution history using lake sediments in four ways:

1. By examining the sources and sinks of heavy metals in the environment

2. By examining the properties of heavy metals in general

3. By discussing the suitability of heavy metals in studies of urban pollution, with particular reference to their modes of transport.

4. By examining the choice of heavy metals used in the investigation to reconstruct pollution history.

i. Sources and sinks of heavy metals in the environment

Fig 2.2 shows the sources of heavy metals to the environment. These can be divided into two broad groups, natural and anthropogenic. The main natural sources are from volcanic and geothermal activity and the process of geologic weathering. The first two are of little significance to the UK, but geologic weathering may release significant amounts of heavy metals from mineralised regions (Fergusson, 1990).
Fig 2.2 Sources of heavy metals in the environment
Table 2.1 compares the relative contributions from natural and anthropogenic sources, and shows the overriding importance of society in the global cycling of heavy metals. These figures show that anthropogenic input of heavy metals to the environment is now an order of magnitude higher than natural sources.

Table 2.1 A comparison of natural and anthropogenic emissions of trace metals to the environment, \( \times 10^4 \) kg yr\(^{-1} \), (Nriagu, 1990)

<table>
<thead>
<tr>
<th></th>
<th>anthropogenic (A)</th>
<th>natural (N)</th>
<th>total</th>
<th>A : N</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>19.0</td>
<td>12.0</td>
<td>31.0</td>
<td>1.58</td>
</tr>
<tr>
<td>Cd</td>
<td>7.6</td>
<td>1.3</td>
<td>8.9</td>
<td>5.85</td>
</tr>
<tr>
<td>Cr</td>
<td>30.0</td>
<td>44.0</td>
<td>74.0</td>
<td>0.68</td>
</tr>
<tr>
<td>Hg</td>
<td>3.6</td>
<td>2.5</td>
<td>6.1</td>
<td>1.44</td>
</tr>
<tr>
<td>Ni</td>
<td>56.0</td>
<td>30.0</td>
<td>86.0</td>
<td>1.86</td>
</tr>
<tr>
<td>Pb</td>
<td>332.0</td>
<td>12.0</td>
<td>344.0</td>
<td>27.67</td>
</tr>
<tr>
<td>Se</td>
<td>6.3</td>
<td>9.3</td>
<td>16.0</td>
<td>3.68</td>
</tr>
<tr>
<td>V</td>
<td>86.0</td>
<td>28.0</td>
<td>114.0</td>
<td>3.07</td>
</tr>
</tbody>
</table>
The anthropogenic sources of heavy metals can be further subdivided into two general groups (Brown et al., 1990; Tarr & Ayres, 1990; Macklin, 1992):

1. Those associated with production-related processes. These include mining and smelting, energy generation, manufacturing and agriculture. Brown et al. (1990)

2. Those associated with consumption-related processes. These include the use, wear and eventual disposal of consumables and commercial products. The weathering and flaking of paints, the burning of pharmaceuticals, batteries, plastics and electrical goods, the wear and weathering of leather, plastics and surfaces which have been electroplated, and the breaking down and burning of treated wood (Tarr & Ayres, 1990; Brown et al., 1990; Macklin, 1992) Table 2.2 shows the individual heavy metals liberated as a result of each of these processes.

Table 2.3 compares the natural global average contributions of heavy metals to those emitted into the environment from high temperature, production related sources. Brown et al. (1990) state that the high temperature processes are those which are the most significant in contributing to atmospheric metal pollution, mainly due to their being emitted in fine particulate or gaseous form. Table 2.3 also illustrates that the relative enrichment of the individual heavy metals to the environment is not equal and that, with the exception of Cd, anthropogenic sources are comparable to,
Table 2.2 Heavy metals released as a result of consumption related activities

1. Weathering and flaking of paints and pigments

   Ag, As, Cr, Cd, Cu, Hg, Pb, Zn

2. Burning of

   a.) discarded pharmaceuticals (Ag, As, Cr, Zn)
   b.) batteries (Hg, Cd)
   c.) electronic tubes (Hg)
   d.) plastics (Zn)
   e.) photographic film (Ag)

3. Wear and weathering of

   a.) electroplated surfaces (Cd)
   b.) leather (Cr)
   c.) plastics (Zn)

4. Breaking down and burning of treated wood

   As, Cr, Cu,
Table 2.3 Average annual global trace element contributions (in thousands of metric tons) to the environment from natural and high-temperature production-related sources (Brown et al., 1990).

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Se</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dust</td>
<td>0.24</td>
<td>0.25</td>
<td>10.0</td>
<td>0.3</td>
<td>0.03</td>
</tr>
<tr>
<td>Volcanoes</td>
<td>7.0</td>
<td>0.5</td>
<td>6.4</td>
<td>0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>Forest fires</td>
<td>0.16</td>
<td>0.01</td>
<td>0.05</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Vegetation</td>
<td>0.26</td>
<td>0.2</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea salt</td>
<td>0.14</td>
<td>0.002</td>
<td>0.1</td>
<td></td>
<td>0.003</td>
</tr>
<tr>
<td>Total</td>
<td>7.8</td>
<td>0.96</td>
<td>18.6</td>
<td>0.4</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mining</td>
<td></td>
<td></td>
<td></td>
<td>8.1</td>
<td>0.005</td>
</tr>
<tr>
<td>Smelting non-ferrous metals</td>
<td>15.2</td>
<td>5.3</td>
<td>77.2</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Fe production</td>
<td>4.3</td>
<td>0.1</td>
<td>50.0</td>
<td>0.01</td>
<td>0.45</td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td>0.04</td>
<td>7.2</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Burnt waste</td>
<td>0.4</td>
<td>1.4</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P fertilizer</td>
<td>2.6</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal burning</td>
<td>0.5</td>
<td>0.05</td>
<td>13.9</td>
<td>0.68</td>
<td>0.63</td>
</tr>
<tr>
<td>Wood burning</td>
<td>0.5</td>
<td>0.2</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Petroleum combustion</td>
<td></td>
<td>273.0</td>
<td></td>
<td>0.06</td>
<td>0.27</td>
</tr>
<tr>
<td>Total</td>
<td>23.5</td>
<td>7.29</td>
<td>439.4</td>
<td>1.085</td>
<td>1.35</td>
</tr>
</tbody>
</table>

1 Other industrial activities
2 Pb is introduced into the environment primarily from the use of leaded petrol
or greater than, those from natural sources. Human society is thus the most important factor in the global biogeochemical cycling of heavy metals in the environment (Nriagu, 1990; Macklin, 1992).

The history of the human use of heavy metals goes back to prehistoric times (Macklin, 1992) when mining and smelting provided the main sources of pollution to the environment. This activity was local or at most regional in impact until the Industrial Revolution since when

"...the production and discharge of trace metals in the environment have been increasing almost at a logarithmic scale."

Nriagu (1990) p 114

The initial discharge of heavy metals into the environment may be through the atmosphere, onto land or directly into the fluvial and limnic systems, but their ultimate dispersal is dependent on the hydrological cycle. The form in which they are released dictates the pathway they take. They may be released in gaseous, particulate, liquid or solid form (Macklin, 1992) and enter the fluvial system in different ways depending on whether they are dispersed from diffuse (non-point) or discrete (point) sources (Mattigod & Page, 1983). Fig 2.3 illustrates the pathways of heavy metals in the freshwater environment from their release to their incorporation in fluvial or limnic sediment. They may remain
Fig 2.3 Pathways of heavy metal transport in the environment
as a sink or be remobilised into other environmental compartments (Macklin, 1992) and thus become non-point sources.

The atmosphere is therefore an important primary source of heavy metals to the environment, but the catchment provides both primary and secondary (remobilised) sources as well as sinks of these trace metals. The sinks of heavy metals therefore provide the focus for studies which attempt to reconstruct the history of heavy metals at the lake-catchment level.

The following sections consider the properties of the heavy metals which facilitate their movement through the aquatic ecosystem.

ii. The chemical properties of heavy metals.

Fig 2.4 shows that heavy metals are generally found in the lower right hand corner of the periodic table. This defines their chemical behaviour (Förstner & Wittmann, 1981), as members of the same group behave chemically in a similar way. Zn and Cd, therefore, often appear together in geochemical processes and Cd may replace Zn in certain enzymes, thus impairing their catalytic function (Manahan, 1993). According to Förstner & Wittmann (1981), metals are characterised primarily by their good conduction of electricity and their electrical resistance which is directly proportional to absolute temperature. Other secondary properties include high
Fig 2.4 The Periodic Table to show the position of Cd, Cu, Zn, Pb and Ni
thermal conductivity, malleability, ductility and high density. It is the property of high density which is mostly used to characterise heavy metals in the environment. Davies (1980), defines the heavy metals as having a density of greater than 6 g cm$^{-3}$.

Due to their chemical properties and relative abundance in the Earth’s crust, heavy metals are:

1. Extracted and frequently used by society
2. Used where living things can come into contact with them
3. Able to significantly disturb the biogeochemical cycle.
4. Toxic to living organisms

(Fergusson, 1990)

Woods' (1974) classification of heavy metals, (in Förstner & Wittmann, 1981), divides them into three categories based on biogeochemical behaviour as:

1. Noncritical to ecosystems
2. Toxic but very insoluble or very rare
3. Very toxic and relatively accessible.

Any study of heavy metal contamination in the environment should therefore pay special attention to the third of Woods categories above as posing the biggest threat to biota. Table 2.4 outlines the densities and crustal abundances of the heavy metals considered in this research project.
Table 2.4 Characteristics of Cu, Cd, Zn, Ni and Pb. From Macklin (1992) after Davies (1980).

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.7</td>
<td>8.9</td>
<td>11.3</td>
<td>8.9</td>
<td>7.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>55.0</td>
<td>13.0</td>
<td>75.0</td>
<td>70.0</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>E</td>
<td></td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>4</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

1 = Density (g cm⁻³)
2 = Mean content in crustal rocks (ppm)
3 = Whether essential (E) to biota
4 = Whether a known pollutant (P)
5 = Woods' category (see above)

The heavy metals can further be subdivided into those which are essential or non-essential to the biosphere. A deficiency of an essential metal can lead to a lack of growth; sufficient leads to optimum growth and an over supply can result in effects on the organism ranging from stunted development to premature mortality (Fig 2.5). Whilst those not having a recognised biological function are classified as non-essential, their function is not absolutely certain.
Fig 2.5 Ecosystem response to metal availability

- Essential Metal Concentration
  - YIELD GROWTH
  - deficient → optimal → toxic → lethal

- Non-Essential Metal Concentration
  - YIELD GROWTH
  - tolerable → toxic → lethal
The toxicity of the various metals depends on many factors, (Table 2.5). These include those factors relating to the properties of the element itself as well as its interaction with organisms. Individual metals betray their toxicity in different ways, Table 2.6 summarises some of these effects.

The availability, uptake and hence toxicity of heavy metals in the environment is dependent on several factors. These include both biotic, as well as abiotic factors, which are summarised in Fig 2.6 and Tables 2.7 and 2.8.

The present study is confined to the sources, transport modes and incorporation of heavy metals in sediments and their bioavailability, rather than any concerns with metabolic pathways within the organisms themselves. In this study, therefore, the impact of the biosphere on the movement of heavy metals in the aquatic environment is considered in terms of its availability as organic matter or sedimenting particles within the water column, rather than in any physiological context.

iii. Transport of heavy metals in the aquatic environment

The transport and fate of heavy metals in aquatic ecosystems is complex due to the difficulty of defining the relative proportions in dissolved and particulate phases, the lack of establishment of equilibrium conditions and the numerous interactions occurring (Salomons & Förstner, 1984).
Table 2.5 Factors affecting the toxicity of heavy metals in solution (after Bryan 1976).

<table>
<thead>
<tr>
<th>Form of metal in water</th>
<th>Ion</th>
<th>Complex ion</th>
<th>Chelate ion</th>
<th>Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inorganic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particulate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colloidal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorbed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Presence of other metals or poisons</th>
<th>Joint action</th>
<th>More-than-additive</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No interaction</td>
<td>Additive</td>
</tr>
<tr>
<td></td>
<td>Antagonism</td>
<td>Less-than-additive</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Factors influencing physiology of organisms and possibly form of metal in water</th>
<th>Temperature</th>
<th>pH</th>
<th>Dissolved oxygen</th>
<th>Light</th>
<th>Salinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage in life history</td>
<td>Changes in life cycle</td>
<td>Age and size</td>
<td>Sex</td>
<td>Starvation</td>
<td>Activity</td>
</tr>
<tr>
<td>Condition of organism</td>
<td>Altered behaviour</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.6 The effects of the toxicity of heavy metals on biota. From Fergusson (1990) and MAFF (1993).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Competition with Zn in occurrence with certain enzymes. Cd can bind irreversibly with active sites on the enzyme, destroying normal metabolism.</td>
</tr>
<tr>
<td>Cu</td>
<td>Essential to the diets of birds and mammals due to its' enzymatic activity. Excess accumulates in the liver.</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb salts relatively insoluble in water. 90% of Pb taken up by living organisms accumulates in the bone remaining immobile for years. Any disturbance of normal metabolic function can remain undetected. Non-essential, Pb is found throughout the body.</td>
</tr>
<tr>
<td>Zn</td>
<td>Essential trace element, found in all cells. Acts as a cofactor of many enzymes. Excess affects children or individual with erratic metabolisms.</td>
</tr>
<tr>
<td>Ni</td>
<td>Toxic to cereals and other crops such as French beans.</td>
</tr>
</tbody>
</table>
Fig 2.6 Biotic and abiotic factors controlling heavy metal availability in the environment
Table 2.7 Biotic and abiotic factors influencing the availability of heavy metals to the environment. After Fergusson (1990).

<table>
<thead>
<tr>
<th>Biotic</th>
<th>Abiotic</th>
</tr>
</thead>
<tbody>
<tr>
<td>The life cycle and life history of the organism</td>
<td>Temperature and oxygen content</td>
</tr>
<tr>
<td>Seasonal variations</td>
<td>Water hardness</td>
</tr>
<tr>
<td>Species specific and individual variability</td>
<td>The presence of organic compounds</td>
</tr>
<tr>
<td>Food contamination</td>
<td>The pH of the surrounding medium</td>
</tr>
<tr>
<td>Trophic level (in an ecological sense)</td>
<td></td>
</tr>
</tbody>
</table>

This section outlines the modes of heavy metal transport in the aquatic environment and relates these to a consideration of deposition and speciation in deposited sediment. Heavy metals can be transported in aqueous solution, as a colloid, or in particulate form. According to Fergusson (1990), this division is arbitrary, being mainly dependent on
Table 2.8 Abiotic factors involved in the availability of heavy metals to the environment. After Fergusson, 1990.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature and oxygen content</td>
<td>Influences redox conditions in water and sediment and hence metal availability. Metal concentrations in interstitial waters associated with anaerobic sediments are 10 times greater than those in supernatant water.</td>
</tr>
<tr>
<td>Water hardness</td>
<td>Insoluble carbonates formed, decreasing heavy metal activity. They can then be adsorbed onto calcium carbonate.</td>
</tr>
<tr>
<td>Organic compounds</td>
<td>Includes living organisms, organic substrates and synthetic compounds such as PCBs released due to biodegradation. Anthropogenically polluted lakes are commonly eutrophic; the balance between productivity, degradation and incorporation of organic compounds may therefore be disturbed, leading to increased heavy metals.</td>
</tr>
<tr>
<td>pH values</td>
<td>Effects of changing pH are indirect as it impacts upon all of the above processes.</td>
</tr>
</tbody>
</table>
particle size. Thus, sizes of 0.45 μm and less are considered to be soluble, sizes greater than 0.45 μm are considered to be either colloidal or particulate, i.e., in suspension or as sediment respectively.

Figure 2.7 illustrates this partition of metals with size, and hence solubility, using Pb and Cd as examples. Figure 2.7 also shows the speciation of heavy metals in water, and the chemical form in which the metal is likely to occur. This depends on several factors including:

1. The solubility, or size, of compounds of the element
2. The oxidation state of the element
3. Whether complexing agents are available
4. Whether complex formation occurs
5. Whether ion-pair formation occurs
6. If particulate material is available, whether adsorption or desorption occurs
7. The nature and availability of biochemical processes

Speciation is important as it fundamentally influences the mobility and toxicity of the metal in the environment (Harrison, 1987). Factor 6 above is particularly important; Förstner & Salomons (1981 a) state that contaminants

"...upon being discharged to surface waters, do not remain solubilised since they are rapidly adsorbed by particulate matter..."  
Förstner & Salomons (1981 a) p 3
**Fig 2.7** Speciation of heavy metals in water dependent on particle size (after Fergusson, 1990)

![Diagram](image)

<table>
<thead>
<tr>
<th>Soluble</th>
<th>Colloidal</th>
<th>Particulate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free metal ion</td>
<td>Metal species attached to high molecular weight organics</td>
<td>Metal species sorbed to colloids</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Pb fulvic acid complexes</td>
<td>PbFe(OH)₃, PbMnO₂</td>
</tr>
<tr>
<td>PbCO₃, PbHCO₃, PbNTA, PbCl⁺</td>
<td>Pb humic acid complexes</td>
<td>Pb amino acids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb organic complexes</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Cd fulvic acid complexes</td>
<td>CdFe(OH)₃, CdMnO₂</td>
</tr>
<tr>
<td>CdCO₃, CdCl₂, CdCl₃</td>
<td>Cd humic acid complexes</td>
<td>Cd amino acids</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd organic complexes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd clays</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb clays, Pb₆(OH)₃-(CO₃)₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CdCO₃(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cds</td>
</tr>
</tbody>
</table>
Before adsorption onto particulates, however, heavy metals are transported in a dissolved form in which factor 1 above is of importance. The residence times in a lake give an idea of the rapidity with which heavy metals preferentially adsorb to particulates and are summarised in Table 2.9 for Lakes Michigan and Washington.

Table 2.9 Mean residence times (in years) of heavy metals in lake waters. After Förstner & Wittmann (1981).

<table>
<thead>
<tr>
<th>Element</th>
<th>Lake Michigan</th>
<th>Lake Washington</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>$8.9 \times 10^1$</td>
<td>$5.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>Cu</td>
<td>$3.7 \times 10^1$</td>
<td>$1.3 \times 10^0$</td>
</tr>
<tr>
<td>Zn</td>
<td>$4.1 \times 10^2$</td>
<td>$1.8 \times 10^8$</td>
</tr>
<tr>
<td>Cd</td>
<td>$4.1 \times 10^2$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

Pb has a relatively short residence time, but Cd has a long one reflecting its weaker binding to particles, ie it behaves as a semi-conservative element (Tisue & Fingleton, 1984).

Sigg (1983) demonstrates that the partition between the dissolved and particulate phases is strongly pH dependant. It is likely, therefore, that the transfer of heavy metals from river water to the water column in lakes will not affect
overall chemical conditions; hence leading to little change in speciation. However, as the pH of rainwater varies between 5 and 7 under natural conditions (Petts & Foster, 1985), and possibly as low as 4.5 in areas subjected to 'acid rain', the heavy metals carried in precipitation are likely to be in dissolved form. When they are deposited in a lake, it is likely that large changes in speciation in the top few centimetres of the lake water, sediment or both will result.

It is possible to evaluate the distribution of heavy metals between the dissolved and particulate phases by calculation of partition coefficients:

$$K_p \left( \text{m}^3 \text{ kg}^{-1} \right) = \frac{C_s \text{ (moles kg}^{-1} \right)}{C_w \text{ (moles m}^{-3} \right)} \quad \text{(Equation 2.2)}$$

where:

- $C_s$ = concentration in particles
- $C_w$ = concentration in soluble form

The coefficients for Zn, Cu, Cd and Pb, valid for Lake Constance, are given in Table 2.10. If the partition coefficient is less than 100 then the amount in solution is 90% of the total. The coefficient for lead is uncertain as its $C_s$ is not really known with any accuracy. It appears to show preference for existing in the particulate phase. A partition coefficient ($K_p$) of $10^3$ indicates that the soluble concentration is 50% of the total. Direct experiments
Table 2.10 Particle-water partition coefficients ($K_b$) determined from their concentrations in water compared to that of settling particles. After (Sigg, 1983).

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1-2</td>
<td>0.3-1.0</td>
<td>5x10^{-1}-0.02</td>
<td>0.05-1.0</td>
</tr>
<tr>
<td>Particles</td>
<td>130</td>
<td>30</td>
<td>0.3</td>
<td>50</td>
</tr>
<tr>
<td>Partition Coefficient</td>
<td>100</td>
<td>35</td>
<td>30</td>
<td>1000</td>
</tr>
</tbody>
</table>

with Cd and Cu have confirmed that they preferentially exist in the dissolved phase (Sigg, 1983), although their partition coefficients for Lake Constance indicate that in that environment, with $K_b$s of 30 and 35 respectively, it would be expected that 90% of Cd and Cu would be in the dissolved phase. Work carried out by Proffitt (1993) on contaminated river water in the River Sherbourne (English Midlands) shows that partition coefficients can be site or environment-specific. Table 2.11 shows the percentage of individual heavy metals present in water in the particulate phase.
Table 2.11 Average percentage of heavy metals carried in the particulate phase of suspended sediments in rivers in the English Midlands. From Proffitt, 1993, p 49.

<table>
<thead>
<tr>
<th>Element</th>
<th>percentage in suspended sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>45.2</td>
</tr>
<tr>
<td>Pb</td>
<td>96.3</td>
</tr>
<tr>
<td>Cu</td>
<td>58.78</td>
</tr>
<tr>
<td>Ni</td>
<td>65.0</td>
</tr>
<tr>
<td>Cd</td>
<td>79.5</td>
</tr>
</tbody>
</table>

The element with the highest proportion transported on particulates is Pb; this is also the element with the highest $K_b$ according to Sigg (1983). Zn has the lowest proportion transported in particulate form in English Midland rivers in contrast to its $K_b$ presented for Lake Constance (Table 2.10), with Cd, Ni, and Cu lying between these two extremes.

a. Speciation of heavy metals in water

The speciation of the heavy elements in water is dependent upon many physical, chemical and biological factors (Brezonik et al., 1991). These are outlined in Table 2.12. These environmental conditions determine the speciation (the chemical form in which the metal occurs) of the heavy metal in
Table 2.12 Environmental conditions affecting the speciation of heavy metals in solution (Brezonik et al., 1991).

Solution conditions

General: Ionic strength (M)  ) No great variations shown  ) in freshwater

Temperature  ) Seasonal significance

pH

Eh

Specific conditions which relate to binding of the metal to the ligand: generally thought to be available to aquatic organisms

Concentrations and nature of inorganic ligands:
Alkalinity ($\text{HCO}_3^-, \text{CO}_3^{2-}$)

Presence of anions in anoxic water: $\text{F}^-$, $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{HS}^-$

Industrial waste contamination: $\text{CN}^-$

Concentrations and nature of organic chelating agents: generally thought not to be available to aquatic organisms

DOM  ) Important in bioaccumulation and toxicity especially with regard to complex formation

Aquatic humus  ) Can be important complexing agents in some surface waters

Natural organic acids  ) Can be important complexing agents in some surface waters

Peptides

Polyaminocarboxylates ) complexing agents in some surface waters

Concentrations and nature of surface sites available on particulate matter for metal binding

Time

An important consideration is the time available for thermodynamic equilibrium to be reached. Reactions involving complex formation on ligands can take time and are dependant on the conditions outlined above.

Reactions involving oxidation and reduction can be slow and can also be dependant on similar conditions to complex formation.
solution. The following section briefly discusses the importance of pH and Eh in heavy metal speciation.

1. pH

Lunt et al. (1989) emphasise the importance of pH in determining the speciation of the metal in the dissolved phase. There can be a very abrupt change over a small pH range of 1-2 units. Förstner & Kersten (1988) illustrate the dependence of metal solubility on pH with case studies undertaken by Dickson (1980) from 16 Swedish lakes (Fig 2.8). These graphs show minimum solubilities for Cd and Pb at neutral pHs and increasing solubility with increasing acidity. pH is therefore an important environmental variable to consider from the point of view of remobilisation of heavy metals, particularly should the conditions change due to acid rain or accidental acid spillage within the catchment.

In the natural environment, the range of conditions tolerable to biota is narrow; hence when considering the chemistry of heavy metals in the natural environment it is only necessary to consider a narrow range under normal circumstances.

The normal pH for natural river water lies between 4 and 9 (Petts & Foster, 1985), although accidental spillages of industrial effluent can occur lowering the pH to as little as 2 (Foster et al., 1990).
Fig 2.8 Dissolved metal concentrations (µg l⁻¹) relative to pH in 16 lakes on the west coast of Sweden (after Förstner and Kersten, 1988)
2. Eh

Eh is a measure of redox potential and defines whether the environment is experiencing oxidising or reducing conditions. Fig 2.9a shows the range of Ehs found in the natural environment. Fig 2.9a is also a combined Eh-pH diagram and illustrates the interaction between these two properties. The zone of stable water trends across the centre of the diagram with the zone of the natural environment in the central one third. Taking individual heavy metal elements, the Eh-pH diagrams for Pb, Cd and Zn are shown in Figs 2.9 b, c and d. Cd exists as Cd$^{2+}$ in aqueous solution up to pH 9, whereas Zn$^{2+}$ exists to pH 7.5 and Pb$^{2+}$ to pH 7. The Eh does not affect the form of these elements in stable water except for Zn in which ZnS appears stable under reducing conditions.

The exact form in which the metal is found will influence its bioavailability and the nature of the interactions of the pollutant with the environment, but its species is determined by the prevailing environmental conditions as outlined above.

b. Transport on particulates

The most important mechanism for the transport of heavy metals and their eventual loss to the water column is through their attachment to settling particles:
Fig 2. 9 Eh / pH diagrams
a. Natural waters (after Petts and Foster, 1985)  b. Pb (after Fergusson, 1990)
"In most aquatic systems, concentrations of trace metals in suspended sediment are far greater than concentrations of trace metals dissolved in the water column."

Horowitz (1985) p 1

This section examines the various ways in which heavy metals can become incorporated into the sediment of lakes by their settling out at the mud-water interface in association with particulate and organic material.

Gibbs (1973) suggests that there are four groups of heavy metal associations in aquatic solid substances. These are:

1. Adsorptive bonding
2. Coprecipitation by hydrous Fe and Mn oxides
3. Complexation by organic minerals
4. Incorporation in crystalline minerals

Considering each of these in turn:

1. Adsorptive bonding

Some materials making up sediments, such as clay minerals, newly precipitated iron hydroxides, amorphous silicic acids and organic substances, have large surface areas. This property enables them to exchange cations by sorption. This occurs due to the attraction between the negatively charged sites on the clay minerals such as SiOH⁻, AlOH₂⁻ and AlOH⁻, or
FeOH\(^+\) groups in iron hydroxides or carboxyl and phenolic OH\(^-\) groups in organic substances, and the positively charged cations, represented by the individual heavy metal. Preferential adsorption of certain cations occurs which selectively balances the overall charge on the particle. Charges are equalised when an equivalent charge is released from the particle when the heavy metal is adsorbed. All fine-grained sediments are able to attract heavy metal ions at the solid-liquid interface because of intermolecular forces due to their large surface area.

