Geochemical investigations of sedimented organic matter in a Scottish mountain lake with respect to late Holocene climate change

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Andrew Dominic McGovern

Department of Geography
University College London

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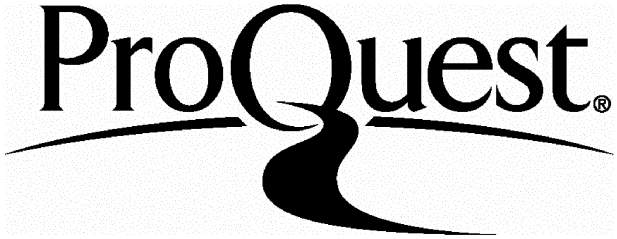

Abstract

Recent research has shown that many mountain lakes are particularly sensitive to environmental change, including climate change. Lochan Uaine, at an elevation of 910 m in the Cairngorms of Scotland, is thought to be one such lake. Previous high resolution analyses undertaken at the lake reveal quasi-cyclic variations in the loss-on-ignition profiles of two cores. It is hypothesised that these cycles are driven by fluctuations in lake primary productivity. In turn, this productivity is thought to be driven by climatic variability, possibly through the influence of winter ice cover duration on growing season.

Fluctuations in LOI comparable to those seen previously are evident in a more recent core from Lochan Uaine (core UACT6) representing the last *c.* 2000 yr of sediment accumulation. This core is dated by correlation of the LOI profile with that of a radiometrically-dated core, although attempts to validate the chronology by identifying microtephra layers were unsuccessful. Analysis of the sediment organic fraction reveals concurrent fluctuations in total organic carbon content, chlorin content, and bulk organic $\delta^{13}C$ with LOI. Although few studies have been undertaken in lake sediments, the chlorin profile is thought to represent variations in lake primary productivity. Similarly, bulk organic $\delta^{13}C$ may reflect variations in the relative inputs of autochthonous and allochthonous material to the sediment. To further investigate these hypotheses, organic geochemical analysis of the unbound lipid fraction is described. Certain lipids identified in the sediment record are assigned to particular organic sources through comparison with published data, analysis of vegetation collected from the lake catchment, and compound-specific $\delta^{13}C$ analysis. Lipid biomarkers attributed to higher plant sources show little downcore variation in concentration, whereas those attributed to algal and bacterial sources show variations similar to the LOI profile. These results support the hypothesis that LOI fluctuations are driven by changes in lake productivity. The productivity changes are discussed in relation to late Holocene climate variability, although an unambiguous correlation between productivity and climate is prevented by the uncertain chronology of UACT6, and our current inadequate understanding of Holocene climate variability in temperate latitudes.

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Note on geochronological protocol

Confusion often arises between chronologies based on calibrated and uncalibrated radiocarbon ages, as the two are not comparable. This thesis will adopt the following protocol. Uncalibrated radiocarbon ages are quoted using the form 1234 ^{14}C yr BP. In some instances '(ref. 1950)' is added after the uncalibrated ^{14}C age for clarity, although this is implicit even where not quoted. Calibrated radiocarbon ages are quoted using either the form 1234 cal yr BP (taking 2000 AD as the reference year), or where appropriate as a date *e.g.* 1234 AD or 1234 BC. Periods of time on the uncalibrated and calibrated radiocarbon timescales are referred to as 123 ^{14}C yr and 123 cal yr respectively.

Chapter 1

Introduction

1.1 Background

1.1.1 Global climate variability

With growing concern over greenhouse gas emissions and associated global warming, the issue of climate change is very much in the public consciousness. Yet climate change is not a recent phenomenon. While there is debate on the impact of anthropogenic activities on climate during the last few hundred years, there is no doubt that the global climate has varied naturally for billions of years, since the formation of the earth itself. During this time a large range of climates have been seen, from 'greenhouse' periods when ice was absent from the poles, to ice ages when the continents were covered by vast ice sheets. This forms the crux of the problem regarding anthropogenically-induced climate change. The twentieth century saw a global temperature rise of around 0.5°C (Briffa and Jones, 1993) - but it is not easy to say how much of this was caused by human activity, and how much was a product of continuing natural climate variability. The difficulty in determining the causes of recent climate change has implications for the prediction of future climate change. It is vital to know whether we can expect temperatures to continue to rise as greenhouse gas emissions continue unabated, or whether the recent warming is merely part of a natural cycle of climate variability, to be followed by a period of cooling in the coming years, decades or centuries.

Predictions of future climate changes rely on the development of computer models to calculate the climatic responses to various forcings (*e.g.* Rind and Overpeck, 1993; Stouffer *et al.*, 1994; Mitchell *et al.*, 1995; Trenberth, 1997; Conway, 1998; Mitchell and Hulme, 1999; Timmermann *et al.*, 1999). Although highly complex, such models are nonetheless comparatively simple representations of the vastly more complex global climate system. Validation of these models is needed to indicate the accuracy of any future climate change predictions. One method for doing this is to run the models using past climatic data (Harrison *et al.*, 1991a; Kohfeld and Harrison, 2000). This allows climate change as calculated by the models to be compared with 'known' climate change. Instrumental records may be used for this purpose. The earliest continuous instrumental records date from as long ago as the late seventeenth century, although near-global coverage is only available for the last century, and data from

Antarctica only from the late 1950s. Prior to the instrumental period climate must be reconstructed from palaeoclimate proxies. For use in models these proxy climate reconstructions should ideally be continuous, accurately datable on a calendrical timescale, and of an annual or better resolution. Proxies that meet these requirements include tree-ring widths and densities, ice cores (isotopes, melt layers), corals, speleothems, and lake varves (Jones *et al.*, 1998). Other climate proxy records exist, as listed in Table 1.1. These generally have lower temporal resolution and are less precisely and accurately datable. With all proxies, there is a tendency for the overall quality of the record to deteriorate with increasing age as records become more scarce, discontinuous, less reliably datable, and so on.

The prediction of future climate change is only one aspect of climate research. An equally important component is the study of the *effects* of climate change. Climate variability affects natural systems on a wide range of spatial scales, from global phenomena such as changing sea levels, to local and regional phenomena, such as vegetational migrations and shifts in vegetational composition. For those climatic proxies listed in Table 1.1 which do not provide data of sufficient length, resolution or accuracy to be used for palaeoclimate model calibration, the real use may be in the records they contain of responses to climate variability.

1.1.2 Evidence for Holocene climate variability

The Holocene is the latest warm period to have occurred during the Quaternary (last *c.* 2 Myr). The Quaternary has been characterised by a succession of glacials and interglacials which have occurred as a response to 'Milankovitch' orbital forcing. On the whole the glacial periods have lasted for longer than the interglacials, and in this respect interglacial periods may be considered to be 'abnormal' for the Quaternary. The last glaciation reached a maximum at around 18,000 ^{14}C yr BP, after which melting of the large northern hemisphere ice sheets occurred. During the Lateglacial Interstadial from *c.* 13,000-11,000 ^{14}C yr BP global climate was relatively mild. A further cold period (the 'Younger Dryas'), most clearly expressed in the Northern Hemisphere, followed from approximately 11,000-10,000 ^{14}C yr BP. The end of this period marks the beginning of the Holocene. By comparison with these large fluctuations between glacial and interglacial conditions, the climate through the

Table 1.1 Comparison of palaeoclimate proxy measurements, the length of record, spatial and temporal resolution, and response time. Example references are given, although the list is by no means definitive. The table is based on those presented by Guiot (1991, Table 1, page 280), Lamb (1995, Table 1, pages 102-107), and Jones *et al.* (1998, Table 1, page 457 and Table 2, page 458).

Proxy source	Variable(s) measured	Climatic information	Length of Holocene record	Temporal resolution	Spatial resolution	Response time	Example references
Instrumental (ground stations, ship-borne, air-borne)	All (air temperature, SST, precipitation, humidity, pressure, wind *etc.*)	All (air temperature, SST, precipitation, humidity, pressure, wind *etc.*)	Earliest temperature records from late 17th Century (Europe)	Greater than seasonal resolution, usually daily	Local, but datasets can be merged to provide up to global resolution	Instantaneous	Manley (1974), Parker *et al.* (1992), Briffa and Jones (1993), Thompson (1995), Jones *et al.* (1998), Mann *et al.* (1998)
Satellite	Temperature, cloud cover *etc.*	Temperature, cloud cover *etc.*	Since 1970s	Very high, daily	Regional to global	Instantaneous	Lean *et al.* (1995), Lean (1996), Waple (1999), Wentz and Schabel (2000), Beer *et al.* (2000)
Historical records (weather registers, diaries, ships logs, chronicles *etc.*), archaeological records	Weather, extreme events (severe winters, droughts, floods, good/bad harvests), ice break-up dates, glacier movements *etc.*	Most climatic parameters, but data tend to be qualitative	Varies, few records date from before 2000 yr BP	Daily to annual, but records tend to be discontinuous	Local to regional	Instantaneous	Gleissberg (1965), Feynman and Fougere (1984), Feng *et al.* (1993), Livingstone (1997), Pfister *et al.* (1998)
Tree-rings	Width, density	Temperature during growing season (width) or late spring and summer season (density)	Some records cover full Holocene	Seasonal, annual; but information can be lost by the need to standardise longer timescales	Local to regional	Few years	Blasing and Duvick (1984), Pilcher *et al.* (1984), Dubois and Ferguson (1985), Baillie and Munro (1988), Stahle *et al.* (1988), Kelly *et al.* (1989), Briffa *et al.* (1990, 1995, 1998), Lara and Villalba (1993), D'Arrigo *et al.* (1993), Feng *et al.* (1993), Baillie (1994), Overpeck *et al.* (1997), Cook *et al.* (1998), Briffa (2000)
	Isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, ^{14}C)	Summer temperature ($\delta^{13}C$), precipitation ($\delta^{18}O$, $\delta^{2}H$), solar variability (^{14}C)	Some records cover full Holocene	Seasonal, annual; but information can be lost by the need to standardise longer timescales	Local to regional	Few years	Stuiver and Braziunas, (1989, 1992, 1993), Lipp and Trimborn (1991), Attolini *et al.* (1991)
Treeline change	Fossil stumps, pollen	Temperature, precipitation	Full Holocene	Discontinuous data (relying on 'threshold' events), resolution relies on the precision and accuracy of the dating method used (tree ring widths, ^{14}C)	Local to regional	Up to 1000 yr, due to slow speed of migration	Dubois and Ferguson (1985), Lowe (1991), MacDonald *et al.* (1993), McConnell and Legg (1995), Haas *et al.* (1998)

Table 1.1 *continued*

Proxy source	Variable(s) measured	Climatic information	Length of Holocene record	Temporal resolution	Spatial resolution	Response time	Example references
Ice cores	Accumulation rate, melt layers	Air temperature, precipitation	Full Holocene	Annual (recent period dated by layer counting), decadal to centennial (older periods dated by flow modelling)	Continental, hemispherical, potentially global	Varies, linked to large scale response of ocean-atmosphere system	Alley *et al.* (1993)
	Isotopes (^{10}Be, ^{14}C, δ^{18}O, δ^{2}H), trapped atmospheric gases and aerosols, dustiness	Moisture source and temperature, precipitation, air temperature (δ^{18}O); climate change linked to solar variability and cosmogenic isotope production	Full Holocene	Annual (recent period dated by layer counting), decadal to centennial (older periods dated by flow modelling)	Continental, hemispherical, potentially global	Varies, linked to large scale response of ocean-atmosphere system	Barnola *et al.* (1987), Beer *et al.* (1988), Bond *et al.* (1993), Taylor *et al.* (1993), Larsen *et al.* (1995), Stuiver *et al.* (1995), Mosley-Thompson(1996), White *et al.* (1996), Morgan and van Ommen (1997), Petit *et al.* (1999)
Glaciers	Advances and retreats (historical records, dated moraines)	Air temperature, precipitation, duration of melt season, sunshine and cloudiness	Some records cover full Holocene	Resolution relies on the precision and accuracy of the dating method used (historical records, ^{14}C)	Regional to continental	10-20 years	Nesje and Dahl (1991), Nesje and Johannessen (1992), Werner (1993), Dahl and Nesje (1994)
Lakes	Varve thickness	Temperature, seasonal temperature differences influencing ice melt, precipitation	Some records cover full Holocene	Seasonal, annual	Local	Days to weeks	Schove (1987), Goslar *et al.* (1995, 2000), Overpeck (1996), Zolitschka (1996), Gajewski *et al.* (1997), Overpeck *et al.* (1997)
	Lake level	Precipitation, evaporation (linked to temperature)	Full Holocene	Resolution relies on the precision and accuracy of the dating method used (historical records, ^{14}C)	Local to regional	15 years (?)	Stine and Stine (1990), Street-Perrott and Perrott (1990), Harrison *et al.* (1991b), Stine (1994), Lent *et al.* (1995), Gasse (2000), Verschuren *et al.* (2000)
	Salinity	Precipitation, evaporation (linked to temperature)	Full Holocene	Resolution relies on the precision and accuracy of the dating method used (^{14}C)	Local to regional	15 years (?)	Fritz *et al.* (1991), Laird *et al.* (1996), Verschuren *et al.* (2000)
	pH	Air temperature	Few hundred years (so far), potentially full Holocene	Resolution relies on the precision and accuracy of the dating method used (^{14}C, varves)	Local to regional	Few years or less	Servant-Vildary and Roux (1990), Psenner and Schmidt (1992), Vyverman and Sabbe (1995), Pienitz *et al.* (1995), Lotter *et al.* (1997b), Sommaruga-Wögrath *et al.* (1997), Koinig *et al.* (1998), Rosén *et al.* (2000)

Table 1.1 *continued*

Proxy source	Variable(s) measured	Climatic information	Length of Holocene record	Temporal resolution	Spatial resolution	Response time	Example references
Lakes (continued)	Isotopes ($\delta^{13}C$ and $\delta^{18}O$ - from carbonate, calcareous and siliceous microfossils, organic matter *etc.*)	Temperature, precipitation (linked to evaporation)	Full Holocene	Resolution relies on the precision and accuracy of the dating method used (^{14}C, varves)	Local to continental	Varies	Stuiver (1970), McKenzie (1985), Siegenthaler and Eicher (1986), Hodell *et al.* (1995), Holmes *et al.* (1995), Curtis *et al.* (1996), Mullins (1998)
	Pollen	Air temperature, precipitation	Full Holocene	Resolution relies on the precision and accuracy of the dating method used (^{14}C, varves)	Local to regional	Up to 5000 years (due to slow vegetation migration after ice retreat)	Huntley and Birks (1983), Huntley and Prentice (1988, 1993), Bennett (1989), Lowe (1991, 1993), Gear and Huntley (1991), MacDonald *et al.* (1993), Huntley (1994, 1999), Mooney (1997), Sawada *et al.* (1999), Rosén *et al.* (2000)
	Other biological proxies (chironomids, chrysophytes, cladocera, diatoms, molluscs, ostracods *etc.*)	Air temperature, seasonal temperatures *etc.*	Full Holocene	Resolution relies on the precision and accuracy of the dating method used (^{14}C, varves)	Local to regional	Varies, generally rapid (few years)	Holmes (1992), Hodell *et al.* (1995), Brooks (1996), Curtis *et al.* (1996), Brooks *et al.* (1997), Lotter *et al.* (1997b), Olander *et al.* (1997), Walker *et al.* (1997), Rosén *et al.* (2000)
Peats	Humification, macrofossils, testate amoebae, $\delta^{18}O$, pollen	Precipitation	Since development of peats *c.* 7000 yr BP	Resolution relies on the precision and accuracy of the dating method used (^{14}C, tephra)	Local to regional	Few years	Aaby (1976), Blackford and Chambers (1991), Blackford (1993), Barber (1994), Barber *et al.* (1994a,b, 1998), Chambers *et al.* (1997), Anderson *et al.* (1998), Mauquoy and Barber (1999a,b), Charman *et al.* (1999), Hong *et al.* (2000)
Speleothems	Growth, isotopes	Precipitation, surface temperature	Some records cover full Holocene	Annual, less if dated by ^{14}C or U-Th	Local to regional	Few years	Baker *et al.* (1993, 1995, 1999), Baker (1999), Lauritzen and Lundberg (1999), McGarry and Baker (2000), Proctor *et al.* (2000)
Corals	Growth, isotopes, trace elements	Sea surface temperature	Few hundred years	Annual, less if dated by ^{14}C	Continental and above	Varies; depends on SST	Beck *et al.* (1992, 1997), Dunbar *et al.* (1994, 1996), Cole (1996), McCulloch *et al.* (1996), Crowley *et al.* (1997), Quinn *et al.* (1998), Gagan *et al.* (2000)
Marine cores	Foraminifera, isotopes ($\delta^{13}C$ and $\delta^{18}O$ of microfossils, carbonate), long chain-length alkenones, pollen *etc.*	Sea surface temperature	Full Holocene	Resolution relies on the precision and accuracy of the dating method used (^{14}C with marine correction)	Continental and above	Weeks to years; depends on SST response to air temperature changes	Pestiaux *et al.* (1987), Bond *et al.* (1993), Sirocko *et al.* (1993), Keigwin (1996), Heusser and Sirocko (1997), Overpeck *et al.* (1997), Perks and Keeling (1998), Hughen *et al.* (1998), Black *et al.* (1999), Sawada *et al.* (1999), Chapman and Shackleton (2000)

Holocene has been relatively stable. However, a growing body of evidence over the last few decades has shown that climatic variations have occurred throughout the Holocene, at a variety of spatial and temporal scales.

Table 1.1 listed some of the proxy records which have been used in the reconstruction of Holocene climate, although the list is by no means exhaustive. A great variety of records may be seen. These proxies respond to different climatic variables such as temperature, precipitation, sunshine and cloudiness. They represent climatic variations at different spatial scales, from local to hemispherical and even global. They differ in the seasonality of their responses, with some proxies responding to summer climate and others to winter climate, and in the temporal resolution of the record provided. They also differ in the time taken to respond to a climatic forcing, and this lag can vary from days to several thousand years. Integration of these proxy sources to create a coherent reconstruction of palaeoclimate is a major challenge in Holocene palaeoclimatology.

Despite the range of climatic proxies available, evidence for large-scale, spatially coherent climatic events during the Holocene is minimal. In Europe, a commonly used climatic model is the Blytt-Sernander scheme (Table 1.2). This suggests that broad climatic variation on millennial timescales occurred during the Holocene. However, this scheme has been criticised by Lowe (1993, page 73): "It appears that the scheme over-generalizes both the spatial and temporal complexity of climatic changes during the Holocene. In addition, the idea of a mid-Holocene thermal maximum does not fit with recent model simulations of Holocene climate based upon the integration of different types of proxy data". The northern hemisphere summer insolation maximum occurred earlier than suggested by the Blytt-Sernander scheme, at *c.* 9000 ^{14}C yr BP (Huntley and Prentice, 1993). The problems with the Blytt-Sernander scheme are thought to be associated with its reliance on vegetation dynamics to infer climate. Not only do many plant communities appear comparatively insensitive to small-scale climatic changes, but the time lags between climatic changes and vegetational responses are potentially large.

Table 1.2 The Blytt-Sernander model of European climate during the Holocene (from Roberts, 1989, page 88).

Period	Inferred climate	Approximate age ^{14}C yr BP
Pre-Boreal	cool/dry	10,000-9,500
Boreal	warm/dry	9,500-7,000
Atlantic	warm/wet	7,000-5000
Sub-Boreal	warm/dry	5,000-2,500
Sub-Atlantic	cool/wet	2,500-present

Evidence for synchronous climatic events over large spatial scales occurring at centennial or shorter timescales is minimal for the Holocene period. A period of low $\delta^{18}O$, accumulation rate, and chloride, calcium and methane concentrations is seen in Greenland ice cores at *c.* 8200 cal yr BP (Chappellaz *et al.*, 1993; Dansgaard *et al.*, 1993; Alley *et al.*, 1997). This is the most prominent event that occurs during the Holocene in Greenland ice core records. Alley *et al.* suggest that this event may be seen in climatic anomalies from palaeoclimate records in North America, the North Atlantic, monsoonal regions of Africa, the Arabian peninsula, northwest India, and Tibet, although they point out that problems of dating and resolution make it difficult to say whether the 8200 cal yr BP event was truly synchronous between these regions. Klitgaard-Kristensen *et al.* (1998) present evidence for a regional cooling in northwest Europe at this time, while Barber *et al.* (1999) propose that the event may have been driven by catastrophic drainage of Laurentide lakes.

During the latter half of the Holocene, studies of regionally synchronous climatic variations have generally focused on two events - the 'Mediaeval Warm Period' and 'Little Ice Age' (Matthes, 1939). These are thought to have occurred at around 1100-1300 and 1500-1850 AD respectively (Bradley and Jones, 1993; Hughes and Diaz, 1994; Lauritzen and Lundberg, 1999; Verschuren *et al.*, 2000). Much of the evidence for these appears to have come from documentary sources. For example, Lamb (1995) cites evidence of the effects of Little Ice Age cooling in Scotland, including reports of permanent snow cover on the Cairngorm summits, an Inuit [sic] landing his kayak near Aberdeen, a decline of the North Atlantic cod fishery, emigration from Scotland and abandonment of settlements due to famines, and a small lake in Strathglass which maintained a permanent ice cover. Similar documentary evidence is

given for warmer temperatures during the Mediaeval Warm Period, both in Britain and across Europe. These documentary sources have generally been interpreted as describing the effects of large scale climatic anomalies which were synchronous across Europe and lasted for several centuries. This interpretation was reinforced by the apparent coincidence between the Little Ice Age and the 'Maunder Minimum' period of low sunspot activity, and between the Mediaeval Warm Period and the 'Grand Maximum' period of high sunspot activity (Eddy, 1976; Waple, 1999), which suggested that these climatic anomalies were driven by solar irradiance variations.

However, recent reassessments of the Mediaeval Warm Period and Little Ice Age events using high resolution climate proxy data question the duration, spatial scale, and regional synchroneity of these events. Tree-ring and ice core data are of particular use for this analysis. Bradley and Jones (1993) state that far from being a 400-500 cal yr long globally-synchronous cold period, the Little Ice Age was actually "...a period of both warm and cold climatic anomalies which varied in importance geographically" (page 374), with the coldest intervals in the Northern Hemisphere occurring from *c.* 1570 to 1730 AD and during the nineteenth century. Likewise, Hughes and Diaz (1994) demonstrate that evidence for a several century long, global Mediaeval Warm Period is unconvincing. Similar views are expressed by Briffa *et al.* (1995), although Briffa *et al.* (1990) state that evidence for a main European phase of the Little Ice Age between 1550 and 1700 or 1800 AD is reasonably compelling.

Despite the lack of evidence for synchronous global scale climatic events during the late Holocene, with the possible exception of the Little Ice Age, there is nonetheless considerable evidence that small magnitude climatic fluctuations have occurred throughout the period. Ice core, tree-ring, speleothem, and coral-based proxy climate reconstructions show considerable variability at annual to decadal timescales (*e.g.* Lipp and Trimborn, 1991; Mosley-Thompson, 1996; Lauritzen and Lundberg, 1999; Gagan *et al.*, 2000). In most cases these are not a response to outside forcings such as insolation changes - there is little evidence that even the well-studied 11 yr solar cycle can be seen in climatic proxy records (R. Thompson, pers. comm.) - nor a response to changes in global 'average' climate, but an expression of forcing from the naturally-

dynamic ocean-atmosphere system at smaller scales. Examples of features of the ocean-atmosphere system which affect regional climates on annual to decadal timescales include the El Niño-Southern Oscillation, and shifts in tropical monsoon belts (Sirocko *et al.*, 1993; Sirocko, 1996; Dunbar *et al.*, 1996; Heusser and Sirocko, 1997; An, 2000). In more maritime areas of northwest Europe, the North Atlantic Oscillation is of particular importance (D'Arrigo *et al.*, 1993; Cook *et al.*, 1998; Rodwell *et al.*, 1999; Perry, 2000; Sarachik and Alverson, 2000; Cullen *et al.*, submitted). Proxy-climate records from ice cores, tree-rings, speleothems, and corals are particularly good at reflecting short term climate variability as they have an annual or sub-annual resolution. However, a major drawback of these proxies is that they provide little indication of environmental responses to climate change.

In terms of future climate change, a warming of a few degrees or a change in precipitation is unlikely to have a *direct* impact on human life. The principal effects will be indirect, through the influence of climate change on the natural environment. Such changes could include sea level rises caused by ice sheet melting, shifting zones of agriculture, increased incidence of flooding in some areas, increased incidence of drought in other areas, and so on. The study of these effects is a vital part of climate research. In the same way that certain proxy records may be used to reconstruct past climate changes, so other proxy records may be used to reconstruct past responses to those changes. The sediment records of lakes are potentially sensitive to climatic influences. They contain an array of indicators, both organic and inorganic, which can provide information on past environmental change. Furthermore, they give the responses of aquatic and terrestrial systems. The study of one such lake forms the focus of this study.

1.1.3 Holocene climate and lake sediments

Not all lake sediments contain climatic information. In mid to high latitudes, the Holocene period has been characterised by comparatively small climatic fluctuations, and only certain lakes are sensitive to these fluctuations. Larger fluctuations are seen in low to mid latitudes where many lakes are sensitive to climate change. Water budgets in low latitude lakes are sensitive both to precipitation, and to temperature

changes through their effect on evaporation. The combined influences of precipitation and temperature changes may show up as changes in salinity (*e.g.* Fritz *et al.*, 1991; Laird *et al.*, 1996; Battarbee, 2000; Verschuren *et al.*, 2000), lake level (*e.g.* Stine and Stine, 1990; Street-Perrott and Perrott, 1990; Harrison *et al.*, 1991b; Lent *et al.*, 1995; Gasse, 2000), or isotope geochemistry of carbonates and fossils of aquatic micro-organisms (*e.g.* Stuiver, 1970; McKenzie, 1985; Holmes, 1992).

Lakes at higher latitudes tend to be less sensitive to changes in water budgets, and other techniques for reconstructing palaeoclimates must be employed. In varved lakes, numerous studies have found a link between varve thickness and climate (Schove, 1987; Goslar *et al.*, 1995, 2000; Overpeck, 1996; Zolitschka, 1996; Gajewski *et al.*, 1997; Overpeck *et al.*, 1997). Biological proxies may also be used to reconstruct climate. These include the remains of aquatic organisms such as chironomid larvae (Brooks, 1996; Brooks *et al.*, 1997; Olander *et al.*, 1997; Walker *et al.*, 1997), cladocera and chrysophytes (Lotter *et al.*, 1997b), or indicators of terrestrial organisms such as pollen (Bennett, 1989; Lowe, 1991; Gear and Huntley, 1991; Bennett *et al.*, 1992; MacDonald *et al.*, 1993; Mooney, 1997; Sawada *et al.*, 1999). There is also growing interest in the use of diatoms, either to reconstruct temperature directly (Servant-Vildary and Roux, 1990; Vyverman and Sabbe, 1995; Lotter *et al.*, 1997b), or to reconstruct lake water pH, which in high mountain lakes is thought to respond to climate (Psenner and Schmidt, 1992; Pienitz *et al.*, 1995; Sommaruga-Wögrath *et al.*, 1997; Koinig *et al.*, 1998). In the latter category, a diatom-pH reconstruction which potentially responds to climate has also been produced for Lochan Uaine (Cairn Toul) in the Cairngorm Mountains of Scotland (Battarbee *et al.*, 1996). A sediment core from Lochan Uaine forms the focus of this study. The diatom-pH reconstruction was one of a suite of analyses undertaken at this lake as part of an earlier study, which together suggested that the lake may be sensitive to climate change (Section 1.1.5).

1.1.4 Lake productivity and the carbon cycle

In many cases, it is not possible to reconstruct past climates directly from measurements of lake sediment properties. Rather, the responses of lake systems to

climatic variations are indirect. It is thus important to understand the processes occurring in lake systems which may lead to the preservation of a proxy climate signal in the sediment record.