The pH of the environment and the resultant charge on the surface of the particle affects its behaviour as shown in Table 2.13. Hydrous oxide surfaces are used as they have been studied in detail and therefore can be used as models of the particles occurring in natural waters (Sigg, 1987)

<table>
<thead>
<tr>
<th>Prevailing environmental conditions</th>
<th>surface charge on particle</th>
<th>type of exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic</td>
<td>negative</td>
<td>cation</td>
</tr>
<tr>
<td>Acidic</td>
<td>positive</td>
<td>anion</td>
</tr>
</tbody>
</table>
Under basic environmental conditions, a hydrous oxide with negative surface charge would be a cation exchanger and sorb heavy metals to its surface. On the other hand, a hydrous oxide under increasingly acidic conditions is more likely to act as an anion exchanger. It has been demonstrated by Guy & Chakrabarti (1975) that the adsorption capacity of different media at intermediate equilibrium concentrations \( (C_{eq}) \) of the individual metal has different properties. The adsorption of Cu, Pb, Cd and Zn onto clay minerals should exhibit no maximum, whereas the adsorption of the same ions onto humic acid and Fe and Mn oxides would exhibit an adsorption maximum. In other words, \( C_{eq} \) is reached where the number of cations adsorbed is equal to their concentration in solution. Adsorption onto clay minerals results in increased adsorption with increased concentration. On the other hand, in the case of sorption with Fe and Mn oxides and humic acids, adsorption is finite. Adsorption of heavy metal ions onto clays may therefore not simply involve the binding of the ion to specific sites on the clay. Indeed, it may be that the heavy metal not only replaces cations on the clay particle, but also diffuses into the crystal lattice of the clay in relatively small amounts. A controlling factor in the sorption of heavy metals to clays may be pH (Förstner & Wittmann, 1981). \( H^+ \) competes with the positively charged heavy metal ion for exchange sites. At increasingly acid pH, the heavy metals may be released from
the binding site as they cannot compete with the high concentrations of H⁺.

2. Coprecipitation by hydrous Fe and Mn oxides

Fe and Mn oxides and hydroxides occur as mineral coatings and as finely divided particulate material in soils and in the aquatic environment.

These coatings and particles are capable of sorbing or coprecipitating heavy metals (Förstner & Wittmann, 1981). They are, therefore, important sinks of these metals and directly control their distribution within the environment. However, the sorbed metal can easily become remobilised should environmental conditions change; more specifically under reducing conditions, whereupon the hydrous Fe and Mn oxides can become a source of heavy metal contamination.

3. Complexation by organic materials

Organic substances in natural ecosystems consist mainly of the remains of biota and their metabolism products and of abiotic, or synthetic, organic materials.

The attachment by complexation onto organic matter by heavy metals is important in that it influences the behaviour of the metal within the aquatic ecosystem. Singer (1977) divided the effects of dissolved organic substances on the behaviour of trace metals into 5 major groups:
a. Complexation of metals with organic matter changes the availability of the metal.

b. The distribution of the metal between the oxidised and the reduced form is changed.

c. By effectively removing the metal from the water column, the organic matter-trace metal complex reduces the toxicity of the metal by essentially removing it from the water column and hence from close proximity to biota.

d. The extent to which metals are subsequently adsorbed onto suspended sediment is directly affected by dissolved organic material.

e. Colloid containing metals are less stable in the presence of such organic matter.

Once formed, the complex can then either be adsorbed onto particulate sedimentary material for incorporation into the bed sediment of the lake, or it can precipitate directly onto the sediment itself.

4. Incorporation in crystalline minerals

Heavy metals may be located in the lattices of minerals; their incorporation is dependent upon ionic radii, valencies and
electronic configuration. The bonding generally occurs in inert positions in the crystal lattice and, once incorporated, the metal may be considered unavailable to the environment.

Whilst it is possible to theorise about these binding sites in isolation, in practise many interactions between the different sites occur in natural situations, eg there is strong evidence to suggest that particulate matter has a thin covering of natural organics (Hart, 1982) which would influence the binding of heavy metals to particulate matter.

2.6 Selection of heavy metals in the research programme.

The elements chosen for this study (Cd, Ni, Cu, Pb and Zn) were selected for 6 main reasons:

1. They have known pollutant properties

2. They are classified in the third of Woods’ three categories, as outlined in Section 2.3i, ie that they are toxic and readily accessible to the environment.

3. Each element is frequently used in consumption and production related processes and hence is commonly found in the urban environment (Tables 2.2 and 2.3).

Pb is the most widely used heavy element industrially (Fergusson, 1990) and, with Cd, is of concern to health. The use of Ni and Cd in battery production is increasing, as is Zn
in the electroplating industry. Cu has been widely used in many processes including the manufacture of electrical cables and in coinage. The use of a Zn : Pb ratio as an index of production (of Zn in, for example, the electroplating industry) versus consumption (of Pb in leaded fuel) has been used by Foster et al., 1994, and appears to show a relative decrease with increasing urbanisation. This ratio will be examined in Chapter 7.

4. Cu, Cd, Pb, Ni and Zn have been widely used in research carried out to assess the extent of heavy metal pollution and information derived from this study would therefore provide comparative data.

5. The five elements chosen are readily analysed using standard acid digestion techniques followed by analysis using atomic absorption spectrophotometry.

6. The elements chosen are readily transferred to the sediment at the mud-water interface. Mobility of heavy metals across the mud-water interface can be viewed as an 'equilibrium' in which the balance is in favour of transfer to the sediments (Jennett et al., 1980).

Mobility of the elements, once incorporated in the sediment, could be a problem in that it could change the
distribution of the metal within the sediment profile. In the case of within-sediment mobility, Alderton (1985) states that:

"Mobilisation of metals and organic compounds within the sediment is assumed to be of minor importance in most instances."

Alderton (1985) p 1

Farmer et al. (1980), found no evidence for diagenetic mobility of Pb, Zn, or Cd in the sediments from Loch Lomond, but did find evidence of mobility of As in that 80% of the total excess for As was found in the upper 4 cm of the core.

The five elements chosen appear to conform to Alderton’s (1985) prerequisites for a pollutant to provide a historical record of enrichment; they have an affinity for the sediment, and do not remain preferentially in the dissolved phase an observation generally supported by the research on contaminated Midland rivers given in Table 2.11, except for Zn.

2.7 Choice of field sites.

As pointed out by Macklin (1992), the heavy metal content of urban soils has been largely ignored in recent research, particularly when consideration is given to the large body of work concerned with agricultural soils in Britain. The same is true of urban lakes, in which very little work has been carried out on the pollution status of inner city lakes and
pools in the UK. Whereas problems exist in assessing background concentrations in urban soils due to overprinting by metal contaminants from, for example, vehicle exhaust emissions, this is not the case when analysing a lake core which represents the gradually accumulated results of historical contamination.

The first site chosen for the present study, Swanswell Pool, is a city centre site (Fig 3.6) which has been a closed basin for the last 150 years (section 3.4.1). It provides some degree of experimental control in that it receives contributions mainly from the atmosphere.

The second site, Wyken Slough, comprises the Slough, an area of marshland and a lake, Wyken Pool itself. It is fed by two inflowing streams, and has a catchment with various sources of pollution. Characteristics of both pools are given in Table 2.14 and further detailed descriptions of both sites are given in Chapter 3.

Section 2.4 outlined the numerous studies undertaken in areas of mining and the effects of the urbanised area at some distance from the source of contamination. However, there has been no assessment of the gradient of atmospheric pollution from the urban area into rural regions using lake sediments. Work complementary to this type of study has been carried out in the Geography Department, Coventry University in two other regions of the UK:

1. Rural locations in North Warwickshire in close proximity to, and downwind of, Midland England industrial conurbations but with no direct catchment sources of metal
Table 2.14 The characteristics of Swanswell Pool and Wyken Slough

<table>
<thead>
<tr>
<th></th>
<th>Swanswell Pool</th>
<th>Wyken Slough</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid reference</td>
<td>SP335795</td>
<td>SP363833</td>
</tr>
<tr>
<td>Resevoir area (ha)</td>
<td>0.73</td>
<td>2.25</td>
</tr>
<tr>
<td>Catchment area (ha)</td>
<td>220.0</td>
<td>450.0</td>
</tr>
<tr>
<td>Resevoir:catchment</td>
<td>1:301</td>
<td>1:200</td>
</tr>
<tr>
<td>Max. altitude (m)</td>
<td>105</td>
<td>112</td>
</tr>
<tr>
<td>Mean water level (m)</td>
<td>70</td>
<td>85</td>
</tr>
<tr>
<td>Relative relief (m)</td>
<td>35</td>
<td>27</td>
</tr>
<tr>
<td>Max. depth (m)</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Mean depth</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Volume (m³)</td>
<td>6389</td>
<td>13050</td>
</tr>
<tr>
<td>Date impounded</td>
<td>1265</td>
<td>c.1850</td>
</tr>
</tbody>
</table>

Present land use % area

<table>
<thead>
<tr>
<th></th>
<th>Urban</th>
<th>Permanent pasture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>c. 40</td>
<td>c. 60</td>
</tr>
</tbody>
</table>

' by the twentieth century, the catchment area was reduced to < 1 ha. The inflowing streams were culverted in 1850 and the hospital spring feeders were cut off in the 1960’s (Chapter 3.4.1 and Table 3.2). The reservoir : catchment ratio was reduced to c. 1 and the catchment altitude reduced to < 2 m above mean water level.
contamination. The two sites are Seeswood Pool and Merevale Lake, with predominantly agricultural and forested catchments respectively. Catchment descriptions are given elsewhere (Foster et al., 1987 and 1991), but the major source of heavy metals to these lakes is from the atmosphere (Foster et al., 1991).

2. Isolated lakes and reservoirs remote from local and regional sources of atmospheric pollution and with no direct catchment derived sources of contamination. (Foster, 1987; Dearing et al., 1989). The two sites are Porth Hellick and Big Pool, Isles of Scilly. Catchment descriptions for these lakes are given elsewhere (Foster et al., 1991), but Big Pool, like Swanswell Pool has no channelled inflow, and for both sites the only source of heavy metals is from the atmosphere.

The data from the current study will be set in the context of findings from the investigations outlined above.

2.8 Sampling strategies.

This section justifies the sampling strategy employed at both sites. As Swanswell Pool has effectively no catchment, sampling concentrated on the lake sediments and on water quality. However, in the case of Wyken Slough, the catchment components are considered individually. Tables 2.15 and 2.16 summarise the sampling strategy employed at each site. Appendix 2 summarises the field handling of the samples and techniques used for analysis.
Table 2.15 Numbers of lake sediment cores and surface samples taken from each site

a.) Swanswell Pool

12 surface samples
12 Mackereth cores sliced at 1 cm intervals:

<table>
<thead>
<tr>
<th>Number of samples per core</th>
<th>Depth to red clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>72</td>
</tr>
<tr>
<td>M2</td>
<td>79</td>
</tr>
<tr>
<td>M3*</td>
<td>84</td>
</tr>
<tr>
<td>M4</td>
<td>50</td>
</tr>
<tr>
<td>M5</td>
<td>55</td>
</tr>
<tr>
<td>M6*</td>
<td>67</td>
</tr>
<tr>
<td>M7</td>
<td>55</td>
</tr>
<tr>
<td>M8*</td>
<td>55</td>
</tr>
<tr>
<td>M9</td>
<td>70</td>
</tr>
<tr>
<td>M10*</td>
<td>47</td>
</tr>
<tr>
<td>M11</td>
<td>56</td>
</tr>
<tr>
<td>M12</td>
<td>33</td>
</tr>
</tbody>
</table>

* cores analysed for heavy metals
### Table 2.15 (continued)

**b.) Wyken Pool**

16 surface samples

16 Mackereth cores sliced at 1 cm intervals

<table>
<thead>
<tr>
<th>Number of samples per core</th>
<th>depth to relict soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>AO* 70</td>
<td>61</td>
</tr>
<tr>
<td>A1 55</td>
<td>36</td>
</tr>
<tr>
<td>A2 73</td>
<td>56</td>
</tr>
<tr>
<td>A3 50</td>
<td>40</td>
</tr>
<tr>
<td>BO* 77</td>
<td>65</td>
</tr>
<tr>
<td>B1 48</td>
<td>30</td>
</tr>
<tr>
<td>B2 27</td>
<td>20</td>
</tr>
<tr>
<td>B3 48</td>
<td>27</td>
</tr>
<tr>
<td>CO* 72</td>
<td>61</td>
</tr>
<tr>
<td>C1 75</td>
<td>70</td>
</tr>
<tr>
<td>C2 45</td>
<td>37</td>
</tr>
<tr>
<td>C3 46</td>
<td>40</td>
</tr>
<tr>
<td>DO* 61</td>
<td>51</td>
</tr>
<tr>
<td>D1 91</td>
<td>80</td>
</tr>
<tr>
<td>D2 50</td>
<td>40</td>
</tr>
<tr>
<td>D3 38</td>
<td>30</td>
</tr>
</tbody>
</table>

* cores analysed for heavy metals
Table 2.16 Cores and samples taken from Wyken Slough

<table>
<thead>
<tr>
<th>Location</th>
<th>Samples Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marsh</td>
<td>2 Russian cores sliced at 2 cm intervals</td>
</tr>
<tr>
<td></td>
<td>Core 1 29 samples</td>
</tr>
<tr>
<td></td>
<td>Core 2 24 samples</td>
</tr>
<tr>
<td></td>
<td>20 surface samples</td>
</tr>
<tr>
<td>Streams</td>
<td></td>
</tr>
<tr>
<td>Eastern stream</td>
<td>21 bed sediment samples</td>
</tr>
<tr>
<td>Western stream</td>
<td>10 bed sediment samples</td>
</tr>
<tr>
<td>Bayton Road</td>
<td>5 bed sediment samples</td>
</tr>
<tr>
<td>Toxic Tip</td>
<td>6 bed sediment samples</td>
</tr>
<tr>
<td>Outlet</td>
<td>1 bed sediment sample</td>
</tr>
<tr>
<td>Soils</td>
<td>2 hand gouge cores sliced at 5 cm intervals</td>
</tr>
<tr>
<td></td>
<td>Core 1 10 samples</td>
</tr>
<tr>
<td></td>
<td>Core 2 10 samples</td>
</tr>
</tbody>
</table>

i. Lake sediment

A sample of sediment from the bed of a lake represents only a part of the material deposited there (Feltz, 1980). It is therefore necessary to remove sufficient material for the samples to be representative of the body of sediment as a whole. Multiple cores were taken in this study since analysis of a single core may yield only limited information, indicating rates of accumulation at a single point in the lake.
basin. A sampling strategy based on a single core would therefore take no account of the differences in spatial loadings of contaminants across the bed of the lake as a whole (Foster et al., 1987).

Dearing (1986) points out the difficulties of accurately locating sampling sites when coring in open water from a boat. This effectively precludes random sampling and for this reason both Swanswell Pool and Wyken Pool were cored on a systematic grid system (Figs 2.10a and 2.10b.)

Dearing (1986) and Foster et al. (1990) have reviewed previous lake studies and their coring densities. The data are reproduced in Table 2.17 including those of Swanswell Pool and Wyken Pool. Whilst there is no recommended optimum coring density, the framework adopted at the two Pools compares favourably with other multiple cored sites.

As Dearing (1986) points out, sampling density depends on physical parameters such as lake area and the irregularity of sedimentation as well as the time and finances available and the amount of energy required to carry out the project. The strategy employed at Swanswell Pool and Wyken Slough was designed with these criteria in mind as well as that of representativeness.

In the case of Swanswell Pool, N-S and W-E transects were established by siting ranging poles along the dam wall and the eastern side of the pool at regular 30 m intervals (Fig 2.10a). A rope was attached to either the dam wall or fountain outlets and an anchor used to steady the boat between the two fixed ropes; any slack being taken up on the ropes so they were kept taut.
Fig 2.10 Sampling strategies at
a. Swanswell Pool
b. Wyken Pool
### Table 2.17. A comparison of coring densities of published lake sediment studies with those of Swanswell Pool and Wyken Pool (Updated from Foster et al., 1990)

<table>
<thead>
<tr>
<th>Site and author</th>
<th>Number of hectares per core</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swanswell Pool</td>
<td>0.06 ha⁻¹</td>
</tr>
<tr>
<td>Wyken Pool</td>
<td>0.14 ha⁻¹</td>
</tr>
<tr>
<td>Llyn Goddienduon, N. Wales (Bloemendal et al., 1979)</td>
<td>0.04 ha⁻¹</td>
</tr>
<tr>
<td>Frains Lake, Michigan (Davis, 1976)</td>
<td>0.3 ha⁻¹</td>
</tr>
<tr>
<td>Havgårdssjön, Sweden (Dearing, 1986)</td>
<td>1.0 ha⁻¹</td>
</tr>
<tr>
<td>Llyn Peris, N Wales (Dearing et al., 1981)</td>
<td>1.3 ha⁻¹</td>
</tr>
<tr>
<td>Merevale Lake, Warwickshire, UK (Foster et al., 1985)</td>
<td>0.08 ha⁻¹</td>
</tr>
<tr>
<td>Seeswood Pool, Warwickshire, UK (Foster et al., 1986a)</td>
<td>0.16 ha⁻¹</td>
</tr>
<tr>
<td>Egari, New Guinea (Oldfield et al., 1985)</td>
<td>1.7 ha⁻¹</td>
</tr>
<tr>
<td>Loe Pool, Cornwall, UK (O’Sullivan et al., 1982)</td>
<td>1.0 ha⁻¹</td>
</tr>
<tr>
<td>Geirionydd, North Wales (Foster et al., 1990)</td>
<td>0.87 ha⁻¹</td>
</tr>
<tr>
<td>Catherine, Northern Ireland (Foster et al., 1990)</td>
<td>1.5 ha⁻¹</td>
</tr>
<tr>
<td>Llangorse, Mid Wales (Foster et al., 1990)</td>
<td>3.0 ha⁻¹</td>
</tr>
<tr>
<td>Roumi, Morocco (Flower et al., 1989)</td>
<td>12.1 ha⁻¹</td>
</tr>
<tr>
<td>Affouah, Morocco (Flower et al., 1989)</td>
<td>1.2 ha⁻¹</td>
</tr>
<tr>
<td>Azigza, Morocco (Flower et al., 1989)</td>
<td>7.4 ha⁻¹</td>
</tr>
<tr>
<td>Bussjo, Scania, Sweden (Foster et al., 1990)</td>
<td>0.12 ha⁻¹</td>
</tr>
<tr>
<td>Lake Geneva, Switzerland (Krishnaswami et al., 1971) one core</td>
<td></td>
</tr>
<tr>
<td>Lake Windermere, English Lake District (Hamilton-Taylor, 1979) two cores</td>
<td></td>
</tr>
<tr>
<td>Lake Monona, Wisconsin, USA (Bortleson and Lee, 1974) two cores</td>
<td></td>
</tr>
</tbody>
</table>
Ranging poles were also set up along the inlet end and western edge at Wyken Pool at 62.5 m intervals (Fig 2.10b). As there was no means of tying the boat off, an anchor was deployed and the boat allowed to drift into position with the prevailing wind.

ii. Marsh

There is evidence to suggest that plants can selectively take up heavy metals in their tissues and hence effectively remove the metal from the environment; this is true of terrestrial plants (Baker et al., 1990; McGraith et al., 1993 a and b) and those growing in wetlands (Harding & Whitton, 1978; Glooschenko et al., 1981; Gambrell et al., 1982; Ajmal et al., 1988). Marsh plants have been used in the water purification process (Lee et al., 1976; Gambrell, 1977; Green, 1993; Upton et al., 1994) and, in the case of soils, it may become economically viable to recover the metals which are assimilated systemically (Baker et al., 1990; McGraith et al., 1993 a and b). Preliminary work at Wyken Slough marsh by Ambridge (1989) indicated that it selectively accumulated heavy metals from the environment and concentrated them in roots and stems of living vegetation. Any study of the reconstruction of the history of this site must therefore consider the action of such sinks as they affect the amount of metals ultimately delivered to the lake.

The marsh at Wyken Slough is associated with the Eastern stream (Fig 2.10 b) and was cored on a systematic grid system (Fig 2.11 a) using a hand gouge (Fig 2.12). Bulked
Fig 2.11 Sampling strategies at Wyken Slough
a. Marsh samples
b. The Wyken Slough catchment
c. Schematic diagram of stream bed sampling sites
(NRA = sampling sites for water quality undertaken by the NRA (Severn Trent Region)
Bayton Road Industrial Estate 4.
Western Stream

Agricultural Inputs 4

1
1
3
1

POWER STATION 12

Eastern Stream

LENTONS LANE

M6

MARSH

6

OUTFLOW

Landfill Sites

Wyken Slough

Sample Sites
samples of the top 10 cm of the core were taken for analysis. Two 1 m Russian cores (Fig 2.12) were also taken from the marsh at the sites marked on Fig 2.11 a to assess the vertical distribution of heavy metals in the marsh. The grid was set out using ranging rods set at 10 m intervals and plotting the crossing points by means of measuring tapes.

iii. Streams

As Thoms (1987) points out, there have been few studies of metal contamination in urban rivers, particularly in the UK. Streams represent an important means of transport of heavy metals through the aquatic ecosystem. They can receive urban stormwater runoff which Ellis (1976) states

"...may well become the major degrading factor in receiving streams."

Ellis (1976) p 730

Section 2.5iiib discussed the transport of heavy metals in the aquatic environment and concluded that the most important mechanism was through their attachment to settling particles (Sigg, 1987; Horowitz, 1991). These particles are transported in the flowing water until they settle out either on the river bed, in a lake or they can be lost to the freshwater part of the hydrological cycle and subsequently deposited in an estuary or out at sea. Urban stream water and sediments should therefore be integrated into any study of catchment response to increased urbanisation and industrialisation.
As outlined in section 2.2, however, river or stream sediments do not retain a historical record of heavy metal pollution. They do, however, act as sinks of pollutants both in the short and long term. This is illustrated with particular reference to the effects of mining (Wolfenden & Lewin, 1978; Brook & Moore, 1988) where river sediments retain the evidence of anthropogenic excess pollutants long after the cessation of mining activity. In the case of urban streams, the concentration of heavy metals contained in the channel substrate can form the basis of an assessment of the amount which may become available to the environment should conditions change.

Samples of bed sediment from inflowing streams at Wyken Slough were taken from sites where access could be gained to surface streams. Much of the stream system flows underground or enclosed in culverts and in many cases the banks have been steeply excavated making sampling hazardous. Fig 2.11 b shows the sampling sites. In order to simplify the interpretation of these data, samples were grouped together on the basis of discrete river reaches, which are represented schematically in Fig 2.11 c.

iv. Soils

As suggested in section 2.2, soils do not lend themselves to an elucidation of the pollution record of an area due to the long industrial history of the UK and consequent overprinting by successive metal contaminants (Macklin, 1988). This overprinting makes it difficult to distinguish between
contemporary and historical contamination events. However, as Table 2.18 shows, the residence times of heavy metals in soils and alluvial deposits is comparatively long (Macklin, 1992) and they therefore represent an important sink of atmospheric wet and dry deposition as well as land-based point sources.

Table 2.18 Residence time (years) of heavy metals in soils and alluvial deposits (from Macklin, 1992)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>75 - 380</td>
</tr>
<tr>
<td>Hg</td>
<td>500 - 1000</td>
</tr>
<tr>
<td>Pb and Zn</td>
<td>1000 - 3000</td>
</tr>
</tbody>
</table>

It is important to take account of the amount of heavy metals in catchment soils for two reasons:

1. The soil acts as an important sink of heavy metals in the environment

2. The soil acts as an important source of heavy metals. This can occur due to simple erosion whereby the soil particles carrying the heavy metals are removed and transported into the fluvial system, or eroded by wind and moved in the atmosphere. This will have two effects: either the catchment soils are heavily contaminated and the pollution signal will be enhanced wherever the soil is eventually deposited, or the soil is
relatively uncontaminated and the pollution signal will be diluted.

v. Water quality

Assessment of water quality was carried out at both Swanswell and Wyken Pools. This took the form of primary and secondary data by means of direct analysis and analysis of data provided by the NRA (Severn Trent region) respectively (Table 2.19 lists the analyses undertaken at Swanswell and Wyken Pools). As outlined in iii above, urban streams are in receipt of excess heavy metals from a variety of sources. Depending on environmental conditions, these are transported in solution or preferentially sorbed to particles settling out of the water column (Sigg, 1987; Horowitz, 1991). Analysis of the conditions prevailing in the water column at both sites would allow the development of four lines of enquiry:

a. The prevailing environmental conditions would be monitored. Wyken Pool inlets and outlet were monitored at monthly intervals for a year. In addition to the collection of primary data at this site, NRA (Severn Trent region) analyses of both the Pool, and sites within the catchment (Fig 2.11 b) were also used. Water quality sampling sites at Wyken Pool were based on an earlier study undertaken by Ambridge (1989) and were chosen to maintain continuity. The sampling sites are shown on Fig 2.10 b, one sample was taken by each inlet, one from below the outlet and one at each end of the lake.
### Table 2.19 Summary of water quality data obtained for Swanswell and Wyken Pools

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>O (mg l(^{-1}))</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>O (%)</td>
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<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
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<td>+</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Eh</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Conductance</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ca</td>
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<td>-</td>
<td>+</td>
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<td>+</td>
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<td>-</td>
<td>-</td>
<td>+</td>
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<td>+</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>NO(_3)</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>NO(_2)</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
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<td>HCO(_3)</td>
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<td>+</td>
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<td>+</td>
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<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>Si</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>TON(^1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>SS(^2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>NH (-N)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Zn(^4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Cu(^+)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Ni(^+)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Pb(^+)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Cd(^+)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

1. Total oxidised nitrogen
2. Suspended solids
3. Ammoniacal nitrogen
4. Total and in filtrate for 1 - 6, total dissolved metal for 7.

1. Swanswell Pool, February, 1988, 1 sample at 3 depths in the water column
2. Swanswell Pool, April, 1988, 3 samples
3. Swanswell Pool, NRA (Severn Trent region) water quality data, 1 sample
4. Wyken Pool, January 1988, 2 samples at 3 depths in the water column
5. Wyken Pool, April 1990, 5 samples
6. Wyken Pool, NRA (Severn Trent region), water quality data, 4 samples
7. Wyken Pool water quality sampling, October 1990 to September 1991, 5 samples per month.