Lake sediments consist of organic and inorganic components. The inorganic component is a product of processes such as catchment erosion, mineral precipitation, and biogenic production of mineral matter such as diatom cell walls. The organic component reflects the balance between organic matter production within the lake and catchment, and processes affecting that organic matter after organism death. A variety of different factors are important in determining lake productivity, particularly the availability of nutrients such as phosphorus and nitrogen. However, it is carbon which arguably offers the greatest opportunities for investigating palaeoproductivity in lake systems. Carbon skeletons form the basis for all organic molecules. Much of this thesis is devoted to an investigation of carbon in lake sediments. Hence, a brief summary of the carbon cycle in lake systems may be useful.

Organic carbon present in lake sediments may derive from a variety of different sources via a variety of different routes. The two major potential sources are the atmosphere and catchment rocks. On a global scale, by far the largest carbon reservoir is the crust, containing approximately 5×10^{16} tonnes of carbon compared to 7.4×10^{11} tonnes of carbon in the atmosphere (Killops and Killops, 1993). However, on a catchment scale the input of carbon to the lake from rocks is dependent on catchment geology. This input will be large in catchments containing carbonate rocks, but much smaller in catchments formed of igneous silicate rocks, such as Lochan Uaine. In lakes with silicate rock catchments, the atmosphere may be a more important source of carbon.

Atmospheric carbon may enter the lake sediment through several different routes. It is assimilated by catchment plants during photosynthesis, and may be transported directly into the lake upon the death of the organism. Alternatively, organic material from dead catchment plants may enter the soil, to be transported into the lake by soil erosion. Aquatic photosynthesisers cannot directly assimilate carbon from the

atmosphere, but must use carbon dissolved in the lake water. This carbon may be deposited directly into the lake sediment following organism death. Given the right conditions, it is also possible for direct precipitation of inorganic carbon to occur, thus providing a mechanism by which carbon may enter the sediment column through a non-biological route.

Assimilation of carbon by organisms does not guarantee eventual deposition in a lake sediment. While an organism is still alive, carbon is released as CO_2 during cell respiration, either directly to the atmosphere in the case of catchment organisms, or dissolved in lake water in the case of aquatic organisms. This carbon may be re-assimilated by the same organism, assimilated by a different organism, or lost from the lake/catchment system altogether. It is not only carbon released while the organism is alive which may be re-used. A variety of physical, chemical and biological processes act to redistribute carbon following the death of an organism. Physical processes include the direct transport of particulate organic material, as mentioned above. Chemical processes include the release of carbon during cell autolysis, and the dissolution of organic compounds. Biological processes include the actions of decomposers and detritivores. Microbial action can result in the release of carbon from dead organic material as CO_2 or methane. As with carbon released during respiration, carbon released following organism death may either be re-assimilated by other organisms, or lost from the system. These processes outlined above may occur at any stage, up to and including burial of organic material within the sediment column. Finally, in any ecosystem there will be a complex interaction between primary producers, grazers, and predators, all of which can serve to redistribute carbon.

Given the importance of carbon in lake systems, it follows that the investigation of organic matter in lake sediment records may provide useful information regarding past lake processes, including palaeoproductivity. It may then be possible to link palaeoproductivity variations to climatic changes. The following section summarises the findings of an earlier study at Lochan Uaine (Battarbee *et al.*, 1996), and discusses why the lake was thought suitable for further investigation.

1.1.5 Previous studies at Lochan Uaine - the TIGGER IIa project

The work undertaken at Lochan Uaine prior to this study formed part of the TIGGER IIa project "Proxy records of climatic change in the UK over the last two millennia", funded by the UK Natural Environment Research Council (Special Topic Grant GST/02/701). The analyses and results are described by Battarbee *et al.* (1996), Barber *et al.* (1999) and Battarbee *et al.* (in press), and all of the following discussion is based on the information contained in these publications.

Cores recovered from Lochan Uaine included a 93.6 cm core, designated UACT4, and a 119.6 cm core, designated UACT3 (the site code, UACT, stands for 'Lochan Uaine, Cairn Toul', and is to distinguish this site from two other lakes with the same name in the Cairngorms). The cores were subsampled at fine resolution 2 mm intervals, and radiocarbon dating shows the cores to represent the last *c.* 4000 yr of sediment accumulation. Dry weight and loss-on-ignition (LOI) analysis revealed quasi-cyclic fluctuations, which were sufficiently similar to allow correlation between the two cores. Microscopic inspection of the sediment inorganic fraction showed it to be comprised mostly of siliceous diatom remains, and concentrations of $1.0\text{-}4.0\times10^{8}$ valves $g_{wet\ wt}^{-1}$ were recorded. This high biogenic fraction suggested that the LOI signal may reflect variations in lake productivity, and it was hypothesised that this productivity may be driven by cyclical climate variations.

Detailed analysis of contiguous samples across one of the LOI fluctuations from UACT4 was performed for bulk organic $\delta^{13}C$, diatom and chrysophyte concentrations, and 'Hard'-IRM (Figure 1.1). Chironomid analysis was performed across the corresponding LOI fluctuation from UACT3 (Figure 1.2), and at a lower resolution for the rest of the core. A clear relationship is seen between LOI and $\delta^{13}C$. Higher LOI values are associated with less negative $\delta^{13}C$. It is thought that the relative lightness of the values is indicative of a strong algal contribution, thus high sediment organic content is associated with an increased algal component (Chapters 4 and 6, this study). If this is the case, the lack of consistent variation between LOI and diatom concentration is harder to explain, although Battarbee *et al.* (in press) propose that small changes in sediment accumulation rate could disguise variations in the

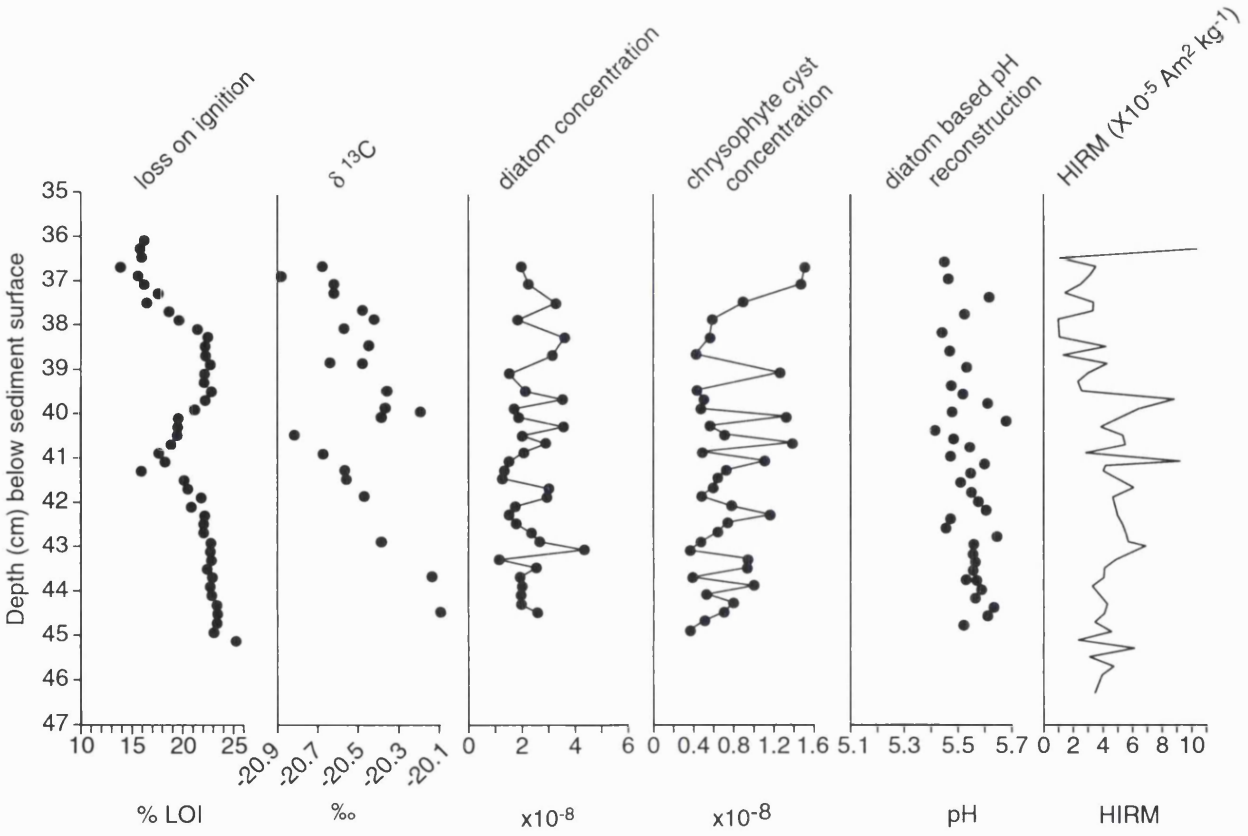


Figure 1.1 Loss-on-ignition, bulk organic $\delta^{13}C$, diatom and chrysophyte concentrations, diatom-based pH reconstruction, and HIRM values, core UACT4 (from Battarbee *et al.*, in press).

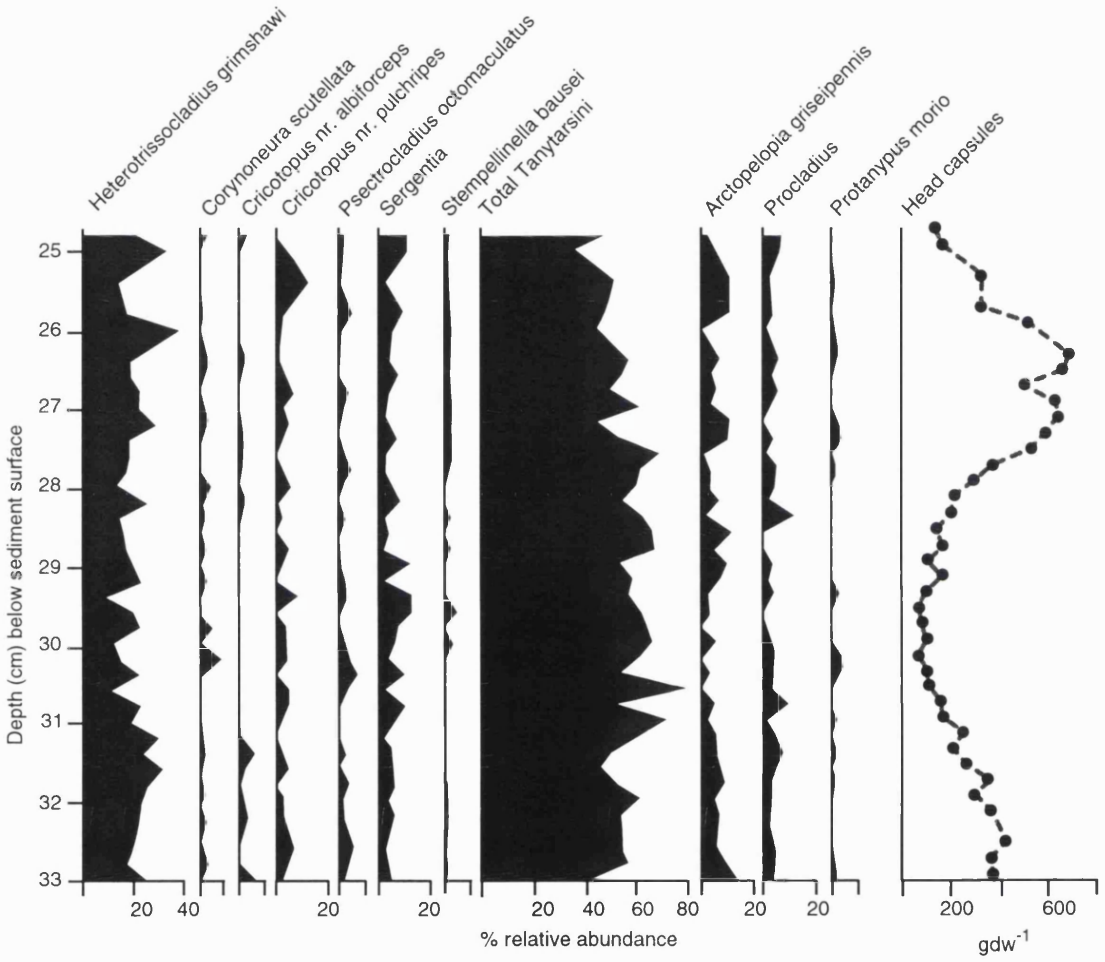


Figure 1.2 Chironomid assemblage and head capsule abundance, core UACT3 (from Battarbee *et al.*, in press).

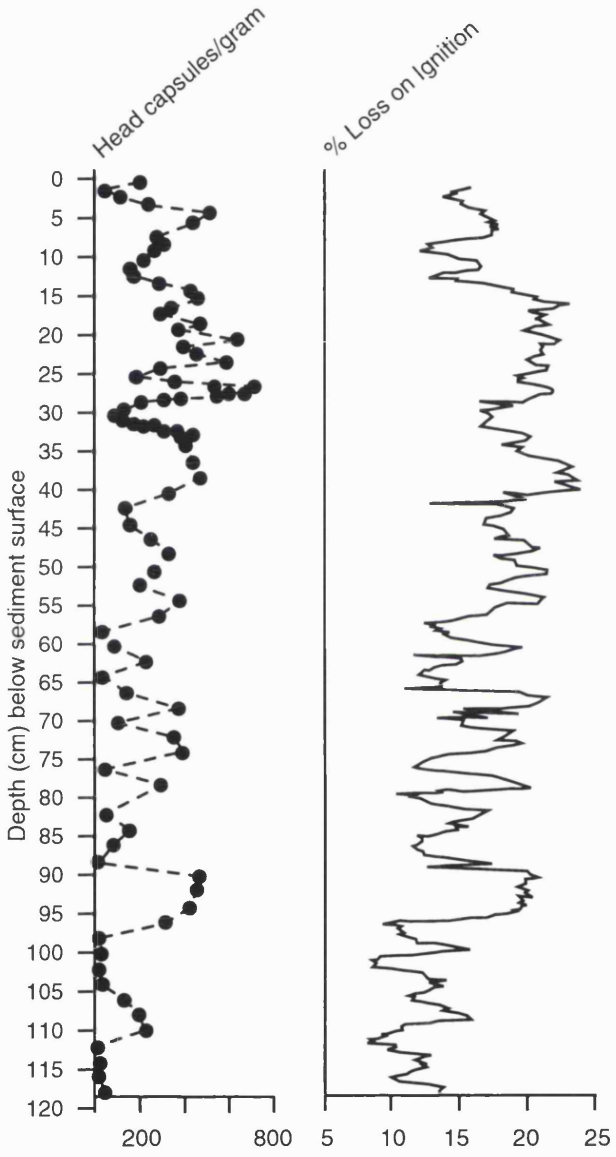


Figure 1.3 Chironomid head capsule abundance and LOI, core UACT3 (from Battarbee *et al.*, in press).

diatom concentration. Other measurements of the sediment inorganic fraction, including magnetic measurements and metal concentrations, also showed no synchronous variations with LOI. Analysis of particle size distribution revealed a correlation between increased mean size and increased LOI, but this was thought to reflect variations in diatom cell size and breakage. These results are discussed in greater detail in Chapter 4.

Chironomid head capsule concentrations show a strong positive correlation with LOI (Figure 1.3). This is interpreted as reflecting an increase in chironomid production in response to an increase in total organic matter production. Declines in Tanypodinae taxa correspond with lower LOI values. Tanypodinae are carnivorous taxa, and their abundance may be expected to reflect the variations in chironomid productivity associated with total organic matter productivity.

The combined evidence of the fluctuations in LOI, bulk organic $\delta^{13}C$, and chironomids, coupled with the evidence that sediment inorganic matter is dominated by diatom biogenic silica, suggests that the LOI fluctuations may be driven by lake primary productivity. In turn, this productivity may be driven by climatic variations. It is possible that the link between climate and productivity at Lochan Uaine is related to the duration of winter ice cover. This is primarily controlled by air temperature. During colder periods the ice cover period may be extended, and the correspondingly shorter duration of the growing season may be responsible for a decline in lake primary productivity. However, it has also been suggested that colder periods are associated with increased lake productivity, due to greater water column mixing and lower retention of nutrients in the catchment (D. Monteith, unpublished). These competing hypotheses are discussed further in Chapter 7.

1.2 Selection of sediment analyses

This thesis aims to explore further the LOI fluctuations evident in the sediment of Lochan Uaine through analysis of the sediment organic matter, and attempts to link the observed variations to potential climatic influences. The decision to focus analyses

on the sediment organic fraction rather than the inorganic fraction was based on several factors. The previous analyses at Lochan Uaine described above suggest that productivity may be important in driving the fluctuations in LOI. They also show that the sediment inorganic fraction may not be particularly responsive to these cycles. The diatom concentration is a potential proxy for lake productivity, yet shows no obvious fluctuations to match those in the LOI profile. This apparent lack of response may be due to changes in sediment accumulation rate varying in phase with the LOI fluctuations (Battarbee *et al.*, in press). There is also the added complication that diatoms contribute both inorganic and organic matter to the sediment, and it is not known whether higher diatom productivity would be reflected by an increase or decrease in LOI (Willemse and Törnqvist, 1999).

The high diatom content of the sediment inorganic matter suggests that other mineral fractions are relatively unimportant as contributors to the sediment. Clastic material from the catchment is identified from visual inspection, and from measurements of magnetic properties and metal concentrations. None of these is observed to vary synchronously with LOI. It is possible that clastic inwash pulses may account for some of the small scale LOI variations in cores from Lochan Uaine (Battarbee *et al.*, in press), but it seems unlikely that they can explain the larger LOI variations.

This evidence suggests that measurements of properties of sediment inorganic matter are of relatively little use in analysing past productivity variations in Lochan Uaine. The organic fraction appears to be of greater use. In particular, the coherent variations in LOI, bulk organic $\delta^{13}C$ and chironomid head capsule concentration provide a strong indication that the LOI cycles are associated with changes in lake primary productivity. For this reason, it was decided to concentrate further analysis of Lochan Uaine sediment on the study of the sedimentary organic fraction. This study focuses on the determination of the sources of input of organic matter to the sediment, with a view to identifying a reliable palaeoproductivity signal.

Various sediment properties are analysed to examine organic matter sources. These properties, and the reasons for choosing to analyse them, are summarised in the following section.

1.2.1 Carbon, hydrogen, nitrogen and carbonate

Carbon and hydrogen are ubiquitous elements in organic matter, and nitrogen is also very common. The total organic carbon content of the sediment is determined by subtracting the carbonate carbon content from the total carbon content. Similarities between the LOI profile and the carbon, hydrogen and nitrogen profiles would show that organic matter is the principal form in which these elements are present in the sediment. However, concentrations of carbon, hydrogen and nitrogen alone do not provide an indicator of organic matter source or total productivity, as these concentrations may be affected by variations in the sediment inorganic content. Numerous authors have used the C/N ratio as an indicator of organic matter source (*e.g.* Håkanson and Jansson, 1983; Meyers and Ishiwatari, 1993; Tyson, 1995; Bianchi *et al.*, 1999). Aquatic micro-organisms such as algae and bacteria generally have high protein contents, and the high nitrogen content of this protein gives aquatic organisms lower C/N ratios than higher plants (Goodell, 1972; Meyers *et al.*, 1984b). The C/N ratio may thus indicate whether the organic matter in a sediment is from an algal/bacterial source, a higher plant source, or a mixture of the two. Variations in the C/N ratio are used to reconstruct the changing importance of inputs from these different sources. The C/H ratio is a less well-established indicator of organic source, particularly in young sediments, but there is a suggestion that it may be used to broadly indicate the origin of organic material (Talbot and Livingstone, 1989).

1.2.2 Bulk organic stable carbon isotope values ($\delta^{13}C$)

Given the strong correlation observed between LOI and bulk organic $\delta^{13}C$ in a section of core UACT4 (Battarbee *et al.*, 1996; Battarbee *et al.*, in press) it is important to try and replicate these results in core UACT6, the subject of this study. C_3 plants as found in the catchment of Lochan Uaine exhibit a well-known range of $\delta^{13}C$ values (*e.g.* Descolas-Gros and Fontugne, 1990; Proctor *et al.*, 1992; Killops and Killops, 1993; Tyson, 1995; Meyers and Lallier-Vergès, 1999). Fractionation in aquatic

macrophytes and micro-organisms is less well-defined, and may exhibit a wider range of values (*e.g.* Nakai, 1972; Schidlowski, 1988; Meyers and Benson, 1988; Michel *et al.*, 1989). Nonetheless, variations in bulk organic $\delta^{13}C$ potentially indicate variations in the importance of inputs from higher plant and algal/bacterial sources.

1.2.3 Chlorins

Few studies of chlorin concentrations in lakes have been made, and their use to date has been restricted principally to marine sediments (Harris *et al.*, 1996). Chlorins are early degradation products of chlorophyll, principally chlorophyll *a* (Harradine *et al.*, 1996a) but also chlorophyll *b* (Talbot *et al.*, 1999b). Several mechanisms have been proposed for chlorin formation in aquatic environments, for example via the grazing of zooplankton on algae (Goericke *et al.*, 1999; Talbot *et al.*, 1999a,b). As such, chlorin concentrations may represent a direct proxy for aquatic productivity. The high resolution stratigraphic analysis of chlorin concentrations in Lochan Uaine represents the first study of this kind, and aims to determine whether chlorins can be used to infer past primary productivity from lake sediments.

1.2.4 Lipids

The sediment properties described above - CHN, carbonate, bulk $\delta^{13}C$, and chlorin content - are all bulk measurements. As such it is often hard to interpret the data. For instance, an increase in bulk $\delta^{13}C$ values could indicate an increased contribution from algal and bacterial organic sources, a decreased contribution from C_3 terrestrial plant sources, or a combination of both. Analysis of sedimentary lipids is undertaken to assess the contributions from these various sources.

Numerous studies show that it is possible to attribute certain lipids to particular source organisms or groups of organisms. Most other organic components such as carbohydrates and proteins cannot be used for this purpose, with the exception of some porphyrins (Hayes, 1993). Among the many thousands of lipid components potentially found in sediments, those which appear to be useful indicators of organic source, and are frequently used as such, include the *n*-alkanes (Ho and Meyers, 1994; Farrimond and Flanagan, 1996; Nott *et al.*, 2000), the *n*-alkanoic acids (Wünsche *et*

al., 1988; Farr *et al.*, 1990; Rieley *et al.*, 1991b; Wilkes *et al.*, 1999), the *n*-alkanols (Cranwell and Volkman, 1981; Kawamura and Ishiwatari, 1985; Robinson *et al.*, 1986; Ficken *et al.*, 1998), and the sterols (Gaskell and Eglinton, 1975; Huang and Meinschein, 1979; Ishiwatari *et al.*, 1980; Meyers *et al.*, 1984b). All of these groups are analysed in the Lochan Uaine sediment, along with various other components of interest.

Although there is a vast literature on the subject of lipid distributions in modern and fossil environments, it was felt important to analyse potential contributors of lipids to the sediment first hand. To this end, specimens of modern vegetation were collected from Lochan Uaine and its catchment. This allows a direct comparison to be made between the lipid signal in the catchment and that in the lake sediment. In particular, the comparison is used to assess degradation of lipids before, during or after deposition. All lipids are susceptible to degradation, but some are more susceptible than others (Giger *et al.*, 1980; Robinson *et al.*, 1984a; Meyers and Benson, 1988; Cranwell, 1981, 1984b). It is important to recognise which sedimentary lipids represent a true signal of changes in vegetation source or productivity, and which represent a signal altered by degradation processes.

1.2.5 Compound-specific $\delta^{13}C$ values

Compound-specific $\delta^{13}C$ values may be measured for the major lipids present in the sediment record. This analysis serves two purposes. Firstly, it can be used to indicate the $\delta^{13}C$ values of different organic sources, in particular the suggestion given previously that C_3 plants from the catchment display lighter $\delta^{13}C$ values than algae and bacteria from the lake. This is important in the interpretation of the bulk organic $\delta^{13}C$ record. Secondly, downcore changes in compound-specific $\delta^{13}C$ values may be compared to the bulk organic $\delta^{13}C$ curve. It is possible that variations in bulk organic $\delta^{13}C$ reflect not only changing contributions from different organic sources, but also a response to other forcings, including climate. Temperature is known to affect $\delta^{13}C$ values in a variety of ways (DeNiro and Epstein, 1977; Schleser, 1995; Mayer and Schwark, 1999; Jahnke *et al.*, 1999). Downcore variations in $\delta^{13}C$ within lipids from a

particular source are unlikely to be caused by the changes in source which influence the bulk $\delta^{13}C$ record, and an alternative explanation must be sought.

1.2.6 Dating

In addition to the analysis of sediment properties, it is essential to date the core if it is to be compared to other records of late Holocene climate variability. Core UACT4 has been dated using ^{210}Pb and thirty-six AMS radiocarbon dates on bulk sediment samples (Battarbee *et al.*, 1996, Battarbee *et al.*, in press). It was decided to use correlation of LOI profiles to transfer the chronology from UACT4 to UACT6. Additionally, an attempt was made to use microtephra layers from Icelandic volcanoes to verify the transferred chronology (Dugmore *et al.*, 1995a; Pilcher *et al.*, 1996; Rose *et al.*, 1996).

1.3 Rationale

Lochan Uaine (Cairn Toul), a high-altitude (910 m) corrie lake in the Cairngorm Mountains, Scotland, was chosen as the focus of this study. Mountain lakes such as Lochan Uaine are potentially sensitive to changes in climate. Additionally, the remote nature of this site suggests that human interference has been minimal prior to industrial-age atmospheric contamination, and any climate signals present should be unobscured by human interference. Previous analysis of cores recovered from Lochan Uaine as part of the TIGGER IIa project (*e.g.* Battarbee *et al.*, 1996) have revealed quasi-cyclic fluctuations in sediment LOI over the last *c.* 4000 ^{14}C yr. Several properties of the sediment organic matter fraction were observed to vary in phase with the LOI fluctuations. Most properties of sediment inorganic matter showed no consistent variations in phase with the LOI fluctuations. These LOI fluctuations are hypothesised to reflect changes in lake primary productivity. Further analysis of the sediment organic matter fraction is required to test the link between LOI and lake productivity. It is also hypothesised that productivity changes in Lochan Uaine may represent a response to climatic forcing. Dating of sediment records from Lochan Uaine allows comparisons to be made with Holocene climate change, as reconstructed from other instrumental and proxy records.

1.4 Study aims

The principal aims of this thesis may be summarised as follows:

1. To establish a chronology for core UACT6 by transferring the $^{210}Pb/^{14}C$ chronology from a previously-dated core through correlation between LOI profiles, and to verify the chronology through analysis of microtephra horizons.

2. To investigate the fluctuations in sediment LOI seen in cores from Lochan Uaine using a variety of methods to analyse the organic fraction of the sediment. These methods include carbon, hydrogen and nitrogen analysis, chlorin analysis, bulk organic $\delta^{13}C$ analysis, lipid analysis, and compound-specific $\delta^{13}C$ analysis.

3. To determine the sources of organic inputs to Lochan Uaine, and how these have changed through time.

4. To establish whether the LOI fluctuations are driven by variations in lake primary productivity.

5. If the LOI cycles are driven by productivity changes, to assess whether these productivity changes are driven by late Holocene climate variability through comparison with instrumental data and other proxy climate reconstructions.

1.5 Structure of thesis

Chapter 2 is divided into two parts. The first part is a site description of Lochan Uaine, covering such aspects as the geology and Quaternary history of the site, the present climate, and descriptions of the lake and its catchment. The second part describes the methodology used to study the sediment. Sediment coring and subsampling, and catchment vegetation sampling are described. This is followed by descriptions of dry weight and LOI analysis, carbon/hydrogen/nitrogen and carbonate analysis, chlorin analysis, bulk organic $\delta^{13}C$ analysis, and lipid analysis. Lipid analysis is further divided into sections on extraction, gas chromatography, gas chromatography-mass spectrometry, and gas chromatography-isotope ratio mass spectrometry. Where relevant, a discussion of the errors associated with a particular method is included. The chapter concludes with a description of tephra extraction and counting procedures.

Bulk sediment lithostratigraphy and the development of a chronology for core UACT6 are described in Chapter 3. This chronology relies on the correlation between LOI profiles of UACT6 and a radiometrically-dated core, UACT4. It is thus necessary to describe lithostratigraphic analyses prior to the section on dating. Dry weight and LOI profiles from cores UACT2,3,4,6,8 and 11 are presented. Core correlations between LOI profiles of UACT4 (the radiometrically-dated core), UACT3 (the back-up core from the TIGGER IIa project) and UACT6 (this study) are described. The remainder of the chapter describes the dating of UACT6, including the attempt to use tephrochronology as an independent means of dating, the construction of a calibrated chronology for UACT4, and finally the transfer of the chronology from UACT4 to UACT6.

Chapter 4 discusses bulk sediment analyses of UACT6. The first section describes carbon, hydrogen, nitrogen and carbonate analyses, and the associated calculation of total organic carbon, C/N ratio and C/H ratio. The relationship between TOC and LOI is also discussed. The second section describes chlorin analysis, and the third section describes bulk organic $\delta^{13}C$ analysis. In all cases the profiles seen in core UACT6 are compared with published data, and discussed in relation to their use in the reconstruction of palaeoproductivity.

Lipid analysis is covered in Chapter 5. The chapter is divided into two main sections and a summary. The first section deals with analysis of modern vegetation reference specimens from the Lochan Uaine catchment. These results are used in the subsequent analysis of lipid distributions in UACT6 as presented in the second section. In both of these sections results are presented separately for total lipid extracts, hydrocarbons, acids, and alcohols and sterols. Throughout the chapter results are discussed in relation to previously published studies.

Chapter 6 describes the compound-specific $\delta^{13}C$ analysis of the main lipid biomarkers identified in Chapter 5. It begins with a review of carbon isotope fractionation in lipids, before presenting the results of the GC-IRMS analyses. These are presented in

the following order: *n*-alkanes, other hydrocarbons, *n*-alkanols, *n*-alkanoic acids. As before, reference is made to previous studies in the literature.

Finally, Chapter 7 presents a summary, discussion and conclusions. Results from the preceding four chapters are summarised. These are discussed in relation to the reconstruction of changing organic matter sources and lake primary productivity. Subsequent sections discuss potential sediment responses to climate change in lake sediments, the dating of the main events seen in the UACT6 sediment record, and the comparison of these dated events with late Holocene climatic changes as determined from instrumental and proxy climate records in Scotland and northwest Europe. Conclusions are presented, and recommendations for future study are made.

Chapter 2

Site Description and Methodology

2.1 Site description

2.1.1 Geology and Quaternary history

Lochan Uaine (57°05'N 3°05'W, Ordnance Survey National Grid Reference NN 960 980) is a small lake lying in a glacial corrie at an elevation of 910 m in the Cairngorm Mountains of northeast Scotland, UK (Plates 1 and 2). The Cairngorm massif is unique in Britain in its extent and elevation. Not only does it contain most of the very highest mountains and all of the highest lakes in Britain, but the large plateau areas at around 1000 m elevation are not seen anywhere else in the country.

The Cairngorms massif has a remarkably uniform geology. It is formed from a granite pluton, and represents the second largest single area of granite in Britain (Harry, 1965). The Main Granite on which Lochan Uaine lies is medium to coarse-grained granitite, the major constituents of which are quartz, orthoclase, oligoclase-feldspar, and biotite. The acidic nature of the rock results in a very low buffering capacity in the lake, and this is reflected in the high sensitivity of Lochan Uaine to pH variations as reconstructed from fossil diatom assemblages (Battarbee *et al.*, 1996; Barber *et al.*, 1999).

During the Quaternary the Cairngorms have probably been glaciated on numerous occasions. Evidence for the earlier glaciations has largely been obscured by scouring during the most recent major glaciation, known as the Devensian in Britain and the Weichselian in Europe, which reached a maximum at around 18,000 ^{14}C yr BP (Lowe and Walker, 1997). During this period the Cairngorms and much of northern Britain were covered by ice. Melting of this ice was complete by around *c.* 13,000 ^{14}C yr BP, except possibly for a small ice sheet on Rannoch Moor. This was followed by a period of comparatively warm climate from *c.* 13,000-11,000 ^{14}C yr BP, usually referred to as the Lateglacial Interstadial (but see Lowe and Walker, 1997, for a discussion of the terminology of the last Glacial/Interglacial transition). The period from *c.* 11,000-10,000 ^{14}C yr BP saw a return to cold climatic conditions known as the Younger Dryas Stadial. In Scotland this resulted in the growth of a large ice cap centered on Rannoch Moor and measuring *c.* 200 km from north to south and *c.* 100 km from east to west (Jones and Keen, 1993; Hubbard, 1999). Of more relevance to this study,

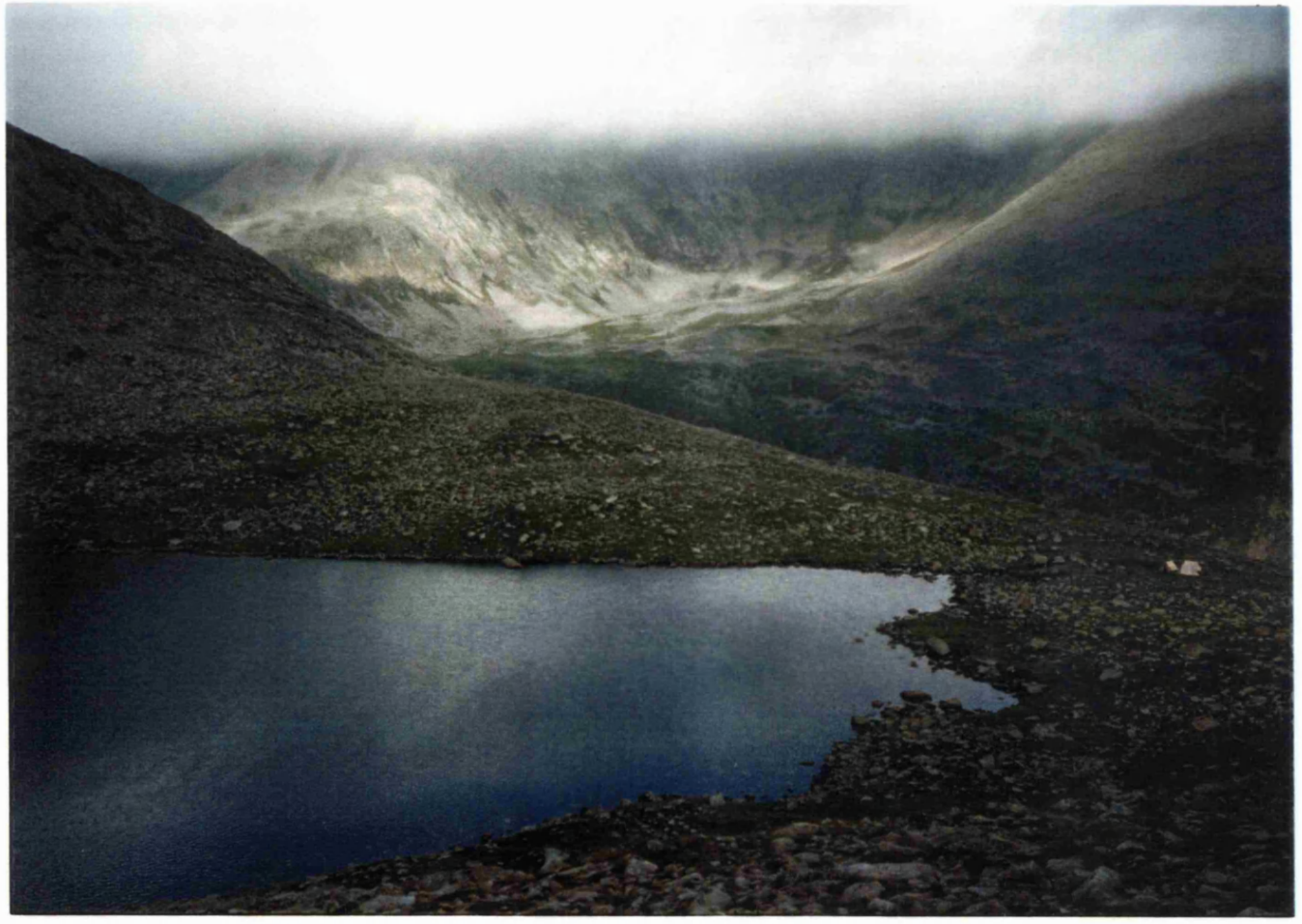


Plate 1 View northwest across the northern end and outflow of Lochan Uaine (Cairn Toul).

Plate 2 View southwest across Lochan Uaine, showing position of coring platform.

glaciers were formed in many of the small corries of the Cairngorm Mountains, including Lochan Uaine (Sissons, 1979; Purves *et al.*, 1999). If a lake was present in the Lochan Uaine corrie during the Lateglacial Interstadial, evidence of this would have been removed by the destructive effects of ice scouring. The maximum possible age of the present-day Lochan Uaine is thus *c.* 10,000 ^{14}C yr. To date no sediments of this age have been found, although the presence of sediments dating from the mid to early Holocene in Lochan Uaine and other Cairngorm lakes is significant. It shows that no glaciers formed in these corries during the supposed 'Little Ice Age' period of the sixteenth to nineteenth centuries, as older sediments would probably have been removed by ice movement (Rapson, 1983, 1985; Battarbee *et al.*, 1996).

2.1.2 Catchment description

The lake area is approximately 50,000 m^2, and the catchment area is ten times larger at *c.* 500,000 m^2 (Figure 2.1). Around three sides of the lake the catchment rises steeply to a high point of 1293 m at the summit of Cairn Toul. A second, smaller corrie is present at the upper southeast corner of the main catchment. The fourth side of the catchment faces northwards, and consists of a low lip of rock over which an outflow stream flows. This stream descends very steeply via a series of waterfalls to the Allt a'Gharbh choire approximately 200 m below, and then flows eastwards into the Lairig Ghru, the main valley through the Cairngorms. At higher elevations the catchment cover is dominated by cliffs, bare rock surfaces and boulder fields, with only minimal vegetation. Many of the rocks have a covering of lichens. At lower elevations and around the lake there is limited vegetation cover. This consists mostly of grass heathland including arctic-alpine species of herbs, ferns and dwarf shrubs. Mosses are abundant, and liverworts are present around the lake margin. Despite the presence of peat-forming species of *Sphagnum* mosses, soils are generally thin and skeletal (Romans *et al.*, 1966) and there are no well-developed peats in the catchment.

At a minimum elevation of 910 m the entire catchment is well above the theoretical tree-line, which has been calculated at 680 m (Pears, 1967, 1968). In reality the present tree-line is at around 490 m, except for a section at Creag Fhiaclach which

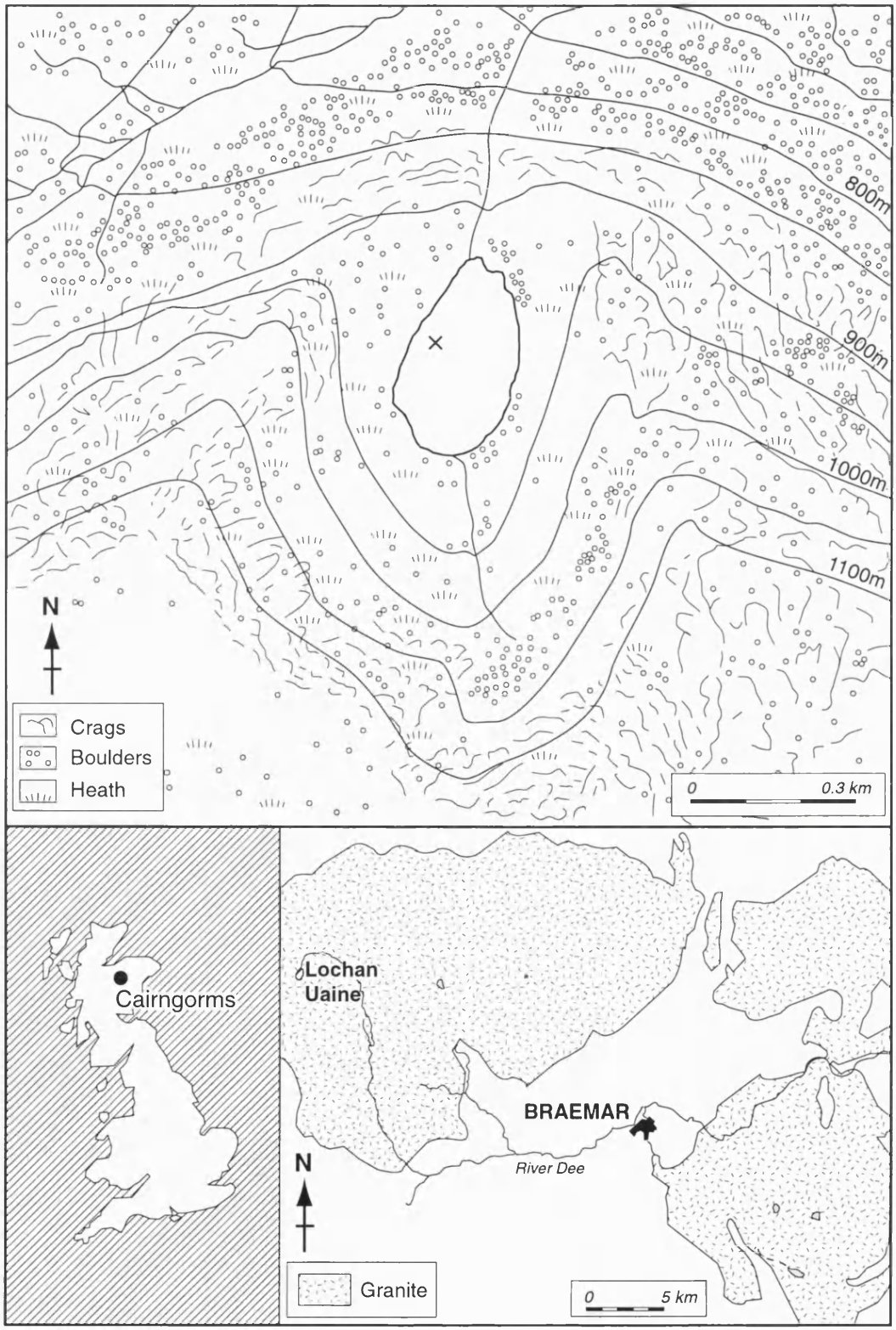


Figure 2.1 Lochan Uaine (Cairn Toul) catchment map (from Battarbee *et al.*, in press).

reaches 640 m (Bennett, 1996). Bennett also notes that although tree-lines were higher during earlier periods of the Holocene, fossil tree stumps have not been found at elevations greater than 790 m. Given the nature and elevation of the catchment it is thought that human influence at Lochan Uaine due to such processes as land clearance or grazing will have been negligible throughout the Holocene, with the exception of the very recent past when the effects of acid deposition have been recorded (Tranter *et al.*, 1988; Landsberger *et al.*, 1989; Jones *et al.*, 1993b; Battarbee *et al.*, 1995, 1996; Barber *et al.*, 1999). This lack of human influence has important implications, as such influences could obscure any responses to late Holocene climate changes contained in the Lochan Uaine sediment record.

The present climate of Lochan Uaine can be inferred from the data provided by the Cairngorm summit automatic weather station (available from the data archive held at http://www.phy.hw.ac.uk/resrev/aws/awsarc.htm). During 1999 a mean temperature of *c.* 3.5°C and a minimum temperature of -9.9°C were recorded. Lochan Uaine is currently frozen for three to four months of the year, although there is evidence that the duration of ice cover has been considerably longer at certain times during the last three centuries (Barber *et al.*, 1999). Precipitation is not recorded at the Cairngorm weather station, but it is known to be lower than mountains along the west coast of Scotland which tend to induce orographic rainfall from moist Atlantic air masses. The high elevation of the Cairngorm plateau gives rise to high wind speeds, and gusts of over 130 mph have been recorded.

2.1.3 Lake description

Lochan Uaine has an area of *c.* 50,000 m^2 and measures roughly 300 m from north to south and 200 m from east to west. Maximum water depth has been measured at 16.5 m, and there is thought to be a maximum sediment depth of no more than 1.5-2.0 m. Sediment accumulation appears to be confined mainly to the deepest part of the basin, and littoral regions are characterised by the presence of large boulders. The lake is ultra-oligotrophic with a secchi depth of at least 15 m. Present day pH has been measured as pH 5.8-5.9 (Battarbee *et al.*, 1996). Macrophytic vegetation consists solely of a sparse covering of aquatic bryophytes at shallower water depths (Light,

1975), while the boulders support an epilithic community dominated by diatoms (Battarbee *et al.*, in press). Analysis of the change in water temperature with depth obtained during August 1997 shows no evidence for a well-developed thermocline, although some stratification is apparent (Figure 2.2). Brief periods of stratification may occur during the warmer months, but these are unlikely to persist for long due to the generally windy environment of the Cairngorms. Longer periods of stratification may occur during winter when the lake is ice-covered.

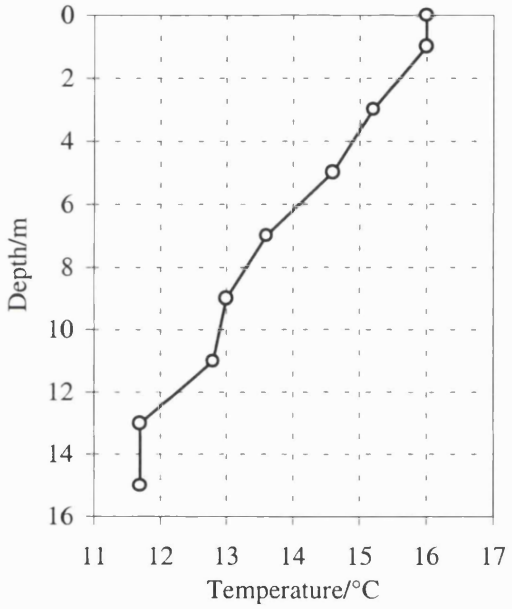


Figure 2.2 Temperature-depth profile for Lochan Uaine, taken at 18:00 on 14-8-97.

2.2 Methodology

2.2.1 Coring

The coring of Lochan Uaine for this study took place during mid August 1997. All of the cores recovered were taken from a raft securely anchored above the deepest point of the lake basin. It was assumed that the sediment accumulation rate was greatest at this point, although without a more detailed survey of lake sediment distribution this cannot be known for certain. Cores which included the mud-water interface were recovered with an 8 cm diameter piston corer, and were transported back to the

laboratory in a vertical position. Cores which did not include the mud-water interface were recovered with a 4 cm diameter modified Livingstone corer (Livingstone, 1955). These were extruded horizontally on site, but were transported back to the laboratory for subsampling. Various problems were encountered with the coring, mainly as a consequence of the water depth (>16 m) which was sufficient to allow flexing of the metal Livingstone rods, despite the use of plastic support casing. It is possible that some cores were recovered at an angle. The main core analysed for this study, UACT6, was not thought to have been affected by this problem as the mud-water interface was horizontal and not visibly disturbed. Also, subsequent analyses of the core have revealed large changes in bulk parameters occurring over a depth of less than one subsampling interval (2 mm). Such changes would likely be smeared or obscured if the core had been taken at an angle. Lotter *et al.* (1997a) demonstrate the high quality of cores recovered using piston coring methods. Individual cores recovered from Lochan Uaine are discussed in more detail in Chapter 3.

Piston cores were subsampled at 2 mm intervals during vertical extrusion using a purpose-built rig. Livingstone cores were subsampled horizontally at 2 mm intervals by slicing with a scalpel. During extrusion and subsampling notes were made of the sediment type and of any changes in appearance, as well as of the presence of identifiable objects such as mineral particles and plant remains. Mineral particles up to 10 mm in length were found in the sediment. These particles were removed where seen to avoid biasing the dry weight and LOI determinations. Following extrusion and subsampling, all sediment samples were placed in cold storage in the dark at 2°C, after which they were freeze-dried and stored in glass vials. For chlorin, bulk organic $\delta^{13}C$, CHN, carbonate and lipid analyses samples were additionally crushed and passed through a 500 μm sieve. At all stages glass and metal objects were solvent washed prior to contact with the sediment to reduce the risk of contamination by organic components. This procedure could not be followed for plastic objects such as core tube and sample bags. In these cases contamination is inevitable, but the contaminating components, principally phthalates, are easily identified during lipid analysis.

2.2.2 Catchment vegetation sampling

Specimens of modern vegetation were taken from the Lochan Uaine catchment to provide reference material for the organic geochemical analysis of core UACT6 (Chapter 5). Approximately 30 different species were collected to represent both the most abundant species in the catchment, and the variety of different vegetation types. An emphasis was also placed on collecting specimens from around the lake rather than higher up in the catchment. This is where the majority of the catchment biomass is found, and is also the most likely source of any catchment-derived material found in the lake sediment. All specimens were stored at 2°C prior to freeze-drying and crushing for lipid analysis.

Eventually only eight of the modern reference specimens were analysed, including a lichen, a moss, a liverwort, a grass, a fern, a dwarf shrub and the aquatic bryophyte present in littoral areas of the lake. An algal scrape was taken from submerged rocks around the lake edge to allow analysis of the epilithic flora, principally consisting of diatoms. During analysis there was found to be insufficient material to produce a detectable signal. As an alternative an algal scrape was taken from a lowland lake in southern England. Although the composition of the species will undoubtedly be very different to that from Lochan Uaine, this was thought unlikely to affect the organic geochemical signal which tends to be sensitive to different plant groups (*e.g.* higher plants *vs* algae) but relatively insensitive to species compositional changes within those groups. In the end, this scrape was thought to contain not just epilithic organisms but detrital higher plant material. A similar problem may affect the ongoing analysis of an algal scrape from Lochnagar in the eastern Cairngorms (J. Scott, pers. comm.). It may be that the best way of avoiding contamination of scrapes of epilithic organisms in future studies is to analyse laboratory cultures.

2.2.3 Dry weight and loss-on-ignition

Analysis of sediment dry weight and loss-on-ignition (LOI) followed the method described by Bengtsson and Enell (1986). For dry weight, *c.* 1 g wet sediment was added to a crucible of known weight (C), and the whole crucible was reweighed (C_W). This was left in an oven at 105°C for 24 hrs to remove the water. After 24 hrs the

crucible was removed, allowed to cool in a dessicator, and reweighed (C_D). Dry weight was then calculated as $\{(C_D\text{-}C) /(C_W\text{-}C)\}x100$, expressed as a percentage of wet weight.

Loss-on-ignition was determined by heating the crucible containing the dry sediment (C_D) in a furnace at 550°C for 2 hrs to oxidise the organic matter, which is released as CO_2. After 2 hrs the crucible was removed, allowed to cool in a dessicator, and reweighed (C_L). LOI was calculated as $\{(C_L\text{-}C) /(C_D\text{-}C)\}x100$, and was expressed as a percentage of dry weight. Dry weight and LOI were determined at contiguous 2 mm intervals for three of the cores recovered in 1997 (UACT6, UACT8, UACT11), the same resolution used for the earlier core studies from Lochan Uaine (Battarbee *et al.*, 1996). Additionally, core UACT2 was analysed. This core was recovered in 1993 as part of the TIGGER IIa project and stored in the dark at 2°C during the intervening period.

2.2.4 CHN, carbonate

Analyses of carbon, hydrogen, nitrogen and carbonate content were performed by the Microanalytical Section, School of Chemistry, University of Bristol, by combustion of a small amount of dry sediment. All values were expressed as a percentage of dry sediment. Total organic carbon (TOC) content was calculated by subtracting the concentration of carbonate from the concentration of total carbon. In reality, given the very low carbonate concentrations (<0.2% sediment dry weight) TOC content is almost identical to total carbon content. CHN and carbonate contents were determined at contiguous 2 mm intervals for core UACT6 only.

2.2.5 Chlorins

Sedimentary chlorin content was determined for contiguous 2 mm intervals throughout UACT6. Samples were analysed in batches of twenty-eight, which consisted of twenty-six core samples and two standard samples. Analysis of standard samples was necessary to correct for any possible instrumental variations occurring between the batches of analyses. The standard consisted of thoroughly homogenised 'representative' sediment sample, formed by taking sediment from *c.* 10 layers from

throughout the core. For each sample, 0.1980 to 0.2020 g of freeze-dried and crushed sediment was weighed into a culture tube and 2 ml of 9:1 acetone/water was added. Samples were sonicated for 15 minutes in ice-cold water, centrifuged at 3000 rpm for 6 minutes, and the supernatant containing the chlorins in solution was transferred to another culture tube. The extraction process was repeated with 2 ml 9:1 acetone/water, and again with 2 ml pure acetone. The culture tubes containing the 6 ml of solvents and extracted chlorins were placed in a water bath at 27°C and blown down under a gentle stream of nitrogen until dry (approximately 90 minutes). Care was taken to keep the samples in the dark as much as possible during the extraction process as chlorins are light-sensitive. Exactly 1 ml of HPLC-grade methanol was added to each culture tube. These were sonicated in ice-cold water for a further 15 minutes and centrifuged at 3000 rpm for two minutes. The reduced duration of centrifugation was necessary to prevent evaporation of solvents which could alter the chlorin concentration in solution, thus artificially increasing the fluorescence value. The supernatant was poured into a third set of culture tubes in preparation for fluorescence analysis. This final step removes any remaining particulate matter.

Samples were analysed on a Waters 470 Scanning Fluorescence Detector connected to a Waters 501 HPLC pump. The fluorescence detector was set to scan at a wavelength of 662 nm, as fluorescence at this wavelength reliably indicates the presence of chlorins. Methanol (HPLC-grade) was used as the carrier solvent. This had been degassed by bubbling helium through the solvent to remove dissolved nitrogen. Twenty microlitres of sample were introduced to the detector by an on-column injection system. The detector was allowed to return to baseline conditions before the next injection took place. Blank injections of methanol were made between samples to clean the injection port. Data were recorded, and peak areas calculated, using X-Chrom analysis software.

To allow determination of chlorin concentrations, a sample of the standard mixture was extracted as detailed above, except at the final stage where the chlorin extract was dissolved in 3 ml rather than 1 ml methanol. This increased volume was necessary to allow analysis on a UV Spectrophotometer. The concentration of chlorins in the

standard mixture was quantified using a Unicam-UN1 Spectrophotometer. The height of the absorption peak at 662 nm was compared to that previously obtained from running a sample of pure pyrophaeophorbide chlorin (Harris and Maxwell, 1995). The chlorin concentration in the standard could thus be quantified.

The inclusion of two standards in each batch of samples run was not only used to correct for instrumental drift between the batches, but is used to indicate the errors involved in the determinations. Analysis of the eighteen sample standards run in total shows that for a mean detector response of 300 units, the standard deviation is 14.7 units. This represents a standard deviation of 4.9%. If we assume the measurements are normally distributed, which seems reasonable, it follows that 95.4% of all values will lie within two standard deviations of the mean, or *c.* ±10%. The downcore variations in chlorin content are much larger than 10%, so it is possible to say that these variations are significant at above the 95% level.