Location sites for water quality samples on Figs 2.10 a (Swanswell Pool) and b (Wyken Pool).
Swanswell Pool relies on mains water for its water supply, has no natural inlets or outlets, therefore inlet water quality should change little and it was felt the time should be spent monitoring Wyken Pool rather than Swanswell. The NRA (Severn Trent region) data and water samples taken 3 months apart in February and April, 1988, were used for certain analyses, these are shown on Table 2.19. Measurements were taken at one site in February 1988, but at three depths in the water column to ascertain whether water quality parameters changed with depth. A more detailed chemical analysis was carried out in April 1988 at three sites to include the site analysed in February, one adjacent to the hospital overflow and one adjacent to the public water supply (Fig 2.9a).

b. The stability of sinks of heavy metals could be assessed and hence their availability should environmental conditions change. In section 2.5 iii a) it was suggested that pH was one of the most important controlling variables in the speciation of heavy metals in water. Temperature, total conductivity (a measure of the total ion concentration in solution, Foster et al., 1981) and pH were therefore measured using ELE Paqualab water quality testing probes, to give an indication of prevailing environmental conditions which would be used to assess the stability of the sinks of heavy metals in the sediment column.

c. Any seasonal control on the transport and deposition of heavy metals could be assessed. Sigg (1983) suggests that the deposition of heavy metals may be seasonal as there are more
settling particles in the summer due to greater biotic activity and therefore incorporation of heavy metals may be greater in the summer than in the winter. This may lead to greater loss of heavy metals through the outflow in winter than in summer due to the lower concentration of particles. Higher productivity and higher sedimentation rates in the summer may more effectively remove the heavy metals from the water column, especially Cu and Zn (Sigg, 1983). Since continuous monitoring was only carried out at Wyken Pool, this aspect of water quality sampling is only considered for this site.

d. Förstner & Wittmann (1981) and Förstner & Kersten (1988) suggest that elevated salt concentrations can lead to the release of heavy metals from sediments. Monitoring of Na, Mg, Ca and K, which compete for sorption sites on solid surfaces, may give an indication of the potential for elevated dissolved metal concentrations due to increased loadings of salt washed off roads and delivered to the fluvial systems by storm sewers.

Table 2.20 summarises the water quality analyses undertaken at both sites and justifies their choice. The next section discusses the framework of sample collection.

2.9 Sample collection

Collection of vertical sections of lake sediment involves the removal of cores. Coring devices are generally of two types:
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Relates to the stability of sinks of heavy metals. At acid pH, H⁺ competes with heavy metals for binding sites leading to metal release. Eh is a measure of redox conditions, at low Eh, metals are released. Increasing temperature leads to increasing toxicity. Conductivity indicates fluctuations in total ion concentrations.</td>
</tr>
<tr>
<td>Eh</td>
<td>Relates to falling particles, gives an indication of productivity and whether eutrophication may be a problem</td>
</tr>
<tr>
<td>Temperature</td>
<td>(SS = suspended sediment)</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Relates to the competition between salts and heavy metals for binding sites. High concentrations of salts can lead to release of heavy metals.</td>
</tr>
<tr>
<td>P0,</td>
<td>Concentration of heavy metals carried in solution</td>
</tr>
<tr>
<td>NO₃,</td>
<td></td>
</tr>
<tr>
<td>NO₂⁻</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>NH₄</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td></td>
</tr>
</tbody>
</table>

See also Tables 2.7, 2.8, 2.12

In the case of recent, soft lake sediment, it is generally not necessary to employ heavy percussion equipment with motor driven devices, but a simple hand-driven corer may be used such as the Russian sampler (Fig 2.12).

Of the end filling devices, the most commonly used are the Mackereth Corer (Mackereth, 1969) which relies on compressed air to drive the sampling tube into the sediment and the Livingstone Corer (Livingstone, 1955) which is a light-weight rod-operated piston sampler.

When coring was undertaken at Swanswell Pool in 1987, a 1 m Mackereth corer was initially used from a small rubber dinghy. This proved unsuccessful as the lake was shallow and the corer tended to bounce off the bottom without taking a sample. A modified Livingstone corer (Fig 2.12) was subsequently adopted in which a perspex tube of up to 2 m in length was driven into the sediment. This technique was successful in these shallow urban lakes and cores of up to 1.8 m long were retrieved. At Wyken Pool, the base of the lake was gritty which tended to split the end of the perspex tube. As a stronger alternative, a grey plastic tube with attachments illustrated in Fig 2.12 was used. A similar technique was also employed to retrieve river bed samples from the inflowing streams of Wyken Slough in order to minimise loss of fines when sampling.

Careful field and laboratory handling of the samples collected was important to minimise disturbance or
Fig 2.12 Coring samplers used in the study

**Russian Corer**

**Modified Livingstone Method**

- Brass attachment:
  - Allen key passes through two holes and slot cut in tube

**Hand Gouge**

- Mackereth tube

- Aluminium attachment

- Rods and T-handle

- Adapted plastic tube

- Slot
contamination. Appendix 2 gives the details of the methods employed.

At the same time that cores were taken from the lake, bathymetry and sediment thickness were measured. Appendix 2 gives the details of the techniques used to construct the bathymetric map.

2.10 Analytical techniques

This section justifies the techniques used to address the aims and objectives outlined in Chapter 1. Table 2.21 summarises the techniques which were applied at Swanswell and Wyken Pools and to the various catchment components of Wyken Slough. The section is divided into two in order to differentiate between the physical and chemical properties. Fe, Mn and P are not discussed in section 2.10 ii with the sediment chemistry as they are used as palaeoenvironmental indicators of redox and productivity respectively rather than purely chemical characteristics. The changing concentration of heavy metals in lake sediments provides the focus for the reconstruction of pollution history in urban lakes, but, as stated by Smol (1992):

"Ideally, none of these approaches should be on a 'stand-alone' basis."

Smol (1992) p 49

Other techniques were therefore chosen to provide additional information which would allow better resolution of the
Table 2.21 Analysis carried out

a.) Swanswell and Wyken Pools
b.) Wyken Slough

### a. Swanswell Pool vs Wyken Pool

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Swanswell Pool</th>
<th>Wyken Pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratigraphy</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Water content</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Organic matter</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Particle size</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Mineral magnetic measurements</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Chemistry: total</td>
<td>4+12 surface</td>
<td>4+16 surface</td>
</tr>
<tr>
<td>sequential</td>
<td>1</td>
<td>1*</td>
</tr>
<tr>
<td>Mollusca</td>
<td>1</td>
<td>bulk</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Fe and Mn</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>'11'Pb and '137'Cs activities</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### b. Wyken Slough

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Marsh</th>
<th>Streams</th>
<th>Soil</th>
<th>Water quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratigraphy</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Water content</td>
<td>+</td>
<td>x</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>Organic matter</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>Particle size</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Mineral magnetic measurements</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>Chemistry: total</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>x</td>
</tr>
<tr>
<td>sequential</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>+ (PO&lt;sub&gt;4&lt;/sub&gt;)</td>
</tr>
<tr>
<td>dissolved</td>
<td>x</td>
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</tr>
<tr>
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<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+ (PO&lt;sub&gt;4&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Fe and Mn</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>x</td>
</tr>
</tbody>
</table>

**Key**

- A = all cores or samples
- 2 = number of cores
- bulk = bulk grab sample rather than a core
- * = analysis undertaken by Ambridge, 1989
- + = samples analysed
- x = samples not analysed
temporal record preserved in the lake sediments. Hence, physical properties such as those of water content, organic matter and stratigraphy have been used to provide a "fingerprint" of the core, and, allied with mineral magnetic measurements, enable correlation of the cores across the lake. Particle size down-core was measured to indicate changing sedimentating properties with time. Fe and Mn were used as proxy palaeo-redox indicators and P was measured to indicate whether eutrophication was becoming an increasing problem. Where possible, Mollusca preserved in the sediment column were also used to indicate past conditions in the lake. To put all these data into an absolute time frame, $^{210}$Pb and $^{137}$Cs dating were applied to selected cores at both sites.

Appendix 2 contains the details of how the analysis was carried out with information regarding instrumentation, chemicals and procedures and Table 2.21 summarises the techniques carried out on the sediments and soils retrieved from Swanswell and Wyken Pools, and Wyken Slough.

i. Physical parameters

It was considered important to record the physical parameters of lake sediments such as water content, organic matter and stratigraphy as any trends in the cores may reflect the biology and chemistry of the material deposited (Bengtsson & Ennell, 1986). Such parameters may also assist in core correlation where rates of deposition vary across the lake bed.
a. Stratigraphy

Variations in the material flux to lakes preserves a record of changes in the depositional and erosional regimes. When multiple coring exercises are carried out these changes can be monitored spatially and marker horizons can provide a means of correlation across the lake. This is useful when used in conjunction with other methods yielding correlatable horizons eg magnetic measurements (section 2.8e).

Stratigraphy was described using the Troels-Smith (1955) classification scheme. It is a comprehensive and widely accepted nomenclature (Goudie, 1981) and as such iscomparable with other similar work. The classification is based on a combination of various physical properties from which the deposit can be defined without recourse to its origin or post-depositional history; unlike the genetic approach which has the disadvantage of requiring knowledge of the formation of the deposit before classification can be made (Goudie et al., 1981; Berglund, 1986).

To be consistent with previous work, and to minimise bias in description, Munsell Colour Charts (1975) were used for colour comparison.

b. Water content.

Water content of lake sediments is distributed spatially in a characteristic way (Håkanson & Jansson, 1983) in that the lowest percentages of moisture are usually found in the shallowest areas, or near river mouths where coarser materials
dominate. The highest moisture content is usually found in the sediments located in the deeper parts of the lake. A downcore decrease in water content is usually observed due to compaction. The vertical, and hence temporal variation, in water content depends on:

1. The rate of sedimentation

2. The quality and characteristics of the deposit

3. The degree of compaction

4. The degree of bioturbation

5. The degree of disturbance within the catchment eg deforestation or building projects.

Water content and bulk density were measured using the procedures described in Appendix 2.

c. Organic matter

Organic matter was measured using loss on ignition at 450°C (Bengtsson & Ennell, 1986) and, under certain conditions, can be used as an estimate of organic carbon in the sample (Mackereth, 1966; Digerfeldt, 1972; Cato, 1977; Håkanson & Jansson, 1983). The correlation between loss on ignition and organic matter is reasonable for non-calcareous sediments

The estimation of carbonate content by loss on ignition at 850°C can only ever be a rough guide as various carbonate compounds volatalize at different temperatures (Ball, 1964). For the purposes of this study, however, estimates of organic matter and carbonate content by loss on ignition at the two temperatures discussed above were considered sufficiently accurate. The methodology is described in Appendix 2.

d. Particle size

The size of the particles can reflect three important characteristics of the composition of sediment (Håkanson & Jansson, 1983):

1. It reflects the processes of sedimentation

2. The capacity of the sediment for entrainment

3. The capacity of the sediment to bind pollutants, particularly when considering the partitioning of heavy metals by particle size (Förstner, 1977; Jones & Bowser, 1979; Förstner et al., 1979; Förstner & Wittmann, 1981).

Research into the partitioning of heavy metals with varying particle size has established that there is usually an increase in heavy metal concentration with decreasing particle size. Förstner & Patchineelam (1980) and Förstner & Wittmann
(1981) present data from Lake Constance and the Lower Rhine in which particle sizes from 63 \( \mu m \) down to 0.06 \( \mu m \) are given, with the maximum concentration of Zn and Ni found in the 0.2 \( \mu m \) fraction.

Förstner & Patchineelam (1980) admit to the inaccuracy of fractionating heavy metals by means of particle size. This is due to the presence of coatings on the grains of Fe and Mn, carbonates and organic matter which all scavenge heavy metals from the environment. When analysing for particle size, sediments can either be left untreated by dispersing in distilled water or various treatments can be carried out on them to ensure separation of the individual grains. Treatment involves removal of cements, such as carbonate or Fe and Mn, binding the particles together. This usually involves an acid digestion which also removes any carbonates present (Foster et al., 1985). The sediment is also treated with hydrogen peroxide to remove organic matter which occurs in long chains or flocculates and which would therefore give rise to spurious particle size results. As a result, the main sites for the binding of heavy metals in the sediments (section 2.3 ii c) are removed and the resulting particle size profile mainly reflects minerogenic elements alone; the fractions within the sediments which often contain the lowest concentration of heavy metals (Förstner & Wittmann, 1981). If the sediment were fractionated for heavy metals analysis on the basis of such a particle size profile, the resulting data would reflect the least important fraction in the sediment containing heavy metals. If, on the other hand, the sediment were analysed without pretreatment, the resulting profile would not reflect
ultimate particle size. In either case, heavy metal partitioning by particle size would seem to be meaningless in lakes with high organic matter, carbonate and iron and manganese concentrations. For the reasons outlined above, therefore, a particle size fractionation of heavy metals was not carried out at either site.

Particle sizing of the mineral fraction without a subsequent heavy metals analysis was carried out on two cores from Wyken Pool and one core at Swanswell Pool, lack of material due to other analyses prevented the analysis of a second core at Swanswell. Particle size was carried out in order to gauge the characteristics of sedimentation and the capacity of deposited sediments for resuspension (Håkanson & Jansson, 1983).

The cores used for particle size from Wyken Pool were taken from near the western inlet and near the eastern inlet (A3 and B1 respectively), that at Swanswell Pool (M8) was taken in a central location in order to avoid waste and brick rubble at the margins (Figs 2.12 a and b).

Details of procedure and sample preparation are described in Appendix 2. Particle size was measured using a Malvern 2600 Laser Diffractor. The M2600 is an optical measurement device which can sense the patterning of scattering monochromatic light. It is connected to a computer which converts the distribution of light energy on the detector rings into a particle size distribution.

The scattering of a beam of laser light by a particle is dependant on size, regardless of its motion or position in a beam of light. The diameter produced by the system is the
diameter of a sphere with the same volume as the particle, or volume diameter.

e. Mineral magnetic measurements

Mineral magnetic measurements were used in three main ways in this study:

1. To enable correlation of the cores across the lake once the grid of cores was complete (Bloemendal et al., 1979; Oldfield et al., 1979, 1983; Beckwith et al., 1984; Hunt et al., 1984; Stott, 1986; Thompson & Oldfield, 1986; Grew, 1990)

2. To aid in the tracing of sediment sources and characterisation of fluvial and limnic sediments. The magnetic characteristics of potential sources such as street dust, fly ash and deposits from the exhausts of internal combustion engines can be compared with the signal obtained from the sediments and a possible source inferred (Thompson et al., 1975, 1980; Thompson & Morton, 1979; Oldfield et al., 1983; Dearing, 1986, 1992; Flower et al., 1989; Gaillard et al., 1991).

3. To study any relationship between magnetic characteristics of the sediments and heavy metal concentrations. This was used to explore the possibility of magnetic characterisation serving as a surrogate measure for estimating certain pollutants present in lake sediments (Hunt et al., 1984; Beckwith et al., 1986; Brilhante, 1989; Foster et al., 1991).
Magnetic measurements are versatile as they are quick to make, relatively cheap, repeatable and non-destructive (Oldfield et al., 1983). They have been used in both lakes and rivers with varying climates in order to correlate cores, provide information on sediment sources and identify sediment mineralogy (Grew, 1990). They measure two characteristics of environmental materials; those occurring naturally and those induced artificially in the mineral assemblage by exposing the samples to varying magnetic fields.

Table 2.22 summarises the important types of magnetic behaviour associated with magnetic minerals and Table 2.23 summarises the characteristics of the various magnetic domains and their effect on associated behaviour. Based on these properties, the following measurements of lake sediments, soils, river bed sediments and marsh sediments were undertaken:

1. Low and high frequency susceptibility ($\chi_L$ and $\chi_H$)
   Units: $\mu m^3 kg^{-1}$

2. Saturated Isothermal Remanent Magnetization (SIRM)
   Units: mAm$^1$ kg$^{-1}$

3. Backfield Isothermal Remanent Magnetization (IRM)
   Units: mAm$^1$ kg$^{-1}$

Fig 2.13 illustrates the hysteresis curve from which these measurements are derived. The following characteristics were calculated from the measurements outlined above:
Table 2.22 Magnetic properties of minerals (adapted from Thompson and Oldfield, 1986 and Grew, 1990)

<table>
<thead>
<tr>
<th>State</th>
<th>Result of application</th>
<th>examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetic (weakest)</td>
<td>Weak negative magnetisation not capable of holding remanence</td>
<td>Wood, water, quartz, calcite</td>
</tr>
<tr>
<td>Paramagnetic (2nd weakest)</td>
<td>Weak positive magnetisation not capable of holding remanence</td>
<td>Olivine, pyroxene Fe and Mn carbonates lepidocrocite</td>
</tr>
<tr>
<td>Antiferromagnetic (3rd strongest)</td>
<td>No net magnetisation capable of acquiring remanence</td>
<td>haematite goethite Fe and Mn ferrite</td>
</tr>
<tr>
<td>As above but canted</td>
<td>Positive magnetisation in one direction</td>
<td>haematite goethite</td>
</tr>
<tr>
<td>Ferromagnetic (1st and 2nd strongest)</td>
<td>Difficult to distinguish between the two. Strong magnetization, capable of partial remanence acquisition</td>
<td>magnetite and maghemite (rare)</td>
</tr>
</tbody>
</table>
Table 2.23 Magnetic domains and their effect on behaviour of magnetic minerals (adapted from Grew 1990)

<table>
<thead>
<tr>
<th>Domain</th>
<th>size and magnetic characteristics</th>
<th>behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multidomain (MD)</td>
<td>Large crystals (&gt;1.0 μm)</td>
<td>Partial magnetic field retained</td>
</tr>
<tr>
<td></td>
<td>Movement of domain walls characterises magnetisation</td>
<td></td>
</tr>
<tr>
<td>Stable single domain (SSD)</td>
<td>No domain boundaries, each grain is its own domain</td>
<td>Higher remanences and more stable than MD</td>
</tr>
<tr>
<td>a. Superparamagnetic (SP)</td>
<td>&lt;0.03 μm</td>
<td>Do not retain remanance at room temperature</td>
</tr>
<tr>
<td></td>
<td>SSD/SP boundary, grains found in soil</td>
<td>Delayed response to changes in the magnetic field High LFX</td>
</tr>
<tr>
<td>b. Viscous (V)</td>
<td>Between MD and SSD</td>
<td>Characteristics between MD and SSD.</td>
</tr>
</tbody>
</table>
Fig 2.13 Hysteresis loop and initial magnetisation curve (after Thompson and Oldfield, 1986)
1. Frequency dependent susceptibility either calculated on a mass specific basis ($\chi_{f,s}$) or as a percentage ($\chi_{f,s,\%}$)

Units: $\text{nm}^2 \text{ kg}^{-1}$

2. S-ratio calculated from the ratio between IRM and SIRM.

3. High Field Remanent Magnetization (HIRM)

    calculated from: $\text{SIRM} (1-S)$

    2

Units: $\text{mAm}^2 \text{ kg}^{-1}$

Table 2.24 summarises the mineral magnetic measurements made. Lake sediments represent a mixture of all the processes occurring within the catchment. As such, the difficulty with characterization by mineral magnetic property is in distinguishing between the individual components of the mixture. Complex interactions occur dependant on mineral type, particle size, autochthonous processes and the effect of biota on the sediment. Additional techniques are therefore advisable to support and strengthen any inferences made on the basis of magnetic measurements.

ii. Sediment chemistry

When considering methods of chemical analysis it is necessary to consider the reasons for requiring these data. The necessity for chemical data in this study are twofold:
Table 2.24 Mineral magnetic measurements (from Dearing et al., 1985; Thompson and Oldfield, 1986; Grew, 1990)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{rt}$</td>
<td>The ratio of magnetisation induced to the intensity of the magnetising field. It is an approximate measure of the total concentration of ferrimagnetic grains, and is sensitive to particle size. Values calculated on a mass specific basis.</td>
</tr>
<tr>
<td>$\chi_{rt-d}$</td>
<td>The difference in susceptibility between low and high ($\chi_{rt}$) frequency measurements. Can identify viscous grains and secondary magnetic minerals due to incorporation of soil particles. Values calculated on a mass specific basis ($\chi_{rt-d}$) or percentage of total $\chi_{rt}$ ($\chi_{rt-d}$).</td>
</tr>
<tr>
<td>SIRM</td>
<td>The remanence retained by a sample upon removal from a saturating magnetic field. SIRM indicates volume concentration of magnetic minerals and also changes in grain size.</td>
</tr>
<tr>
<td>IRM</td>
<td>Reflects the approximate concentration of remanence carrying haematite.</td>
</tr>
<tr>
<td>S-ratio</td>
<td>Demagnetising parameters, these are useful in the identification of grain size components in homogeneous samples and the proportion of ferrimagnetic to antiferromagnetic minerals.</td>
</tr>
<tr>
<td>HIRM</td>
<td></td>
</tr>
<tr>
<td>SIRM / $\chi_{rt}$</td>
<td>Scattergrams used to indicate variations in grain size in single mineral samples. In a mixture, the ratio can indicate differences in the proportions of minerals in the mixture.</td>
</tr>
</tbody>
</table>
1. To assess the total amount of heavy metals in the sediments, and calculate the flux and accumulation rate. This can be applied to an assessment of background levels and subsequent changes in concentration and loading.

2. To partition the heavy metals according to sites within the sediment and hence assess their availability should environmental conditions change.

Two methods are therefore required in order to fulfil these aims: a method giving the concentration of heavy metals in the bulk sediment, or a total digest, and a method which yields the concentration of heavy elements in selected fractions within the sediments, or a sequential digest. There are other methodologies for obtaining data on heavy metal concentration in sediments which are outlined in Table 2.25. This Table shows that the atomic absorption method is sensitive, accurate (Förstner & Wittmann, 1981) and is the most widespread method used in the analysis of water and effluents (Bengtsson & Enell, 1986).

a. Total digestion method

The wet digestion method was chosen for this study to conform with similar studies carried out in the English Midlands (Foster et al., 1987, 1991; Foster & Dearing, 1987a). The facilities were readily available and the techniques well known.
Table 2.25 Comparison of various methods of trace metal analysis (after Förstner and Wittmann, 1981)

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>Approximate range of concentration (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Gravimetry</td>
<td>...</td>
</tr>
<tr>
<td>Titrimetry</td>
<td>...</td>
</tr>
<tr>
<td>Colourimetry</td>
<td></td>
</tr>
<tr>
<td>Fluorescence</td>
<td></td>
</tr>
<tr>
<td>Kinetics</td>
<td></td>
</tr>
<tr>
<td>Inverse voltametry</td>
<td></td>
</tr>
<tr>
<td>Flame emission spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Atomic absorption spectroscopy</td>
<td></td>
</tr>
<tr>
<td>Atomic absorption spectrophotometry (AAS)</td>
<td></td>
</tr>
<tr>
<td>Non-flame AAS</td>
<td></td>
</tr>
<tr>
<td>Gas chromatography</td>
<td></td>
</tr>
<tr>
<td>X-ray fluorescence (XRF)</td>
<td>...</td>
</tr>
<tr>
<td>Radiometry</td>
<td></td>
</tr>
<tr>
<td>Activation analysis</td>
<td></td>
</tr>
<tr>
<td>Mass spectrometry</td>
<td></td>
</tr>
</tbody>
</table>

--- applicable in most circumstances

----- applicable in single cases
Table 2.26 Total digestion methodologies (from Förstner and Wittmann, 1981).

1. Hydrofluoric acid (HF) digestion

   Usually used in combination with H₂SO₄, HClO₃, and HNO₃. HF dissolves the basic silica and silicate matrix of the sediment. Metal sulphates are often difficult to dissolve, combination with HClO₃ produces perchlorates which are easier to get into solution (Förstner and Wittmann, 1981). Addition of HNO₃ reduces the possibility of explosion.

2. HCl - HNO₃

   Useful for volatile elements such as Hg, As and Cd. Provides a high degree of metal extraction, but silicates are not completely dissolved. Metals in association with organic matter are dissolved and some of the metals in the crystal lattices are removed (Agemian and Chau, 1976).

3. Lithium metaborate fusion

   Results from fusion techniques are not comparable with wet digests (Greenwood, 1991), but it is faster than acid digestion and dissolves most minor minerals (Alloway, 1989).

All of the above provide a solution of heavy metals which readily pass through an AAS.
In order to measure the concentrations of elements in sediment by the wet digestion method, they must first be dissolved. Dissolution is achieved by digestion in strong acid solutions. There are various digestion methodologies, ranging from vigorous treatment with hydrofluoric acid and aqua regia to less comprehensive digests of concentrated acids (Table 2.26). The laboratory facilities available were not considered suitable for the use of hydrofluoric acid and a less vigorous method was used which nonetheless gives a high degree of metal extraction, but did not dissolve residual silica. Alloway (1989) called this "pseudo-total analysis" but noted that, as most heavy metal pollutants are not bound to the silicate phases, a digest solution of concentrated acids other than HF would prove vigorous enough to dissolve heavy metals not bound to the silicates. This method has also been used in previous related studies and, by using the same methodology, the data should be directly comparable (Renberg, 1986; Foster et al., 1991).

b. Sequential extraction

Techniques to determine the associations of elements with specific sedimentary phases are useful to assess the potential availability of toxic compounds for biological uptake (Salomons & Förstner, 1980). It is important to know this for four main reasons:

1. To assess whether the sediments are a permanent sink for trace metals or whether remobilization is likely to occur.
2. To assess the bioavailability of the contaminants in the sediments for aquatic life.

3. To assess the behaviour of the pollutants in dredged material during and after disposal to landfill or upon land spreading.

4. To assess the subsequent bioavailability of the trace metals in the landfill site.

The total concentration of heavy metals within the bulk sediment gives no information on which of the elements may take part in short term geochemical processes or are bioavailable. Tessier et al. (1979) go further:

"Use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable."

Tessier et al. (1979) p 844

In order to partition the metals within the sediment a sequential extraction procedure was needed. There are a wide range of sequential digestion procedures in use (Table 2.27 a), but unfortunately none of these are comparable. A digest had already been carried out on one core at Wyken Pool (Ambridge, 1989) and it was decided to use the same methodology on one core at Swanswell Pool, that given by Tessier et al. (1979) (Table 2.27 b). Only one core at each
site was sequentially digested mainly due to the length of time taken to perform the analysis. Up to 6 weeks was needed to process 16 samples and the resultant solutions often proved difficult to analyse on the atomic absorption spectrophotometer (AAS) as deposit built up on the burner sometimes necessitating the instrument having to be switched off, allowed to cool and cleaned after every 4-5 samples (see details in Appendix 2).