2.2.6 Bulk organic $\delta^{13}C$

Between 1-2 μg of freeze-dried, crushed sediment were enclosed in a tin foil capsule for analysis. The samples were run on a Finnigan MAT Delta-S isotope ratio mass spectrometer configured for elemental analysis. All sample runs were duplicated, and further analyses were performed if discrepancies were seen between the two values obtained. Samples were run non-sequentially, and a C_{19} hydrocarbon standard was run between every 10-15 sediment samples to check that measurement errors were within acceptable limits. Bulk $\delta^{13}C$ was not determined for contiguous 2 mm samples throughout the whole of core UACT6 but for about half of the *c.* 240 samples. In some core sections $\delta^{13}C$ was determined in contiguous samples, whereas in other sections the resolution was lower. Around half of the values determined for the top 15 cm of core were excluded from analysis due to instrumental error. As a consequence the sampling resolution from 0-15 cm depth was lower than for the rest of the core. Average $\delta^{13}C$ values from core UACT6 are listed in Appendix A.

Isotopic fractionation is calculated relative to PeeDee belemnite (PDB) as shown in Equation 2.1, where R is the ratio $^{13}C/^{12}C$.

$$\delta^{13}C = \frac{R(\text{sample}) - R(\text{standard})}{R(\text{standard})} \times 1000 \quad [2.1]$$

In all but eight cases the $\delta^{13}C$ values obtained from duplicated measurements of a sample are within 1‰ of each other. Similarly, analysis of $\delta^{13}C$ values of the C_{19} hydrocarbon standards run with the sediment samples produces a standard deviation of 0.23‰ (N=32). Assuming a normal distribution of values, 95.4% of $\delta^{13}C$ determinations should be within two standard deviations of the measured value, or ±0.46‰. This suggests that the downcore variations of nearly 4‰ observed in the UACT6 bulk organic matter are genuine features, as they are significant at above the 95% level.

2.2.7 Lipid analysis

Eight modern vegetation reference specimens from the Lochan Uaine catchment were selected for lipid analysis. These were selected to represent the major plant groups in the catchment rather than the most abundant species. Lipid composition is more likely to vary between different groups than between different species of the same group, and the intention was to use lipid analysis to determine the broad inputs of organic matter to the lake sediment. The reference specimens chosen included a lichen, a moss, a liverwort, a grass, a fern, a dwarf shrub, and an aquatic bryophyte. An algal scrape from submerged rocks in Lochan Uaine did not provide sufficient material for analysis, and a scrape from a lowland lake in southern England was used as a substitute.

Due to the length of time required for lipid extraction, sample preparation and analysis it was not possible to analyse lipid contents contiguously through core UACT6. Twenty-eight samples were chosen from UACT6. While these were approximately evenly spaced throughout the core, a conscious effort was made to choose samples from maxima and minima in profiles of LOI and bulk organic $\delta^{13}C$. This was to allow the lipid record to be used to investigate the variations in bulk parameters, and to see whether similar variations are observed in lipid concentrations. Of the twenty-eight samples used for lipid analysis, sixteen samples were selected for compound-specific

isotope analysis. This analysis was performed on the hydrocarbon, acid, and alcohol/sterol fractions only. The sixteen samples analysed were from the same depths for each fraction, and additionally two further hydrocarbon samples were analysed. As for the lipid analysis, samples for compound-specific isotope analysis were chosen to coincide with maxima and minima in bulk parameters, while also being roughly evenly spread downcore.

2.2.7.1 Extraction

All samples were freeze-dried, crushed and passed through a 500 μm sieve. Due to the high resolution 2 mm sampling interval it was necessary to combine core samples across three contiguous levels to provide a sufficient quantity of extract for lipid analysis. This was achieved by taking 0.5 g dry sediment from each sample to give a total sample mass of 1.5 g, representing a sediment depth of 6 mm. An attempt was made to combine only contiguous samples having similar organic content, so that the contribution of organic matter from each 2 mm sample to the combined sample would be similar (Appendix B). Smaller amounts of modern plant material were used due to their higher lipid content.

Samples were placed in a 12 ml glass centrifuge tube and 100 μl internal standard was added to each. This contained five components relating to different lipid classes, each with a concentration of 200 μg ml^{-1} (Table 2.1).

Table 2.1 Internal standard mixture used in lipid analysis

Component	Lipid class
5α-cholestane	Hydrocarbon
Hexadecyl octadecanolate	Ketones and wax esters
2-hexadecanol	Alcohols and sterols
5β-pregnan-3α-ol	Alcohols and sterols
Heptadecanoic acid	Acids

The recovery of these standards was assessed by comparing the peak areas of the two standards added to the alcohol and sterol fraction, 2-hexadecanol and 5β-pregnan-3α-ol. A very close correlation was observed, with an R^2-value of 0.969 (Figure 2.3). This shows that the recovery of standards added to samples is highly reproducible,

and it can thus be assumed that GC peak areas of components found in the sediment have equally high reproducibility.

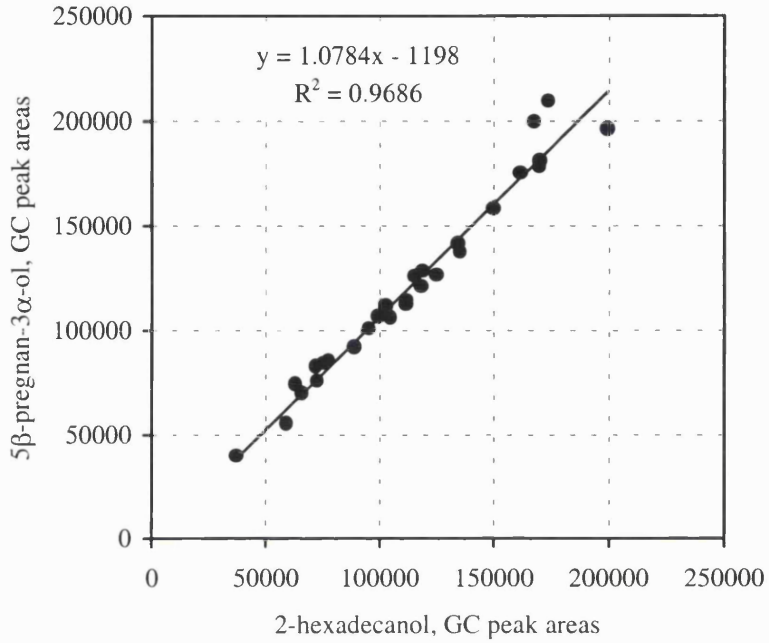


Figure 2.3 Comparison of standards added to the alcohol/sterol fraction of twenty-eight samples from core UACT6. The slope of the regression line (y = 1.0784x) indicates that the standard mixture appeared to contain roughly 8% more 5β-pregnan-3α-ol than 2-hexadecanol. Arbitrary scale.

Lipids were extracted by sequential sonication and centrifugation (10 min sonication followed by 10 min centrifugation at 3000 rpm). Three extractions were carried out with 100% methanol (MeOH), three with 1:1 v/v MeOH/dichloromethane (DCM), and five with 100% DCM, in that order. Seven millilitres of solvent were used at each stage. After each centrifugation the supernatant was decanted into a round-bottomed flask, and the solvents were removed by evaporation under vacuum. A short silica column was made by adding 1 cm^3 silica gel (stored at 130°C) to a glass pipette plugged with solvent-extracted cotton wool. DCM/isopropanol (2:1 v/v) was used to rinse the column, remove the lipids from the round-bottomed flask, and elute them through the column. This stage removes sugars and any particulate matter. Anything that eluted through the column was collected in a pre-weighed glass vial and blown

down under a gentle stream of nitrogen. Samples were immediately removed from nitrogen blow-down when dry to prevent the loss of more volatile components. The vial was reweighed to allow the mass of total lipid extract (TLE) to be calculated.

The TLE was separated into neutral and acid fractions by solid phase extraction using an aminopropyl Bond Elut column (Figure 2.4). The column was prewashed with 2:1 v/v DCM/isopropanol, and the TLE was dissolved in a small quantity of the same solvent and added to the column. Care was taken not to allow the activated aminopropyl surface of the column to dry out. The neutral fraction was eluted from the column into a round-bottomed flask with 12 ml 2:1 v/v DCM/isopropanol, and the acid fraction was similarly eluted with 12 ml 2% acetic acid in diethylether.

The neutral fraction was further separated into hydrocarbon, aromatic, ketone and wax ester, alcohol and sterol, and polar fractions by 'flash' column chromatography. Silica gel (0.6 g) was added to the 'flash' column and the column eluted with hexane. Again without allowing the silica to dry, the neutral lipid extract was added and the fractions were eluted from the column by addition of solvents in the order and quantities given in Table 2.2. The first 1 cm^3 of hexane was used to dissolve the neutral lipid extract.

Table 2.2 Sequential fractionation of neutral lipid extract by 'flash' column chromatography

Fraction	Solvent added	Quantity / cm^3
Hydrocarbons	Hexane	3.0
Aromatics	9:1 v/v Hexane/DCM	1.5
Ketones and wax esters	DCM	5.5
Alcohols and sterols	1:1 v/v DCM/MeOH	3.0
Polar fraction	MeOH	2.5

The five fractions were blown down with nitrogen to remove the solvents. Hydrocarbons required no further preparation prior to GC analysis. The other four fractions, and the acid fraction, needed to be derivatised. For those lipids extracted from sediment samples, each fraction was dissolved in 300 µl DCM. Twenty microlitres of this were placed in a vial and blown down with nitrogen, and 30 µl of the derivatising agent BSTFA [*N,O*-bis(trimethylsilyl)trifluoroacetamide] were

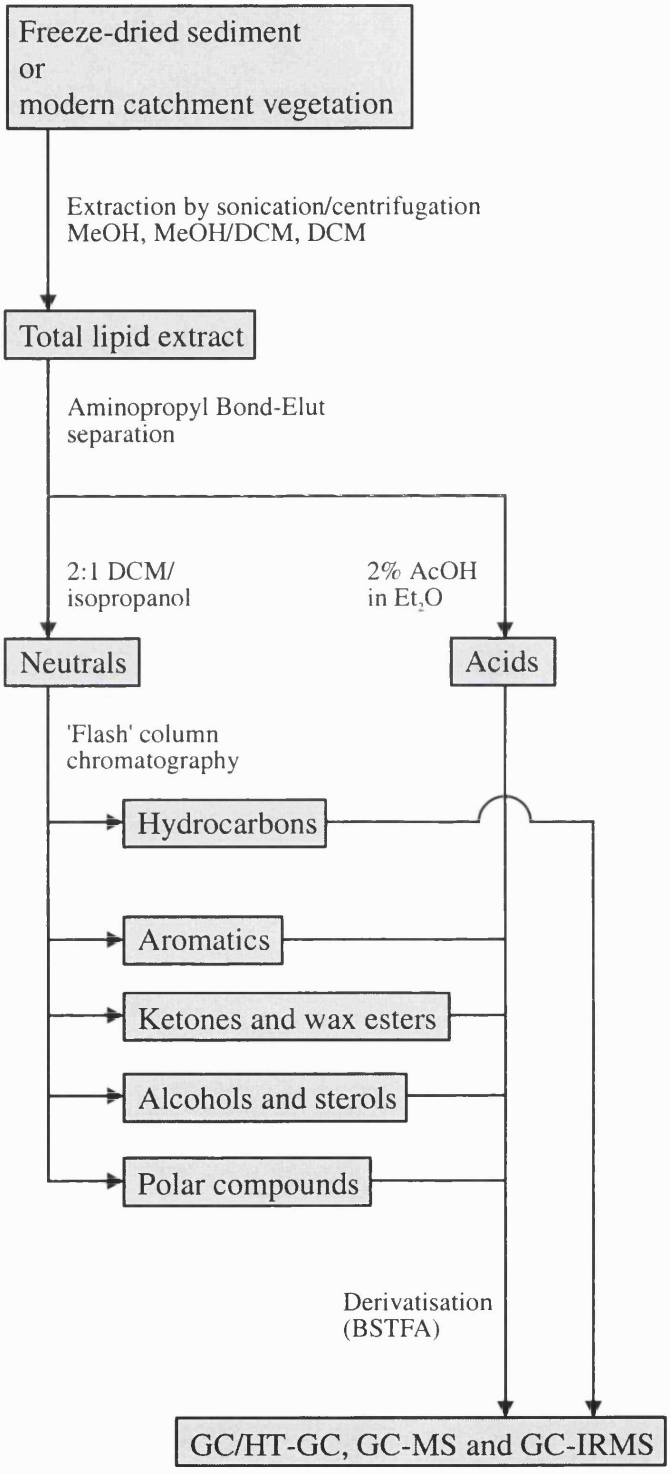


Figure 2.4 Lipid analysis protocol.

added. Different concentrations were used for lipids extracted from modern plant material. All vials were sealed with Teflon tape, placed on a heating block at 70°C for 90 minutes, and after cooling the BSTFA was removed on the nitrogen blow-down.

2.2.7.2 Gas Chromatography (GC), Gas Chromatography-Mass Spectrometry (GC-MS), and Gas Chromatography-Isotope Ratio Mass Spectrometry (GC-IRMS)

Hexane (20 µl) was added to each derivatised fraction (50-70 µl for hydrocarbons) and 1 µl was taken for GC, GC-MS or GC-IRMS analysis (Appendix C). GC analysis of hydrocarbon, acid, aromatic, and alcohol/sterol fractions used a HP 5890 gas chromatograph with a dimethyl polysiloxane coated phase capillary column (CPSil 5CB; Chrompack; 50 m column length, 0.32 mm internal diameter, 0.12 µm film thickness). A high temperature (HT) column was used for the ketone/wax ester and polar fractions. Helium was used as a carrier gas for the elution of the hydrocarbons, and hydrogen was used for all other fractions. For standard GC runs the oven temperature was programmed to remain at 40°C for 1 min, increase from 40-200°C at a rate of 10°C/min, increase from 200-300°C at 3°C/min, and remain at 300°C for 20 min. HT-GC runs were held at 50°C for 2 min, increased to 350°C at 10°C/min, and held at 350°C for 10 min. The total run lengths were 70.33 and 42.00 min respectively.

GC-MS analysis was performed using a Carlo Erba Mega GC (70 eV EI, on-column injection) linked through a direct interface to a Finnigan 4500 MS. The columns and temperature programmes used were the same as for the GC analyses, and helium was used as the carrier gas. Lipids were identified at first by mass spectral analysis, and thereafter by comparison of GC retention times under constant operating conditions (column type, column length, temperature programme, column head pressure, carrier gas, *etc.*).

GC-IRMS analysis of hydrocarbon, acid, and alcohol/sterol fractions used a Varian 3400 GC coupled to a Finnigan MAT Delta-S isotope ratio mass spectrometer (Matthews and Hayes, 1978). All samples were run in duplicate, and the mean value

calculated. This mean value was used in all subsequent analyses. Acid and alcohol/sterol fractions were derivatised with BSTFA prior to GC-IRMS. This process adds a three-carbon containing TMS group to each protic site in a molecule, and it is necessary to correct $\delta^{13}C$ values to allow for this addition of exogenous carbon (Rieley, 1994). Derivatised and underivatised samples of a standard were run several times to calculate the $\delta^{13}C$ of the TMS group (Equation 2.2). Both hexadecanol and cholesterol were used as standards, although the example given shows only the results for cholesterol. It was necessary to repeat the analysis whenever a new batch of BSTFA was used for derivatisation.

$$N_{STD}.\ \delta^{13}C_U + 3.\delta^{13}C_{TMS} = (N_{STD} + 3).\ \delta^{13}C_D \qquad [2.2]$$

N_{STD}	Carbon number of standard (16 for hexadecanol, 27 for cholesterol)
$\delta^{13}C_U$	$\delta^{13}C$ of underivatised standard
$\delta^{13}C_D$	$\delta^{13}C$ of derivatised standard
$\delta^{13}C_{TMS}$	$\delta^{13}C$ of TMS group carbon

Example

For cholesterol:	N_S	= 27
	$\delta^{13}C_U$	= -22.73‰
	$\delta^{13}C_D$	= -23.30‰
Therefore:	$\delta^{13}C_{TMS}$	= -28.43‰

Once the $\delta^{13}C$ of the TMS group is known, it is possible to correct $\delta^{13}C$ values of samples accordingly (Equation 2.3). A standard of known $\delta^{13}C$ was run regularly to check the accuracy of the analyses.

$$\delta^{13}C_{SD}.(N_S + 3) = \delta^{13}C_{SU}.N_S + 3.\delta^{13}C_{TMS}$$

$$\Rightarrow \quad \delta^{13}C_{SU} = \{\delta^{13}C_{SD}.(N_S + 3) - 3.\delta^{13}C_{TMS}\}/\ N_S \qquad [2.3]$$

N_S	Carbon number of sample component
$\delta^{13}C_{SD}$	$\delta^{13}C$ of derivatised sample component
$\delta^{13}C_{SU}$	$\delta^{13}C$ of sample component corrected for TMS group

There are several indications as to the accuracy of compound-specific $\delta^{13}C$ determinations. Firstly, the C_{19} standards run at regular intervals during the GC-IRMS analyses were found to have a standard deviation of 0.44‰ (N=10), and assuming a normal distribution the 95.4% confidence interval is plus or minus two standard deviations, or ±0.88‰. This figure is slightly misleading as it represents 'ideal' conditions - the C_{19} hydrocarbon was the only component eluting during these standard runs and the isotope ratio can thus be accurately determined according to the method described by Freeman *et al.* (1990). A better indication of accuracy is provided by analysis of the internal standards added to the lipid extracts. In the case of 5α-cholestane which was added to the hydrocarbon sample, a standard deviation of 0.52‰ (N=32) is calculated. This indicates a 95.4% confidence level of ±1.04‰. However, it should be noted that the hydrocarbon fraction is particularly 'clean' in that there are few components present other than the homologous *n*-alkane series. The acid and alcohol/sterol fractions contain numerous components other than the corresponding *n*-alkyl series, increasing the chance of co-elution of components. As Freeman *et al.* (1990) point out, this is a serious problem in compound-specific isotope analysis as there is no reliable procedure for deconvoluting the contributions of co-eluting components. It is likely that the 95% significance limit for these fractions is considerably greater than ±1‰. Furthermore, some of the important components analysed, in particular the C_{17} *n*-alkane, are present in low concentrations by comparison to the most abundant components. These low concentrations increase the errors associated with GC peak integration and $\delta^{13}C$ determination.

2.2.8 Dating

No radiometric dating was carried out directly on UACT6. A chronology based on ^{210}Pb and ^{14}C dates was transferred from UACT4 to UACT6 by comparison of LOI profiles. The construction of a chronology for UACT6 is described fully in Chapter 3.

2.2.9 Tephra extraction and shard counts

Extraction of tephra shards for counting followed the technique of Rose *et al.* (1996) given in Figure 2.5. Wet sediment (1.0-1.5 g) was placed in a 12 ml glass centrifuge tube of known weight. The sediment was dried at 40°C and the centrifuge tube was

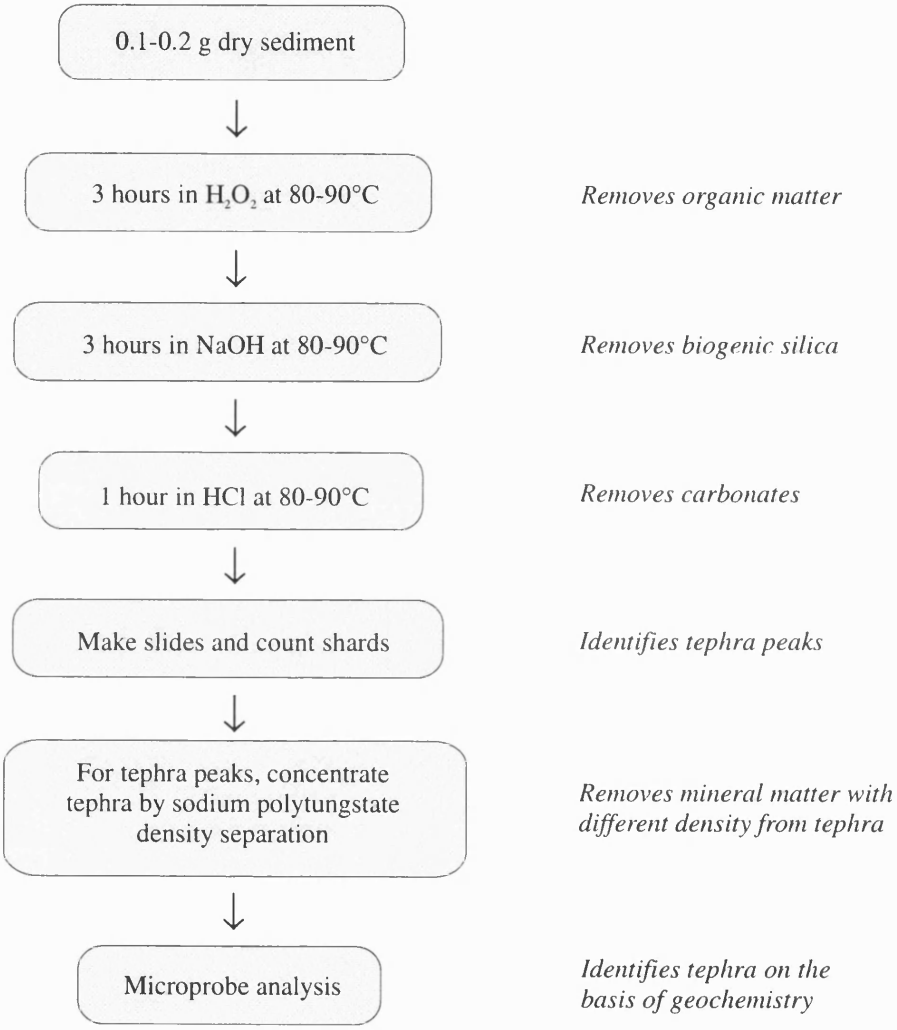


Figure 2.5 Tephra analysis protocol.

re-weighed, allowing the weight of dry sediment to be calculated (typically in the range 0.1-0.2 g). A small amount (1-2 ml) of 30% hydrogen peroxide was added to each centrifuge tube, and the samples left overnight. This was then topped up with 5 ml 30% H_2O_2 and left in a water bath at 90°C for three hours to remove organic matter. Samples were removed from the water bath and allowed to cool. The centrifuge tubes were topped up with distilled water and centrifuged at 1500 rpm for 5 minutes, and the supernatant was decanted off. Five millilitres of 0.6M NaOH were added to each tube, and these were placed in a water bath at 90°C for three hours. Rose *et al.* (1996) found that this period was long enough to remove most of the less robust forms of silica, such as the biogenic silica from which diatom cell walls are made and which form a major component of the sediment at Lochan Uaine. More robust forms of silica, such as the mineral silica which accounts for 50-80% by weight of tephra shards, did not show any appreciable dissolution after three hours. Following this stage, samples were removed from the water bath and allowed to cool. Centrifuge tubes were topped up with distilled water, centrifuged at 1500 rpm for 5 minutes, and the supernatant was removed. Five millilitres of 3M HCl were added to each sample, and were left in a water bath at 90°C for 1 hour to remove any soluble minerals, specifically carbonates (although these were not found to be a major constituent of the sediment at Lochan Uaine). Samples were washed a minimum of four times by topping up with distilled water, centrifuging at 1500 rpm for 5 minutes, and removing the supernatant, and the residue was transferred to a pre-weighed glass vial. These were re-weighed, and the weight of tephra suspension in each vial was calculated.

Each tephra shard suspension was thoroughly mixed to homogenise the suspension. A known weight of the suspension, typically 10-20 mg, was removed and placed in a plastic centrifuge tube. Approximately 1 ml distilled water was added and the suspension transferred onto a 19 mm glass coverslip by pipette. These were covered to reduce the risk of contamination, and allowed to dry. Coverslips were mounted onto slides using Naphrax mountant.

A Leitz petrological microscope at x400 magnification was used for counting. Tephra shards were identified on the basis of colour, morphology, and isotropy under plane-polarized light. The entire area of each coverslip was scanned for tephra shards. Tephra shard concentrations per gram dry sediment could then be calculated according to Equation 2.4.

$$T_{conc} = [(S_{total}/S_{cover})N]/D \quad [2.4]$$

T_{conc} Tephra shard concentration (number of shards per gram dry sediment)
S_{total} Total mass of tephra suspension (grams)
S_{cover} Mass of tephra suspension applied to coverslip (grams)
N Number of tephra shards counted on whole coverslip
D Mass of dry sediment used in preparation of tephra suspension

During counting it became apparent that although some particles could be confidently identified as tephra particles, many more particles could not be identified unambiguously as such. For this reason, tephra shards were noted as being either 'definite' or 'possible'. Other properties of the shards were noted, including colour, morphology (platey, vesicular, stringy) and length. Estimates were also made of the relative concentrations of tephra and other mineral particles of comparable size. It was found that the concentration of tephra never exceeded 1% of mineral particles, and in most instances was below 0.1%. This is in sharp contrast to the high concentrations of tephra seen by Bennett *et al.* (1992) in a lake sediment in Shetland.

It was originally intended to identify tephra layers on the basis of shard geochemistry, determined by electron probe microanalysis (Figure 2.5). However, this technique was not used due to the nature of the tephra profiles. The results of tephra analysis are discussed in Chapter 3.

Chapter 3

Lithostratigraphy and Chronology

3.1 Introduction

This chapter describes the development of a chronology for core UACT6, the main core analysed in this study. As the chronology is based on the correlation of LOI profiles between UACT6 and a dated core, UACT4, it is first necessary to present the high resolution lithostratigraphic analyses of these and other cores from Lochan Uaine. A section on lithostratigraphy is followed by a discussion of the establishment of an LOI-based correlation between the cores. Dating of the cores is described, including sections on the raw radiocarbon dates obtained for UACT4, and tephra analysis of UACT4 and UACT6. The final section discusses the construction of a core chronology for UACT6, including calibration of the UACT4 radiocarbon dates and the transfer of this chronology to UACT6. All work on cores UACT1 to UACT5 was carried out as part of a previous study (Battarbee *et al.*, 1996; Barber *et al.*, 1999; Battarbee *et al.*, in press), with the exception of the UACT4 radiocarbon calibration. Cores UACT6 to UACT12 were recovered and analysed as part of this study.

3.2 Lithostratigraphy

3.2.1 Cores from Lochan Uaine

Three coring trips have been made to Lochan Uaine. The first two, which took place in summer 1993, formed part of the UK Natural Environment Research Council TIGGER IIa project, "Proxy records of climate change in the UK over the last two millennia" (Battarbee *et al.*, 1996; Barber *et al.*, 1999; Oliver *et al.*, 1999; Battarbee *et al.*, in press). Five cores were recovered at this time, labelled UACT1-5. Core UACT1 was recovered on a preliminary trip to the site to determine the best coring position, and UACT2-5 were recovered on the subsequent visit. Table 3.1 lists details of these cores and the analyses performed on each.

The most recent coring trip to Lochan Uaine took place in August 1997 as part of this study. A further seven cores were recovered, labelled UACT6-12. Details of these cores are given in Table 3.2. The cores were taken along a west-east transect across

the lake, and from a maximum water depth of 16.5 m (Figure 3.1). Variations in the piston cores were seen during extrusion, as listed in Appendix D.

Table 3.1 Cores recovered from Lochan Uaine for the TIGGER IIa project, summer 1993. Further details of these cores may be found in Battarbee *et al.* (1996) and Barber *et al.* (1999). All cores were taken from *c.* 16 m water depth and included the mud-water interface.

Core	Corer	Length cm	Sampling interval	Analyses	Notes
UACT1	Glew				Core recovered on preliminary vsit to site
UACT2	Piston	100	2 mm	Dry weight, LOI	Core possibly taken at an angle
UACT3	Piston	119.4	2 mm	Dry weight, LOI, wet density, pollen, chironomids (whole core, high resolution from 25-33 cm), metals and base cations	Back-up core for UACT4
UACT4	Piston	93.6	2 mm	Dry weight, LOI, wet density, Troels-Smith, ^{210}Pb-dating (0-5 cm), ^{14}C-dating (36 samples), diatoms and pH reconstruction (0-45 cm), chrysophyte cyst concentrations (36-45 cm), bulk organic δ^{13}C (36-45 cm), lipids (4 samples, 36-45 cm), tephra, biogenic silica (5 samples, top 20 cm), granulometry (top 40 cm organics not removed, 60-76 cm organics removed), magnetics	Master core for TIGGER IIa project
UACT5	Glew	30	5 mm (0-8 cm), 10 mm (8-30) cm	Dry weight, LOI, wet density, carbonaceous particles	

Table 3.2 Cores recovered from Lochan Uaine, August 1997.

Core	Corer	Length cm	Sampling interval	Analyses	Notes
UACT6	Piston	46.2	2 mm	Dry weight, LOI, carbon-hydrogen-nitrogen, carbonate, bulk organic δ^{13}C, chlorins, lipids, compound-specific δ^{13}C, tephra	Mud-water interface intact
UACT7	Livingstone	80-90	Not sampled	-	Core disturbed - casing broke during coring, position in stratigraphic sequence not well constrained
UACT8	Piston	109.6	2 mm	Dry weight, LOI	Mud-water interface not present
UACT9	Livingstone	40	Not sampled	-	Position in stratigraphic sequence not well constrained
UACT10	Piston	62.2	2 mm	-	Mud-water interface possibly present, but disturbed by piston bung
UACT11	Livingstone	100	2 mm	Dry weight, LOI, pollen (4 basal samples - analyst: S. Peglar)	Core top *c.*50 cm below mud-water interface
UACT12	Piston	31.8	2 mm	-	Highly disturbed

Dry weight and LOI analyses were performed as routine on cores chosen for analysis. Profiles for cores UACT2,3,4,6,8 and 11 are given in Figures 3.2 to 3.6. Where appropriate, wet density (UACT3,4) and carbonate (UACT6) measurements are included. Marked downcore variations in dry weight and LOI are seen to varying degrees in all cores. It is these variations which determined the selection of cores for further analysis, and upon which inter-core correlations and the construction of core chronologies are based.

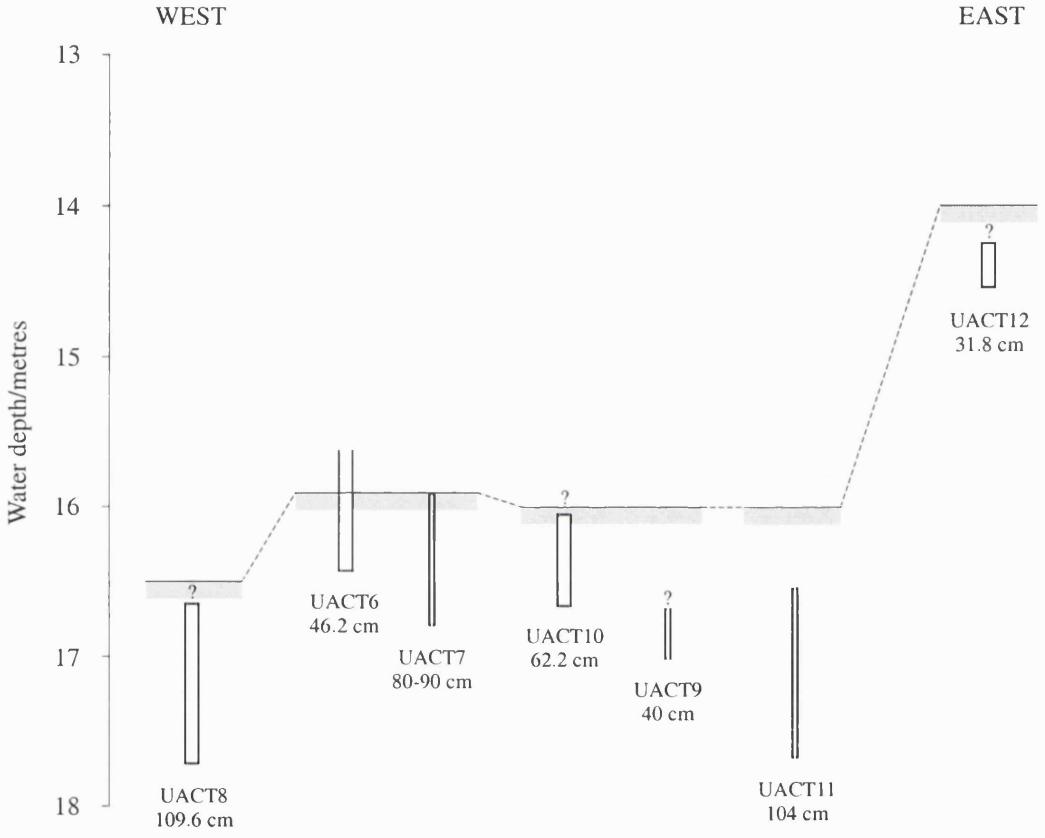


Figure 3.1 Diagrammatic representation of cores taken along a west to east transect in Lochan Uaine, August 1997. The symbol *?* represents uncertainty in the position of the core top relative to the mud-water interface. Wide cores were taken with an 8 cm diameter piston corer; thin cores were taken with a 4 cm diameter Livingstone corer.

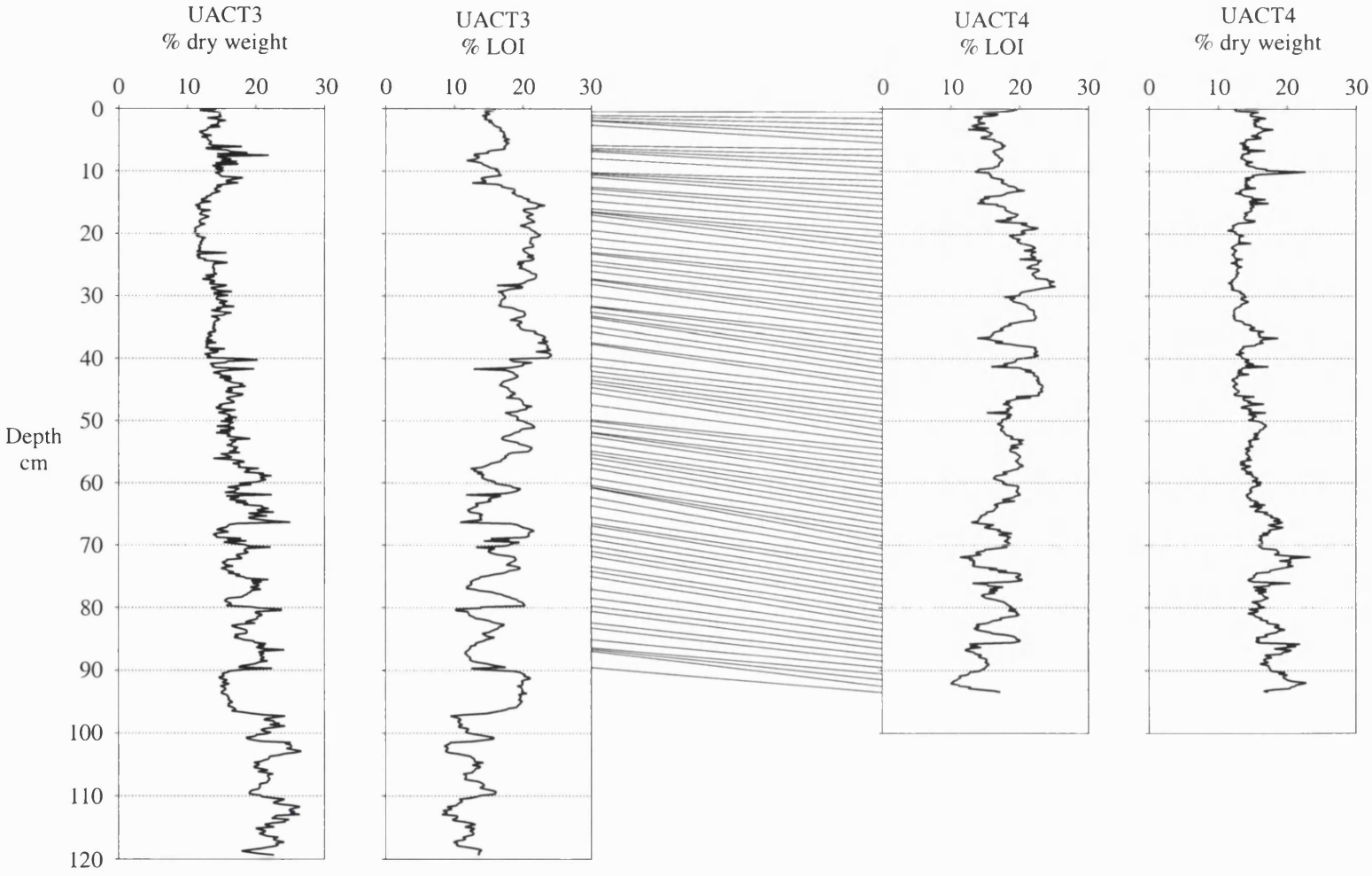


Figure 3.2 Correlation between UACT3 and UACT4, from the TIGGER IIa project (Battarbee *et al.*, 1996; Barber *et al.*, 1999).

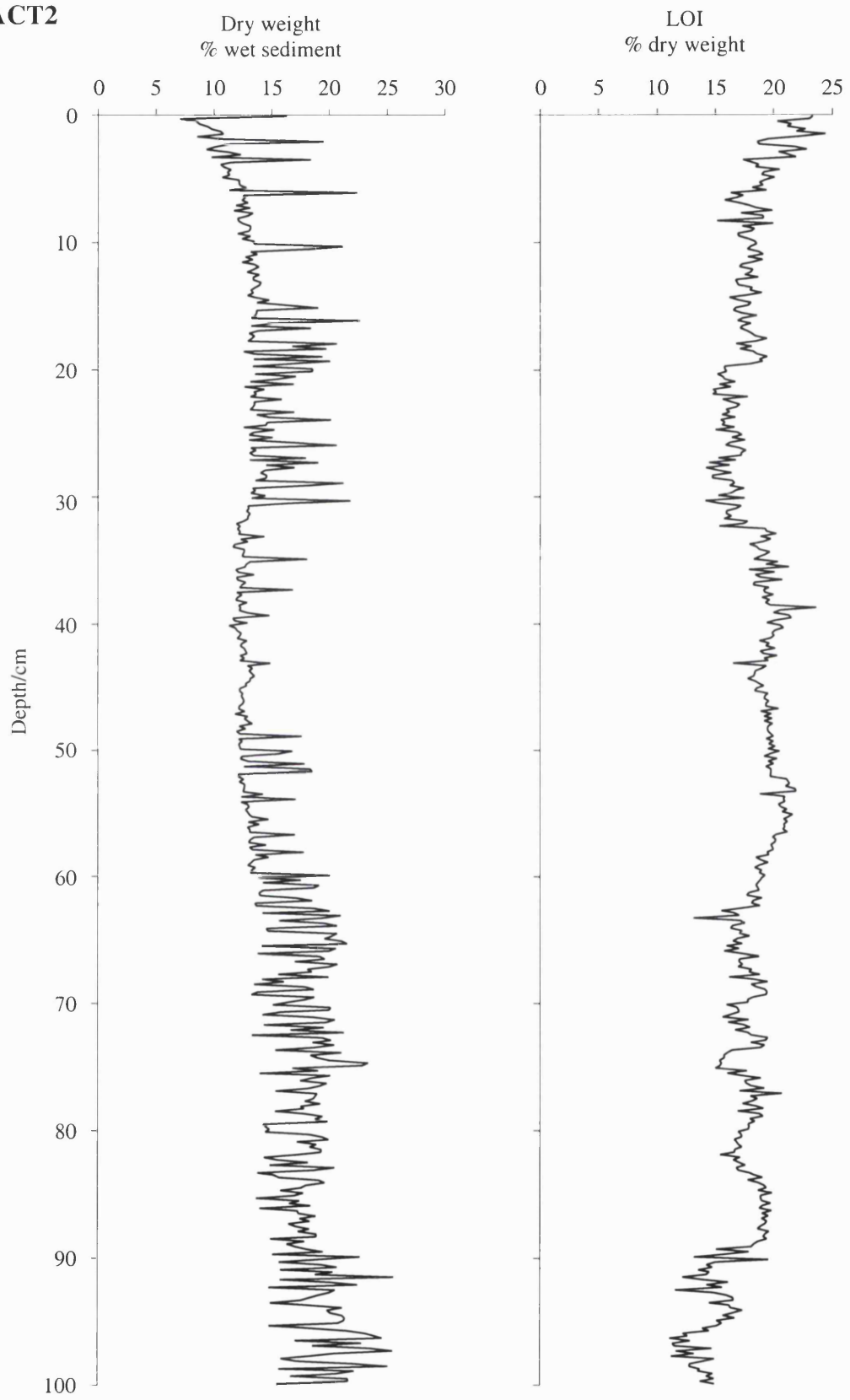


Figure 3.3 Dry weight and LOI, core UACT2.

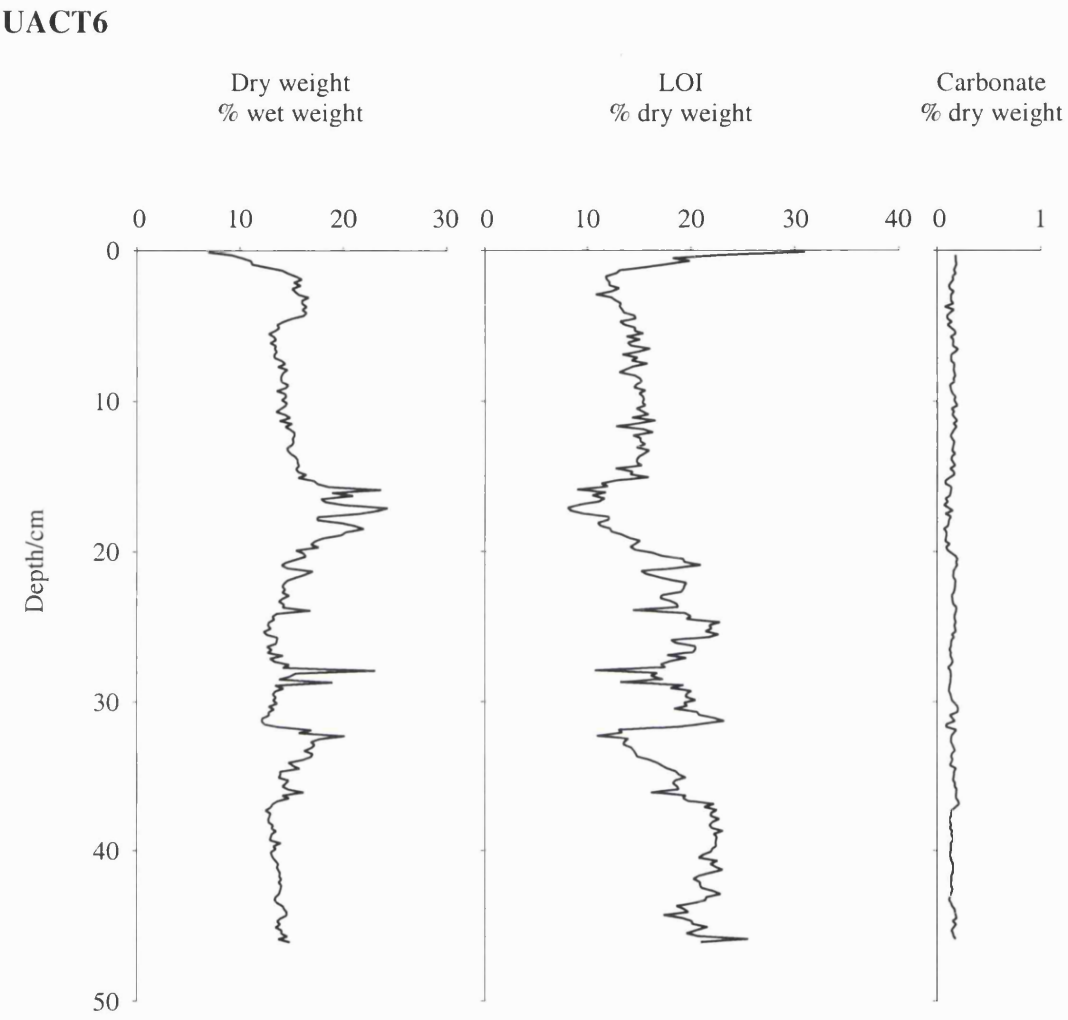


Figure 3.4 Dry weight, LOI and carbonate, core UACT6. Note that the carbonate scale has 10x exaggeration.

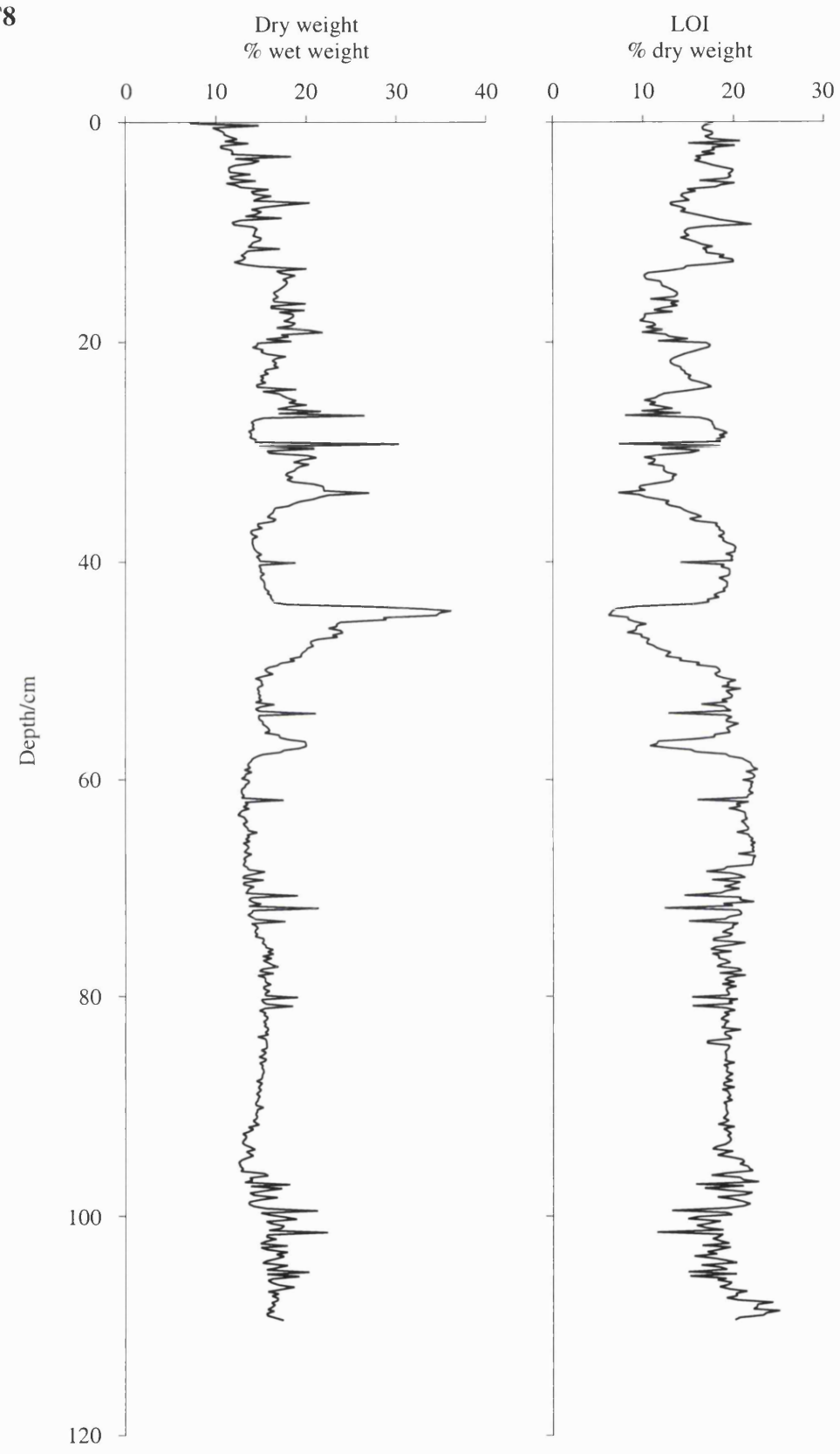


Figure 3.5 Dry weight and LOI, core UACT8.

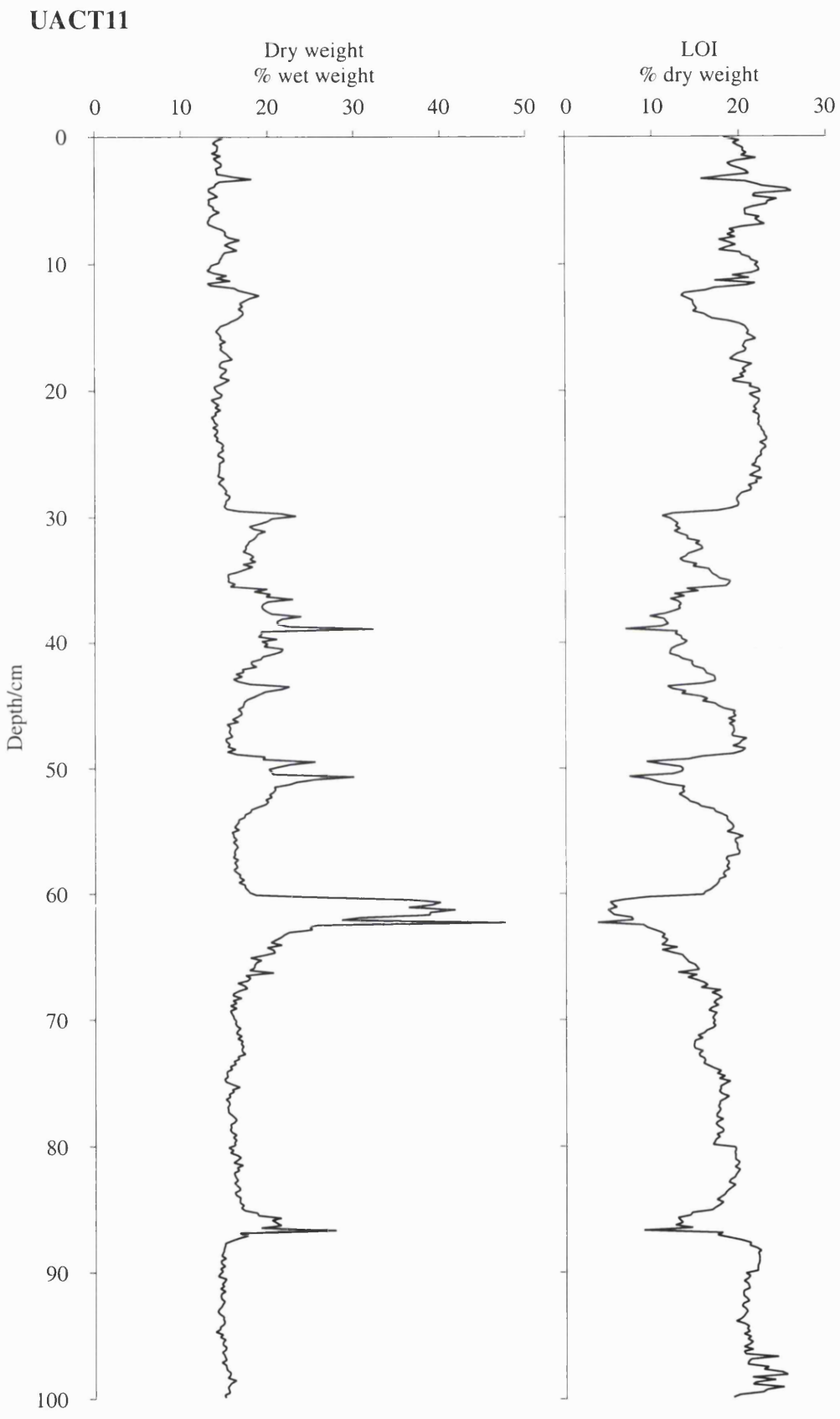


Figure 3.6 Dry weight and LOI, core UACT11.

3.2.1.1 Cores UACT3 and UACT4

These two cores formed the basis of the Lochan Uaine component of the TIGGER IIa project (Battarbee *et al.*, 1996; Barber *et al.*, 1999; Battarbee *et al.*, in press). A strong correlation was seen between the dry weight and LOI profiles of the two cores, allowing them to be matched level for level by a sequence slotting algorithm (Figure 3.2). UACT4 has a slightly higher accumulation rate than UACT3 and was thus chosen for radiometric dating. However, UACT3 is the longer core (119.4 cm), and the base of UACT4 correlates with a depth of only 89.6 cm in UACT3. Hence UACT3 contains older sediment than that dated in UACT4. Assuming that the UACT4 radiocarbon chronology is approximately accurate (Section 3.3.2), the major variations in LOI appear to recur at approximately 200 year intervals, although the dating errors make it impossible to say whether the variations are truly cyclic (*i.e.* have a constant return frequency) or merely episodic.

3.2.1.2 Core UACT2

Originally intended as a back-up core for the TIGGER IIa project, UACT2 was analysed for dry weight and LOI in 1997, having been stored in the dark at a temperature of 2°C since it was recovered in 1993. The long period of storage accounts for the large fluctuations between contiguous samples visible in the dry weight profile (Figure 3.3). This is caused by the leakage of water from some sample containers during storage, which increases the sediment dry weight. LOI will not have been affected by this problem, and is thus a more reliable measure of sediment lithostratigraphy. The LOI profile did not exhibit the same variations as seen in UACT3 and UACT4. When inter-sample noise is smoothed out, the LOI oscillations of UACT2 from 0-60 cm depth exhibit a lower frequency and amplitude than is seen in other cores. Only below 60 cm are the frequency and amplitude of the oscillations comparable to those of UACT3 and UACT4. Field notes suggest that the core was taken at a slight angle, which may have destroyed the fine detail of the cycles (N. Cameron, pers. comm.). The lack of these cycles in UACT2 made correlation with UACT3 and UACT4 on the basis of LOI values impossible, and no further analyses are carried out on this core.

3.2.1.3 Core UACT6

This was the only core recovered during the 1997 coring trip to contain an undisturbed mud-water interface (Plate 3). Although less than 50 cm long, the core displayed similar variations in dry weight and LOI to cores UACT3 and UACT4 (Figure 3.4). Assuming that no sediment was lost from the core tops during coring, the mud-water interface can be used as an unambiguous horizon in all cores to aid the correlation of the cores and subsequent construction of core chronologies. For this reason core UACT6 was chosen as the main focus of this study.

3.2.1.4 Core UACT8

Two main problems were encountered with core UACT8. Firstly, the mud-water interface was not present. This may be due to incorrect calculation of the water depth during piston coring, or possibly to drift of the coring platform into shallower water prior to coring. It is thought that the piston drive began some distance below the mud-water interface. The second problem was the opposite of that seen in UACT2. Well-defined fluctuations in dry weight and LOI were seen in the top 60 cm of core, similar to those found in cores UACT3, 4 and 6. From 60 cm to the core base (109.6 cm) practically no fluctuations were seen above the inter-sample noise (Figure 3.5). It is possible that this represents a real sediment profile, possibly from older sediment than that seen in other cores. However, it is thought more likely that the profile is an artefact of sediment disturbance. During coring the Livingstone rods were seen to be flexing significantly. This could cause the core to be driven at an increasingly large angle from the vertical. As with UACT2, this has the effect of mixing the sediment vertically and destroying the fine detail of the lithostratigraphy. For this reason, no further analyses were carried out on core UACT8.