2.11 Palaeoenvironmental indicators

Lake trophic level and hydroseral development can be assessed by means of the remains of biota preserved in the sediment at the bottom of a lake. P, Fe and Mn reflect changing trophic level and redox conditions, so a combination of these factors is useful in determining changing environmental conditions with time.

i. Mollusca, pollen and diatoms

The use of pollen, diatoms, molluscs, etc. to infer environmental change, particularly during the Quaternary, is well documented (Sparks, 1961; Birks & Birks, 1980; Lowe & Walker, 1984; Faegri & Iverson, 1989). The change in species diversity and numbers within a sediment core may correlate with fluctuations in heavy metal concentration indicating the response to increases in urbanisation in the catchment by invertebrates and flora.
Table 2.27 a Sequential digest methodologies after Förstner and Salomons (1981 b)

<table>
<thead>
<tr>
<th>Sediment fraction</th>
<th>Extraction methodology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractable</td>
<td>BaCl, MgCl, NH₄OAc</td>
</tr>
<tr>
<td>Detrital/ non-detrital</td>
<td>EDTA, 0.1M HCl, 0.3M HCl, 0.5M HCl, 0.1M HNO,</td>
</tr>
<tr>
<td>Mn and Fe</td>
<td>Acidified hydroxylamine, ammonium oxalate, hydroxylamine-acetic acid, dithionite/citrate</td>
</tr>
<tr>
<td>Carbonate</td>
<td>CO₂ treatment, acidic cation exchange, NaOAc/HOAc (pH 5)</td>
</tr>
<tr>
<td>Organic</td>
<td>H₂O₂, H₂O₂-NH₄OAc, H₂O₂-HNO₃, organic solvents, 0.5N NaOH, 0.1N NaOH/HSO₄, Na</td>
</tr>
<tr>
<td>Detrital silicates</td>
<td>HF/HClO₄</td>
</tr>
</tbody>
</table>
Table 2.27 b Fractions selected for sequential chemical analysis (After Tessier et al., 1979)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Form of heavy metal</th>
<th>Sensitivity to environmental change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Exchangeable</td>
<td>Adsorption to clays, hydrated iron and manganese oxides and humic acids</td>
<td>Changes in water ionic composition</td>
</tr>
<tr>
<td>2. Bound to carbonates</td>
<td>association with sediment carbonates</td>
<td>Changes in pH</td>
</tr>
<tr>
<td>3. Bound to Fe and Mn oxides</td>
<td>Nodules, concretions and cements of Fe and Mn oxides scavenge trace metals</td>
<td>Thermodynamically unstable under anoxic conditions ie. low Eh</td>
</tr>
<tr>
<td>4. Bound to organic matter</td>
<td>Living organisms, detritus, coatings on mineral particles</td>
<td>Degradation of organic matter under oxidising conditions can release soluble trace metals.</td>
</tr>
<tr>
<td>5. Residual</td>
<td>Primary and secondary minerals holding metals in crystal lattices</td>
<td>Not usually released under normal range of environmental conditions.</td>
</tr>
</tbody>
</table>
Pollen grains at both sites were found to be too poorly preserved and too few in number to be useful. A preliminary examination of 5 samples from one core from Swanswell Pool (R Flower, University College, London) found that diatoms were well preserved and numerous. However, lack of time to extract and identify diatom remains meant that these procedures were not attempted.

Mollusca were well represented and preserved at Swanswell Pool, but less so at Wyken Pool. One core from Swanswell Pool was therefore analysed for Mollusca to infer the changing environmental conditions at the site with time. Grab samples of sediment at the mud-water interface from Wyken Pool were taken to assess the present-day conditions at the site for freshwater Mollusca.

ii. Phosphorus

The phosphorus content of the sediments was measured in order to assess the trophic status of the lakes and changing trophic level through time, rather than as a simple measure of chemistry. The possibility of eutrophication in shallow polluted lakes is a common problem (Cooke et al., 1986; Ryding & Rast, 1989). Ryding & Rast (1989) point out that even if the source of the excess nutrients is decreased a net outflow of phosphorus continues for some time afterwards. This has future management implications should the sediments have a high phosphorus content.

Total phosphorus was measured using the method described in Foster et al. (1986b) so that the analysis was comparable
with data from other sites. P analysis was undertaken by colourimetry (details in Appendix 2) on the digests obtained from the total extraction procedure, details of which are also given in Appendix 2.

iii. Fe and Mn.

Fe and Mn concentrations reflect changing redox conditions at the mud-water interface (Oldfield, 1977). Changing redox conditions reflect phosphorus exchange at the sediment-water interface and thus trophic level (Håkanson & Jansson, 1983). A combination of palaeoenvironmental indicators, phosphorus, Fe and Mn concentrations hence provide an indication of nutrient availability and utilisation within the lake and also the activity of the heavy metals scavenging factors as shown in Fig 2.6. Fe and Mn determination was carried out by AAS on the digests obtained from the total extraction, details of which are given in Appendix 2.


The radioisotopes $^{210}$Pb and $^{137}$Cs were used to date the sediments as the period of interest is less than 150 years. Facilities were available within the Physics Department at Coventry University to carry out the analysis.

i. $^{210}$Pb

The $^{210}$Pb dating method was devised by Goldberg in 1963
and has been in common use over the last 30 years (Olsson, 1986). $^{210}\text{Pb}$ has a half life of $22 \pm 0.22$ years and should therefore be useful for dating sediments up to 150 years of age.

Figure 2.14 illustrates the two sources of $^{210}\text{Pb}$ to the lake sediments:

1. Supported, or that derived from erosion within the catchment

2. Unsupported, or that transported in the atmosphere and deposited on the lake surface.

In order to date sediments using this method, it is necessary to be able to distinguish between the total $^{210}\text{Pb}$ and the supported $^{210}\text{Pb}$.

There are three assumptions implicit when dating sediments using this method:

1. That the $^{210}\text{Pb}$ does not migrate in the sediment column

2. That the flux of $^{210}\text{Pb}$ to the sediments is constant

3. That the residence time of $^{210}\text{Pb}$ in the sediments is constant.

The age of the sediment at any particular depth is calculated from its unsupported $^{210}\text{Pb}$ activity relative to
Fig 2.14 Sources of $^{210}\text{Pb}$ to sediments (Goudie et al., 1981)
that at the surface and the radioactive half life et al. (Pennington, 1976).

Olsson, (1986) recommends that

"...a few determinations from every core ...from the top down to a level corresponding to 100-150 years"

Olsson (1986) p 299

However, lack of project funding meant that only one core from each lake could be dated.

There are several variables which have to be taken into account when using this method:

1. The concentration of $^{210}\text{Pb}$ can be elevated near a coal burning power station (Eakins, 1983)

2. The concentration of $^{210}\text{Pb}$ can also be elevated if there has been any nuclear testing, although this is unlikely to be significant in the English Midlands.

3. The residence time of $^{210}\text{Pb}$ in the atmosphere ranges from 9 days up to a few weeks, therefore deposition may not be uniform.

4. Bioturbation or mixing may smooth out the profile and the curve of concentration of $^{210}\text{Pb}$ with depth may show a flattened area at the crest.
5. Some mobilization of lead in interstitial water may occur, especially if the sediment has a high water content.

6. Sediment resuspension or focusing may give a low $^{210}\text{Pb}$ level where appreciable erosion has taken place, and enhanced lead levels where focusing has occurred (Oldfield & Appleby, 1984).

7. Catchment derived unsupported $^{210}\text{Pb}$ may prove to be a significant source of error. This may be due to disturbance of the catchment when, for example, residential housing estates or industrial complexes are built and is obviously a factor to consider in urban areas (Oldfield & Appleby, 1984).

8. Variable allochthonous sedimentation may affect the $^{210}\text{Pb}$ record, but Oldfield & Appleby (1984) report that it is not significant as a source of error.

Sediments are dated using this method by determining both the total $^{210}\text{Pb}$ and the supported $^{210}\text{Pb}$. The latter is found by measuring the $^{226}\text{Ra}$, and subtraction of this value from the total $^{210}\text{Pb}$, represents the unsupported $^{210}\text{Pb}$ in the sample.

ii. $^{137}\text{Cs}$

The above limitations illustrate the need for more than one dating method to be carried out to verify results. Another well-documented method for radiometrically dating sediments is that of measuring $^{137}\text{Cs}$. This isotope has been artificially
produced as a consequence of nuclear weapons testing from 1954 and accidents such as that of Chernobyl in 1986.

Pennington et al. (1976) used $^{137}$Cs and $^{210}$Pb to date the recent sediments of Blelham Tarn in the English Lake District and found the radioisotopic dates to be consistent. Pennington’s study was also able to use palaeomagnetic measurements as well as $^{14}$C to confirm the consistency of the dating methods, and a total of 8 cores were analysed.

The fallout of $^{137}$Cs began in 1954 and the peak in activity took place in 1963. As with $^{210}$Pb, there are several factors that have to be considered when using $^{137}$Cs as a dating tool:

1. Bioturbation is a problem in that it can smooth out the record.

2. $^{137}$Cs may be mobile in the sediment under certain conditions

3. Delayed $^{137}$Cs input from soil erosion can be a source of error.

Dating using this method involves ascertaining the depth at which $^{137}$Cs is measurable in the lake sediment; this would represent 1954 when fallout began. The rise in $^{137}$Cs content can then be confirmed by a peak in activity representing 1963. Fig 2.15 shows the estimated annual deposition of $^{137}$Cs at Windermere (Pennington et al., 1973) and the actual distribution of $^{137}$Cs in the upper 25 cm of the sediments at

114
Fig 2.15 Deposition of $^{137}$Cs to the sediments of Lake Windermere
a. Actual deposition  
b. Annual deposition (after Pennington et al 1973)

A

0 1 2 3 pCi/cm²

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

1963 peak

1954, deposition of $^{137}$Cs began

B

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 pCi/cm²

1971

1970

1969

1968

1967

1966

1965

1964

1963 peak

1988

1985

1984

1983

1982

1981

1980

1951

1958

1957

1956

1955

1954

1953

1954, deposition of $^{137}$Cs began
Windermere. The 1963 peak in activity is marked on the traces and 1954 is marked for when fallout began.

2.13 Statistical analysis

The results obtained from the analytical techniques described in this Chapter were subjected to statistical analysis. The objectives of these tests were to identify whether particular properties of the sediments could be discriminated independently or whether they shared a high degree of colinearity. In order to identify these characteristics, statistical analyses aimed to answer the following questions:

1. Are the data bases suitable for parametric statistical tests?

2. Are there correlations between magnetic parameters, in which case are some of the measurements redundant?

3. Are there correlations between the individual heavy metals, in which case can the presence of one indicate the presence of others?

4. Are there correlations between the magnetic parameters and the heavy metals, in which case can magnetic measurements serve as a surrogate measure of heavy metals either as a group or as individual elements?
5. Can a small number of common properties be extracted from the large number of variables?

6. How consistent are the results from the 4 cores taken from each of the lakes?

7. What is the relationship between the catchment components at Wyken Slough and the sediment deposited in the lake?

Statistical analysis was carried out using SPSS PC. in Appendix

2.14 Summary

This chapter has set out the rationale behind the present study in terms of previous limnological work. It has identified a gap in studies of pollution history in that few studies of entirely urban lakes have been carried out. Using a paired lake catchment approach, it suggests a practical framework using a variety of techniques to address this deficiency. These techniques include a sampling strategy, chemical and physical analysis and the subsequent statistical testing of the results obtained.

Chapters 4, 5 and 6 describe the results obtained from Swanswell Pool, Wyken Pool and the Wyken Slough catchment respectively, in terms of the framework outlined in this Chapter.
Chapter 3

Site description and histories

3.1 Introduction

This chapter describes the development of the sites as indicated by documentary evidence, and their current appearance. Section 3.1 discusses the background to the Coventry region in terms of its underlying geology, geomorphology and climatology. Section 3.2.3 traces the origins of the Industrial Revolution in the City of Coventry. This has an important bearing on changing contaminant loadings through time, as discussed in Chapter 7. The catchments of Swanswell Pool and Wyken Slough are considered in Section 3.3 and their histories discussed in Section 3.4.

3.2 Background to the Coventry region

3.2.1 Geological and Geomorphological setting

Coventry is situated in Midland England on the eastern side of the East Warwickshire Plateau (Fig 3.1), an inlier in the New Red Sandstone of the Midland Plain, which is cut by several fast flowing streams, generally flowing in a westerly or southerly direction (Coventry Geographical Association, 1971).
Fig 3.1 Geology of the Coventry area (after Dix and Hughes, 1960)

Key

- Older Drift
- Keuper Marl
- Keuper Sandstone
- Enville Beds with Corley Conglomerate and conglomerate
- Keele Beds
- Etruria Marl and Coal Measures
- Halesowen Beds
- Cambrian
- Pre-Cambrian

City boundary

20 km

1 km
Although strategically the site of the City was not important, Coventry initially developed on the slightly higher ground to the south of the River Sherbourne with the land sloping away on all sides, particularly to the east, where there is a resistant band of Carboniferous sandstone and conglomerate. The surface strata in the Coventry area are the Upper Coal Measures of the Keele and Enville beds. The geological sequence generally becomes younger in a southerly direction.

The Keele beds are clays and sandstones and yield reasonable soils when weathered. The Enville Beds are red clays, marls and sandstones with occasional conglomerates and breccias. The sandstones form an extensive aquifer which has several wells and boreholes providing potable water as well as water which can be used for industrial purposes.

To the west of Coventry, lying unconformably on the Carboniferous rocks, are the Keuper Sandstones and Marls of Triassic age. Any remaining deposits are of alluvium or are Pleistocene deposits such as the sand and gravels which are well represented to the east of the City (Old et al., 1990).

3.2.2 Hydrology and climate

The River Sherbourne flows southeast across the present day City to join the River Sowe and in doing so breaches the "cliff" of conglomerate and sandstone. This produces a flat-floored, fairly steep-sided valley with a narrow floodplain.
The Pickford Brook joins the Sherbourne from the east and the Radford and Swanswell Brookes join the River Sherbourne from the north with a prominent spur of sandstone separating the latter two at about 130 m OD.

Fig 3.2 shows the relief and drainage of the Coventry area. The highest points are to the west at an altitude of about 150 m OD. To the north of Swanswell Brook the less resistant Upper Coal Measures present an area of flat land at 100-120 m OD. An extension of this flatter area to the south of the river forms the watershed between the Sherbourne and the streams to the southwest which join the Finham Brook.

Figures 3.3 a and b summarise the data for the Coventry meteorological record (Cockerton, 1991). The bar charts represent two years, 1990 and 1977 and indicate the average total sun and rain (Fig 3.3a) and minimum, maximum and average temperature (Fig 3.3b) for each month with the average over the year for temperature data at 'month' 13. The climate represented is a typical northern hemisphere temperate one with highest temperatures and sunshine hours recorded in May to August and the wettest months in November to February. The mean annual rainfall for the region is 678 mm from data taken over 125 years from 1867 to 1992 (Sheard, 1994).

3.2.3 The historical development of Coventry

From nearly 70 inhabitants reported in the Domesday Survey of 1086, Coventry grew to become an important centre
Fig 3.2 Topography of the Coventry area (after Foster et al., 1994)
Fig 3.3 Coventry area climatological data
a. total sun and total rain
b. average minimum temperature, average maximum temperature and average temperature
Average minimum temperature

Average temperature

Average maximum temperature
for the manufacture of silk ribbons and watches between 1765 and 1850. When competition suffocated these industries, the late nineteenth and early twentieth centuries saw the rise of the bicycle and motor industries as well as aeroplane manufacture, munitions factories and machine tools. The population expanded, particularly in the twentieth century (Fig 3.4), and the City expanded with it (Fig 3.5).

By 1930, however, aided by the general slump of the 1920’s, 40 firms ceased production. The slimmed down motor manufacturers were able to use their modern methods to effect during the Second World War and the technology was expanded into aeroplane manufacture with the building of new premises.

Whilst the larger factories engaged in heavy manufacture closed, for example Smith’s Stamping Works, Albion Drop Forgings and Hawker Siddeley,

"...the premises left vacant...were easily let as trading estates." Richardson (1972) p 141

and industrial estates, such as at Bayton Road in the catchment of Wyken Pool, were built in the 1960’s and 70’s.

Thus, whilst many authors date the onset of the Industrial Revolution from lake sediment pollution histories as early as 1872 (Batterbee et al., 1988) or even the mid nineteenth century (Oldfield et al., 1983) in fact the Industrial Revolution in Coventry began to make its mark, both in the increase in manufacturing industry as outlined above and in
Fig 3.4 Population of Coventry since the Domesday survey

(after Stephens, 1969 and various others)
Fig 3.5 The growth of Coventry 1610-1807 (P Clarke, pers. comm.)
the increase in population as illustrated in Figs 3.4 and 3.5 in about 1900. The reasons for this were probably due to the decline of the domestic manufacturing industry leaving the City without an industrial base as the Industrial Revolution progressed in other areas. Richardson (1972) emphasises the role of the Common land in Coventry in physically impeding the spread of manufacturing industry:

"As long as the Commons remained, the city’s expansion was impeded, one of the reasons why Coventry missed the Industrial Revolution."

Richardson (1972) p 9.

The increase in contaminants released in association with burgeoning industry and increased urbanisation would therefore be expected to have started later in Coventry than elsewhere. The heavy metal concentrations in the lake sediments of the two research sites would therefore be expected to reflect this late initiation of Coventry into the Industrial Revolution.

3.3 The Research Catchments

The two sites selected for detailed investigation were the Swanswell Pool and Wyken Pool (Fig 3.6). A brief description of the present day lakes and their associated catchments is given below before considering their documented histories.
Fig 3.6 Location of Swanswell and Wyken Pools
a. Coventry
b. Coventry boundaries
c. Wyken Slough catchment

Lake or Pool
River
City Centre
City Boundary

Surface Stream
Culverted Stream
Marsh
Residential Area
Industrial Estate
Waste Tip
Railway
Motorway
Canal

Wyken Slough
Swanswell Pool
Coventry Slough

Coventry

0 km 2.5
3.3.1. Swanswell Pool

Swanswell Pool is a small freshwater lake (0.73 ha) situated in the centre of the City of Coventry between the old city wall and the mid nineteenth century development of Hillfields (Fig 3.8). Originally a green field site, the lake is now surrounded by a small park (< 1 ha) which effectively forms its surface water catchment. The park in turn is bounded by the Coventry and Warwickshire Hospital, the Stoney Stanton Road and the main West Midlands Passenger Transport Executive (WMPTE) bus depot at Pool Meadow. Fig 3.6 b illustrates how close the Pool is to the City Centre.

The Pool is bounded by concrete coping stones which are surrounded by either paved or metalled pathways. These pathways pass through the grassed areas and out onto public footpaths. The park presently contains mature sycamore trees (*Acer pseudoplatanus*) and willow (*Salix spp.*).

The main inlet to the pool is located in the northeast corner and the outlet to a surface drain is in the southeast corner. The only other source of water for Swanswell Pool in the recent past, apart from the runoff from pathways and direct rainfall input, may have been sporadic leakage from the hospital settling tank located some 50m to the north of the Pool. This source has now been connected directly to the storm drain system, (J. Batty, NRA (Severn Trent Region), pers comm).

There is a small island located near the northern end of the Pool which was occupied by mature trees including Willow
(Salix sp.). The island is reinforced by brickwork around the sides. The structure of the island has recently become unstable and several of the trees were lost when the island began to disintegrate. Water birds such as the Mute Swan (Cygnus olor), ducks (Anas platyrhynchos) and moorhens (Gallinula chloropus) nest and raise young successfully both on the island and on the metal cages along the dam wall. The Pool was stocked with Bream (Abramis brama) in the past and anglers have been observed catching small live specimens. Dead specimens have also been found, particularly in hot conditions when the water becomes deoxygenated. There is little or no littoral or benthic flora, but there are examples of free-floating vegetation present in the form of algae and pondweed (Potamogeton and Chara sp). Red Tubifex worms and a variety of molluscs represent the invertebrate fauna, although an exhaustive survey of biota has not been carried out at this site and no ecological surveys are known to exist.

3.3.2 Wyken Pool

Wyken Pool is a much larger freshwater feature than Swanswell Pool, being 2.25 ha in area with a surface water catchment of 450 ha. This catchment collects runoff from residential areas as well as from industry, landfill leachates and a water reclamation works. The Pool is surrounded by parkland and permanent pasture which is used for grazing and retains mediaeval ridge and furrow features. Immediately to the north
of the site is an area of marshland designated as a Local Nature Reserve (LNR) in 1990.

The Pool has two major channelled inflows. The Wyken Slough Brook drains the western side of the catchment. Fig 3.6c shows the Brook passing through two landfill sites one of which discharges through a disused water treatment plant, and a major industrial area, the Bayton Road Industrial Estate. The second inflow is referred to here as the Eastern Stream, and drains predominantly agricultural land, although there is some storm drainage from the M6 motorway which was built in 1971, Lentons Lane and Hawksbury Lane. Both streams negotiate the Coventry Canal and pass under the M6 motorway which dominates the northern end of the Pool as is shown in Plate 1. The Wyken Slough Brook passes, via a drainage ditch, into the Pool in the north-western corner. The Eastern Stream drains through the area of marshland and into the Pool. The marshland extends down the eastern side of the Pool as is shown in Fig 2.7b with a finger-like projection about half way down. This marshy ground extends to the outlet.

The public footpath passes W-E to the north of the Pool, the inlets flowing under it enclosed in a pipe in the case of the Eastern Stream, and under a footbridge in the case of Wyken Slough Brook. At the outlet, a footpath passes over a footbridge. Between the footbridge and a controlling overspill weir is an area of marsh which forms an important habitat for swans which have been observed nesting here (see Plate 2). The weir plate was installed to provide a water balance mechanism.
Plates 1 and 2

1. (top) Domination of the site by the M6

2. (bottom) Swans nesting at Wyken Pool
for the downstream River Sowe (R. Ashby, Coventry City Engineers, pers comm).

There are various water fowl on the lake including geese, both Canada (Branta canadensis) and common (Anser sp.), mute swans (Cygnus olor) (Plate 2), Mallard (Anas platyrhynchos) and moorhens (Gallinula chloropus). Littoral vegetation is present, particularly in marsh areas, which mostly consists of rushes and reeds (Typha latifolia and Phragmites communis). Tables 3.1 a and b show the results of a recent ecological survey carried out by Ambridge (1989) and a more extensive project undertaken by a local school (Jones 1982) which show the range of fauna living in the Pool.

There are few trees, although Poplar (Populus sp) line the footpath to the north with hawthorn (Crataegus monogyna) hedges. There appears to be little thriving nekton and local anglers suggested that the Pool was not well stocked with fish. No free-floating plants were seen, although the thick mats of algae found on the lake bottom were unidentifiable due to a covering of organic matter and silt.

Although Wyken Pool may be a settling tank for particulate pollution derived from its catchment, it is still capable of sustaining a range of aquatic life.
### Table 3.1 a Fauna at Wyken Pool after Ambridge (1989).

Individuals caught per 5 minute fishing effort

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<tr>
<th></th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
<th>Site 4</th>
<th>Site 5</th>
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Key to common names

- **Segmentina complanata*** = Flat Ramshorn Snail
- **Lymnaea peregra** = Common Wandering Snail
- **Potamopyrgus jenkinsii** = Jenkins Spire Shell Snail
- **Acroloxus lacustris** = Lake Limpet
- **Corixa sp** = Lesser Water Boatman
- **Chironomid sp** = Blood Worm Larvae
- **Gasterosteus aculeatus** = Nine-spine Stickleback
- **Tubificid** = River Worm

For location of sampling stations, see Fig 2.7b

*=*Hippeutis complanatus
Table 3.1b Fauna at Wyken Pool

b. After Jones (1982) relative abundance per 5 minute fishing effort.

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\* see Table 3.1a, others see key next page
Key to Table 3.1 b

Planorbis planorbis
Planorbis (carinatus?)
Lymnaea stagnalis
Gyraulus laevis
Sphaerium lacustre
Erpobdella octoculata
Lumbriculus variegatus
Cyclops strenuus
Daphnia pulex
Argulus (foliaceus?)
Gammarus pulex
Asellus aquaticus
Notonecta
Gyrinus (natator?)
Laccophilus hyalinus
Baëtis (rhodani?)
Perla

The Ramshorn
Keeled Ramshorn
Great Pond Snail
Smooth Ramshorn
Pea Mussel
Leech
Segmented Bristle Worm
Water Flea
Common Water Flea
Fish Louse
Freshwater Shrimp
Water Louse
Water Boatman
Whirligig Beetle
Diving Beetle
Mayfly Nymph
Stonefly
3.4 Site histories

3.4.1 Swanswell Pool.

The complete history of Swanswell Pool from its probable construction as a medieval fishpond associated with Coventry Priory is detailed in Charlesworth (1990). The history of the Pool up to about 1800 is summarised in Table 3.2 and the five maps in Figs 3.7 & 3.8 a - d illustrate the changing nature and land use of the environs of the Pool.

John Speede's map of 1610 (Fig 3.7) shows the Pool without inlets, but with two outlets, and serves to illustrate how the Pool was situated originally outside the boundary of the City of Coventry. Thomas Sharps' map of Coventry (1807) shows Swanswell Pool with the much smaller New Pool to the southwest (Fig 3.8 a). There is no inlet shown on this map, although one is shown on later maps, so this omission may have been a cartographic oversight. There are allotments or ornamental gardens around the Pool with many trees, and pasture land divided into fields by hedges. The outlet appears to have been used for irrigation.

By 1828, New Town was laid out in the Hillfields area and eight streets to the east of Swanswell Pool were constructed. The map of 1837 (Fig 3.8 b) shows the building of New Town and warehouses and streets are also shown. The Springfield Brook, feeding Swanswell Pool is shown meandering through the countryside.
Fig 3.7 John Speede's 1610 map "The ground plott of Coventre"
Fig 3.8 Historical maps of pre-20th century central Coventry

30 m a. 1807

120 m b. 1837

300 m c. 1851

150 m d. 1886
<table>
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<th>Year (AD)</th>
<th>Event / Evidence</th>
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<td>pre 1000</td>
<td>No evidence of pre-Roman settlement in Coventry</td>
</tr>
<tr>
<td>1000</td>
<td>&quot;Coventry&quot; from Anglo Saxon &quot;Cufa’s Tree&quot;</td>
</tr>
<tr>
<td>1016</td>
<td>St Osburg’s nunnery founded</td>
</tr>
<tr>
<td>1043</td>
<td>St Osburg’s nunnery sacked by the Danes</td>
</tr>
<tr>
<td>1162-74 or 1177-81</td>
<td>Foundation of Benedictine monastery by Leofric and Godiva.</td>
</tr>
<tr>
<td>1265 +/-90</td>
<td>Coventry not mentioned in Domesday although the area belonging to Godiva is described.</td>
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<td>1355</td>
<td>Charter of Earl Hugh of Chester does not mention the existence of Swanswell Pool</td>
</tr>
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<td>1411</td>
<td>Possible formation of Swanswell Pool by damming of the Endermere Brook</td>
</tr>
<tr>
<td>1425</td>
<td>Tripartite Indenture of Edward III: first mention of Swanswell Pool by name</td>
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<tr>
<td>1439</td>
<td>J Lancaster (1974) represents Swanswell Pool with the Priory’s Mill and Orchard.</td>
</tr>
<tr>
<td>1480</td>
<td>St. John’s Hospital land lay between Swanswell Pool and the city wall.</td>
</tr>
<tr>
<td>1540</td>
<td>Master of St John’s Hospital had the pasture below Swanswell Pool.</td>
</tr>
<tr>
<td>1545</td>
<td>Prior Deram complained to the Court Leet regarding the townspeople washing in the Pool</td>
</tr>
<tr>
<td>1551</td>
<td>Crown lease of Swanswell Pool and New Pool to Henry Over</td>
</tr>
<tr>
<td>1551</td>
<td>Swanswell Pool granted to John Hales after the Dissolution</td>
</tr>
<tr>
<td>1579</td>
<td>Grant of Swanswell Pool and New Pool to Coventry Corporation</td>
</tr>
<tr>
<td>1610</td>
<td>John Speed’s map, the first cartographic representation of Swanswell Pool, shows the Pool as pear-shaped, no inlets but with 2 outlets. Situated outside the city wall in open countryside. The island is not shown.</td>
</tr>
<tr>
<td>1632</td>
<td>Construction of Swanswell Waterworks</td>
</tr>
<tr>
<td>1646</td>
<td>Bewley family took a 200 year lease on the Swanswell Waterworks.</td>
</tr>
<tr>
<td>1709</td>
<td>Thomas Bewley (Mayor of Coventry) may have owned Swanswell Pool.</td>
</tr>
<tr>
<td>1748-9</td>
<td>Samuel Bradford’s map shows the Pool divided into Swanswell and New Pools with a spur of land projecting northwards into the Pool. 2 outlets and 2 inlets. The island is not shown, the Pool is surrounded by pasture.</td>
</tr>
</tbody>
</table>
After 1848, an estate of houses was built to the south of Swanswell Pool and New Pool was infilled to make way for White Street. The Ordnance Survey map of 1851 (Fig 3.8 c) shows Swanswell Pool surrounded by streets, with New Town now considerably larger and Swanswell Pool truncated at its southern end with the loss of New Pool. Springfield Brook is shown running to the east of the Pool, in pipes or open conduits; the Pool relying on local springs for its water supply.