3.2.1.5 Core UACT11

This core was obtained with a 4 cm diameter Livingstone corer. It was intended to extend the sediment sequence beyond that obtainable with a piston corer, and to correlate the sequences using dry weight and LOI profiles, hence the drive was started at a depth of *c.* 50 cm below the mud-water interface. The core lithostratigraphy (Figure 3.6) exhibits the fluctuations characteristic of cores UACT3, 4 and 6,

Plate 3 Cores UACT8 (left) and UACT6 (right).

although they appear to have a lower frequency in UACT11. This may be due to the core representing a faster accumulation rate than other cores. Alternatively, it may reflect a change in the nature of the fluctuations which is not seen in the top metre of the sediment record. Because of the differences in fluctuations between UACT11 and those cores containing the mud-water interface, no obvious correlations between the LOI profiles are apparent. To determine the likely age of the basal sediment, four samples were chosen for pollen analysis, at depths of between 88 and 100 cm. The analysis and interpretation of results were carried out by S. Peglar, and are summarised below.

All four samples show similar pollen assemblages and are dominated by *Betula* and *Corylus* pollen. Typical high altitude 'montane' taxa are present but rare. These include *Juniperus communis*, *Empetrum nigrum*, *Cerastium cerastioides*-type, *Sedum*, *Thalictrum*, *Trollius europaeus*, *Huperzia selago*, *Lycopodium annotinum* and *Selaginella selaginoides*. Aquatic species are even sparser, and only a single grain of *Sparganium emersum*-type was found. Aquatic species are uncommon above the present-day treeline. The low abundances of montane species and virtual absence of aquatic species caused Peglar to conclude that the samples were sedimented during a period when Lochan Uaine lay well above the treeline. The local flora was very sparse, hence the pollen is dominated by windblown pollen of high pollen-producing taxa growing at lower altitudes.

Similar pollen assemblages dominated by *Betula* and *Corylus* are found in the area; in a blanket peat at Loch Einich (Birks, 1975), and in lake sediments at Abernethy Forest (Birks, 1970; Birks and Mathewes, 1978). These are dated to 8700-7200 ^{14}C yr BP. Furthermore, local expansion of *Pinus* and *Alnus* in the area started between 7500 and 7200 ^{14}C yr BP. Pollen from both genera is found only in low concentrations in the samples analysed. Peglar concluded that the basal sediments of UACT11 are most likely to have been deposited between 8700 and 7500 ^{14}C yr BP. By contrast, the oldest sediment in UACT4 is dated to 4670±70 ^{14}C yr BP (Battarbee *et al.*, 1996). It thus appears that UACT11 contains a significantly older part of the

Lochan Uaine sediment record than UACT4. The same is found with UACT3 as discussed above.

3.2.2 Core correlation

As a result of the difficulty in obtaining a sufficient number of radiocarbon ages for a high resolution study of core UACT6, it was decided to construct a core chronology on the basis of lithostratigraphic correlation with UACT4, the dated core from the TIGGER IIa project. The strong correlations between dry weight and LOI measurements of UACT3 and UACT4 have previously been established using a sequence slotting algorithm (Figure 3.2). Although the correlation between UACT6 and UACT4 was not as well-defined, the main features were nonetheless apparent.

The most likely correlation between UACT6 and the two longer cores is given in Figure 3.7. The correlation is made visually, as it is felt that use of a numerical sequence slotting programme is only justified where a far better correlation is apparent between cores. The top half of UACT6 (0-*c.* 25 cm depth) appears to have a slightly higher overall accumulation rate than UACT4, which itself has a higher accumulation rate than UACT3. From 25 cm depth to the core base the overall accumulation rate is lower than for the corresponding section of UACT4, and slightly lower than for UACT3. The base of UACT6 at 46.2 cm is thought to correspond to a depth of 48 cm in UACT3, and 53 cm in UACT4.

Differences between the cores exist. For example, the section from 3-15 cm depth in UACT6 exhibits low variability in LOI values. This is not seen in either UACT3 or UACT4. Such features may be due to variations in accumulation rates within and between cores (see below). Disturbance during coring cannot be ruled out, but is thought unlikely due to the lack of smearing in the signal, as shown by the sharp features apparent in the UACT6 LOI profile, and the lack of visible disturbance at the mud-water interface at the time of coring.

UACT6 exhibits larger amplitude variations than UACT3 and UACT4, and more overall noise between samples. Maximum and minimum values of LOI in UACT6 are

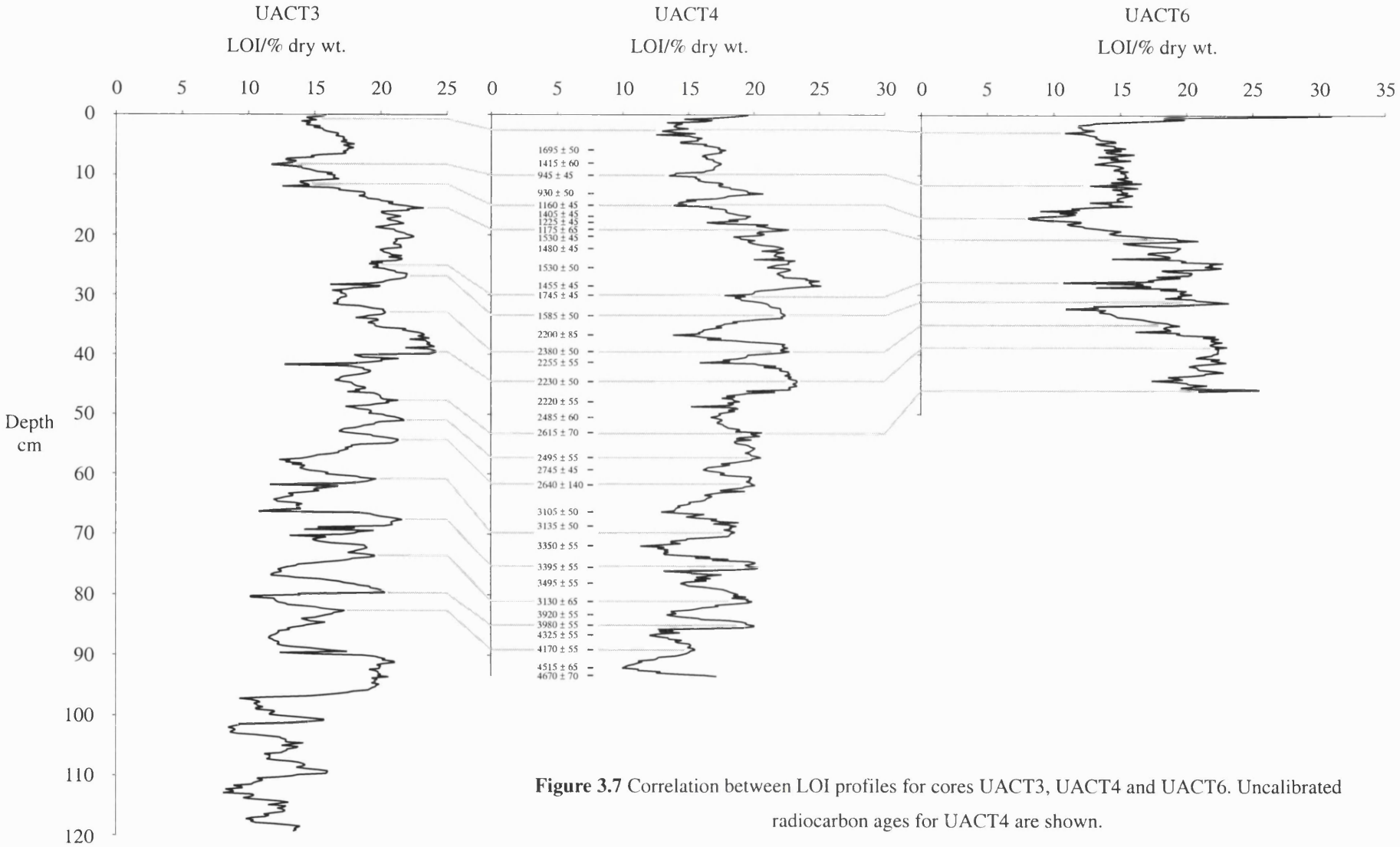


Figure 3.7 Correlation between LOI profiles for cores UACT3, UACT4 and UACT6. Uncalibrated radiocarbon ages for UACT4 are shown.

larger or smaller respectively than for UACT3 and UACT4. In particular, the topmost samples of UACT6 show a rise in LOI to >30% at the surface. A corresponding, but smaller magnitude, rise is seen in UACT4, and barely any increase in UACT3. This is possibly due to differences in subsampling of the cores by different analysts. Topmost samples of UACT6 have a high water content, and appear to consist principally of organic material in suspension. This may reflect a delay in the mineralisation of organic matter at the mud-water interface, or the presence of rapidly-degradable organic components such as polysaccharides. The conditions at the mud-water interface of cores UACT3 and UACT4 during subsampling are not known.

Although core UACT6 was analysed by a different analyst from cores UACT3 and UACT4, the possibility of differences in LOI due to the use of different methods is considered slight. All cores were analysed in the same laboratory, using the same equipment and following a standard procedure (Bengtsson and Enell, 1986). LOI is sometimes thought to be unreliable in sediments with a high clay content where water may be chemically bound to the clay as iron, aluminium or manganese oxides (Mackereth, 1966; Håkanson and Jansson, 1983; Sutherland, 1998). This water is not removed during drying at 105°C, but is lost by dehydration at 550°C, thus contributing to the 'organic' weight. However, this problem is thought to be minimal at Lochan Uaine as the sediment has a low clay content, and is dominated by silt-sized siliceous diatom remains. The LOI results are corroborated by measurements of TOC which show a highly significant correlation with LOI, with an R^2-value of 0.865 (Chapter 4). Furthermore, differences are seen between the LOI profiles of UACT3 and UACT4. These profiles were both measured by the same analyst, suggesting that differences between core profiles are real and not due to inconsistencies in the methods used by different analysts.

Average sediment accumulation rates differ between the three cores, as noted previously with respect to the correlation of the base of UACT6 with the corresponding depths in UACT3 and UACT4. These were given as 46.2 cm, 48 cm and 53 cm respectively. In addition, accumulation rates are not constant within any one single core. This is demonstrated by the alternate bunching and spreading of the

lines depicting depth correlations between UACT3 and UACT4 (Figure 3.2). These are small variations, generally within the range of at most a couple of centimetres. Nonetheless, the varying accumulation rates have implications for radiocarbon dating, in particular the use of a linear regression to construct the main depth-age model. These problems are discussed in more detail below (Section 3.5.1).

Assuming that the correlation between cores UACT4 and UACT6 is accurate, it should then be possible to use the dating of UACT4 as a means to date UACT6. It is first necessary to evaluate the accuracy and precision of the dating of UACT4, with the aim of establishing a calendrical depth-age model. The use of calendar dates, rather than uncalibrated radiocarbon ages, is essential to allow comparisons to be made between the sediment record and other non-radiometrically dated sequences, such as ice core, tree ring and instrumental records.

3.3 Dating of cores UACT4 and UACT6

This section examines the dating of cores UACT4 and UACT6. Various techniques were used in the dating of UACT4. These included radiocarbon dating, ^{210}Pb dating and the associated ^{137}Cs and ^{241}Am techniques, and tephrochronology. Work on UACT4 was carried out by numerous research institutions as part of the TIGGER IIa project, as described by Battarbee *et al.* (1996), Barber *et al.* (1999) and Battarbee *et al.* (in press). Tephrochronology wais used to try to date core UACT6. Core UACT5 has been analysed for spheroidal carbonaceous particles (N. Rose, unpublished), but the short length and lower sampling resolution of this core prevent correlation with any other cores from the site, and this work is not discussed further. Calibration of radiocarbon dates and the constructon of core chronologies based on all the available data is covered in a subsequent section (Section 3.5).

3.3.1 ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am

Gamma spectrometry of ^{210}Pb and ^{226}Ra, using the method described by Appleby *et al.* (1986), was used to establish the chronology for the recent sediment of UACT4. The results were listed by Battarbee *et al.* (1996) and Battarbee *et al.* (in press) and

are shown in Figure 3.8. Equilibrium of ^{210}Pb activity with supporting ^{226}Ra activity occurs at a depth of only 3.6 cm, suggesting a date of *c.* 1876 AD for this level and a correspondingly low sediment accumulation rate. Unsupported ^{210}Pb activity declines roughly exponentially with depth, and there is little difference between the constant initial concentration (CIC) and constant rate of supply (CRS) dating models (Appleby and Oldfield, 1978, 1983; Olsson, 1986). This allows a ^{210}Pb depth-age model to be constructed for the upper 3.6 cm of UACT4 (Figure 3.8). Battarbee *et al.* (1996) conclude that the sediment accumulation rate since *c.* 1876 is uniform at around 0.0051 ± 0.0006 g cm^{-2} yr^{-1}, or 0.030 ± 0.004 cm yr^{-1}. These accumulation rates are comparable with those from similar low productivity lakes, such as Lochnagar and Lochan Uaine (Ben Macdui) in the Cairngorms (Rapson, 1985; Dalton *et al.*, 2000), Lake Illisarvik, arctic Canada (Michel *et al.*, 1989), in sections of cores from Linnévatnet, Svalbard (Snyder *et al.*, 1994), and prior to 1950 AD in Sombre Lake, maritime Antarctic (Appleby *et al.*, 1995).

Also shown on Figure 3.8 is the ^{137}Cs activity for the top of UACT4. Battarbee *et al.* (1996) and Battarbee *et al.* (in press) found that it was not possible to validate the ^{210}Pb depth-age model by ^{137}Cs due to the slow accumulation rate and the high caesium mobility. The highest ^{137}Cs activity is found in the topmost sample and significant activity is detected below 3 cm depth, prior the start of nuclear testing in 1954 AD as indicated by ^{210}Pb dating (Appleby *et al.*, 1995). Another product of atmospheric nuclear weapons testing, ^{241}Am, is detected in the 0.4-0.6 cm level. This probably corresponds to a date of 1963 AD (Appleby *et al.*, 1991), a date that is in agreement with the ^{210}Pb depth-age model (Battarbee *et al.*, 1996).

3.3.2 Radiocarbon dating - raw data

Thirty-six AMS radiocarbon dates were obtained for bulk sediment from UACT4 (Battarbee *et al.*, 1996). The results are given in Figure 3.9 and Appendix E. Overall a strong linear trend is apparent, with radiocarbon age increasing with core depth. At several points within the core inversions occur where an older sample lies above a younger sample. This appears to be at odds with the basic sedimentological principle that younger sediments are found above older sediments, but there are several

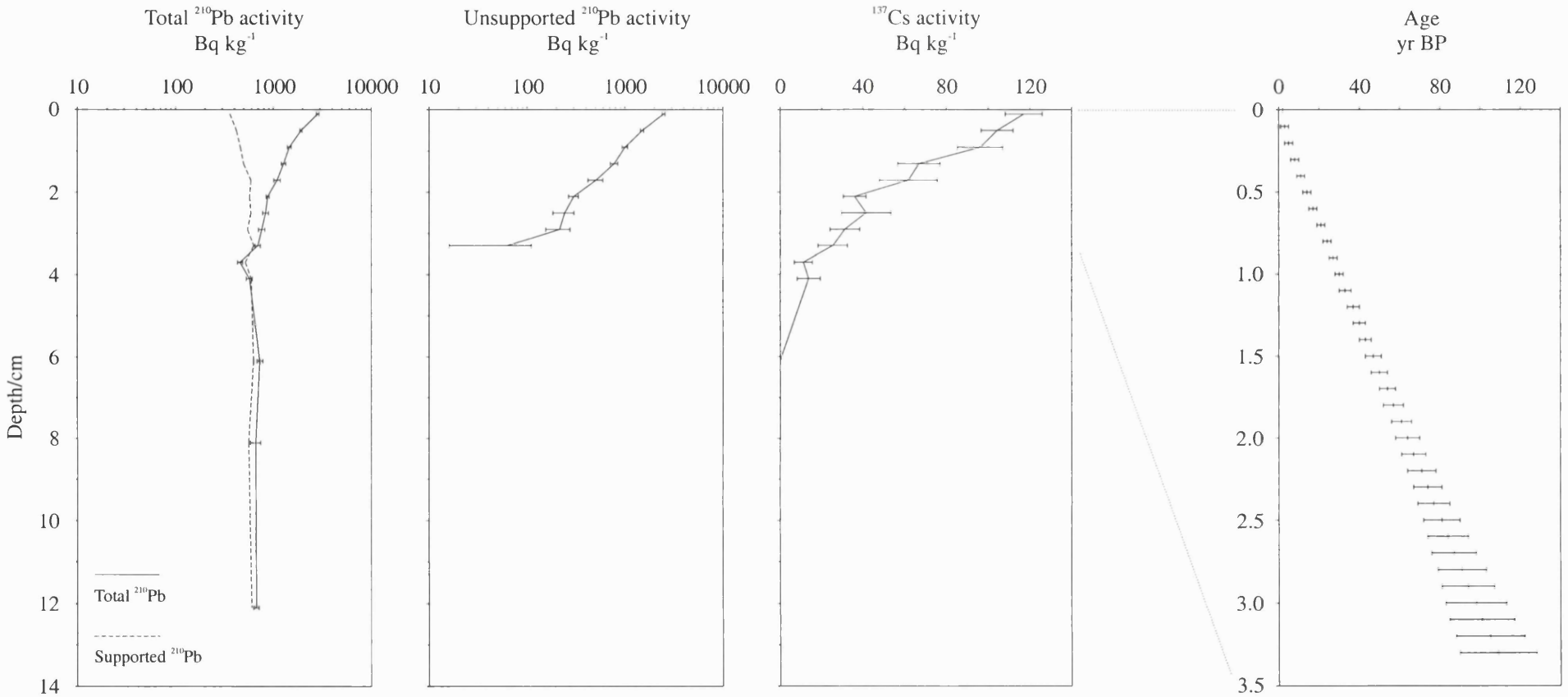


Figure 3.8 Dating of top of core UACT4 by ^{210}Pb activity. Both CIC and CRS dating models gave similar results, allowing construction of the depth-age model, far right (after Battarbee *et al.*, 1996; Battarbee *et al.*, in press).

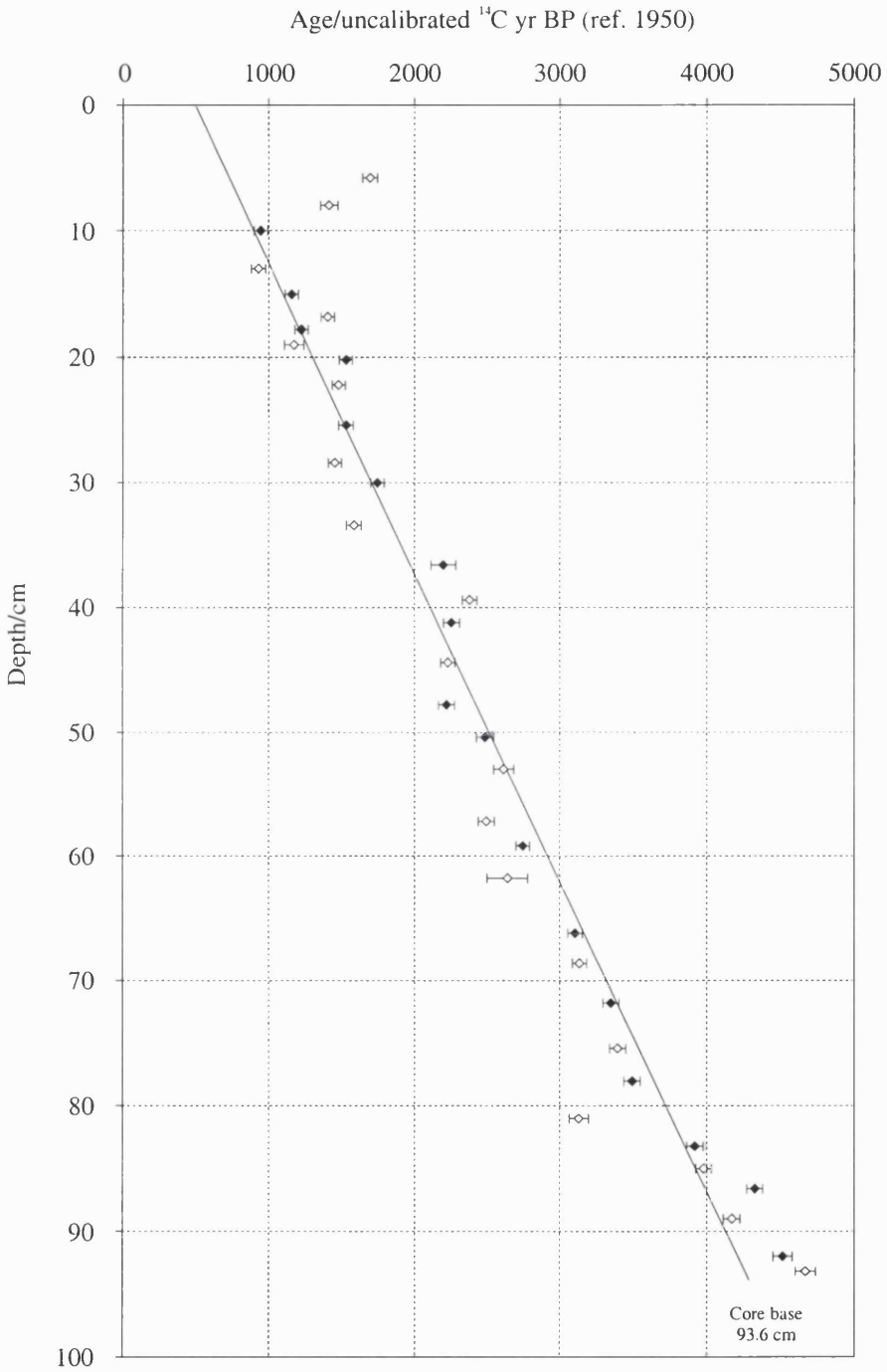


Figure 3.9 Uncalibrated radiocarbon ages of UACT4 *vs* depth. Filled symbols are from LOI minima, open symbols are from LOI maxima. 1σ error bars and the best fit linear regression ($R^2 = 0.962$; top two samples excluded) are shown.

possible explanations. Firstly, the age inversions could be due to the deposition of older, and hence less active, carbon from the catchment or atmosphere. This is frequently seen as a consequence of peat erosion during the Holocene, either through natural processes or through a change in catchment land use (O'Sullivan *et al.*, 1973; Battarbee *et al.*, 1985; Stevenson *et al.*, 1990, 1992). In the industrial era, inactive carbon released as a consequence of fossil fuel burning can enter lake sediments, either directly in the form of particulate matter such as spherical carbonaceous particles (Rose, 1994, 1995), or indirectly through the assimilation of old carbon from the atmosphere by photosynthetic organisms. The 'hard water' reservoir effect is unlikely to be significant at Lochan Uaine due to the absence of carbonate rocks in the catchment (Olsson, 1986; Peglar *et al.*, 1989; Pilcher, 1991a). A second possible explanation for the age inversions is that they are a natural consequence of the nature of the radiocarbon curve. The production of ^{14}C in the atmosphere by cosmic ray bombardment is not constant, but varies depending on factors such as the strength of the earth's magnetic field. Variations on a variety of different timescales can result in inversions in the radiocarbon calibration curve, whereby older samples can have a higher ^{14}C content, and thus appear younger, than more recent samples (Taylor *et al.*, 1996). The inversions in the UACT4 radiocarbon record may reflect short term variations in ^{14}C productivity during the Holocene. Finally, measurement error cannot be ruled out. In particular, contamination of samples during collection, preparation and analysis can have a major influence on the radiocarbon ages obtained.

In UACT4, samples were chosen for dating which lie at extremes of LOI (Battarbee *et al.*, 1996). If the LOI cycles are caused by episodic inwash of catchment material, either mineral or organic, a consistent difference might be seen between the ^{14}C ages from the maxima and minima in the cycles. For example, inwash of old carbon due to soil erosion should produce consistently older ^{14}C ages. There is some evidence for a consistent difference in radiocarbon ages of samples from LOI maxima and minima in UACT4. This is seen more clearly in Figure 3.10 which shows the age deviation from the best fit linear regression. In some parts of the core there is a general trend for samples from LOI minima to be comparatively older than those from LOI maxima, as in the section from 55-75 cm depth. In other core sections this trend is not seen.

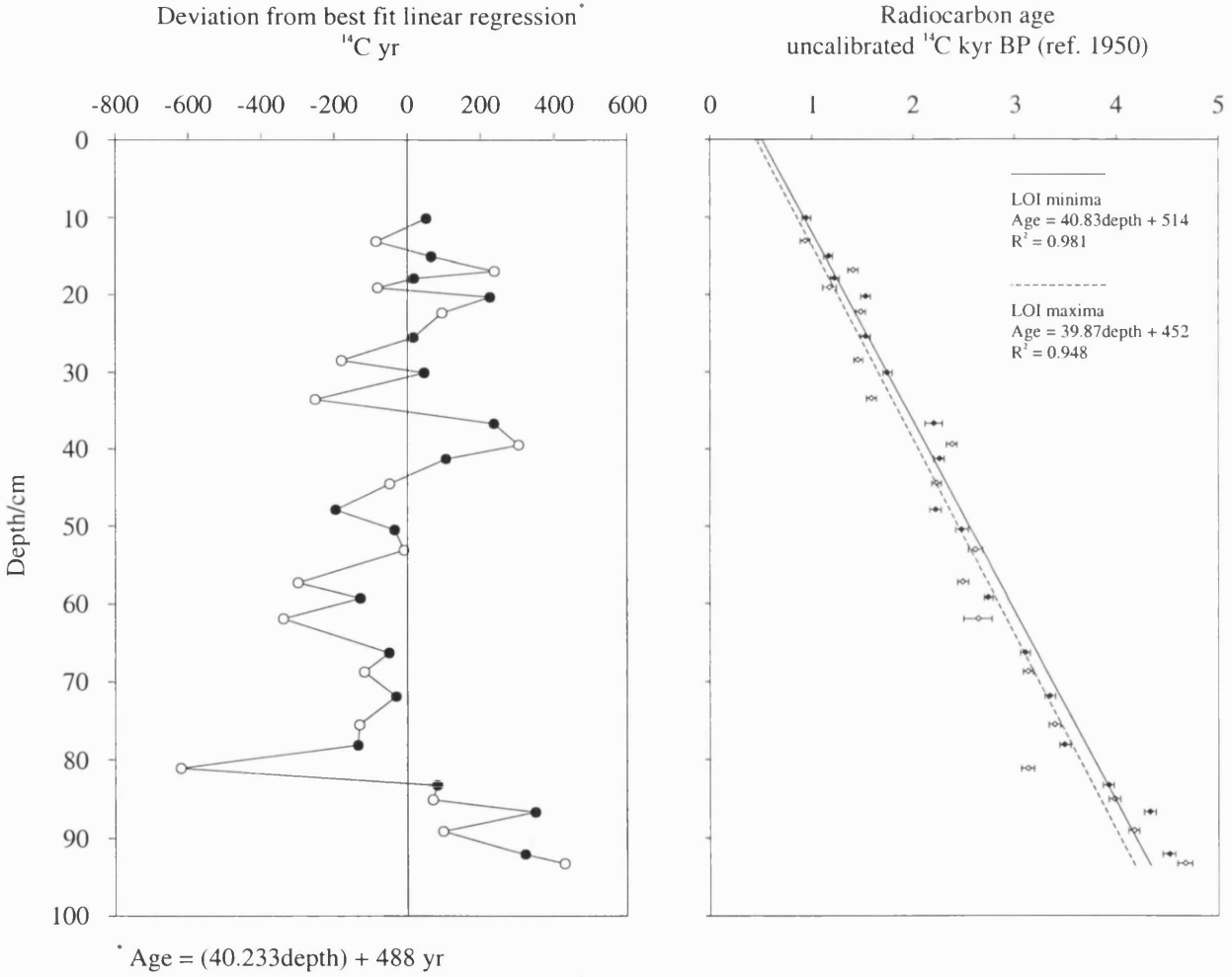


Figure 3.10 Deviation in uncalibrated radiocarbon ages from the best fit linear regression (left), and comparison of regressions through ages from LOI maxima and LOI minima (right), core UACT4. The two anomalous samples in the top 10 cm were excluded from the analysis and are not shown. Filled symbols represent LOI minima, open symbols are from LOI maxima.

Comparison of linear regressions through radiocarbon ages from LOI maxima and LOI minima reveals a consistent downcore difference between the two sets of ages. This increases from 62 ^{14}C yr at the surface to 151 ^{14}C yr at the core base. These differences lie within the 2σ error ranges of most of the radiocarbon ages. Also, their magnitude is lower than the error seen by extending the linear regression for all radiocarbon ages to the surface (Figure 3.9). This produces an age of 488 ^{14}C yr BP (ref. 1950) for the surface sediment. It is possible that there was an input of old carbon to UACT4 throughout the period of sediment accumulation which became more significant, and hence produced older radiocarbon age estimates, during periods of relatively low organic deposition. A similar input of old carbon from the catchment of a soft-water lake in southwest Sweden was described by Björck *et al.* (1998), who recorded bulk sediment dates 100-500 yr older than those obtained from AMS dating of terrestrial macrofossils. The low abundance of terrestrial macrofossils at Lochan Uaine prevents their use for radiocarbon dating. Oldfield *et al.* (1997b) also found that bulk AMS ^{14}C measurements from a soft-water lake in northern Sweden gave significantly older dates than those from terrestrial macrofossils. They attributed this to a possible carbon reservoir effect in the aquatic ecosystem, or from sediment focusing of older marginal material into the deepest part of the lake.

Sediment inputs to lakes such as Lochan Uaine are complex. Organic matter originates both autochthonously from organisms such as algae and bacteria, and allochthonously from catchment vegetation. Likewise, sediment mineral matter contains an autochthonous component, principally of biogenic silica from diatoms, and an allochthonous component of clastic material. Changes in the relative proportions of these inputs make it difficult to ascertain whether an increased input from the catchment is associated with higher or lower LOI values. As a result, it is not possible to say whether older ^{14}C ages caused by the inwash of catchment soil should be associated with LOI maxima or LOI minima. However, analysis of the organic component of Lochan Uaine sediment undertaken as part of this study suggests that greater relative catchment input is associated with LOI minima. There are three main reasons for this relationship. Firstly, the chlorin concentration of core UACT6 shows a strong positive relationship with LOI when expressed as a proportion of TOC

(Section 4.4). Chlorins are thought to be indicative of lake primary productivity. Low chlorin concentrations are thus associated with low autochthonous input to the sediment organic fraction, suggesting a correspondingly greater relative input from the catchment. As low chlorin concentrations coincide with low LOI values, the relative input of catchment organic matter during these periods is increased. Secondly, there is some evidence that low LOI values are correlated with greater bulk organic carbon isotope fractionation (Section 4.5). This is noticeable in the event occurring between 15-20 cm depth of UACT6, but not in other parts of the core (Figure 4.14). Overall, the relationship between LOI and $\delta^{13}C$ is not significant at the 95% level. For the section from 15-20 cm, the more negative $\delta^{13}C$ values suggest a greater relative contribution from catchment vegetation, which is associated with low LOI. The third reason for linking LOI minima with high relative catchment input comes from analysis of lipids (Chapter 5). Certain biomarker indicators of lake productivity, notably the C_{17} *n*-alkane and a C_{25} highly branched isoprenoid hydrocarbon (HBI), are positively correlated with LOI. As with chlorins, this suggests that the relative input to the sediment from autochthonous sources is lowest during LOI minima. By contrast, little correlation is evident between LOI and biomarkers of catchment vegetation. This suggests a constant input of catchment material to the sediment. Assuming that catchment material contains a greater old carbon component than autochthonous material due to the presence of eroded soils, this may explain the apparent presence of old carbon throughout the core as seen by the intercept with the surface at 488 ^{14}C yr BP (ref. 1950). The older ages measured from LOI minima may then result from the decreased input of autochthonous material, which would otherwise have the effect of 'diluting' the old carbon input from the catchment and giving rise to younger age estimates.

Finally, the topmost two dated samples appear to have anomalously old radiocarbon ages (Figure 3.9). Downwards extension of the ^{210}Pb chronology suggests that these samples were probably deposited around the start of the industrial era, yet they give ages of 1695±50 ^{14}C yr BP (5.8-6.0 cm) and 1415±60 ^{14}C yr BP (8.0-8.2 cm). It is possible that these anomalous ages are due to contamination by old carbon released by fossil fuel burning. Furthermore, dating of young samples <*c.* 300 years in age is

problematic (Taylor, 2000). The top two radiocarbon ages are thus excluded from all subsequent analyses. Calibration of radiocarbon ages, including correction for the possible presence of old carbon from the catchment, is discussed in full in Section 3.5.

3.4 Tephrochronology

As a result of the problems with the radiocarbon dating of core UACT4, and the additional difficulties of transferring this chronology to core UACT6, it was decided to try and establish an independent means of constructing the chronologies. Analysis of volcanic ash particles, known as tephra, provides a potentially useful tool for doing this (Grange, 1931; Uragami *et al.*, 1933; Thorarinsson, 1981a,b; Einarsson, 1986). Cores UACT4 and UACT6 were both analysed for tephra. The analysis of core UACT4 was performed by N. Rose as part of the TIGGER IIa project (Battarbee *et al.*, 1996; Barber *et al.*, 1999; Battarbee *et al.*, in press). Core UACT6 was analysed as part of this study.

3.4.1 Tephra in British Holocene sequences

The identification and analysis of tephra in British Holocene sites is a relatively recent science. Dugmore (1989) was the first to identify such tephras, at Altnabreac in northeast Scotland. Subsequently, tephra layers have been found at numerous sites in Scotland, the north of Ireland, and northern England, and have recently been found at several more southerly sites in England and Wales (V. Hall, pers. comm.). This allows regional tephrochronologies to be constructed with the aim of making tephra analysis a routine part of Holocene palaeoecological studies in the British Isles (Dugmore *et al.*, 1995; Pilcher *et al.*, 1996; Pilcher and Hall, 1992, 1996).

Tephra studies have numerous potential applications. Individual layers of tephra represent time-synchronous horizons across their region of deposition, and as such they may be used to correlate between sequences. Furthermore, tephras which can be attributed to an eruption of known age provide an important means of dating sequences. Well-dated sequences can be used to estimate rates of sediment deposition, and in sequences containing several dated horizons changes in deposition

rate may be calculated. It may be possible to assess the environmental and climatic significance of past volcanic events by examining changes in pollen, diatoms and other palaeoecological markers in relation to tephra horizons (Blackford *et al.*, 1992; Hall *et al.*, 1994a; Caseldine *et al.*, 1998). On a Holocene timescale tephra layers are deposited near-instantaneously, hence the stratigraphic depth covered by a single tephra layer indicates the amount of post-depositional reworking and the overall resolution of the sediment record. Finally, the areal extent of Holocene tephras aids the study of the eruptions themselves, and provide insights into such factors as the amount of material involved and the mechanisms of dispersal and deposition, including the height of the volcanic plume, wind speed and direction, and precipitation.

Since the pioneering study of Dugmore (1989), tephra in British Holocene depositional sequences has been studied with increasing frequency. These studies have focused mostly on peat bogs with only a few examples of tephra analysis in lake sediments. The locations and identities of most Holocene age tephras found in Britain to date are given in Tables 3.3-3.5. The dates given are those quoted by the authors, hence the Hekla 4 tephra is listed as an uncalibrated radiocarbon age for Scottish sites, and as a calibrated date for Irish and English sites. A chronology of all known Middle and Late Quaternary Icelandic tephras in the North Atlantic region is given by Haflidason *et al.* (2000).

These tephra layers have several features in common. They are all thought to originate from Icelandic volcanoes, with deposits from Hekla being of particular importance. This Icelandic source explains the distribution of British tephra deposits. These are found almost exclusively in northern areas, principally Scotland and the north of Ireland. Several tephras have now been found in northern England (Pilcher and Hall, 1996) and as far south as Wales (V. Hall, pers. comm.). Identification of tephras from other volcanic centres in Europe at these sites would be of great importance as it would allow the linking of regional tephrochronologies, but to date no such tephras have been discovered in Britain.

Table 3.3 Holocene tephra layers identified in Scottish deposits (after Dugmore *et al.*, 1995).

Name of tephra	Date/Age	Sites	References
Hekla AD 1510 (Loch Portain A)	1510 AD[1]	Lairg (Sutherland), Loch Portain (Western Isles)	Dugmore *et al.* (1995, 1996)
Loch Portain B	*c.*450 BP[2]	Lairg (Sutherland), Loch Portain (Western Isles)	Dugmore *et al.* (1995)
Glen Garry	*c.*2,100 BP[2]	Slethill (Caithness), Loch Leer (Caithness), Altnabreac (Caithness), Glen Na Beiste (Caithness), Lairg (Sutherland), Beinn Eighe (Highlands), Glen Garry (Highlands), New Pitsligo (Grampian)	Dugmore and Newton (1992), Dugmore *et al.* (1995)
Kebister	*c.*3,600 BP[3]	Kebister (Shetland)	Dugmore *et al.* (1995), Dugmore and Newton (1998)
Hekla 4	*c.*3,830 BP[2]	Kebister (Shetland), Hoy (Orkney), Slethill (Caithness), Loch Leer (Caithness), Altnabreac (Caithness), Lairg (Sutherland), New Pitsligo (Grampian)	Dugmore (1989), Dugmore and Newton (1992), Bennett *et al.* (1992), Blackford *et al.* (1992), Dugmore *et al.* (1992, 1995)
Hoy	*c.*5,600 BP[2]	Hoy (Orkney)	Dugmore *et al.* (1995)
Lairg A + Lairg B	*c.*6,000 BP[4]	Lairg (Sutherland)	Dugmore *et al.* (1995)
Saksunarvatn	9350±90 BP[2]	Dallican Water (Shetland)	Bennett *et al.* (1992)

[1] Based on historical records
[2] Uncalibrated radiocarbon age
[3] Based on stratigraphic position within a radiocarbon-dated profile
[4] Estimate based on stratigraphic position

Table 3.4 Holocene tephra layers identified in Irish deposits.

Name of tephra	Date/Age	Sites	References
Hekla AD 1510	1510 AD[1]	Garry Bog, Sluggan Bog	Pilcher *et al.* (1996), Hall *et al.* (1994b)
Öræfajökull AD 1362	1362 AD[1]	Garry Bog, Sluggan Bog	Pilcher *et al.* (1995, 1996), Hall *et al.* (1994b)
Hekla 1	1104 AD[1]	Garry Bog, Sluggan Bog, Owenbeg	Pilcher *et al.* (1995, 1996)
'AD 860 layer'	776-887 AD[2]	Sluggan Bog, Barnsmore (one geochemical population only)	Pilcher *et al.* (1995, 1996), Hall *et al.* (1993, 1994b)
Hekla 4	2,395-2,279 BC (2σ)[2]	Garry Bog, Sluggan Bog, Malin Head, Slieve Meelbeg (Mourne Mountains), Lough Henney, Fallahogy Bog, Ballynahone More Bog, West Corlea?	Pilcher *et al.* (1995, 1996), Hall *et al.* (1994a,b), Pilcher and Hall (1992), Caseldine *et al.* (1998)
Lairg B	4,778-4,614 BC (2σ)[2]	Garry Bog, Sluggan Bog, Fallahogy Bog, Ballynahone More Bog	Pilcher *et al.* (1996)
Lairg A	5,048-4,859 BC (2σ)[2]	Garry Bog, Sluggan Bog, Fallahogy Bog, Ballynahone More Bog	Pilcher *et al.* (1996)

[1] Based on historical records
[2] Calibrated radiocarbon date

Table 3.5 Holocene tephra layers identified in English deposits (Pilcher and Hall, 1996).

Name of tephra	Date/Age	Sites	References
Glen Garry	c.2,100 BP[1]	Fleet Moss, Harthorpe Moss	Pilcher and Hall (1996)
Hekla 4	2,310±20 BC[2]	Fleet Moss, Fenton Cottage	Pilcher and Hall (1996), Wells *et al.* (1997)

[1] Uncalibrated radiocarbon age
[2] Calibrated radiocarbon date

All of the Icelandic tephras found in British Holocene sequences are 'microtephras' - that is, the sizes and concentration of tephra shards are too low to be visible to the unaided eye. As with tephra distribution, this is a product of the distance from Iceland to Britain, around 1000 km. Particles of coarse sand size or larger (>250 μm) are heavy and rain out of the atmosphere close to the eruption site (Twomey, 1977; but see also Betzer *et al.*, 1988; Ram and Gayley, 1991). By contrast, the clay-sized fraction (<2 μm) is very light, and particles reaching the stratosphere can remain in suspension for several years and be distributed globally. Tephra deposits in Britain are mostly of an intermediate size range, the silt and fine sand component (V. Hall, pers. comm.). This is sufficiently light to allow transport of several thousand kilometres under favourable conditions, but these particles are unlikely to remain airborne for more than a few days. Due to the distance involved, even large Icelandic eruptions producing >1 km^3 uncompacted tephra deposit only low volumes of tephra over Britain, and these layers are not visible to the unaided eye (Dugmore *et al.*, 1996). Most microtephra layers are identified by extraction from the surrounding matrix, mounting on a microscope slide, and counting of contiguous samples at a suitable magnification (Persson, 1971; Dugmore, 1989; Rose *et al.*, 1996; Turney, 1998). Identification of tephra layers is also aided by the use of complementary methods, including downcore titanium concentrations (Lowe and Turney, 1997), X-radiography (Dugmore and Newton, 1992; Boygle, 1999), reflectance and luminescence scanning (Caseldine *et al.*, 1999), thin sectioning (Merkt *et al.*, 1993), and magnetic susceptibility (van den Bogaard *et al.*, 1994; Child *et al.*, 1998).

The majority of British Holocene tephra studies focus on ombrotrophic peat bog sequences rather than lake sediments. The main advantage of peat bog studies is that the predominantly organic matrix may be removed easily, leaving a mineral residue containing a high concentration of tephra shards. In the majority of lake sediments the inorganic component is much larger than in peats. This is due to the presence of clastic material from the lake catchment, and biogenic silica from lacustrine organisms such as diatoms and chrysophytes. It is thus more difficult to separate the tephra component (Rose *et al.*, 1996; Turney, 1998). For this reason, most studies of lake sediment tephras globally are confined to volcanic regions where the tephras are of

sufficient thickness to be visible to the unaided eye. Fewer studies of 'invisible' microtephra horizons exist. In Britain, Bennett *et al.* (1992) and Hall *et al.* (1994b) describe microtephras in Holocene lake sediments, while Roberts (1997), Lowe and Turney (1997) and Turney *et al.* (1997) identified microtephras in British lake sediments of Lateglacial age. Outside Britain, microtephras of Holocene and Lateglacial age are seen in lake sediments from Norway (Mangerud *et al.*, 1984; Birks *et al.*, 1996), Sweden (Wastegård *et al.*, 1998, 2000; Björck and Wastegård, 1999), Germany (Merkt *et al.*, 1993), and Antarctica (Dyson, 1988; Hodgson *et al.*, 1998).

3.4.2 Results of tephra analysis

Tephra analysis was undertaken on two cores from Lochan Uaine following the methods described in Chapter 2. Core UACT4 was analysed by N. Rose (Battarbee *et al.*, 1996). Core UACT6 was analysed as part of this study. In both cases contiguous 2 mm samples were counted.

3.4.2.1 Core UACT4

The tephra profile of core UACT4 is given in Figure 3.11. Two main peaks in tephra concentration are apparent. These maximise at depths of *c.* 32 and 88 cm, with shard concentrations of 15,000 and 8,000 $g_{dry\ wt}^{-1}$ respectively. It is noticeable that these peaks are not stratigraphically well-constrained, as seen in many peat bogs, but are relatively diffuse. Both peaks appear to cover 10-20 cm depth. This has important implications regarding the use of such tephra layers as a dating tool, as discussed in a later section. In addition to these main peaks there are several minor peaks, and a low background of tephra throughout the entire core. Battarbee *et al.* (1996) suggested that the lower main peak at *c.* 88 cm may correspond to the Hekla 4 eruption on the basis of the radiocarbon dating from UACT4. It is also possible that the smaller peak at 14-15 cm depth represents the Hekla 1510 AD event. However, an attempt to identify the tephra peaks by geochemical methods was unsuccessful.

3.4.2.2 Core UACT6

Preparation of tephra slides from UACT6 employed the biogenic silica removal technique of Rose *et al.* (1996) but not the density separation technique of Turney

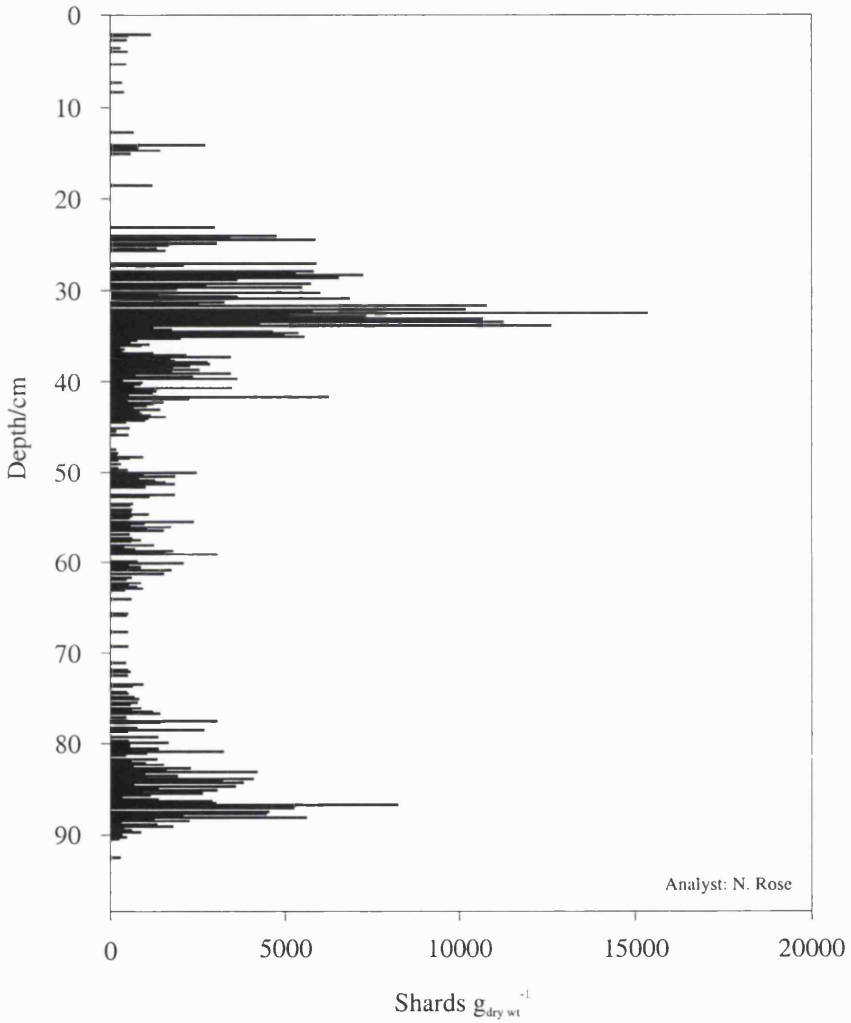


Figure 3.11 Tephra concentration profile, core UACT4 (from Battarbee *et al.*, 1996).

(1998). The earlier analysis of UACT4 described by Battarbee *et al.* (1996) followed the same methods, and major peaks in tephra concentration were seen (Figure 3.11). It was not felt that it would be necessary to remove clastic mineral matter prior to the tephra shard counting stage. This mineral matter would only be removed once tephra layers had been identified and it was necessary to increase the shard concentration of these samples for geochemical typing by electron probe microanalysis. Tephra slides from UACT6 thus contain large amounts of inorganic matter. This consists primarily of silt-sized quartz grains with lesser amounts of other minerals. Biogenic silica skeletons of diatoms and chrysophytes are also present, although it is assumed that the majority of these are removed by sodium hydroxide digestion during sample preparation (Rose *et al.*, 1996). In this lake sediment, sieving is ineffective at removing the majority of mineral particles (Hall *et al.*, 1994b) as these lie in the same size range as the tephra.

The presence of mineral matter on the UACT6 tephra slides creates various problems during the counting. The large number of mineral particles means that tephra shards are only ever present in low concentrations. Estimates of relative particle abundances made during counting suggest that in no sample did tephra account for over 0.1% of the total number of particles, and in most cases the value was below 0.01%. This contrasts sharply with the findings of Bennett *et al.* (1992). They record shard concentrations of up to 80% of total inorganic objects in sediments of Dallican Water, Shetland, for the early Holocene Saksunarvatn tephra. At 30-65% LOI these sediments had a higher organic content than at Lochan Uaine, and hence a lower mineral content in which any tephra deposits would be 'diluted'. Shetland is also several hundred kilometres closer to Iceland, and greater tephra concentrations would be expected compared to the Cairngorms. Nonetheless, the difference in shard concentrations between sediments at the two sites is substantial. The low concentrations in UACT6 also create difficulties during counting as it is necessary to scan large amounts of material to locate the tephra shards.

Identification of tephra shards is made more difficult by the high mineral content of the samples. Although large, vesicular shards are easily identifiable by their

morphology, smaller or less vesicular shards are harder to distinguish from the quartz. In most cases isotropy under plane polarised light can be used to distinguish non-crystalline tephra from crystalline minerals (Hunt and Hill, 1993), but given the large number of quartz particles it is possible that some lie in an orientation so as to appear to have the same optical properties as tephra. The adherence of small (<5 μm) particles to larger particles can also affect the optical properties of the larger particle. This is seen in several instances. Finally, fragments of glass from the edge of the coverslip are frequently seen. In some cases these have the appearance of long, thin, non-vesicular tephra shards, and being made of glass they have identical optical properties. These coverslip fragments can generally be recognised by their greater regularity compared to tephra, and care was taken to identify them correctly.

Due to the problems of tephra enumeration outlined above, tephra shards were classified into two main groups - those particles that were 'definitely' tephra shards, and those that were 'possibly' tephra shards. The downcore profiles of definite and total ('definite' + 'possible') tephra shards are given in Figure 3.12. Overall, roughly 25% of the total tephra shards were labelled as being 'definite'. The profiles of definite and total tephra shards are similar. Tephra is found throughout core UACT6, with the greatest concentrations occurring from *c.* 5-25 cm depth. The single highest concentration recorded amongst the definite shards is 19,000 $g_{dry\ wt}^{-1}$ at 20.8-21.0 cm depth, and amongst the total possible shards it is 76,000 at 14.4-14.6 cm depth. These totals represent only a small fraction of the total inorganic matter in the sediment. On no single slide were more than four definite tephra shards found, or more than 13 possible shards. On the same slides it is estimated that many thousands of non-tephra mineral particles were present. Tephra at Lochan Uaine is thus far less concentrated than that found by Bennett *et al.* (1992) at Dallican Water in the Shetlands as described previously.

The low concentrations of tephra and the high concentrations of other mineral matter in UACT6 should not prove a major obstacle to electron probe microanalysis of tephra shards. Mineral matter may be removed by the density separation method of Turney (1998). However, this is not attempted due to the nature of the downcore

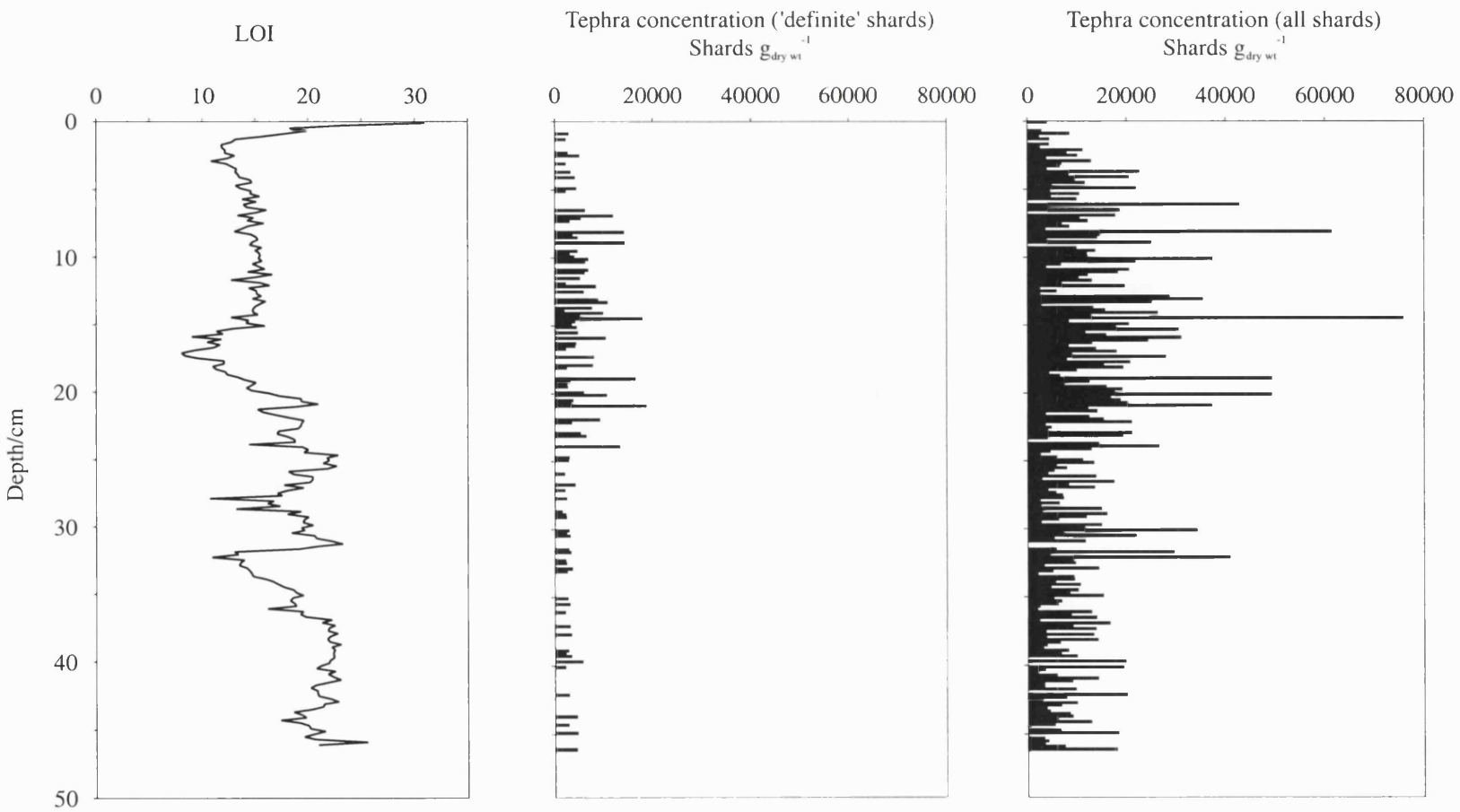


Figure 3.12 Tephra concentration profiles, core UACT6.

tephra profiles. Tephra is found throughout the core in low concentrations. No major peaks are visible which may suggest the presence of a discrete tephra layer. The principal aim of the tephra analysis at Lochan Uaine is to provide an independent means of validating the radiocarbon-derived timescale, but this is only possible if discrete tephras from well-dated eruptions are identified. Even if tephra shards from UACT6 are geochemically typed, the diffuse nature of the tephra record prevents the establishment of a stratigraphically well-constrained age. A poorly-constrained age is of no use in the validation of the radiocarbon chronology.