The water supply to the citizens of Coventry in the seventeenth century depended to a great extent on springs in the Swanswell Pool area. However, by 1843, only 280 of the 7000 houses in the City were being supplied by the Swanswell Waterworks and, following the 1844 Coventry Water Act, the supply was taken over by new works at Spon End.

The Ordnance Survey map of 1886 (see Fig 3.8 d) shows Swanswell Pool virtually as it is today, surrounded by housing, industry (the "City Mill (corn)" is shown to the south) and the Coventry and Warwickshire hospital to the north. No inlets or outlets are shown.

Correspondance in the local newspapers during October 1988 (Coventry Evening Telegraph), suggested that the Pool suffered bomb damage during the Second World War and needed repairs to stop leakages, although no firm documentary evidence has been found to support this suggestion. There is evidence of the severe damage suffered by the hospital during air raids, and it would seem possible that the Pool was hit by bombs:
"All around the hospital grounds glowed literally hundreds of incendiary bombs.."

Longmate (1976) p 91

Urban development continued around the Pool and in 1946, following a series of pollution events, the Hospital spring feeders which maintained the level of water in the Pool after 1850 were cut off and a metered water supply was used (NRA (Severn Trent Region) pers comm). In the mid 1960’s, a larger dimension inflow pipe was installed to feed ornamental fountains and hence the metered water consumption was increased.

In 1949, the City Corn Mill occupied the site where the West Midlands Passenger Transport Executive (WMPTE) bus depot now stands. This Mill abstracted 50,000 gallons of water per day from the Pool, which was returned directly to the Pool after use.

A new block was added to the hospital in the 1950’s and surface water sewers laid originally to link up with the various sumps and wells to supply the Pool were diverted into the Springfield Brook (NRA (Severn Trent Region), pers comm). The Brook itself was culverted in the 1960’s, approximately 2 m below the present-day surface of the Pool.

In recent years there have been periodic spillages from the underground hospital settling tank (a 2 m deep storage reservoir) with high ammoniacal nitrogen and BOD. The surface water sewer taking outflow from the hospital flowed directly
into the Pool from the north. Severn Trent Water Authority have diverted this source of pollution into the nearest surface sewer system.

The Pool has, therefore, undergone wide ranging changes to its catchment, starting with agriculture and pasture and latterly with 140 years of urbanisation and industrialisation.

3.4.2. Wyken Pool

The development of Wyken Pool, in contrast to Swanswell Pool, is poorly documented. Evidence suggests that it formed after mining subsidence in about 1850 (Coventry City Council, pers comm). Cartographic evidence presented in Fig 3.9 a shows "Marcher Brooke" flowing where Wyken Pool is now on the Ordnance Survey map surveyed in 1835. The Second Edition Ordnance Survey was produced in 1883 (Fig 3.9 b) and clearly shows the Pool to the south of Aldermans Green with Wyken Colliery to the east.

In 1850 there were two main collieries in the area. Hawksbury Colliery (now been renamed Main Pit Farm) and Victoria Colliery (Stephens, 1969).

Victoria Colliery was permanently closed after a series of fires in the workings in 1870. All mines in the area have been disused since 1886 and only old shafts and workings are left. A map of the Wyken Colliery dated 1905 in the Coventry Record Office (CRO), shows mining to the east of the site, most of which was from the Ell and Ryder seams. These seams appear to
have been worked out between 1845 and 1881. Other dates appear around the site of the Pool itself (1864, 1872, 1881) and presumably refer to active mining beneath the site. Notes from (pers. comm. British Geological Society, 1993) the Geological Survey by Howell (1855/6), and lodged in the Geological Survey record office do not mention the Pool and, as the base map for the survey was produced in 1835, this does not show the Pool either. Enquiries at the British Coal record Office also failed to produce any evidence which might tie the date of formation of Wyken Pool more closely than between the dates of the two Ordnance Surveys.

Industrial Growth and development in the Wyken Catchment.

Ribbon weaving remained the main industry in the Foleshill area of Coventry until 1860. There were 300 power looms there in 1866, although by then most were idle. Since the First World War, most firms centered on Foleshill were concerned with engineering, textiles and the construction industry.

Photographic evidence of the Wyken Pool was obtained from the boatman's family, who lived there in the 1920's and 30's, and are presented in Plates 3 to 6. Williams (1993) interviewed the family who gave evidence for the existence of two islands in the Pool on which the boats used to be tied (Fig 3.10).

Newspaper articles (Coventry Evening Telegraph) from 1958 indicate the decline in quality of the Pool. On November 21,
Plates 3 and 4 Wyken Pool in the 1920's

3. (top) The Pool and boatman's house

4. (bottom) The boatman fishing on the Pool
Plates 5 and 6 Wyken Pool in the 1920's: boating on the Pool
Fig 3.10 Map drawn by surviving boatman's family of Wyken Pool in the 1920's (Williams, 1993)
1958, 1000 fish, mainly roach and bream, were killed, when Wyken Pool was polluted.

"...the fish were being poisoned by a discharge of industrial waste, carried by a stream which flows into the Slough (sic)."

The same source, in September 1968, reported that

"...many fish were killed in July this year..." and that "the source of the pollution has not been disclosed"

but it was thought that flooding in the catchment carried the pollution to the Pool.

Wyken Brook was canalised in 1975 to improve drainage due to problems with the area flooding periodically and presumably causing the pollution events outlined above. At the same time, some dredging of the southern edge of the lake margins were carried out although little disturbance of the majority of the lake bed occurred (R. Ashby, Coventry City Engineers, pers comm).

3.4.3. The Wyken Slough Catchment.

Fig 3.11 shows the development of housing in the Longford area. This area is to the north of Coventry and includes the catchment area of Wyken Pool. Large housing estates were built
Fig 3.11 The Longford area, housing development pre-1914 to 1971.
during the 1950’s and 60’s, mainly to the south of Wyken Pool, but the Longford area was also subject to extensive building programmes (Coventry Geographical Association, 1971).

The historical aspects of a landfill site at Hawksbury are confidential and no records exist of what was dumped there prior to 1974 when the Control of Pollution Act 1974 (now superceded by the Environmental Protection Act 1990, Part II) required disposal records to be maintained of all chemicals disposed of in this way. Unfortunately, there are also no records from 1974 as the tenure of a succession of new owners was too short for the legislation to be enforced. However, the site is subject to flooding and hence any pollutants it may contain could be moved downstream by flood water.

The Bayton Road Industrial Estate was built in about 1969 on the site of an abandoned colliery (J. Batty, STWA, pers comm) and at one time "bright" processing (ie the cleaning of copper and brass with nitric and sulphuric acids) as well as zinc-cadmium battery manufacture occurred there. Part of Bayton Road was sewered until 1988 by a pumped system. This periodically failed, leading to contamination of surface waters with foul sewage. Improved sewerage has been installed adjacent to the Wyken Brook and its lower reaches, close to the marsh.

The Power Station site, including land on the opposite side of the canal, has been used for non-toxic landfill. The first Waste Disposal License was issued in 1984, but the site
has been inactive since 1990 (Environmental Health, Coventry City Council, pers. comm.)

By 1981, the "Coventry Evening Telegraph" carried reports of volunteers needed to help clear the Pool of rubbish.

"...the Slough (sic) was popular for boating, fishing and rambling. But the water has become polluted, the land is used as an unofficial tip and buildings have been badly vandalised."

Two skips of rubbish were removed from the site by the volunteers. The Friends of Wyken Slough were formed in 1982, but their hut was gutted by fire in 1986 and removed in 1990.

The marsh to the south of the Pool was designated a Site of Importance for Nature Conservation (SINC) in 1977. Unlike Sites of Special Scientific Interest (SSSI), SINC's do not have any legal standing. On September 12 1990, Coventry City Council declared the site a LNR.

Wyken Pool and the land around it, known collectively as "Wyken Slough" (Slough= marsh) is to be incorporated into an 11 mile "green ribbon" walk through Coventry (Fig 3.12), which may herald a brighter future for the site.

Table 3.3 summarises the major changes to both lake basins in the last 140 years and illustrates the increasing urbanisation and industrialisation taking place around them.
Table 3.3 Major changes to Swanswell and Wyken Pools from 1850

<table>
<thead>
<tr>
<th>Date</th>
<th>Swanswell Pool</th>
<th>Date</th>
<th>Wyken Pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>1850</td>
<td>Springfield Brook diverted to the east of Swanswell Pool</td>
<td>1850</td>
<td>Subsidence of marshy ground under Marcher Brook</td>
</tr>
<tr>
<td>1940-45</td>
<td>Possible bomb damage during the Second World War</td>
<td>1886</td>
<td>closure of mining activities around the Pool</td>
</tr>
<tr>
<td>1946</td>
<td>Hospital spring feeders cut off and metered water supply installed</td>
<td>1920-30</td>
<td>2 island used to tie boats up</td>
</tr>
<tr>
<td>1949-50</td>
<td>Building of the WMPTE bus depot, Pool Meadow</td>
<td>1958-68</td>
<td>Local newspaper articles on the declining conditions at Wyken Pool</td>
</tr>
<tr>
<td>1950</td>
<td>New hospital block built to the west of Swanswell Pool</td>
<td>1969</td>
<td>Construction of Bayton Road Industrial estate</td>
</tr>
<tr>
<td>1960’s</td>
<td>Culverting of Springfield Brook 2 m below present Pool surface</td>
<td>1971</td>
<td>M6 built</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1977</td>
<td>Marsh designated a SINC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1990</td>
<td>Site designated a LNR</td>
</tr>
</tbody>
</table>
Wyken Pool is the largest expanse of water in Coventry and is an obvious attraction for wildfowl. The rough grassland, scrub and marsh near the Pool also supports a rich variety of wildlife. From Wyken Slough, you can walk under the motorway to the banks of the Oxford Canal and Hawkesbury Junction Conservation Area. The canal towpath forms part of the new Centenary Way Long Distance Footpath, which runs from Kingsbury Water Park and finishes at Mean Hill near Stratford.

The Sowe Valley is an area of Green Belt open space which follows part of the course of the River Sowe for about eight miles. The Valley runs from Hawkesbury Junction Conservation Area in the north, to Stonebridge Meadows Local Nature Reserve in the south.

The Valley links Coventry with the countryside and is particularly important for landscape, amenity, outdoor recreation, local history, education and nature conservation.

Fig 3.12 Coventry Leisure Services produced map of the "green ribbon" walk through Coventry incorporating Wyken Slough
The Swanswell Pool

4.1 Introduction

This chapter describes the results of field surveys and analyses carried out on the water and sediment samples collected from Swanswell Pool and listed in Table 2.21. The following data are considered first:

1. Following descriptions of the bathymetry and sediment thickness of the lake, are classifications of the lake sediment type and its macrofossil content (Chapter 4.1.2), sediment density and organic matter content (Chapter 4.1.3).

2. The chemical analysis of the lake sediments is divided into two sections: phosphorus and heavy metal concentrations. The latter is further subdivided into a discussion of the spatial distribution of the metals in the surface lake sediments and, in four cores, their change in concentration with sediment depth. Two cores were analysed to chemically fractionate the sediments which would enable the sites of attachment of the heavy metals within the sediment to be assessed (Chapter 4.2.4).

3. Mineral magnetic, radioisotope and particle size analyses complete the description of the physical parameters and are presented in Chapters 4.5 to 4.7.
4. Statistical analysis of the data is presented in section 4.3. This was primarily used to establish whether any relationship existed between individual parameters, but also to assess the usefulness of some of the measurements that were made for the purposes of environmental reconstruction.

5. A consideration of the Swanswell Pool lake sediments is completed by an examination of the molluscan content of a sediment core from Swanswell Pool.

6. Water quality is considered in section 4.5. Measurements were made in situ, and in the laboratory. NRA (Severn Trent Region) data are also discussed.

4.2 Characteristics of Swanswell Pool and its sediments

The results of analyses used to reconstruct the pollution history of Swanswell Pool are presented in this section. These include the bathymetry of the lake basin as well as physical and chemical analyses of the sediments deposited within it. Physical characteristic, such as visible stratigraphy, fossils and bulk density, all provide a means to correlate synchronous horizons across the lake.

4.2.1 Bathymetry and sediment thicknesses.

A bathymetric map, based on hand line depth measurements, is given in Figure 4.1. The maximum depth of water, 1.4 m, was recorded in the southeastern corner of the Pool. Over the rest
Fig 4.1 Bathymetry of Swanswell Pool

Survey Date: 9th. February 1988
Overflow Level: 0m

Water Depth (m)
of the Pool water depths varied between 0.5 and 0.75 m. At
the time of sampling there was no head of water over the
overspill weir located in the south-east corner of the Pool.
Water depths are reported to the level of the weir plate.

Sediment thicknesses were measured by probing with survey
rods at intersections of the coring grid (Fig 2.10 a) and
plotted by hand. The results of this analysis are given in the
form of an isopach map in Figure 4.2. The thickest sediment,
over 2.5 m, is located in the central third of the Pool. The
island appears to interrupt the general pattern of
sedimentation and, on its western side, the sediment is
between 2 and 2.5 m thick. The sediment gradually reduces in
thickness towards the edges of the Pool, but is truncated to
the north and south where the isopachs are much more closely
spaced. To the south of the Pool, adjacent to the dam wall,
the 1 and 2 m isopach lines converge at the wall, suggesting
that the wall was constructed over the original southern end
of the Pool (see Figs 3.7 and 3.8). The isopach lines
therefore indicate that Swanswell Pool was larger in the past,
a factor reinforced by the documentary evidence presented in
Chapter 3.

4.2.2 Core stratigraphies

The stratigraphies for the sediment cores retrieved from
Swanswell Pool are shown in Figure 4.3, and the macrofossil
record is shown in Figure 4.4.

From Fig 4.3, it is possible to provide a general
stratigraphic description for the lake sediments using Munsell
Fig 4.2 Sediment thickness

Survey Date: 9th. February 1988
Overflow Level: 0m

Sediment Thickness (m)
Fig 4.3 Lake sediment type at Swanswell Pool

12
11
10
9
8
7
6
5
4
3
2
1

- Fine detritus mud
- Clay
- Transition zone

25 cm depth
Fig 4.4 Macrofossils in the sediments from Swanswell Pool (based on the Troels-Smith (1955) classification scheme)

- Chara with mollusc shells
- Gyttja with filamentous algae
- Whole mollusc shells
- Transition zone between gyttja and red clay
- Gyttja with filamentous algae and mollusc shells
- Lime mud with Chara
- Weed, possibly Stonewort

25 cm depth
Charts (1975) for the colours. The upper sediments were a uniform black to grey-black organic gyttja composed of fine silts and clays but with some macroscopic plant and molluscan shell remains. The macrofossils were mainly present in discrete horizons, the most significant being a layer of weed, possibly the Stoneworts Chara vulgaris or Nitella flexilis. The plants were not sufficiently well preserved for more exact identification, but cores M1, M2 and M12 contained remains of the lime coating associated with the stems of these algae (Clegg, 1989). Mollusc shells also appeared to be represented in discrete horizons, sometimes in association with a filamentous algae which could not be identified. Molluscan remains are considered in more detail in section 4.4. Core M5 contained very little plant material and few horizons of shells. Pebbles were present in some of the cores at various depths.

A sharp, but not horizontal boundary, separated the upper sediments from a red to reddish brown minerogenic clay beneath. These lower sediments contained few shells or plant remains in comparison with the gyttja above. Of the 12 cores sampled on the grid at Swanswell Pool, 3 did not penetrate deeply enough into the sediment to contain any of the red clay. The average depth of the red clay-gyttja boundary was 42 cm although core M1 reached a depth of 72 cm without encountering the red clay. Core M2, near to the dam wall in the southeast corner of the Pool, penetrated the red clay at 78 cm; the deepest point at which the boundary was encountered. The shallowest the boundary was encountered was
in core M9, located between the western edge of the Pool and the island, where red clay was found at 29 cm.

There are therefore several horizons of both Mollusca and algae present in several of the lake cores. However, none of these are present in all the cores to provide a correlatable horizon across the lake. Similarly, 3 of the cores did not penetrate the red clay, so this was not correlatable across the whole lake using visual stratigraphy alone. From the visual stratigraphy, however, the sediments reveal a twofold sedimentation pattern: an earlier, predominantly minerogenic phase depositing the red clay and a later predominantly organic phase represented by the gyttja. Provisionally this may be interpreted in terms of the red clay being deposited whilst the Springfield Brook was still contributing sediment to the Pool (Chapter 3.4.1) and the transition to deposition of gyttja when the Brook was culverted to the east of the Pool in about 1850.

4.2.3 Bulk density and loss on ignition

Results obtained for wet and dry bulk density are shown in Figs 4.5 and 4.6. Wet bulk density did not increase markedly downcore at any of the sites, varying from 0.6 to 1.2 g cm$^{-3}$ at the top of the core and from 1 and 1.7 g cm$^{-3}$ at the bottom of the core. The dry bulk density showed some variation between sites, and a gradual increase downcore; particularly at the boundary between the gyttja and the red clay in those cores which extended deep enough. The values ranged from 0.04 to 0.14 g cm$^{-3}$ in the gyttja. The highest value, in core M8,
Fig 4.5 Wet bulk density of cores M7 - M12

Red clay / black gyttja boundary if present
M2 = 78 cm, M3 = 48 cm, M6 = 45 cm, M7 = 48 cm, M8 = 34 cm, M9 = 26 cm, M10 = 47 cm, M11 = 36 cm, M12 = 31 cm

Fig 4.6 Dry bulk density of cores M1 - M6
was 1.18 g cm$^{-3}$. In the red clay values varied between 0.4 and 1.0 g cm$^{-3}$. Core M8, from the eastern side of the Pool, had consistently higher dry bulk density values whilst core M1, located in the southeastern corner, had consistently lower values. The ratio between dry and wet bulk densities (Fig 4.7) increases from between 0.04 and 0.14 in the upper samples to about 0.5 at the bottom of the cores, but no significant change is apparent at the boundary between the red clay and gyttja.

The profiles for organic matter and carbonate content in cores M4 and M11 are shown in Fig 4.8. The general trends are for both of these parameters to decrease with increasing depth, although the carbonate contents are more variable. The organic matter content of core M11, situated in the centre of the transect taken in the north of the pool, declines from a value of 20% to 7% at the boundary with the red clay at a depth of 36 cm. The rise to 10% within the red clay is maintained to the bottom of the core. Values for organic matter are generally higher in core M4, varying from a maximum of 26% in the upper samples down to 10% at the bottom of the core. Core M4 does not penetrate the red clay therefore there is no equivalent decrease in organic matter to that observed in core M11, although there is an isolated decrease to 19% at a depth of 15 cm. Values are over 20% in the upper samples of the lake cores and this is high in comparison with other Midland England lakes such as Merevale Lake and Seeswood Pool (Foster et al., 1987) with organic matter values of 0.75 - 5.9% and 9.2 - 11.6% respectively. Swanswell Pool would appear to be in receipt of high organic matter contributions.
Fig 4.7 Dry : Wet bulk density ratio from cores M3, M6, M8 and M11

![Graph showing dry to wet bulk density ratio across different depths for cores M3, M6, M8, and M11.]

Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm

Fig 4.8 Organic matter and carbonate content of cores M4 and M11

![Graph showing organic matter and carbonate content across different depths for cores M4 and M11.]

M4 Organic Matter
M4 Carbonate
M11 Organic Matter
M11 Carbonate
either from the catchment, or internally due to high productivity. As explained in Chapter 3.4.1, Swanswell Pool has no contributing catchment apart from limited runoff from the surrounding park. Chapter 3.3.1 detailed the waterfowl living on and around the Pool. It therefore seems likely that the organic matter reflects high internal productivity at this site. This could be due to the waterfowl living on and around the Pool, (see Chapter 3.3.1) which are known to cause high sediment organic matter (Gere & Androvics, 1992).

The carbonate content in core M11, whilst decreasing from 33% in the top sample to 22.5% at the bottom, initially exhibits an increase downcore. This trend is interrupted by a marked drop to 26.5% between 17 and 25 cm depth. The subsequent rise in carbonate content downcore is again interrupted at the boundary with the red clay where carbonate content decreases to 15% before rising again to the bottom of the core. The carbonate content is generally higher in core M4 than in core M11. Initially exceeding 61%, it falls to 34% at 33cm depth. The deepest sample at 50cm reaches a value of 62%, but those between 36cm and 49cm, whilst fluctuating slightly, still decrease towards the basal sediments. Unlike in sea water, carbonate is not entirely removed by biota (Stumm & Morgan, 1981), although comparison of the stratigraphies (Fig 4.4) with Fig 4.8 indicates increased carbonate content of the sediment where shells remains and the carbonate-rich Stoneworts appear.
4.2.4 Sediment Chemistry

The results of sediment chemical analysis are presented in the following section which is divided into three parts. With the aim of reconstructing pollution history in the lake, downcore trends of metal concentration are presented first followed by analysis of the spatial distribution of metals in the upper 1 cm of lake sediment in the 12 cores taken in the grid shown on Fig 2.7a.

As discussed in Chapter 2.11, P, Fe and Mn are used in this study as indicators of past nutrient and redox status, and their distribution is also considered both downcore and spatially.

The third section is concerned with the non-metallic elements. These can indicate past sedimentation regimes, such as increased erosion (Engstrom & Wright, 1984) which may help to identify changing sediment sources or changing sediment yield. Non-metallic elements may also indicate changing salt concentrations over time which could lead to the release of heavy metals into the water column (Chapter 2.8 v).

1. Heavy metal analysis

a. Trends in heavy metal concentration with depth.

This section is divided into two parts, with a consideration of the analysis for the total heavy metal concentration downcore presented first followed by a discussion of the
results of a sequential extraction carried out on one lake core.

i. Total extraction of heavy metals

The general trend in the lake cores is for a decrease in the concentration of heavy metals with depth; the exception being Ni (Fig 4.9 a) which exhibits an increase in the basal sediments below the interface between the organic gyttja and the red clay. Ni concentrations range from a maximum of 140 µg g⁻¹ at a depth of 20 cm in core M10 to a minimum of 4 µg g⁻¹ at a depth of 9 cm, also in core M10. The decrease in Ni concentration in the top few cm is followed by a substantial rise; the largest being found in core M10, and the smallest peak in core M3. Concentrations then decrease to the boundary with the red clay whereupon they increase again.

The profile for Cd (Fig 4.9b) fluctuates between the limits of detection and 18 µg g⁻¹ with generally the lowest concentrations found in core M10 and the highest in core M8. In general, concentrations are higher in the upper sediments of the core, although average values in core M6 do not decrease below 20 cm depth.

Pb concentrations (Fig 4.9c) show great variability in all cores, although the underlying trend is for this metal to decrease in concentration with depth. Values vary from a maximum of 550 µg g⁻¹ recorded from the top sample of core M8 down to between 29 and 35 cm depth in core M6 where Pb concentration is below the limit of detection.

170
Fig 4.9 Total heavy metal content of lake sediment cores

- a. Ni
- b. Cd
- c. Pb
- d. Zn
- e. Cu

Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm
Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm
Zn concentration decreases in the top few cm of all cores, exhibits a slight increase and then decreases, until by 30 cm depth it is mostly undetectable. The increase in core M8 is found lower than the other cores at 15 cm and reaches a maximum concentration of 3700 μg g⁻¹.

Cu (Fig 4.10 e) exhibits a fall in concentration in the upper 30 cm of all cores. In core M10, Cu is undetectable at 9 cm, immediately before the highest concentration of 57 μg g⁻¹ at 10 cm depth is recorded. The sample at 9 cm depth in core 10 has low concentrations for all the heavy metals analysed, whereas at 34 cm in the same core there is a marked peak in all metals concentrations.

Table 4.1 summarises the maximum total concentrations of heavy metals recovered in the Swanswell Pool lake sediments.

Table 4.1 Maximum concentrations of heavy metals from the Swanswell Pool lake sediments (μg g⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Ni</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3700</td>
<td>140</td>
<td>600</td>
<td>550</td>
<td>18</td>
</tr>
</tbody>
</table>

The heavy metal chemistry is dominated by Zn, followed by Cu and Pb, with Ni and particularly Cd present in lower concentrations. However, Chapter 2.4, Table 2.4, shows that Cd
is not an essential element and would be toxic to biota even in small amounts (Macklin, 1992 and Table 2.6).

The trend of heavy metal accumulation over time in Swanswell Pool is of increasing concentration from just above the red clay / gyttja boundary to the present day. In order to assess the magnitude of this increase, background values from uncontaminated deposits should be compared with the values obtained from Swanswell Pool. Section 4.2.2 suggests that the gyttja / red clay boundary may represent the time when the Springfield Brook was cut off from the Swanswell Pool. The relatively low and constant heavy metal concentrations in the red clay tend to support this assumption. If it is the case that the boundary between the two sediment types represents 1850, then the red clay could provide samples of sediment laid down before the Industrial Revolution and therefore before the onset of contamination by anthropogenic heavy metal release. Comparison of average heavy metal concentrations from the red clay and published background values (Förstner & Salomons, 1981) would also provide confirmation of their pre-Industrial Revolution origins. Table 4.2 presents a comparison between background concentrations and average concentrations of heavy metals in the red clay at Swanswell Pool. This shows that Zn, Ni, and Cu are all comparable with the published data, but Pb and Cd are slightly higher, which may reflect the local geology rather than any enrichment due to cultural effects. The red clay was therefore used as a background value in any calculations of anthropogenic excess heavy metal delivery to Swanswell Pool.
Table 4.2 Comparison between heavy metal concentrations in published background values of sediments and average values for the red clay from Swanswell Pool (μg g⁻¹).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
<th>Column 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>105</td>
<td>115</td>
<td>118</td>
<td>95</td>
<td>65</td>
</tr>
<tr>
<td>Ni</td>
<td>51</td>
<td>46</td>
<td>66</td>
<td>68</td>
<td>55</td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
<td>51</td>
<td>45</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>Pb</td>
<td>16</td>
<td>30</td>
<td>34</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td>0.8</td>
</tr>
</tbody>
</table>

1. Fossil lake sediments (Ries Lake n=25)
2. Fossil river sediments (Rhine n=4)
3. Recent lake sediments from remote areas (n=87)
4. Shale standard

Source: Förstner & Salomons (1981a)

5. Red minerogenic clay at the base of Swanswell Pool (n=63)

From background values and maximum concentrations of heavy metals obtained from the lake cores, enrichment factors can be calculated. This is a measure of cultural enhancement of heavy metal content (Förstner & Wittmann, 1981), where the enrichment factor (F) is defined as:
Table 4.3 gives values of $F$ for the lake sediments from Swanswell Pool. All metals are significantly enriched, in particular Zn and Cd. To put these values into perspective, they are compared with those for Wyken Pool in Table 5.4 in Chapter 5.2.4 and also with other published values of $F$ from lakes in the USA.

**Table 4.3 Cultural enrichment factors ($F$) for Swanswell Pool lake sediments**

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Ni</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>55.4</td>
<td>2.6</td>
<td>20.0</td>
<td>11.0</td>
<td>22.5</td>
</tr>
</tbody>
</table>

**ii. Sequential extraction of heavy metals**

This section is discussed under two separate headings to discriminate between the partitioning of heavy metals in the sediments and also the overall trend of metal concentrations with depth in the sediment column.
1. Partitioning of heavy metals in the sediments of Swanswell Pool

Table 4.4 lists the primary and secondary sinks within the sediments for the individual metals. Fe and Mn oxides dominate for Pb, Ni and Zn, probably in the form of cements or coatings on grains (Tessier et al., 1979) whilst a secondary sink for Pb and Ni is organic matter. Zn and Cu are found predominantly in the exchangeable fraction, whilst carbonates are the only other form in which Cu is detectable. With the exception of the residual minerals in which the concentration of Cd remains at minimal levels throughout, there is no fraction which can be said to dominate the retention of Cd. There is no evidence to suggest any fundamental change in partitioning of the heavy metals through time in Swanswell Pool. Release of heavy metals from Fe and Mn cements and organic matter would only occur with changing redox conditions (Chapter 2.4 iiib), exchangeable sites would provide the most concern since Zn or Cu could be released in acidic conditions (Chapter 2.4 iiib). Chapter 3.4.1 highlighted the periodic spillages that have occurred in Swanswell Pool in the past. Section 4.5 discusses water quality in Swanswell Pool and this will be applied back to the partitioning of heavy metals in sediments described in this section.
Table 4.4 Fractions associated with the highest proportion of metals in the upper zone.

<table>
<thead>
<tr>
<th>element</th>
<th>fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Fe and Mn; organic matter</td>
</tr>
<tr>
<td>Ni</td>
<td>Fe and Mn; organic matter</td>
</tr>
<tr>
<td>Zn</td>
<td>Fe and Mn; exchangeable</td>
</tr>
<tr>
<td>Cd</td>
<td>none dominates</td>
</tr>
<tr>
<td>Cu</td>
<td>exchangeable; carbonate</td>
</tr>
</tbody>
</table>

2. Trends of metal concentration with depth in the sediment of Swanswell Pool

The fractionation of the lake sediments in core P2 (Fig 2.7 a) yielded profiles which can be divided into two broad zones. In the upper zone, down to about 70cm (the red clay was encountered at 90 cm), concentrations of the metals are generally higher than in the sediments below (Figs 4.10 a - e). There are, however, fractions in which the concentration of all metals vary little, if any, downcore. These are identified in Table 4.5.

Pb (Fig 4.10 a) is as variable in the fractionation profile as in the total digest, although the concentration of Pb in the red clay is lower than that in the sediments above. The Zn and Ni (Fig 4.10 b and c) profiles are marked by peaks
Table 4.5 Fractions with no variation downcore.

<table>
<thead>
<tr>
<th>element</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>exchangeable; carbonate</td>
</tr>
<tr>
<td>Ni</td>
<td>residual; carbonate</td>
</tr>
<tr>
<td>Zn</td>
<td>residual</td>
</tr>
<tr>
<td>Cd</td>
<td>residual</td>
</tr>
<tr>
<td>Cu</td>
<td>residual; Fe and Mn; organic matter</td>
</tr>
</tbody>
</table>

in concentration between samples 7 and 13 in which they are particularly enriched in association with Fe and Mn oxides. Subsequently, concentrations in all the fractions fall to background levels with increasing depth. There is an isolated peak in the concentration of Ni bound to organic matter in sample 27. A peak in Cd concentration occurs in sample 12 in all but the residual minerals (Fig 4.10 d). A single peak in the Cd content of the organic matter fraction occurs in sample 15. The peak for Cu (Fig 4.10 e) in the upper sediments is slightly broader, encompassing samples 6 to 14 in the exchangeable fraction. The trend in Cu bound to carbonates is for decreasing concentrations with increasing depth, apart from a peak in sample 4. Below sample 14, Cu is only detectable in the exchangeable fraction.
Sample 9, at a depth of 45 cm, marks a peak in the concentration of all the elements, although not necessarily in all of the fractions.

The overall trends in the sequential extractions reflect those found in the total extraction; that of increasing metal concentration towards the present day and with low, constant values from just above the gyttja / red clay boundary to the base of the core.

b. The spatial distribution of heavy metals in the top 1 cm sediments of the Pool.

The results of heavy metal analysis of the upper 1 cm samples from each of the cores in the grid at Swanswell Pool are presented in Figs 4.11 a-e. The pattern for all of the heavy metals is similar, except for Pb. There are two areas of the Pool in which the concentrations of Cd, Cu, Ni and Zn are highest. These are in the north of the Pool, near the hospital settling tank inflow, and in the southern end of the lake at some distance away from the outflow weir. In the case of Pb (Fig 4.11 a), the areas of highest concentration are towards the eastern margins of the Pool, one in the north, to the east of the hospital settling tank, and the second in the south east, near the dam wall. With the exception of Cu and Pb, the concentrations of heavy metals near the outlet are higher than those near the hospital settling tank inflow.

Higher Pb values are found around the northeastern and southeastern margins of the pool, with the minimum value interposed between the two areas of maximum concentration.
Fig 4.11 Spatial distribution of heavy metals in surface lake sediments:
a. Pb  
b. Cu  
c. Cd  
d. Ni  
e. Zn

A

Lead (µg g⁻¹)

<300
300-400
>400

0 m 30

Overflow
Concentrations of Pb tend to decrease towards the central eastern areas of the pool. Values vary from 474 to 233 μg g⁻¹. 

Concentrations of Cu (Fig 4.11 b) vary from 54.44 μg g⁻¹ in the northeast corner to 24.8 μg g⁻¹ in the southeast near the overflow. Values tend to decrease in the central and eastern areas, but the range of values is relatively small.

Cd concentrations (Fig 4.11 c) vary from 14.65 μg g⁻¹ in the south to less than 4 μg g⁻¹ in the northeastern corner. Concentrations tend to decrease southwards and towards the margins of the pool.

Maximum concentrations of Ni (Fig 4.11 d) are to be found in the south of the pool at over 120 μg g⁻¹. The minimum concentration of 42.6 μg g⁻¹ is found in the northeastern corner. Apart from these two extremes, values do not vary greatly across the rest of the surface sediments, although the tendency is for concentrations to decrease southwards.

Zn concentrations (Fig 4.11 e) vary between about 3000 μg g⁻¹ in the south, and 1510 μg g⁻¹ in the area to the east of the island. Values tend to decrease around the margins of the pool and towards the overflow.

The historical problems with spillages from the hospital settling tank overflow outlined in Chapter 3 may still be reflected in the sediments with higher concentrations of most heavy metals found in the north of the Pool. Sediment focusing may also be responsible in part for the distribution of metals in the surface sediments, reflecting differential settling of coarser particles near the hospital overflow and finer particles near the Pool overflow accounting for an area of high values there.
2. P, Fe and Mn content of lake sediments

This section is divided into two parts to present the results of the distribution of P, Fe and Mn with depth in the lake sediments and also spatially in the surface samples of the lake.

a. Downcore trends in P, Fe and Mn content

The general trend in P concentration downcore (Fig 4.12 a) is for a perceptible decrease with depth. Concentrations vary from between 200 and 1200 µg g⁻¹ in the upper sediments to between 180 and 400 µg g⁻¹ towards the bottom of the core (cores M6, M8 and M10). Core M3 has a minimum concentration of 200 µg g⁻¹ at 47 cm depth and a maximum of 600 µg g⁻¹ at 53 cm, the base of the core. All cores except core M10, in which concentrations gradually decline, exhibit an increase in concentration in the upper 9 cm. Core M8, for example, approaches 1200 µg g⁻¹ at a depth of 4 cm. The peak in core M10 occurs at a depth of 21 cm where values reach 1660 µg g⁻¹. Secondary peaks are also evident in core M8 at 21 and 23 cm, rising to 1020 and 620 µg g⁻¹ respectively. Whilst P in cores M3, M6 and M8 subsequently decreases in concentration with depth, core M10 exhibits isolated peaks at 29 and 34 cm and a sustained rise from 35 to 45 cm reaching a maximum of 780 µg g⁻¹.

P concentrations do not indicate excessive productivity and hence it is unlikely that Swanswell Pool has suffered problems associated with eutrophication in the past.
Fig 4.12 Downcore trends in P, Mn, Fe and Fe/Mn in lake cores

a. P  b. Mn  c. Fe  d. Fe/Mn

Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm
Red clay / black gyttja boundary
M3 = 48 cm, M6 = 45 cm, M8 = 34 cm, M10 = 31 cm
The high organic matter values obtained for the upper lake sediment may be due to the lack of channelled inflow.

Fe and Mn (Fig 4.12 b and c) show similar trends with a decrease in concentration at about the boundary between the gyttja and the red clay in each core followed by a rise within the red clay to a concentration above that of the surface sediment samples. Once again the samples at 8 cm and 34 cm in core M10 show a trough and a peak respectively in Fe concentration and, although this is paralleled in Mn concentrations, it is not as pronounced within the range of values recorded. Fig 4.12 d gives the Fe / Mn ratio from each core. The ratio fluctuates in the cores between 20 and 100, with the highest average ratio shown by core M8 and the lowest generally in core M10. Each core exhibits fluctuations within the gyttja which cannot be correlated between cores. The ratio does, however, tend to rise upon sampling the red clay which indicates a deficiency in Mn. Core M10 shows the greatest fluctuation in the Fe / Mn ratio, possibly indicating changing redox conditions which may have been associated with mobilisation of heavy metals. However, profiles for the other three cores analysed do not show such variability so the evidence for heavy metals release in the past throughout the lake is inconclusive.

b. Spatial variability in the upper 1 cm of sediment

The spatial distribution of P in the upper 1 cm slice of lake sediment (Fig 4.13 a) varies from a maximum of 940 µg g⁻¹ in the south to a minimum of less than 250 µg g⁻¹ in the
Fig 4.13 Spatial distribution of P, Fe, Mn and Fe / Mn in the surface sediments of Swanswell Pool
a. P
b. Fe
c. Mn
d. Fe / Mn

A
Phosphorus (µg g⁻¹)

>800
400-800
<400

0  m  30
Overflow
B  
Iron (mg g⁻¹)

- >17.5
- 12.5-17.5
- <12.5

C  
Manganese (mg g⁻¹)

- <2.5
- 2.0-2.5
- <2.0
northeastern corner and in the south near the dam wall. A second peak in concentration occurs to the east of the island at 800 μg g⁻¹. The general trend is for decreasing concentrations towards the margins of the lake, particularly in the south and northeast.

Fe and Mn (Fig 4.13 b and c) are both low to the south of the island and high in the north of Swanswell Pool, but the Fe / Mn ratio (Fig 4.13 d) is lowest around the island and higher towards the edges of the Pool, perhaps indicating greater reducing conditions in relatively shallower water. Mitsch & Gosselink (1993) relate redox conditions to the presence of oxygen-consuming and oxygen-producing organisms and mixing of surface waters by wind and convection currents. The presence of shallow water and possibly disturbed and shallow sediment (Fig 4.2) would not provide suitable conditions for plants to root. A combination of this and the shelter offered by the island walls and concrete pool banks would ensure minimal mixing and hence, reduction of the underlying lake sediment.

3. Non-metallic elements

Results from the analysis of Na, Mg, Ca and K from core M10 are presented in Fig 4.14. Na shows a decrease in concentration downcore from 2000 μg g⁻¹ in the upper sample to 1100 μg g⁻¹ at the bottom of the core. Mg and K exhibit similar behaviour with little variation down to a depth of 30 cm followed by a marked rise to the base of the core. There is a peak in the concentration of Ca at a depth of 9 cm, where the peak in the heavy metals also occurred. The Ca trace is
Fig 4.14 Downcore trends in non-metallic elements
Na, K and Mg (mg/g)

Red clay / black gyttja boundary, M10 = 34 cm
highly variable, but the general trend is for an increase downcore until the boundary with the red clay at between 33 and 35 cm depth where there is a marked decline in concentration with increasing depth. This decline is followed by a peak at 37 cm below which its concentration declines towards the bottom of the core.

Apart from Ca, there does not appear to be great variation in the concentration of the non-metallic elements until the junction with the red clay. This reflects little change in sedimentation both in terms of source and delivery. The Ca profile differs from the other three non-metallic elements, but it may be connected to metabolism by organisms such as snails or Ca-depositing algae. Comparison of Fig 4.14 with Fig 4.4 shows some similarities between the incidence of snail and Chara remains and the Ca profile. It is probable, therefore, that the Ca profile reflects cycling by biota rather than any change in sedimentation.

4.2.5 Mineral magnetic properties of the lake sediment

Chapter 2.10 ie) discussed the main reasons for obtaining the mineral magnetic characteristics of lake sediments to trace pollution history. These were for correlation of a grid of cores, tracing the sources of sediment to the lake and to establish whether it would be possible to use magnetic measurements as a surrogate for heavy metals analysis. The latter will be addressed in section 4.3a iii, but the rest of
this section will be divided into three subsections. The first will describe the results obtained. This will be followed by an application of those characteristics to a matrix of $\chi_{1r}$ and SIRM profiles representing the grid of cores and an attempt to use these to correlate across the lake. Lastly, mineral magnetic characteristics will be used to resolve the changing nature of the sediments through time.

a. The mineral magnetic characteristics of the lake sediments

Figs 4.15 a and 4.15 b show traces for $\chi_{1r}$ and SIRM respectively for cores M6 and M12. The highest values for $\chi_{1r}$ in both cores are found in the top 10 samples, this is followed by a trough of lower values. There are two peaks in both cores at depths of between 20 and 24 cm where values of $\chi_{1r}$ are over 7.5 $\mu$m$^3$ kg$^{-1}$. Values rise in both cores at the junction with the red clay. SIRM profiles are similar to those of $\chi_{1r}$ with high values in the uppermost sediments, a central peak at about 20 cm depth, and the junction with the red clay is indicated by markedly higher values in the case of core M6, and slightly higher values in core M12.

Values of $\chi_{rs}$ (Fig 4.15 c) for both cores fluctuate around the limits of detection. The upper 9 cm of core M6 has a maximum $\chi_{rs}$ of 50 nm$^3$ kg$^{-1}$, whilst core M12 reaches 15 nm$^3$ kg$^{-1}$ at a depth of 2 cm. There would therefore appear to be little or no input of magnetic minerals of a pedogenic origin.
Fig 4.15 Mineral magnetic characteristics in lake sediments
a. $\chi_{lf}$  b. SIRM  c. Xfd  d. S-ratio  e. HIRM

Red clay / black gyttja boundary
M6 = 45 cm, M12 = 31 cm
Fig 4.15 Matrix of $\chi_{Ir}$ and SIRM for all lake cores

*$^{137}\text{Cs date, see 4.2.6*)*}
which are usually characterised by high $\chi_{r,a}$ (Thompson & Oldfield, 1986).

S-ratio and HIRM profiles are presented in Figs 4.15 d and 4.15 e and are mirror images of one another. The S-ratio reflects ferrimagnetic mineralogy and HIRM reflects canted antiferromagnetic mineralogy. The trace for the S-ratio, with high values in each core, (between 0.6 and 1.0) indicate a high ferrimagnetic component, possibly magnetite. The maintainence of these high values to the junction with the red clay indicates that the source of the gyttja probably has not changed through time. The values for HIRM in core M6 are much lower than those of M12, but vary little until the junction with the red clay when values rise to over 1.5 mAm$^{-1}$ kg$^{-1}$ from 38 cm to the red clay boundary. The HIRM trace for M12 fluctuates markedly from low values in the topmost samples to 17 cm where HIRM reaches 3 mAm$^{-1}$ kg$^{-1}$. Values decrease until the red clay boundary where HIRM begins to increase, reaching 2.3 mAm$^{-1}$ kg$^{-1}$ at 32 cm.

b. The use of a matrix of $\chi_{r,t}$ and SIRM profiles in core correlation

A matrix to show $\chi_{r,t}$ and SIRM profiles throughout the grid of lake cores is presented in Fig 4.15 f. On the basis of these magnetic properties, the lake can effectively be divided into two sub-basins, with the profiles in the northern transects exhibiting marked fluctuations in both SIRM and $\chi_{r,t}$. 

201
more particularly within the upper black gyttja. The two transects in the southern half of the pool exhibit profiles which are less variable. The profiles within the red clay also tend to exhibit little variation, with the exception of core M9 in which there are three peaks common to both parameters at depths of 40, 45 and 54 cm.

The boundary between the red clay and the black gyttja is characterised by a peak in both magnetic parameters in all cores except core M7. The largest peak in $\chi_{1t}$ at this boundary is in core M12.

Maximum $\chi_{1t}$ values of up to 0.9 $\mu$m$^2$ kg$^{-1}$ in the upper sediments are found in the northern sub-basin. The highest values in the south are slightly more than half of those in the north, reaching a maximum of 0.48 $\mu$m$^2$ kg$^{-1}$ in core M5.

Highest SIRM values parallel those of $\chi_{1t}$, with the largest values recorded in the sediments in the northern sub-basin. The highest value in the upper sediments approaches 30 Am$^2$ kg$^{-1}$ in core M9 at a depth of 14 cm, the highest value to the south, apart from those found near the red clay boundary is 9 Am$^2$ kg$^{-1}$ in core M1 at a depth of 21 cm.

Correlation between the magnetic traces for cores along the two transects in the north of the Pool is fairly clear, as is that between the cores along the two transects in the south of the Pool. It is not possible to match the profiles obtained in the northern transects with those in the south on the basis of magnetic characteristics alone, apart from correlating from
north to south using the visible stratigraphies (Fig 4.3 and 4.4).

The correlatable feature in the northern sub-basin is a trough in both SIRM and $\chi_1$, below the high values in the upper sediments. There is also a peak in both magnetic parameters associated with the boundary between the red clay and the black gyttja. The trough in the black gyttja overlies a peak, which is not associated with the red clay boundary peak. Core 12 exhibits a double peak just above the red clay boundary. There are peaks in the red clay in cores M8, M9 and M12, which may be synchronous, but it is not possible to extrapolate between the cores as the relationship is inconsistent.

In the southern cores there are two locations in the profiles where correlation is possible. The upper few samples exhibit higher SIRM and $\chi_1$, values and at the point these values decline sharply, a time synchronous correlation may exist. Below this horizon is a plateau of unvarying values terminated by a single or double peak; a second correlatable feature. Below this peak, values become more variable with most of them increasing. However in cores M1, M4 and M5 SIRM and $\chi_1$, generally decrease.

Difficulties in correlation are encountered in the cores located around the margins of the pool. In a small water body such as the Swanswell Pool the majority of the cores are near the banks where they may be disturbed. Cores M6, M2 and M3 probably represent the least disturbed cores from the suite and consequently show similar profiles with least variation.
It is noticeable that those cores taken from the marginal areas of the pool with the shallowest depths of water and sediment offer the least convincing correlatable horizons.

c. Mineral magnetic characteristics as an indicator of changing sediment source with time

Subsection a.) mentioned the use of $\chi_{r_4}$ values in identifying sediment sources, as the low values indicated a lack of magnetic minerals of pedogenic origin. The high and consistent $S$-ratio suggests no change in the source of the gyttja. To specifically apply mineral magnetic measurements to assess whether sediment source has changed with time, scattergrams of $\chi_{r_1}$ against SIRM were used. This ratio can be used as a guide to magnetic particle size (Thompson & Oldfield, 1986) and also reflects magnetic mineralogy in the sample. Fig 4.16 presents data kindly provided by J A Lees (Geography Division, Coventry University) showing the division of a scattergram of $\chi_{r_1}$ and SIRM into lines of gradient characteristic of materials such as polluted road dusts, synthetic magnetic materials and natural sediments from rivers and soils.

Scattergrams of $\chi_{r_1}$ against SIRM in the lake sediment cores are presented in Fig 4.17. Two distinct trends on each graph can be seen; a low SIRM/ $\chi_{r_1}$ ratio corresponding to the black organic gyttja, which is more ferrimagnetic, and a high SIRM/ $\chi_{r_1}$ ratio corresponding to the red clay and indicating a trend towards a canted antiferromagnetic mineralogy.
Figure 4.16: SIRM/$\chi_{lf}$ ratios for sets of polluted materials
(unpublished data, J A Lees)

Values for SD and MD magnetite and haematite are recalculated from Thompson & Oldfield (1986)

- Materials containing haematites
- Materials containing magnetites
Superimposed on these scattergrams are lines of gradient representing ratios of 1:10, 1:20, 1:40 and 1:80. The majority of the gyttja plots between ratios of 10 and 40. Decreasing ratios indicate an increasingly ferrimagnetic mineralogy, such as magnetite, and increased magnetic grain size. Increasing ratios indicate an increasing canted antiferromagnetic component, such as haematite. Core M2 is the longest of the four cores plotted with 79 samples (Fig 4.17 a). The samples can be resolved into several different groups relating to their position in the core. From the basal sediments to the uppermost samples, the low ratio indicates increasing ferrimagnetic minerals, such as magnetite, and increasing grain size, which may be indicative of an increasing proportion of particulate pollutants which are ferrimagnetic multidomain grains (Thompson & Oldfield, 1986 and Fig 4.16). Whilst cores M7, M9 and M10 do not show this resolution, the general trend of increasing antiferromagnetic minerals and decreasing ferrimagnetic minerals is present, the samples within the red clay indicating the gradual change in sediment source as they lie on a different line of gradient to the gyttja.

Mineral magnetic measurements therefore show the change in sediment source at the boundary between the red clay and the black gyttja and the dominance of pollution particles in the uppermost sediments of Swanswell Pool commensurate with the dominance of atmospherically derived sources to the sediment. However, use of magnetic properties to fingerprint the cores
of a small urban lake with a complex history is problematic. The question of the application of magnetic measurements to both Swanswell and Wyken Pools was addressed by Foster & Charlesworth (1994). The following paragraph comments on Swanswell Pool; Wyken Pool is covered in Chapter 5.2.5.

Table 4.6 gives the coefficient of variation (CV) at two standard deviations (95%) for various properties of the surface lake sediment samples and for one core at Swanswell Pool. In the case of the mineral magnetic characteristics, the spatial variability is similar to or less than that of the downcore variability which indicates that in general mineral magnetic properties may reflect the characteristics of the lake such as sorting processes, the presence of magnetotactic bacteria (Fassbinder et al., 1990; Mann et al., 1990) or greigite (Snowball & Thompson, 1992) as much as trends through time. The CV for heavy metals, however, is much higher downcore than spatially which indicates that the core may provide a reasonable representation of trends in pollution history in Swanswell Pool.

4.2.6 Dating using $^{137}$Cs and $^{210}$Pb

In order to put the history of heavy metal pollution in Swanswell Pool into an historical context, one lake sediment core was subjected to radioisotope dating as outlined in Chapter 2.12. The results are presented in 2 subsections which will discuss $^{210}$Pb and $^{137}$Cs separately.
Table 4.6 Coefficient of Variation at 2 standard deviations (95%) for surface sediments and a lake sediment core from Swanswell Pool. From Foster & Charlesworth (1994)

<table>
<thead>
<tr>
<th></th>
<th>Surface samples n=12</th>
<th>Core n=72</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBD</td>
<td>120.0</td>
<td>71.1</td>
</tr>
<tr>
<td>$\chi_{s-f}$</td>
<td>75.4</td>
<td>150.4</td>
</tr>
<tr>
<td>SIRM</td>
<td>100.3</td>
<td>121.0</td>
</tr>
<tr>
<td>IRM</td>
<td>129.7</td>
<td>170.7</td>
</tr>
<tr>
<td>S-ratio</td>
<td>24.7</td>
<td>200.0</td>
</tr>
<tr>
<td>HIRM</td>
<td>100.0</td>
<td>396.2</td>
</tr>
<tr>
<td>Pb</td>
<td>44.6</td>
<td>112.2</td>
</tr>
<tr>
<td>Cu</td>
<td>72.1</td>
<td>135.2</td>
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<tr>
<td>Ni</td>
<td>55.5</td>
<td>111.6</td>
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<tr>
<td>Zn</td>
<td>66.1</td>
<td>206.8</td>
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<tr>
<td>Fe</td>
<td>41.9</td>
<td>125.1</td>
</tr>
<tr>
<td>Mn</td>
<td>131.2</td>
<td>83.5</td>
</tr>
</tbody>
</table>

DBD = dry bulk density
Results of the analysis undertaken in the Physics department at Coventry University are presented in Table 4.7 and Fig 4.18.

i. $^{137}$Cs

$^{137}$Cs activity is below the limits of detection of the instrument by 27 cm depth. There is a large percentage error at 25 cm and a low activity which strongly suggests that 25-27 cm depth in core M7 could therefore represent 1954. This gives a sediment accumulation rate in the last 39 years of 0.625 cm yr$^{-1}$. The red clay in core M7 is reached at a depth of 48 cm. The intervening 21 - 23 cm, therefore, represent the sediment accumulated between 1850 and 1954; a sediment accumulation rate of 0.221 cm yr$^{-1}$. However, as sediments accumulate, they are compressed, as illustrated by bulk density data (Fig 4.6) in that the upper sediments have a lower bulk density than those towards the base of a core. Taking this into account, the equivalent depth of sediment can be calculated using dry bulk density. The upper 26 cm, if the same bulk density as those sediments below, would occupy 18.54 cm, some 6.5 cm less. The accumulation rate for the sediments since 1954 can therefore be corrected to 0.4635 cm yr$^{-1}$ using $^{137}$Cs as a means of dating.
Table 4.7a Activity of $^{137}\text{Cs}$ and $^{210}\text{Pb}$ in core M7 from Swanswell Pool (mBq g$^{-1}$).

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>$^{137}\text{Cs}$ Total</th>
<th>%</th>
<th>$^{210}\text{Pb}$ Total</th>
<th>Supported $^{210}\text{Pb}$</th>
<th>Unsupported $^{210}\text{Pb}$</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>36.6</td>
<td>35</td>
<td>190.0</td>
<td>4.4</td>
<td>185.6</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>31.8</td>
<td>30</td>
<td>168.1</td>
<td>2.4</td>
<td>165.8</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>52.1</td>
<td>30</td>
<td>188.4</td>
<td>4.4</td>
<td>184.0</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>55.2</td>
<td>25</td>
<td>121.6</td>
<td>4.0</td>
<td>117.6</td>
<td>50</td>
</tr>
<tr>
<td>12</td>
<td>33.6</td>
<td>30</td>
<td>81.3</td>
<td>3.0</td>
<td>78.3</td>
<td>50</td>
</tr>
<tr>
<td>14</td>
<td>57.0</td>
<td>25</td>
<td>96.1</td>
<td>4.5</td>
<td>91.6</td>
<td>50</td>
</tr>
<tr>
<td>18</td>
<td>42.4</td>
<td>25</td>
<td>61.1</td>
<td>2.4</td>
<td>58.6</td>
<td>42</td>
</tr>
<tr>
<td>20</td>
<td>33.8</td>
<td>30</td>
<td>73.9</td>
<td>3.9</td>
<td>69.9</td>
<td>46</td>
</tr>
<tr>
<td>25</td>
<td>4.8</td>
<td>65</td>
<td>32.6</td>
<td>2.2</td>
<td>30.4</td>
<td>60</td>
</tr>
<tr>
<td>27</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>30</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Where ND = not detectable
Fig 4.18 Downcore $^{137}$Cs activity in core M7 (mBq/g)
ii. $^{210}$Pb

Unsupported and supported $^{210}$Pb appear to be below the limits of detection by 25-27 cm depth. However, the unsupported $^{210}$Pb levels are very high in the upper samples in comparison with the supported ones. Table 4.7b compares ratios of surface activities from Swanswell with those from Merevale Lake and Seeswood Pool (unpublished data kindly provided by I D L Foster, Geography Division, Coventry University) both Merevale and Seeswood Pools are rural lake catchments in the English Midlands (Foster et al., 1987).

Table 4.7b $^{210}$Pb activities from Swanswell Pool compared with those from other Midland England lakes.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Total</td>
<td>190.0</td>
<td>159.7</td>
<td>64.8</td>
</tr>
<tr>
<td>b) Supported</td>
<td>4.4</td>
<td>38.1</td>
<td>31.1</td>
</tr>
<tr>
<td>c) Unsupported</td>
<td>185.6</td>
<td>121.6</td>
<td>33.7</td>
</tr>
<tr>
<td>b:c</td>
<td>42.2</td>
<td>3.2</td>
<td>1.1</td>
</tr>
<tr>
<td>a:c</td>
<td>0.98</td>
<td>0.76</td>
<td>0.51</td>
</tr>
</tbody>
</table>

1 = Swanswell Pool
2 = Merevale Lake
3 = Seeswood Pool
It is apparent that the total $^{210}$Pb in the surface sample at Swanswell Pool is considerably higher than that at Merevale or Seeswood, and that the proportions of total : unsupported, and supported : unsupported are also very different. As explained in Chapter 2.12 i, the unsupported component of the $^{210}$Pb measured is from direct atmospheric sources, indirect atmospheric sources (via the catchment in re-eroded soils, channel banks etc) and radon decay in the water column (Oldfield & Appleby, 1984). However, the principal source of unsupported $^{210}$Pb is generally accepted to be directly from the atmosphere with the indirect and water column sources contributing very little to the total inventory (Oldfield & Appleby, 1984). The ratios in Table 4.7 b emphasise the dominance of atmospherically derived $^{210}$Pb at Swanswell Pool. Of the total $^{210}$Pb, 98% is unsupported, and the ratio of unsupported to supported is 42.2, almost 15 times that at Merevale and 40 times that at Seeswood.

An average estimate of the mean annual deposition rate of unsupported $^{210}$Pb from direct fallout from the atmosphere has been estimated at 0.35 pCi cm$^{-2}$ yr$^{-1}$ (P Appleby, pers comm). This is close to published values from average flux rates calculated from lake sediments of 0.55 pCi cm$^{-2}$ yr$^{-1}$ (Oldfield & Appleby, 1984). Converting these values to mBq cm$^{-2}$ yr$^{-1}$ so that they are comparable with those obtained for Swanswell Pool, the mean annual deposition rate would be between 12.95 and 20.35 mBq cm$^{-2}$ yr$^{-1}$. The dry bulk density for the top sample of M7 from Swanswell Pool is 0.185 g cm$^{-3}$ (Fig 4.6) and
the accumulation rate calculated for the sediments from 1954 to the present day based on the $^{137}$Cs date is $0.4635 \text{ cm yr}^{-1}$. The annual deposition rate for Swanswell Pool is therefore:

$$185.6 \text{ mBq g}^{-1} \times 0.185 \text{ g cm}^{-2} \times 0.4635 \text{ cm yr}^{-1} = 15.92 \text{ mBq cm}^{-2} \text{ yr}^{-1}$$

The total $^{210}$Pb in Swanswell Pool is therefore directly comparable with other published data. $^{210}$Pb activity does not register below 25 cm in core M7. Many reasons are postulated in the literature for an incomplete profile and these are discussed in Chapter 2.12 i, and, as applied to Swanswell Pool, these include:

1. Migration of $^{210}$Pb in the sediment column. Smoothing of the curve would be expected in the upper 10 cm due to bioturbation, but the $^{210}$Pb does not register below 25 cm, so whilst bioturbation may be responsible for some movement in the upper sediments, this does not explain the lack of this radioisotope in the lower ones. Some mobilization of $^{210}$Pb may occur in pore water, but according to Eakins (1983) there is indirect evidence that this process is minimal due to sharp peaks in some profiles which would be smoothed if migration had occurred.
2. The flux of $^{210}$Pb should be constant. This cannot be guaranteed in urban lakes whose catchments are characterised by disturbance. However, in the case of Swanswell Pool, there has been no catchment, apart from a small park, since 1850 (Chapter 3.4.1) and sediment is derived from the atmosphere or is autochthonous in origin. Bulk density, loss on ignition and heavy metal profiles give no evidence of change in sediment delivery regime at the site, so it is to be assumed that the flux of $^{210}$Pb has been reasonably constant over time.

3. The residence time of $^{210}$Pb in the atmosphere is constant. Oldfield & Appleby (1984) admit that whilst the relationship between input and fallout is not conclusive, it is a good approximation. Calculations presented above show that the annual accumulation rate of $^{210}$Pb in Swanswell Pool is comparable with calculated values of atmospheric flux so it is likely that the input of $^{210}$Pb has been constant.

4. Sediment resuspension and focusing will lead to lowered levels at sites of active erosion and enhanced levels at sites of active deposition. Oldfield & Appleby (1984) suggest that a study should never rely on a single core, but should instead establish a chronology from a set of representative cores. Unfortunately, this was not possible in the duration of this study, but should provide the focus for future work.
The reason for the lack of $^{210}\text{Pb}$ below 25 cm is therefore not known, but it may be connected with sediment entrainment and focusing.

4.2.7 Particle size analysis

Particle size analysis was carried out on core M8 from Swanswell Pool. The core was chosen as it penetrated the red clay and there was sufficient sediment left to perform a particle size analysis after analysis of heavy metal content.

The mean particle size in core M8 (Fig 4.19) declines gradually with depth from 34 $\mu$m in the top sample to the boundary with the red clay where it decreases to 14.5 $\mu$m. A small peak below the boundary at a depth of 36 cm with a mean particle size of 26 $\mu$m, is followed by a further decrease to 16 $\mu$m in the basal sample of the core. Span is a measure of the spread of particle size about the average and is used to define sorting or dispersion of the sediment (Allen, 1990). Span (Fig 4.19) does not fluctuate greatly in core M8, where values range from about 2 to 4. The lower values are found in the red clay.

Examples of Laser Granulometer traces from individual samples showing the distribution of particle size are shown in Fig 4.20. The top 32 cm is generally characterised by multimodal distributions with up to 5 peaks, mainly dominated by the 25 $\mu$m fraction in the top 9 cm and the 20 $\mu$m peak from 10 cm to 25 cm. Below 25 cm, the dominant peak is at 10 $\mu$m.
Fig 4.19 Particle size distribution in core M8

Red clay / black gyttja boundary
M8 = 34 cm,
Where span is an index of sorting

median
mean
span
Fig 4.20 Examples of the multimodal character of individual lake sediment samples.
Fig 4.20 illustrates this multimodal characteristic with a gradual decrease in size of the dominant peak.

The tail above 100 μm indicates the percentage of grains in the fine sand range. However, 100% of all grains in the samples tested were below 118 μm; i.e. mostly finer than fine sand.

Fig 4.21 shows the change in particle size with depth in core M8. The clay fraction is less than 2% of the total throughout the core. The values for the other size fractions remain fairly constant in the upper 28 cm of the core. The proportion of fine sand in the upper sediments contributes 10%, that of the coarse silt 40%, and medium silt 31%. Changes in the proportions of particle sizes occurs just above the boundary with the red clay at about 31 cm. The percentage of fine sand falls to zero at 34 cm; rising slightly in the basal sediments. Fine and coarse silt appear to be mirror images of one another: a decline in the one is mirrored by a rise in the other. At the boundary with the red clay, the percentage of fine silt increases by 22%, the coarse silt declines by 20% to values of 34% and 18.5% respectively. Medium silt rises from 34% at a depth of 28 cm to a maximum of over 50% at 34 cm. The values of each fraction are highly variable below this boundary.

In general, the core is dominated by the medium silt fraction which contributes over 50% of the sediment, particularly at the boundary with the red clay. The trends of
Fig 4.21 % change in particle size with depth in core M8

% particle size fractions

depth (cm)

- fine sand
- coarse silt
- medium silt
- fine silt
- clay
medium and fine silt are identical. Until the boundary with the red clay, there does not appear to be evidence to suggest any great changes in sediment regime during the deposition of the gyttja.

4.3 Statistical analysis

Statistical analysis was carried out on a number of data sets:

The 12 lake cores separately
The 12 surface samples
The 12 lake cores together
The 4 lake cores with heavy metals data together
The 4 lake cores with heavy metals data separately

Table 2.21 shows the range of laboratory analyses carried out on these data sets. Descriptive statistics including skewness and kurtosis, as well as correlation analysis, were carried out on all the above data sets. Regression was carried out on selected data sets as explained in section 4.3a iii below. Principal Component Analysis (PCA) was carried out on the 4 lake cores with heavy metal data separately.

The objectives of statistical analysis were introduced in Chapter 2.13 and were mainly to identify whether particular properties of the sediments could be discriminated independantly, or whether they shared a high degree of
collinearity. In order to do this, statistical tests were applied to the 7 questions put forward in Chapter 2.13.

To ascertain whether the data was suitable for parametric statistical tests, they were subjected to a number of transformations and skewness and kurtosis values were computed. It was found that transforming the data did not consistently improve the distribution and that the raw data approximated a normal distribution. The raw data were therefore suitable for parametric tests.

Collinearity between mineral magnetic parameters and between heavy metals was determined using correlation. The use of magnetic measurements as a surrogate measure of heavy metals was investigated by means of regression.

PCA was used to reduce the number of variables to a set of dominant factors. As some variables appeared to load on more than one component, varimax rotation was carried out so that one variable would load highly on one component only. This effectively separated the variables into discrete clusters and enables determination of controlling factors.

The results of statistical analysis is divided into 2 subsections, firstly that covering descriptive statistics, correlation and regression, and secondly a description of the results obtained from PCA.
a. Descriptive statistics, correlation and regression

This is divided into four subsections in order to determine relationships between magnetic parameters and between the heavy metals. It also seeks to determine whether there is any relationship between heavy metals and mineral magnetic characteristics of the sediment and whether mineral magnetism can be used as a predictive tool in urban lakes. Lastly, the particle size characteristics of the lake sediment are compared with heavy metal concentrations to determine whether particle size might affect metal concentrations.

Table 4.8 gives a summary of the results from Swanswell Pool. Comparative tables which include Wyken Pool and Wyken Slough are presented and discussed in Chapter 6.

i. Relationship between mineral magnetic parameters in lake sediment cores and surface samples

Correlations between magnetic parameters highlight a high level of interdependence. Table 4.9 illustrates this with a correlation matrix taken from the sum of all the cores analysed in Swanswell Pool. With a critical R value for the correlation coefficient of 0.0815, correlations between measured parameters such as $\chi_i$ and SIRM are consistently high. Correlations between derived parameters such as HIRM, $\chi_{r4}$ and the S-ratio are also highly significant.
Table 4.8 Summary descriptive statistics of the lake sediments from Swanswell Pool (n=156)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Minimum</th>
<th>Maximum</th>
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</thead>
<tbody>
<tr>
<td>$\chi_t$</td>
<td>0.29</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\chi_{ts}$</td>
<td>3.91</td>
<td>0.0</td>
<td>49.3</td>
</tr>
<tr>
<td>SIRM'</td>
<td>5.88</td>
<td>0.1</td>
<td>20.1</td>
</tr>
<tr>
<td>S ratio</td>
<td>0.71</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>HIRM'</td>
<td>0.77</td>
<td>0.0</td>
<td>5.4</td>
</tr>
<tr>
<td>DBD'</td>
<td>0.38</td>
<td>0.0</td>
<td>1.2</td>
</tr>
<tr>
<td>WBD'</td>
<td>1.29</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>DWR</td>
<td>0.29</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe$^t$</td>
<td>35.62</td>
<td>2.5</td>
<td>187.4</td>
</tr>
<tr>
<td>Mn$^t$</td>
<td>1.13</td>
<td>0.1</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe/Mn</td>
<td>56.53</td>
<td>28.8</td>
<td>102.8</td>
</tr>
<tr>
<td>Cd$^t$</td>
<td>5.82</td>
<td>0.0</td>
<td>17.4</td>
</tr>
<tr>
<td>Pb$^t$</td>
<td>198.93</td>
<td>0.0</td>
<td>553.8</td>
</tr>
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<td>Ni$^t$</td>
<td>46.07</td>
<td>4.0</td>
<td>138.7</td>
</tr>
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<td>Zn$^t$</td>
<td>1034.59</td>
<td>28.0</td>
<td>3642.1</td>
</tr>
<tr>
<td>Cu$^t$</td>
<td>179.77</td>
<td>0.0</td>
<td>574.0</td>
</tr>
<tr>
<td>P$^s$</td>
<td>325.24</td>
<td>12.0</td>
<td>1663.9</td>
</tr>
<tr>
<td>Na$^s$</td>
<td>2.15</td>
<td>1.4</td>
<td>2.6</td>
</tr>
<tr>
<td>K$^s$</td>
<td>4.21</td>
<td>2.0</td>
<td>8.4</td>
</tr>
<tr>
<td>Ca$^s$</td>
<td>81.08</td>
<td>31.7</td>
<td>166.6</td>
</tr>
<tr>
<td>Mg$^s$</td>
<td>4.58</td>
<td>2.5</td>
<td>5.6</td>
</tr>
</tbody>
</table>

* n=31

Units
1 $\mu$m$^t$ kg$^{-1}$
2 nm$^t$ kg$^{-1}$
3 mAm$^t$ kg$^{-1}$
4 g cm$^{-3}$
5 mg g$^{-1}$
6 $\mu$g g$^{-1}$

225
Table 4.9 Correlation between mineral magnetic parameters for composite data from all lake cores at Swanswell Pool (575 samples, critical $R = 0.0815$ at 99%)

<table>
<thead>
<tr>
<th>$\chi_{1r}$</th>
<th>$\chi_{n_r}$</th>
<th>$\chi_{r_d}$</th>
<th>SIRM</th>
<th>IRM</th>
<th>HIRM</th>
<th>S-ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_{1r}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi_{n_r}$</td>
<td>0.9986**</td>
<td>-</td>
<td>0.8728**</td>
<td>0.8739**</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\chi_{r_d}$</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIRM</td>
<td>0.8594<strong>0.8613</strong></td>
<td>0.9475**</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IRM</td>
<td>0.4838**0.486 **0.1061*0.685 <strong>0.5212</strong></td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIRM</td>
<td>0.175 <strong>0.179</strong></td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** denotes significance of 99.9%
* denotes significance of 99%
ii. Relationship between heavy metals in lake sediment cores and surface samples

There is a high level of correlation between the heavy metal concentrations in individual cores and in the composite data set. Table 4.10 shows the correlation matrix of heavy metals from all cores at the Swanswell Pool. Apart from cores M6 and M10, in which Cd and Ni respectively do not correlate with any other heavy metal, the correlation coefficients displayed are high when compared against the critical value of R for the appropriate sample size. With the exception of core M10, the correlation between Ni and Zn is particularly high. Correlations are generally lower in core M10 than in the other 3 cores. When all the lake cores are taken together (Table 4.11), the highest correlation is that between Cu and Pb with an R value of 0.8691.

Fewer significant correlations are found between heavy metals in the top 1 cm of each lake core, as shown in Table 4.12. The highest correlation coefficient is between Cd and Ni with an R value of 0.9053.

Correlations between heavy metals are thus inconsistent, especially in the surface samples. The relationship between Zn and Cd highlighted in the literature (Manahan, 1993) and discussed in Chapter 2.5ii does not appear in correlations from Swanswell Pool.
Table 4.10 Swanswell Pool correlations between heavy metals in individual lake cores

Core M3 (50 samples, critical R = 0.2734 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-</td>
<td>0.7088**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.7091**</td>
<td>0.9034**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.4117*</td>
<td>0.5081**</td>
<td>0.5204*</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.7374**</td>
<td>0.8881**</td>
<td>0.935**</td>
<td>0.6739**</td>
<td>-</td>
</tr>
</tbody>
</table>

Core M6 (46 samples, critical R = 0.288 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>0.9074**</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.6698**</td>
<td>0.6415**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.7945**</td>
<td>0.7433**</td>
<td>0.8511**</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Core M8 (34 samples, critical R = 0.3335 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-</td>
<td>0.799**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.9287**</td>
<td>0.9144**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.5639**</td>
<td>0.773**</td>
<td>0.7331**</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.7313**</td>
<td>0.8928**</td>
<td>0.8942**</td>
<td>0.9356**</td>
<td>-</td>
</tr>
</tbody>
</table>

Core M10 (47 samples, critical R = 0.2734 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>0.7754**</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.412*</td>
<td>0.4924**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.4323*</td>
<td>0.6623**</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

228
Table 4.11 Swanswell Pool correlation between all lake cores with heavy metal analysis.
(177 samples, critical R = 0.1946 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.2978**</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.3245**</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.4188**</td>
<td>0.4443**</td>
<td>0.2173*</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.5657**</td>
<td>0.5236**</td>
<td>0.3768**</td>
<td>0.8691**</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.12 Swanswell Pool correlation between heavy metals in surface lake sediment samples.
(12 samples, critical R = 0.6021 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Ni</td>
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<td>-</td>
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<tr>
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<td>0.6478*</td>
<td>-</td>
<td></td>
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<tr>
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<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
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<td>-</td>
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iii. Correlation and regression between heavy metal concentration and mineral magnetic parameters.

Tables 4.13 and 4.14 give correlation matrices of heavy metals and mineral magnetic parameters for individual lake cores. There is little correlation shown in core M3, except between Ni, $\chi_p$, $\chi_h$, and the S-ratio. The correlation coefficient values are low and do not exceed 0.5, although they are still significant at the 99.9% level. There is also little correlation in core M10. Here, the three derived magnetic parameters, $\chi_r$, S-ratio and HIRM correlate with Cd and Cu; Ni and Cu; and Zn respectively, but only the relationship between Ni and the S-ratio exceeds a coefficient of 0.4 and it is the only value significant at the 99.9% level.

The top 1 cm samples of the lake cores exhibit no significant correlation between heavy metals and magnetic parameters.

Regression was also carried out between heavy metals and magnetic parameters on individual cores. This was to determine whether mineral magnetic characteristics could be used to predict the levels of heavy metals in a sample. Cores M6 and M8 were chosen for this analysis as there was little correlation between these parameters in cores M3 or M10. The data were selected on the basis of a correlation coefficient at the 99.9% significance level and high values, such as Cu with $\chi_p$ in core M6 (0.7133**, Table 4.13). The scattergrams
Table 4.13  Swanswell Pool correlations between heavy metals and mineral magnetic parameters

All cores with heavy metal analysis: no correlation

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<th>Core M3 (50 samples, critical R = 0.275 at 99%)</th>
<th>$\chi_{1t}$</th>
<th>$\chi_{ht}$</th>
<th>$\chi_{r,4}$</th>
<th>SIRM</th>
<th>IRM</th>
<th>HIRM</th>
<th>S-ratio</th>
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<td>Cd</td>
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<td>0.4993**</td>
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<td>Pb</td>
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<th>SIRM</th>
<th>IRM</th>
<th>HIRM</th>
<th>S-ratio</th>
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<td>0.6118**</td>
<td>0.5035**</td>
<td>0.5211**</td>
<td>0.4645**</td>
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<td>0.6656**</td>
<td>0.6946**</td>
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<td>Cu</td>
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<td>0.6007**</td>
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<td>0.4672*</td>
<td>0.5606**</td>
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<table>
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<th>IRM</th>
<th>HIRM</th>
<th>S-ratio</th>
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<td>0.7074**</td>
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<td>0.4672*</td>
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<td>0.4018**</td>
<td>0.5041*</td>
<td>0.5777**</td>
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</table>
Table 4.13 (continued) Swanswell Pool correlations between heavy metals and mineral magnetic parameters

Core M10 (47 samples, critical R = 0.2875)

\[
\begin{array}{cccccc}
\chi_{s'}, \quad \chi_{a'}, \quad \chi_{t'd} & \text{SIRM} & \text{IRM} & \text{HIRM} & \text{S-ratio} \\
\text{Cd} & 0.394* & & & \\
\text{Ni} & & 0.473** \\
\text{Zn} & & 0.3525* \\
\text{Pb} & & \\
\text{Cu} & 0.4224* & & 0.3576* \\
\end{array}
\]

Top 1 cm lake core samples: no correlation

are presented in Figs 4.22 to 4.25 with the associated percentage explained variance and regression equations. In linear regression, the fitted line is described by an equation of the form

\[ Y = a + bX \]

Where Y is the dependent variable and X is the independent variable. Y is therefore to be predicted from X. The gradient
**Fig 4.22 Core M8 regression**

a. Zn with $\chi_{\text{ff}}$

b. Pb with $\chi_{\text{ff}}$

\[
y = 178.22 + 2856.4x \quad R^2 = 0.361
\]

**Fig 4.23 Core M8 regression**

a. Ni with $\chi_{\text{ff}}$

b. Cu with $\chi_{\text{ff}}$

\[
y = 14.195 + 66.946x \quad R^2 = 0.590
\]
Fig 4.24 Core M8 regression, Ni with SIRM

\[ y = 13.399 + 3.157x \quad R^2 = 0.481 \]

Fig 4.25 Core M6 regression

a. Cu with \( \chi_{is} \)
b. Pb with \( \chi_{is} \)
of the regression lines are all positive indicating that as the mineral magnetic parameter increases, so does the heavy metal concentration.

The $R^2$ value quantifies how strong the relationship is between heavy metals and mineral magnetic characteristics. The $R^2$ value represents the coefficient of determination, this represents the proportion of $Y$ explained by the regression equation. The closer the $R^2$ value approaches 100%, the more the variation in $Y$ is explained by the regression equation (Gordon et al., 1992). With $R^2$ values of 33.84% and 38.1% for cores M6 and M8 respectively, the parameters tested which explain the least variance are Zn with $X_1$. The majority of the other combinations explain more than 50% of the variance in the data. However, cores M6 and M8 are alone in exhibiting any such relationship, and the results from core M6 indicate significant correlation between Cu and Pb with $X_1$, only so the relationships demonstrated are not consistent. When consideration of all the cores with heavy metals is made, there is no demonstrable relationship between heavy metals and magnetic parameters in the bulk data set.

The scattergrams indicate two populations of points; those with high values for both the magnetic parameter and heavy metal concentration, and those with low values for both. The low values in each case represent the samples at the base of the core, the higher values are a mixture of the samples from the middle to the top of the core.
v. Relationships between particle size and heavy metal concentration.

As discussed in Chapter 2.8.10, there are many studies which have found an inverse relationship between increasing heavy metal concentration and decreasing particle size (Forstner & Patchineelam, 1980; Forstner & Wittmann, 1981; Horowitz, 1991). Whilst this study did not attempt to partition the heavy metal concentration in the sediment according to particle size, particle size analysis was carried out separately on core M8 for which there was also heavy metals data. The mean particle size (Fig 4.19) varied from about 10 to 35 μm (fine to medium silt). Table 4.14 shows the correlation matrix between the mean, median and span (the sorting index) of lake sediment particle size from core M8 with heavy metal concentration. There is no correlation between the heavy metals and span, but there is a correlation greater than the 99% significance level between the median and mean particle size and all heavy metals. There is particularly significant correlation (at the 99.9% significance level) between Pb and Cu and both the median and mean particle size. Cd and Ni show the lowest levels of correlation. It has been shown (Tables 2.10 and 2.11) that Pb has the highest $K_b$ and that it is most strongly sorbed to particulate matter. Zn transported in rivers in the English Midlands (Proffitt, 1993) however, is preferentially transported in solution, although its' $K_b$, according to Sigg (1983) is more than that of either Cu and Cd. Sigg (1983) suggested that 90% of the Cd and Cu would be preferentially transported in solution.
Table 4.14 Correlation between particle size and heavy metals from core M8 (34 samples, critical R = 0.3494 at 99%)

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Zn</th>
<th>Pb</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>0.4230*</td>
<td>0.5099*</td>
<td>0.74**</td>
<td>0.4902*</td>
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<tr>
<td>Mean</td>
<td>0.4353*</td>
<td>0.5271**</td>
<td>0.7458**</td>
<td>0.51*</td>
<td>0.6996**</td>
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<tr>
<td>Span</td>
<td>no correlation with heavy metals</td>
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<td></td>
<td></td>
<td></td>
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</tbody>
</table>

* denotes significance at 99.9%
** denotes significance at 99%

With increasing solubility, therefore, the correlation between particle size and sediment associated heavy metals appears to get poorer. However, Honeyman & Santschi (1988) state that the $K_b$ for an element is site specific and may reflect many environmental variables (see Table 2.12). The availability, heterogeneity and state (aggregation, dissolution and presence of other substances on the sorption sites) of the particles also affects the rate of removal of metals from solution (Honeyman & Santschi, 1988). Foster et al. (1994) have shown that the proportion of soluble heavy metals was affected by the total concentration in solution such that as the total heavy metal concentration increased, the relative amount sorbed to particulates decreased. Direct causality therefore
cannot be inferred since the relationship between particles and sorbed heavy metals is far from being a simple one.

Whilst the complex interactions between particles and heavy metals are beyond the scope of this study, it would provide a suitable subject for further work.

b. Principal Component Analysis (PCA)

PCA reduces the number of variables to a set of dominant factors which enables the associations to be isolated. The first factor accounts for as much of the variation in the original data set as possible. The second factor then accounts for as much of the remaining variance as possible which is not correlated with the first factor. PCA does this by examining the data set, determining interrelationships and creating a new data set from the original, effectively reducing the number of variables. In such a large set of data as has been collected in this study, PCA is therefore a useful statistical tool (Gordon et al., 1992). At Swanswell Pool, it was applied to the lake sediment cores with heavy metals data and included all the other parameters measured such as bulk density and mineral magnetic properties.

Figs 4.26 a – d plot the eigenvalues and Tables 4.15 to 4.17 present the varimax rotated factor matrices from the lake cores. Table 4.18 a lists the percentage contribution to the total variance of the individual factors in the data set. In all the cores the first two factors contributed over 55% to the total variance. The factor matrix plots utilised factors 1 and 2 only (Figs 4.27 a – d).
### Table of Eigenvalues

<table>
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<th>Factor</th>
<th>Eigenvalue</th>
<th>Pct of Var</th>
<th>Cum Pct</th>
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**Fig 4.26 Eigenvalues**

- a. core M3
- b. core M6
- c. core M8
- d. core M10
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Table 4.15 Varimax rotated factor matrix (n = 19, critical R = 0.5721 at 99%)

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|       | LFX       | .54386    | .80368    | -.03525   | .15453    |
|       | HFX       | .47787    | .84005    | -.02858   | .05931    |
|       | SIRM      | .14209    | .95840    | .12289    | .08689    |
|       | IRM       | .20405    | .95840    | -.06109   | .07220    |
|       | FDX       | .65797    | .32087    | -.05210   | .39331    |
|       | S_RATIO   | -.01659   | .04071    | .71298    | -.61332   |
|       | HIRM      | .12809    | .87485    | .20832    | .13677    |
|       | DBD       | -.95382   | -.11994   | .04713    | -.03701   |
|       | WBD       | -.83159   | -.19691   | .21812    | -.00665   |
|       | DWR       | -.96184   | -.14326   | -.05002   | -.08677   |
|       | CD        | .08128    | -.15036   | -.00258   | -.35578   |
|       | ZN        | .79917    | .12903    | .25836    | -.23499   |
|       | PB        | .75510    | .41860    | .14589    | .04981    |
|       | NI        | .77018    | .12582    | .40902    | -.24692   |
|       | CU        | .89589    | .27536    | .24013    | .05817    |
|       | FE        | .22448    | .65451    | .61170    | .17743    |
|       | MN        | .18948    | .59618    | .65312    | -.02589   |
|       | FE_MN     | .34444    | .54611    | .27788    | .50295    |
|       | P         | .77358    | .36684    | .13864    | .13083    |
### Rotated Factor Matrix:

<table>
<thead>
<tr>
<th></th>
<th>FACTOR 1</th>
<th>FACTOR 2</th>
<th>FACTOR 3</th>
<th>FACTOR 4</th>
<th>FACTOR 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFX</td>
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<td>-0.06102</td>
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<tr>
<td>HFX</td>
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<td>0.16141</td>
<td>0.08074</td>
<td>-0.06924</td>
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<tr>
<td>SIRM</td>
<td>0.09727</td>
<td>0.91492</td>
<td>0.18426</td>
<td>0.32738</td>
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<tr>
<td>IRM</td>
<td>0.16434</td>
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<td>0.26714</td>
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<td>0.05486</td>
</tr>
<tr>
<td>FDX</td>
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<td>-0.17701</td>
<td>-0.04895</td>
<td>0.39254</td>
</tr>
<tr>
<td>S_RATIO</td>
<td>0.24350</td>
<td>0.17937</td>
<td>0.22828</td>
<td>-0.86293</td>
<td>0.22142</td>
</tr>
<tr>
<td>HIRM</td>
<td>-0.06354</td>
<td>0.55888</td>
<td>-0.03830</td>
<td>-0.79629</td>
<td>-0.16538</td>
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<td>DBD</td>
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<td>-0.13752</td>
<td>0.11029</td>
<td>-0.22837</td>
<td>-0.12228</td>
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<td>WBD</td>
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<td>0.02033</td>
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<td>DBR</td>
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<td>-0.00677</td>
<td>0.10517</td>
<td>0.03510</td>
</tr>
<tr>
<td>CD</td>
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<td>0.22104</td>
<td>0.84015</td>
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<td>0.00651</td>
</tr>
<tr>
<td>ZN</td>
<td>0.50833</td>
<td>0.30596</td>
<td>0.73781</td>
<td>0.06724</td>
<td>-0.0663</td>
</tr>
<tr>
<td>PB</td>
<td>0.82812</td>
<td>0.34944</td>
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<td>0.07869</td>
<td>0.00880</td>
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<tr>
<td>NI</td>
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<td>0.50834</td>
<td>0.59070</td>
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<td>CU</td>
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<td>0.47974</td>
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<td>FE</td>
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<td>0.35125</td>
<td>0.30640</td>
<td>0.77569</td>
<td>0.29773</td>
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<tr>
<td>MN</td>
<td>-0.03290</td>
<td>0.29058</td>
<td>0.59276</td>
<td>0.67718</td>
<td>0.17223</td>
</tr>
<tr>
<td>FE_MN</td>
<td>0.30900</td>
<td>-0.08227</td>
<td>0.68734</td>
<td>0.03127</td>
<td>0.16537</td>
</tr>
<tr>
<td>P</td>
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<td>0.05921</td>
<td>-0.15950</td>
<td>-0.05673</td>
<td>0.51138</td>
</tr>
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<td>0.36736</td>
<td>-0.20663</td>
<td>0.18399</td>
</tr>
<tr>
<td>MEAN</td>
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<td>0.11759</td>
<td>0.36879</td>
<td>-0.28399</td>
<td>-0.01941</td>
</tr>
<tr>
<td>SFAN</td>
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<td>0.15988</td>
<td>0.04957</td>
<td>0.00011</td>
<td>0.83876</td>
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</table>

Table 4.16 Varimax rotated factor matrix (n = 22, critical R = 0.4921 at 99%), core M8
Rotated Factor Matrix:

<table>
<thead>
<tr>
<th>Variable</th>
<th>FACTOR 1</th>
<th>FACTOR 2</th>
<th>FACTOR 3</th>
<th>FACTOR 4</th>
<th>FACTOR 5</th>
<th>FACTOR 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFX</td>
<td>0.04762</td>
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<td>0.85695</td>
<td>0.01146</td>
<td>0.16900</td>
<td>0.28214</td>
</tr>
<tr>
<td>HFX</td>
<td>-0.05514</td>
<td>0.35727</td>
<td>0.84000</td>
<td>0.01294</td>
<td>0.16379</td>
<td>0.27556</td>
</tr>
<tr>
<td>SIRM</td>
<td>0.04744</td>
<td>-0.12005</td>
<td>0.68551</td>
<td>-0.08984</td>
<td>-0.01231</td>
<td>0.68386</td>
</tr>
<tr>
<td>IRM</td>
<td>-0.00045</td>
<td>0.10946</td>
<td>0.56585</td>
<td>-0.14335</td>
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<td>0.77448</td>
</tr>
<tr>
<td>FDX</td>
<td>0.11659</td>
<td>0.22109</td>
<td>-0.00881</td>
<td>-0.11597</td>
<td>0.57748</td>
<td>0.38099</td>
</tr>
<tr>
<td>S_RATIO</td>
<td>-0.20040</td>
<td>0.70328</td>
<td>0.04664</td>
<td>0.29118</td>
<td>0.05254</td>
<td>0.52789</td>
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<tr>
<td>HIRM</td>
<td>0.14736</td>
<td>0.65790</td>
<td>0.62394</td>
<td>1.00026</td>
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<td>DBD</td>
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<td>WBD</td>
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<td>0.04540</td>
<td>0.11325</td>
<td>0.14594</td>
<td>0.16673</td>
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<td>-0.28865</td>
<td>-0.00203</td>
</tr>
<tr>
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<td>-0.23286</td>
<td>-0.10329</td>
<td>0.85470</td>
<td>0.04348</td>
<td>-0.00862</td>
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<tr>
<td>CU</td>
<td>-0.35046</td>
<td>0.28439</td>
<td>0.05509</td>
<td>-0.17925</td>
<td>0.81443</td>
<td>-0.00862</td>
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<tr>
<td>FE</td>
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<td>-0.07678</td>
<td>0.75727</td>
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<td>0.11996</td>
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<tr>
<td>MN</td>
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<td>-0.10948</td>
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<tr>
<td>FE_MN</td>
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<td>-0.21784</td>
<td>0.12655</td>
<td>0.87208</td>
<td>0.00763</td>
<td>0.05773</td>
</tr>
<tr>
<td>NA</td>
<td>-0.12865</td>
<td>0.79184</td>
<td>0.13335</td>
<td>-0.19007</td>
<td>-0.03879</td>
<td>-0.06616</td>
</tr>
<tr>
<td>K</td>
<td>0.14378</td>
<td>-0.75349</td>
<td>-0.14006</td>
<td>0.45805</td>
<td>-0.09920</td>
<td>-0.05676</td>
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<tr>
<td>CA</td>
<td>0.28255</td>
<td>0.34249</td>
<td>-0.13931</td>
<td>-0.29138</td>
<td>0.72481</td>
<td>0.17444</td>
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<tr>
<td>MG</td>
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<td>0.68747</td>
<td>0.45929</td>
<td>0.08377</td>
<td>0.19118</td>
<td>0.03317</td>
</tr>
<tr>
<td>P</td>
<td>0.11501</td>
<td>0.00261</td>
<td>-0.73869</td>
<td>0.05490</td>
<td>0.20936</td>
<td>-0.11083</td>
</tr>
</tbody>
</table>

Table 4.17 Varimax rotated factor matrix (n = 23, critical R = 0.535 at 99%), core M10
Table 4.18 a Percentage variance of Principal Components in Swanswell Pool lake cores

<table>
<thead>
<tr>
<th>Core</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3</td>
<td>39.279</td>
<td>31.016</td>
<td>6.437</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td>53.847</td>
<td>16.074</td>
<td>8.052</td>
<td>3.279</td>
<td></td>
</tr>
<tr>
<td>M8</td>
<td>44.705</td>
<td>18.241</td>
<td>9.759</td>
<td>7.1</td>
<td>5.486</td>
</tr>
<tr>
<td>M10</td>
<td>35.381</td>
<td>20.276</td>
<td>16.581</td>
<td>5.633</td>
<td>4.319</td>
</tr>
</tbody>
</table>

Table 4.18 b lists the parameters which dominate the factors. Some of the heavy metals and all the bulk density parameters feature in factor 1 in all the cores except M3, which is dominated by the measured magnetic parameters, HIRM, Fe and Mn.

Apart from core M3 where factor 2 features mainly heavy metals and some bulk density characteristics, mineral magnetic parameters and Fe and Mn feature strongly in the remaining three cores. X-Y plots of the 2 dominant factors (Figs 4.27 a - d) indicate the strength of the relationship between the variables in the 2 dominant factors. Only the variables with the highest level of component loading (those above the critical value indicated on Tables 4.11 to 4.13) are indicated on these plots; unlabelled points represent those variables with the weakest loading.
Fig 4.27 Rotated factor plot
a. core M3
b. core M6
c. core M8
d. core M10
Table 4.18 b Dominant parameters identified by Principal Component Analysis in factors 1 and 2

<table>
<thead>
<tr>
<th>Core</th>
<th>Factor 1</th>
<th>Factor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M3</td>
<td>Magnetics</td>
<td>Heavy metals</td>
</tr>
<tr>
<td></td>
<td>Fe and Mn</td>
<td>P</td>
</tr>
<tr>
<td>M6</td>
<td>Heavy metals</td>
<td>Magnetics</td>
</tr>
<tr>
<td></td>
<td>bulk density</td>
<td>Fe and Mn</td>
</tr>
<tr>
<td>M8</td>
<td>Heavy metals</td>
<td>Magnetics</td>
</tr>
<tr>
<td></td>
<td>bulk density</td>
<td></td>
</tr>
<tr>
<td>M10</td>
<td>Heavy metals</td>
<td>Magnetics</td>
</tr>
<tr>
<td></td>
<td>bulk density</td>
<td></td>
</tr>
</tbody>
</table>

4.4 Mollusca.

The molluscan fauna of Swanswell Pool have been discussed in detail by Foster et al. (1988). The Mollusca diagram (Fig 4.28) indicates that conditions clearly worsened for Mollusca towards the top of the core. There is a progressive decline in suitable habitat which may reflect decreasing water flow through the pool, which allowed the development of a weed obligate, still water community. This occurs above a depth of 26 - 30 cm, at the boundary between the red clay and the black, organic gyttja and may represent the conditions prevalent when Swanswell Pool was isolated from its inflowing stream as outlined in Chapter 3. The substrate was then
Fig 4.28 Mollusc diagram from Swanswell Pool
disturbed to such a degree above a depth of 11 - 16 cm in the sediment column, that virtually all molluscan species disappeared. It was suggested in Foster et al. (1988), that the disturbance may date back to the 1920's and 30's when Swanswell Pool was used for boating. Species diversity and individual numbers of Molluca decline in the upper two samples, where they are dominated by Sparks' (1961) "catholic" group; those that are tolerant of a wide range of substrate and oxygenation conditions. However, Swanswell Pool does support a limited fauna at present as well grown individuals of L. Peregra were found on weed removed from the Pool during coring.

4.5 Water quality analysis

This section is divided into three subsections, the first two detail primary data collected during February and April 1988 when in situ analyses and water chemistry in the laboratory were carried out respectively. The third subsection discusses secondary water quality data obtained from the NRA (Severn Trent Region). These data were obtained to determine prevailing environmental conditions to assess whether there was any likelihood of heavy metals bound to sediment particles being released into the water column and thus becoming a hazard to the ecosystem.
4.5.1. In situ analysis

Summary data for water quality characteristics of the Swanswell Pool are presented in Table 4.19. The measurements were taken from a boat in February, 1988, at three depths in the water column, at the point marked S1 on Fig 2.10 a.

Table 4.19 Water quality characteristics of Swanswell Pool in the field at a single site at three depths in the water column

<table>
<thead>
<tr>
<th>Site</th>
<th>Depth m</th>
<th>pH</th>
<th>O mg l(^{-1})</th>
<th>O % sat</th>
<th>Temp °C</th>
<th>Eh mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0</td>
<td>8.7</td>
<td>13.2</td>
<td>100</td>
<td>3.8</td>
<td>109</td>
</tr>
<tr>
<td>S1</td>
<td>0.5</td>
<td>8.7</td>
<td>13.1</td>
<td>99.2</td>
<td>3.8</td>
<td>115</td>
</tr>
<tr>
<td>S1</td>
<td>0.75</td>
<td>8.6</td>
<td>12.7</td>
<td>96.2</td>
<td>3.8</td>
<td>76</td>
</tr>
</tbody>
</table>

Location of S1 on Fig 2.10 a

Based on a survey undertaken in February, 1988.

The water sample was highly alkaline, with an average pH of 8.7. Dissolved oxygen levels reduced from 100% saturation at the surface down to 96.2% at the mud-water interface. Lowered dissolved oxygen at the mud-water interface probably reflects water trapped in benthic weed giving rise to partially deoxygenated conditions. There was no variation in temperature, which remained at 3.8°C from the surface downwards. Eh, the measure of redox potential, decreases with
depth, reaching +76 mv at the mud-water interface. The Eh of the intermediate sample was slightly higher than the one at the surface.

4.5.2. Chemical analysis of water samples

A second water quality survey was undertaken in April 1988. In this case three samples were taken from sites marked on Fig 2.10 a and analysed in the laboratory. The results are presented in Table 4.20. The most likely source of pollution in the future at Swanswell Pool is the hospital overflow, and although the NRA (Severn Trent Region) stated that leakage was unlikely (J. Batty, pers comm), this was sampled as were the mains water which supplies the Pool and the lake water itself.

The pH of the lake water at Swanswell Pool was 7.4, in marked contrast to the readings obtained during the February 1988 survey, when the pH was found to be 8.7, possibly illustrating the changing environmental regime at this site or the difference between the field and the laboratory-based meters, since the samples were returned to the laboratory for analysis using a bench pH meter rather than the field probe used in the first investigation.

Conductance was highest in the sample taken from the public water supply with that from the main body of the lake intermediary between this and the sample taken from near the hospital overflow. The sample taken from the public mains was highest in Ca, Mg, NO₃, SO₄, HCO₃ and Si and lowest in Na, K, NH₄, NO₂, Cl and PO₄. The sample near the hospital inflow was highest in Na, K, NH₄, NO₂ and PO₄, and lowest in Ca, Mg, SO₄.
Table 4.20 Chemical analysis of water samples from Swanswell Pool.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4</td>
<td>7.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Conductance&lt;sup&gt;b&lt;/sup&gt;</td>
<td>520.0</td>
<td>459.0</td>
<td>744.0</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;c&lt;/sup&gt;</td>
<td>36.3</td>
<td>28.8</td>
<td>54.4</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.9</td>
<td>6.4</td>
<td>16.3</td>
</tr>
<tr>
<td>Na&lt;sup&gt;c&lt;/sup&gt;</td>
<td>25.5</td>
<td>28.2</td>
<td>21.6</td>
</tr>
<tr>
<td>K&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.3</td>
<td>4.0</td>
<td>3.3</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.0</td>
<td>0.08</td>
<td>0.0</td>
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<td>3.1</td>
<td>5.5</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>0.08</td>
<td>0.0</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>36.0</td>
<td>53.0</td>
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</tr>
<tr>
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<td>109.8</td>
<td>214.2</td>
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<tr>
<td>Cl&lt;sup&gt;c&lt;/sup&gt;</td>
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</tr>
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<td>0.01</td>
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<td>0.61</td>
<td>2.3</td>
<td>3.55</td>
</tr>
</tbody>
</table>

<sup>a</sup> Location of sampling points also shown on Figure 2.9 a

S1 Swanswell Pool
S2 Hospital drain overflow
S3 Public water supply

<sup>b</sup> μS cm<sup>-1</sup>
<sup>c</sup> mg l<sup>-1</sup>

Analysis based on one sample from each location taken on 7 April 1988.
and HCO₃. The sample from the lake water was highest in Cl and lowest in NH₄, NO₃, and Si. These analyses suggest that the sample taken from the hospital inflow still contains high levels of NO₃ and NO₂ in comparison with the public water supply and the Swanswell Pool.

4.5.3. NRA (Severn Trent Region) records of water quality.

The data available from the NRA (Severn Trent Region) relevant to Swanswell Pool consists of a single sampling point located at the surface water sewer taking outflow from the nearby hospital. These data are summarised in Table 4.21. The water quality at this point is highly variable with periodically high BOD and ammoniacal nitrogen. There is also a history of periodical spillages to this site (J. Batty, NRA (Severn Trent Region), pers comm).

The BOD measurements are not directly comparable with the oxygen concentration given in Table 4.19, but NH₄-N, Cl, pH and NO₃-N are. Ranges for pH given by the NRA (Severn Trent Region) fluctuate around neutral for the nine samples taken. The maximum value for NH₄-N of 3.7 mg l⁻¹ indicates the magnitude of the spillages occurring from the settling tank, especially in comparison with the value obtained from the samples taken in April 1988 of 0.08 mg l⁻¹. The value given by NRA (Severn Trent Region) for Cl with a mean of 53.0 mg l⁻¹ is slightly higher than those taken in April 1988, but they fall within the range of values given by the NRA (Severn Trent Region). Suspended solids were not measured in the 1988
samples but those given by NRA (Severn Trent Region) vary from 177.0 to 21.0 mg l$^{-1}$ with a mean of 67.9 mg l$^{-1}$.

Table 4.21 Summary water quality statistics from NRA (Severn Trent Region) of a surface water sewer Swanswell recreation ground (1985-1987).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>Suspended solids</th>
<th>BOD+ATU</th>
<th>Ammoniacal Nitrogen</th>
<th>Chloride total oxidised</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg l$^{-1}$</td>
<td>mg l$^{-1}$</td>
<td>mg l$^{-1}$</td>
<td>mg l$^{-1}$</td>
</tr>
<tr>
<td>maximum</td>
<td>7.6</td>
<td>177.0</td>
<td>54.0</td>
<td>3.7</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>minimum</td>
<td>6.8</td>
<td>21.0</td>
<td>8.2</td>
<td>0.02</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mean</td>
<td>7.3</td>
<td>67.9</td>
<td>30.1</td>
<td>0.7</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sample</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>size</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tables 4.22 and 4.23 summarise average water quality data from the NRA (Severn Trent Region) and Bottrill (1994) for rivers in Warwickshire and Prescribed Concentrations or Values (PCVs) for potable water. The water in Swanswell Pool does not exceed any of the PCVs for potable water for the analyses undertaken. In comparison with the study undertaken by
Table 4.22 Average NRA (Severn Trent Region) water quality data from various rivers in Warwickshire and potable water
Prescribed Concentrations or Values (PCVs)

<table>
<thead>
<tr>
<th></th>
<th>Cl $\text{mg l}^{-1}$</th>
<th>TC* $\mu\text{S cm}^{-1}$</th>
<th>DO $\text{mg l}^{-1}$</th>
<th>T $^\circ\text{C}$</th>
<th>pH</th>
<th>Class**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.7</td>
<td>854.7</td>
<td>10.27</td>
<td>11.4</td>
<td>7.92</td>
<td>2</td>
</tr>
<tr>
<td>n=</td>
<td>16</td>
<td>16</td>
<td>25</td>
<td>25</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>266.0</td>
<td>1269.7</td>
<td>10.87</td>
<td>10.3</td>
<td>7.8</td>
<td>2</td>
</tr>
<tr>
<td>n=</td>
<td>26</td>
<td>26</td>
<td>25</td>
<td>25</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>151.7</td>
<td>1053.0</td>
<td>10.3</td>
<td>11.0</td>
<td>7.4</td>
<td>3</td>
</tr>
<tr>
<td>n=</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>45.0</td>
<td>581.7</td>
<td>11.4</td>
<td>9.4</td>
<td>7.8</td>
<td>1B</td>
</tr>
<tr>
<td>n=</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>56.0</td>
<td>882.7</td>
<td>10.4</td>
<td>9.87</td>
<td>7.9</td>
<td>2</td>
</tr>
<tr>
<td>n=</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>400.0</td>
<td>1500.0</td>
<td>5.0</td>
<td>&gt;25.0</td>
<td>5.5-9.5</td>
<td>-</td>
</tr>
</tbody>
</table>

1 = River Avon at Tewkesbury (grid ref SO 893 332)
2 = River Sowe at Baginton (grid ref SP 338 752)
3 = River Sowe at Stoneleigh (grid ref SP 332 728)
4 = Finham Brook at Finham Bridge (grid ref SP 331 740)
5 = River Leam at Leamington (grid ref SP 308 654)
6 = PCV water quality standards

* TC refers to total conductivity

** Class refers to the chemical classification of river water quality where class 4 refers to a river which is grossly polluted and class 1 are rivers of high water quality.

n= number of samples

From Severn Trent Water Authority, 1988/1989 (1 - 5) and 1994 (6).
### Table 4.23 Average water quality data from rivers in Warwickshire (Bottrill, 1994) and Prescribed Concentration or Value (PCV)

<table>
<thead>
<tr>
<th></th>
<th>Arable n=5</th>
<th>Pasture n=10</th>
<th>Forest n=8</th>
<th>Urban n=8</th>
<th>PCV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>43.5</td>
<td>17.62</td>
<td>15.8</td>
<td>29.5</td>
<td>150.0</td>
</tr>
<tr>
<td>K</td>
<td>11.57</td>
<td>5.97</td>
<td>5.56</td>
<td>5.89</td>
<td>12.0</td>
</tr>
<tr>
<td>Ca</td>
<td>51.4</td>
<td>40.5</td>
<td>39.0</td>
<td>35.5</td>
<td>250.0</td>
</tr>
<tr>
<td>Mg</td>
<td>45.4</td>
<td>32.3</td>
<td>24.6</td>
<td>18.8</td>
<td>50.0</td>
</tr>
<tr>
<td>CO₃</td>
<td>32.6</td>
<td>18.96</td>
<td>6.9</td>
<td>5.7</td>
<td>NS</td>
</tr>
<tr>
<td>HCO₃</td>
<td>250.2</td>
<td>240.0</td>
<td>190.6</td>
<td>204.3</td>
<td>NS</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.47</td>
<td>0.18</td>
<td>0.1</td>
<td>0.12</td>
<td>2.2</td>
</tr>
<tr>
<td>NH₄</td>
<td>0.16</td>
<td>2.82</td>
<td>0.25</td>
<td>5.38</td>
<td>0.5</td>
</tr>
<tr>
<td>NO₃</td>
<td>1.1</td>
<td>1.05</td>
<td>1.5</td>
<td>0.46</td>
<td>50.0</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.05</td>
<td>0.147</td>
<td>0.018</td>
<td>0.12</td>
<td>0.1</td>
</tr>
<tr>
<td>Cl</td>
<td>32.4</td>
<td>32.8</td>
<td>24.9</td>
<td>32.0</td>
<td>400.0</td>
</tr>
<tr>
<td>SO₄</td>
<td>25.8</td>
<td>0.03</td>
<td>9.0</td>
<td>12.3</td>
<td>250.0</td>
</tr>
<tr>
<td>Si</td>
<td>0.9</td>
<td>0.56</td>
<td>0.44</td>
<td>0.37</td>
<td>NS</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
<td>7.39</td>
<td>7.5</td>
<td>7.84</td>
<td>5.5-9.5</td>
</tr>
</tbody>
</table>

All concentrations are in mg l⁻¹  
n=number of samples  
NS=No Standard
Bottrill (1994) of some Warwickshire rivers, both Si and SO$_4$, would appear to be high, but the value is still 22% of the maximum PCV for potable water.

There would not appear to be any likelihood of remobilisation of heavy metals bound to sediments as long as environmental conditions remain stable.

4.6 Summary

Swanswell Pool is a shallow, freshwater lake which contains up to 3.0 m of sediment. At an average depth of about 50 cm in the sediment column is a transition from black organic gyttja to a red minerogenic clay. The supposition that the red clay / gyttja boundary represents the isolation of Swanswell Pool from its catchment is further confirmed by palaecological evidence of the trends in Mollusca. The visual stratigraphy is confirmed by mineral magnetic measurements which indicate the greater haematite content in the red clay and the predominance of magnetite, possibly as MD particulate pollutants, in the gyttja. The red clay therefore represents material which accumulated whilst the Springfield Brook flowed into the Pool and comprises catchment-derived sediment. The black organic gyttja has accumulated since the channelization of Springfield Brook and the only possible source for this is the atmosphere with small amounts of runoff from the surrounding park.

The upper sediments show an increase in heavy metals up core. Since Swanswell Pool has had no channelled inflow since 1850, the majority of this is mainly derived from the atmosphere with some contribution from urban runoff. Trends in
heavy metal concentrations indicate increasing anthropogenic release of these elements. Sequential extraction emphasises the importance of Fe and Mn oxides and organic matter in the incorporation of metals into the sediment. Organic matter indicates a highly productive lake, although P concentrations do not suggest eutrophication problems. Sigg (1987) suggested that the main scavengers of heavy metals are probably falling particles, the high nutrient content of the sediments and high values for suspended sediment and P0, in the lake water indicate that there is no shortage of particles available for the sorption of heavy metals and their subsequent incorporation into the sediment.

Mineral magnetic measurements suggest that the upper sediments are dominated by multidomain pollution particles. This assertion is supported by $^{210}$Pb data which has high ratios of supported to unsupported $^{210}$Pb reflecting the dominance of the atmosphere in providing the sediment source.

The statistical analysis of the grid of cores from Swanswell Pool has shown that there is a high level of collinearity between the magnetic parameters and also between the individual heavy metals. The correlation between heavy metals and magnetic parameters is inconsistent, but scattergrams pick out at least two populations of samples representing the top and basal samples in the black gyttja. PCA indicates that heavy metals accounts for much of the variation in the data in the majority of the cores, although again this is inconsistent as magnetic parameters dominate in core M3.
Whilst $^{137}$Cs has enabled a tentative date to be suggested for core M7 at Swanswell Pool, $^{210}$Pb could not confirm this date. The flux of $^{210}$Pb to the surface sediment samples at Swanswell Pool, however, show that the atmosphere dominates the source of $^{210}$Pb. This was confirmed by comparison of activities from rural lakes in Midland England.

The lake water appears to be of good general quality for an urban area and present conditions do not imply any remobilisation of heavy metals into the water column is likely.