3.4.3 Correlation of tephra profiles from UACT4 and UACT6

The tephra record from UACT6 is not in good agreement with that previously established for UACT4. Figure 3.13 shows both records with the core correlation established from the LOI profiles. According to this correlation, the topmost of the two main peaks in UACT4 should also be seen in UACT6, maximising at around 30 cm depth. This is not seen. The highest tephra shard concentrations in UACT6 occur from *c.* 5-25 cm depth, correlating with a period of much lower concentrations in UACT4. In both cores, the sections with highest concentrations do not display consistently high values throughout, but contain numerous levels with few or no tephra shards. This may be due to the low number of shards identified in each level. The concentrations shown in Figure 3.13 appear high, but in reality no more than five definite tephra shards are identified on any one slide. This reflects the very low concentrations of tephra present in the sediment. The maximum concentrations of shards measured in the two cores are around 15,000-20,000 $g_{dry\ wt}^{-1}$. By comparison, diatom cells are present in concentrations of around 1-4x10^8 $g_{wet\ wt}^{-1}$, estimated to correspond to around 1-4x10^9 $g_{dry\ wt}^{-1}$. This represents a difference of five magnitudes. Clastic mineral particles from the catchment are not present in the same high quantities as diatoms, but tephra is nonetheless thought to constitute no more than *c.* 0.1% of total mineral particles, and mostly less than 0.01%. The low tephra presence may account for the lack of similarity between the UACT4 and UACT6 tephra profiles.

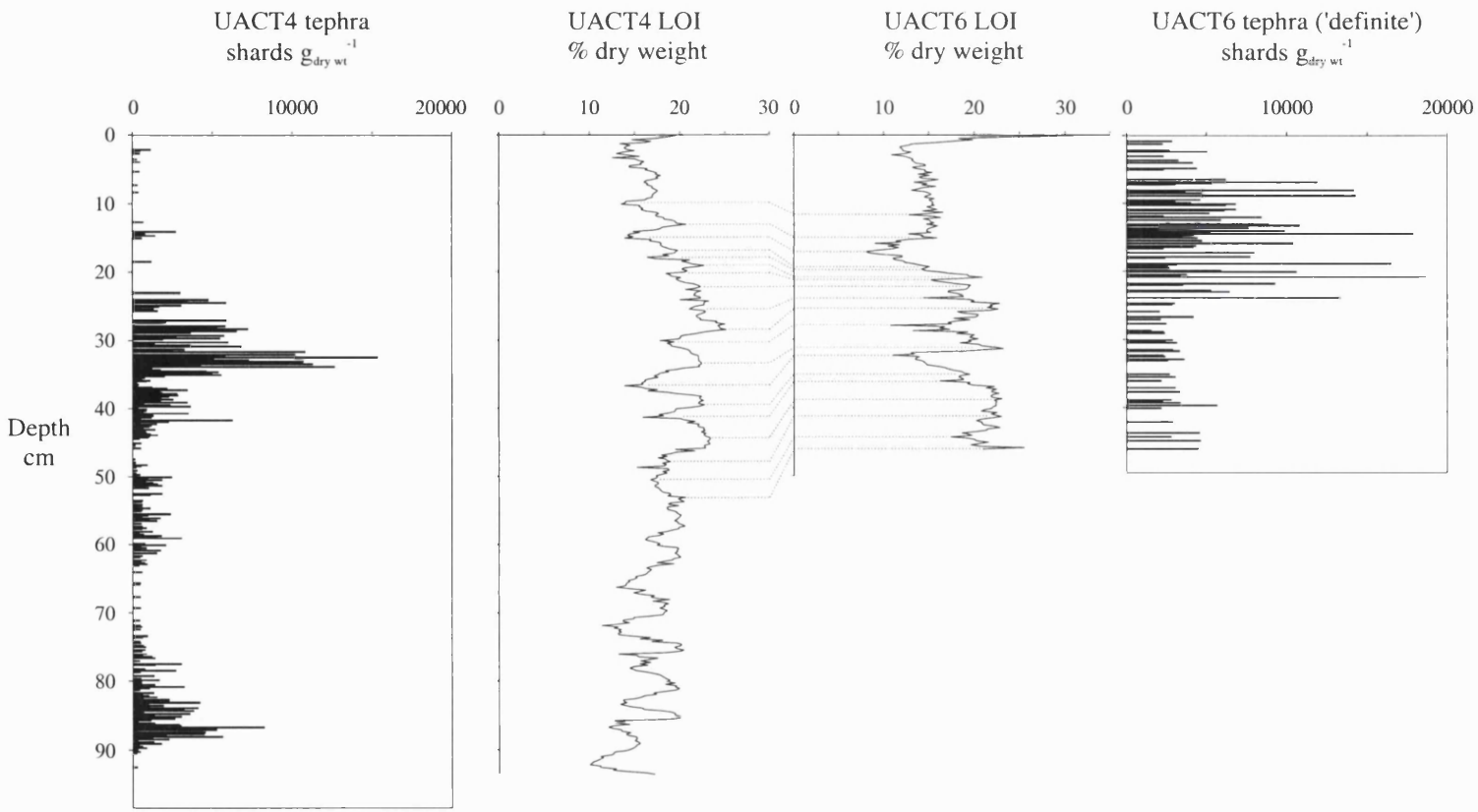


Figure 3.13 Comparison of tephra profiles from UACT4 and UACT6, with LOI-based core correlation.

3.4.4 Microtephras in lake sediments

The problem of stratigraphically diffuse tephra horizons in lake sediments is not unique to Lochan Uaine. Although a distinctive peak in concentration of the early Holocene Saksunarvatn tephra was seen by Bennett *et al.* (1992) at Dallican Water, Shetland, the total spread of shards spanned a depth of around 50 cm. As at Lochan Uaine, a low background of tephra shards was found throughout the sediment core. Diffuse peaks were also seen for a more recent double tephra layer. Geochemical analyses of these layers were inconclusive, and the authors acknowledged the possibility of disturbance to the sediment profile: "Whether the double peak of tephra at Dallican Water represents two separate events or one event disturbed by within lake processes must await investigation at other sites" (Bennett *et al.*, 1992, page 254). The same conclusion was reached by Wastegård *et al.* (1998), who attributed a double peak in the Lateglacial-age Vedde Ash in Lake Madtjärn, Sweden, to sediment reworking or bioturbation. They also suggested that a small number of shards found up to 6 cm above the main tephra layer may indicate inwash of tephra from the lake catchment. Diffuse tephra layers in lake sediments, probably due to sediment reworking, bioturbation or catchment inwash, are also recorded in Norway (Mangerud *et al.*, 1984), Germany (Merkt *et al.*, 1993), Scotland (Turney *et al.*, 1997), the Faroe Islands (Mangerud *et al.*, 1986), Iceland (Thompson *et al.*, 1986), Alaska (Child *et al.*, 1998), and Antarctica (Dyson, 1996; Hodgson *et al.*, 1998), although in some cases the tephra is spread over only a few centimetres depth and a single peak is clearly visible. Thompson *et al.*'s (1986) analysis of Hekla tephras in Lake Svinavatn demonstrated how inwash of tephra from the catchment results in an exponential decay in tephra concentration following the main deposition peak. They estimated that in the region of 3% of tephra deposited on the catchment is subsequently transported to the lake sediment. Lake Svinavatn is a large (11.7 km^2) lowland lake with a low relief catchment, and the corresponding proportion of tephra redeposited from catchment to lake in a small, steep-sided upland catchment such as Lochan Uaine is not known. Some studies have found no significant diffusion of tephra in lake sediments (Merkt *et al.*, 1993; Björck and Wastegård, 1999). Merkt *et al.* attribute this low diffusion to the prevention of catchment erosion by a surrounding dense boreal forest.

It is thought that the diffuse tephra profiles seen in Lochan Uaine may reflect reworking of tephra. This may either be through the erosion of catchment soils on which tephra has been deposited, or from sediment focusing of marginal lake sediments into the deepest part of the basin. It is not thought that bioturbation is an important process at Lochan Uaine, as all cores taken show sharp features in LOI profiles which bioturbation would be expected to obscure. The differences in tephra profiles between cores UACT4 and UACT6 are harder to explain. They may be related to the low tephra concentrations compared to other mineral particles, as it was necessary to count large numbers of non-tephra particles to find even a few tephra shards. Differences in tephra identifications between the two analysts who counted the two cores may also be significant.

Identification of low tephra concentrations is not a problem if other mineral matter can be removed. Biogenic silica may be removed using the technique of Rose *et al.* (1996), and mineral matter of a differing density from tephra may be removed with the density separation technique of Turney (1998). Using these methods, Turney *et al.* (1997) identified tephra peaks of the Lateglacial-age Vedde Ash in concentrations as low as 50 shards cm^{-3}. However, the diffuse nature of the Lochan Uaine tephra profiles suggests that geochemical typing of tephra shards would not help to validate the radiocarbon chronology, as the tephra do not come from stratigraphically well-defined layers. Also, the peaks in UACT4 do not show the exponential decay in concentration as proposed by Thompson *et al.* (1986) with their model of tephra deposition and catchment inwash. It is thus not known whether the maximum values within each diffuse tephra peak represent the moment of atmospheric tephra deposition, or a subsequent inwash or redeposition of tephra in a greater concentration than was originally deposited. Despite these problems at Lochan Uaine, it is possible that other similar sites may contain better Holocene tephra records. Work is currently underway on cores from Lochnagar to ascertain this (Dalton *et al.*, 2000).

3.5 Construction of core chronologies

Of the three main cores studied at Lochan Uaine, radiometric dating is available for UACT4 only, while tephra profiles are available for UACT4 (Battarbee *et al.*, 1996; Battarbee *et al.*, in press) and UACT6, although no tephra peaks are identified through geochemical analysis. No independent dating is available for UACT3. This section describes the construction of the core chronology for UACT4, and the subsequent transfer of this chronology to UACT3 and UACT6 through lithostratigraphic core correlation.

3.5.1 UACT4 Core chronology

Several methods were used to establish a depth-age model for UACT4. The topmost sediments are dated by ^{210}Pb, and similar results are seen with both the CIC and CRS models (Figure 3.8). ^{137}Cs is not used due to the high mobility of caesium in the sediment, but the presence of ^{241}Am in a single level provides a marker horizon in agreement with the ^{210}Pb chronology. Thirty-six radiocarbon dates are available for the whole core, although the two samples in the upper 10 cm are thought to be contaminated with old carbon from industrial age fossil fuel burning and are excluded from all subsequent analyses. Finally, although no tephra layers are identified as originating from known, dated eruptions, it is possible that the downcore distribution of tephra peaks may have chronological significance when compared to the radiocarbon profile.

The principal method used for constructing a whole core depth-age model was radiocarbon dating. Uncalibrated radiocarbon ages from UACT4 were presented above (Figure 3.9). It is necessary to calibrate these dates for two reasons. Firstly, radiocarbon ages are not directly comparable to calendrical dates due to the *c.* 3% error in the Libby ^{14}C half-life calculation (Libby, 1955; Godwin, 1962; Stuiver and Polach, 1977; Mook, 1986), and due to the secular variations in ^{14}C production throughout the Holocene (Stuiver and Becker, 1993; Taylor *et al.*, 1996). This difference prevents the linking of calendrical ^{210}Pb dates and uncalibrated, non-calendrical ^{14}C ages to produce a master chronology for the whole core. Secondly, it is not possible to compare uncalibrated ^{14}C timescales with records based on

calendrical timescales, such as tree rings, ice cores and historical climate records. Such comparisons are essential if the impacts of climate change on Lochan Uaine sediments are to be evaluated.

3.5.1.1 Correction of radiocarbon ages for contamination by old carbon

The thirty-four radiocarbon ages used for the dating show a very strong linear relationship, and the R^2-value of 0.962 is significant at above the 99.5% level (Figure 3.9). However, the intercept with the surface at 488 ^{14}C yr BP (ref. 1950) suggests a consistent source of old carbon in the lake sediment, with a suggestion that this may be more important during periods of low organic input (Figure 3.10; Section 3.3.2). The presence of old carbon prevents accurate calibration of the radiocarbon ages, as the calibration would be performed on erroneous uncalibrated ^{14}C ages. For this reason, two radiocarbon calibrations are performed to allow comparison between chronologies constructed with and without a correction for the possible presence of old carbon. To correct for old carbon, 488 ^{14}C yr are subtracted from all thirty-four radiocarbon ages (Appendix E). The error ranges are not altered. This creates a linear regression through the ^{14}C ages which intercepts the surface at 0 ^{14}C yr BP (ref. 1950). Although the surface sediment is known to represent the present day from the ^{210}Pb chronology, this is not inconsistent with a surface *radiocarbon* age of 1950. All radiocarbon ages are quoted relative to 1950, and the difference between this and the actual date of the surface sediment is corrected for during the radiocarbon calibration. These ^{14}C ages corrected for a 488 yr offset are then used in the calibration.

It is worth commenting on the use of a linear regression model in the correction for old carbon. This assumes a constant rate of sediment accumulation. In reality, this is unlikely to be the case. The lithostratigraphic core correlation (Figures 3.2 and 3.7) demonstrates that differences exist between the relative sediment accumulation rates of the three main Lochan Uaine cores. Given that the accumulation rate is not constant, a non-linear regression will be more accurate. However, it is not possible to determine the correct non-linear regression to be used. Battarbee *et al.* (1996) found a quadratic curve to give a better fit to the ^{14}C ages, as did Mauquoy and Barber (1999a) in their study of northern England peat bog sequences. This is to be expected,

as a quadratic curve will always give a closer fit to any set of points that do not lie in a straight line. Likewise, higher order polynomial curves will give increasingly better fits to the data (*e.g.* Chambers *et al.*, 1997), and taken to the extreme a 34th order polynomial will give a perfect fit to the 34 radiocarbon ages. However, as the goodness of fit of the model increases so the predictive power of that model decreases. Ideally the model used should have both a good fit and a high predictive power. As the linear regression through the radiocarbon dates is significant at above the 99.5% level, it is not thought that use of a non-linear regression is justified as the increase in goodness of fit by doing so is minimal. Use of a linear regression is not a perfect solution to the problem of constructing the radiocarbon depth-age model. Importantly, the average sediment accumulation rate suggested by the regression, 0.25 mm yr^{-1} (^{14}C years), is lower than that calculated from ^{210}Pb dates, 0.30 mm yr^{-1} (calendar years), even allowing for the difference between uncalibrated radiocarbon ages and calendrical dates. There is evidence in the magnetic measurements of UACT4 to indicate a recent (last few hundred years) increase in sediment accumulation rate (Battarbee *et al.*, 1996), and this may explain the observed differences between the ^{210}Pb and ^{14}C-derived accumulation rates. Fitting a quadratic curve to the uncalibrated radiocarbon ages gives an accumulation rate that increases from 0.22 mm yr^{-1} at the base of UACT4 to 0. 27 mm yr^{-1} at the surface (P. Appleby, pers. comm.). This value is closer still to the accumulation rate obtained from ^{210}Pb dating, although there is still a *c.* 500 yr offset in age where the quadratic curve intercepts the surface.

3.5.1.2 Calibration

The calibration of the radiocarbon dates from UACT4 was performed with the program CALIB version 4.1 (Stuiver and Reimer, 1986, 1993) using the atmospheric sample dataset INTCAL98.14C (Stuiver *et al.*, 1998a,b). 'Calculation Method B' was used throughout, which calculates the probability distribution around the calendar age intercepts, and estimates the relative importance of each age range. Two calibrations were carried out as detailed above - one on unaltered ^{14}C ages, and one on ^{14}C ages corrected for the 488 yr old carbon offset suggested by the linear regression. The results of both calibrations are listed in Appendix E and shown in Figure 3.14.

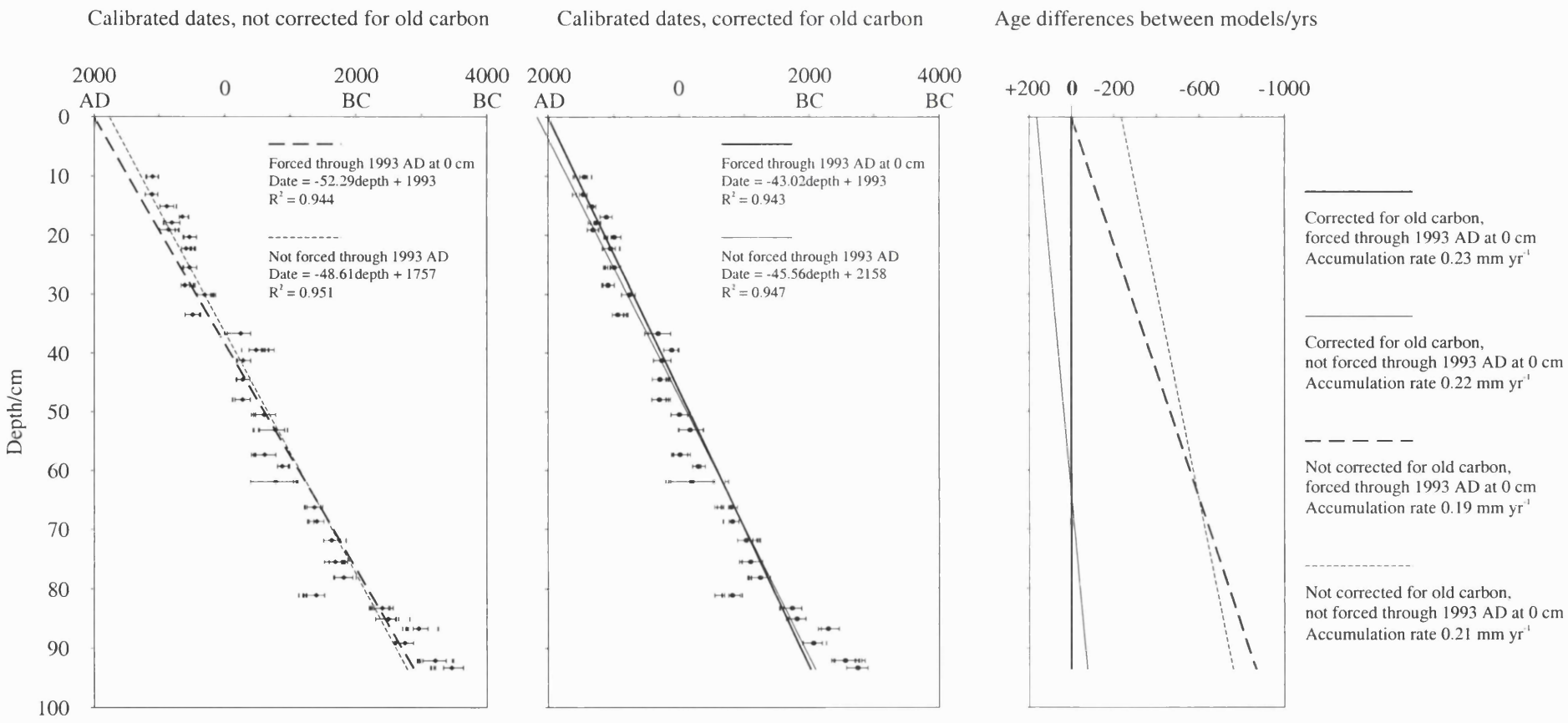


Figure 3.14 Radiocarbon calibration models for core UACT4. Four models are shown: with or without the 488 yr old carbon correction, and with or without forcing through 1993 AD at the surface to agree with the ^{210}Pb depth-age model. Also given are the differences in date estimations between the models, shown relative to the model thought most likely to represent an accurate depth-age curve for UACT4. This model contained the correction for old carbon, and the forcing through 1993 AD at 0 cm.

Neither set of calibrated dates when fitted with a linear regression intercepts the surface at 1993 AD, the year when the core was taken. The uncorrected dataset gives a date of 1764 cal AD at 0 cm, or 229 cal yr too old. The dates corrected for the 488 yr old carbon offset give a value of 2165 cal AD at the surface, or 172 cal yr too young. As the recent chronology of UACT4 is well established by ^{210}Pb dating, it is possible to force the calibrated ^{14}C linear regressions to intercept with 1993 AD at the surface. In both cases this results in a change in accumulation rate and a small decrease in the R^2-value, although the regression is still significant at above the 99.5% level (Figure 3.14). The accumulation rates vary from 0.19 mm yr^{-1} for ^{14}C ages not corrected for old carbon and forced through 1993 AD at 0 cm, to 0.23 mm yr^{-1} for ^{14}C ages corrected for old carbon and forced through 1993 AD at 0 cm. The total difference in date estimations between the four models is smallest at the surface (401 cal yr), and greatest at the core base (868 cal yr). Over the *c.* 4-4.5 kyr timescale represented by UACT4 these differences are not inconsiderable. These difficulties with the radiocarbon chronology were one of the primary reasons for the tephra analysis undertaken on the core.

3.5.1.3 Validation of combined ^{210}Pb/^{14}C chronology by tephra analysis

The aim of the tephra analysis of UACT4 is to provide an independent means of dating the core and, importantly, of validating the radiocarbon chronology. The tephra profile of Battarbee *et al.* (1996) was presented above (Figure 3.11). Unfortunately, geochemical typing of tephra shards was not successful. This is thought to be due mainly to the large amounts of non-tephra mineral matter present in the samples, although Battarbee *et al.* (1996) do not employ the flotation technique of Turney (1998) to isolate the tephra shards. The lack of geochemical typing prevents identification of individual tephra peaks. It is thus not possible to use the tephra peaks to validate the radiocarbon chronology.

Despite the failure to identify tephra layers in UACT4 geochemically, it is interesting to compare the peaks in shard concentration with the calibrated radiocarbon chronologies. The possible origins of the tephra peaks has been mentioned previously. In particular, it is suggested that the peak with a maximum at 14 cm depth may be the

Hekla 1510 eruption, while the lower peak with a maximum at 87 cm may be the Hekla 4 eruption dated to 2310±20 cal BC by Pilcher *et al.* (1995). The dates of these peaks as calculated from the four radiocarbon calibration models are given in Table 3.6. The closest dating of the possible Hekla 1510 tephra is seen with the two models corrected for the 488 yr old carbon offset, while the closest dating of the potential Hekla 4 tephra is provided by the two models with no old carbon correction. In both cases the differences may be attributable in part to the diffuse nature of the tephra peaks. This is particularly true of the possible Hekla 4 tephra which is spread over a depth of *c.* 10 cm. Depending on the model used this represents a duration of around 430-520 cal yr, which is a significant fraction of the *c.* 800 cal yr age differences between the four calibrated date models given in Table 3.6. The possible Hekla 1510 tephra is spread over 1 cm depth, representing an age error of 40-50 cal yr compared to the *c.* 440 cal yr spread of the estimated dates. This problem of diffuse tephra peaks would remain even if the tephras are geochemically identified. Without accurate geochemical identification of the UACT4 tephras, however, it is unwise to place any interpretation on these results.

Table 3.6 Possible identification of tephra peaks in UACT4, and corresponding dates under the four radiocarbon calibration models. Age deviation from the accepted dates of the tephras are given in italics.

Possible tephra layer:	Hekla 1510	Hekla 4
Depth in UACT4:	14 cm	87 cm
Date of eruption:	1510 AD	2310±20 BC*
No old carbon correction, not forced through 1993 AD at surface	1083 AD *-427 cal yr*	2465 BC *-155 cal yr*
No old carbon correction, forced through 1993 AD at surface	1268 AD *-242 cal yr*	2549 BC *-239 cal yr*
488 yr old carbon correction, not forced through 1993 AD at surface	1527 AD *+17 cal yr*	1798 BC *+512 cal yr*
488 yr old carbon correction, forced through 1993 AD at surface	1398 AD *-112 cal yr*	1743 BC *+567 cal yr*

* Date from Pilcher *et al.* (1995)

Given the above discussion, the model corrected for old carbon and forced through 1993 AD at 0 cm is favoured for providing the master chronology for core UACT4. There are two principal reasons for preferring this model. Firstly, the intercept with

1993 AD at 0 cm is in agreement with the ^{210}Pb dates, although the sediment accumulation rates are slightly different. Secondly, a correction for the possible input of old carbon to the sediment is provided. The source of this old carbon is not known, although it may originate from the inwash of catchment soils, sediment focusing of older marginal material in the lake, or some aquatic reservoir effect (Oldfield *et al.*, 1997b; Björck *et al.*, 1998). There is some indication that radiocarbon ages from LOI minima give relatively older ages than those from LOI maxima, and there may also be a continuous background input of old carbon to the sediment.

3.5.2 UACT3 Core chronology

No radiometric or tephrochronological dating of UACT3 was carried out. Rather, the chronology determined for core UACT4 can be transferred to UACT3 by correlation of the dry weight and LOI profiles. The core correlation determined by Battarbee *et al.* (1996) was presented in Figure 3.2. Although UACT3 is longer at 119.4 cm, the sediment accumulation rate is slightly lower than that of UACT4 by around 1% overall. The relative accumulation rates of the two cores vary downcore. The base of UACT4 at 93.6 cm, dated to *c.* 2030 cal yr BP using the preferred calibration model, correlates to a depth of 89.5 cm in UACT3. By extrapolation, the base of UACT3 is estimated as around 3100 cal yr BP, although a substantial error will be associated with this estimate. For example, a similar extrapolation using the UACT4 calibration model without an old carbon correction and forcing the regression through 1993 AD at the surface gives a date of 4200 cal yr BP for the base of UACT3, a difference of *c.* 1100 cal yr from the previous estimate. A similar difficulty is encountered with the dating of UACT6, discussed below. As UACT3 was not analysed as part of this project but as part of the TIGGER IIa project, the dating of the core is not discussed further here.

3.5.3 UACT6 Core chronology

Core UACT6 is not dated directly by the ^{210}Pb or ^{14}C methods, but relies on correlation with UACT4 through the dry weight and LOI profiles, as did UACT3. The tephra analysis carried out in an attempt to validate the transferred chronology from UACT4 was described above. However, the poor results from this analysis

prevent the identification of discrete tephra horizons, and it is thus not possible to use the tephra analysis for dating purposes.

The best correlation between UACT4 and UACT6 was given in Figure 3.7. Figure 3.15 shows the steps in the construction of the depth-age model for UACT6. This uses the preferred calibration model for UACT4, namely that allowing for a 488 yr old carbon offset in the uncalibrated radiocarbon ages and forcing the best fit linear regression to intercept with the surface at 0 ^{14}C yr BP (ref. 1950). The regression through the calibrated dates is then also forced to intercept the surface at 1993 AD, in agreement with the ^{210}Pb depth-age model. Two possibilities exist for transferring the UACT4 calibrated date model to UACT6. The first is to transfer the calibrated radiocarbon dates directly from UACT4 to UACT6. All radiocarbon-dated samples from UACT4 are taken from LOI maxima and minima, so it is possible to transfer these dates to the corresponding LOI maxima and minima from UACT6. The depth-age model for UACT6 is then based on a linear regression through these dates. The second possibility is to calculate the dates for LOI maxima and minima in core UACT4 according to the best fit linear regression model for that core, and then to transfer these dates to the corresponding LOI maxima and minima in UACT6. As before, a depth-age model for UACT6 can be constructed based on the linear regression through these dates. The first of these two methods is preferred. Assuming the correlation between the LOI maxima and minima in the two cores is correct, a direct transfer of calibrated radiocarbon dates from UACT4 to UACT6 will only transfer those errors present in the original calibration. By contrast, the method of using dates calculated from the UACT4 linear regression model will transfer additional errors associated with this model. Specifically, the linear regression model assumes a constant sediment accumulation rate throughout the core. Correlation of the three main Lochan Uaine cores demonstrates that there are changes in downcore sediment accumulation rate within and between all three cores (Figure 3.7). This second method thus transfers errors in calculating the accumulation rate of UACT4 onto core UACT6, whereas the first method avoids this problem. The four year gap between the coring of UACT4 in 1993 and UACT6 in 1997 is not thought to add significantly to any dating errors already present in the model.

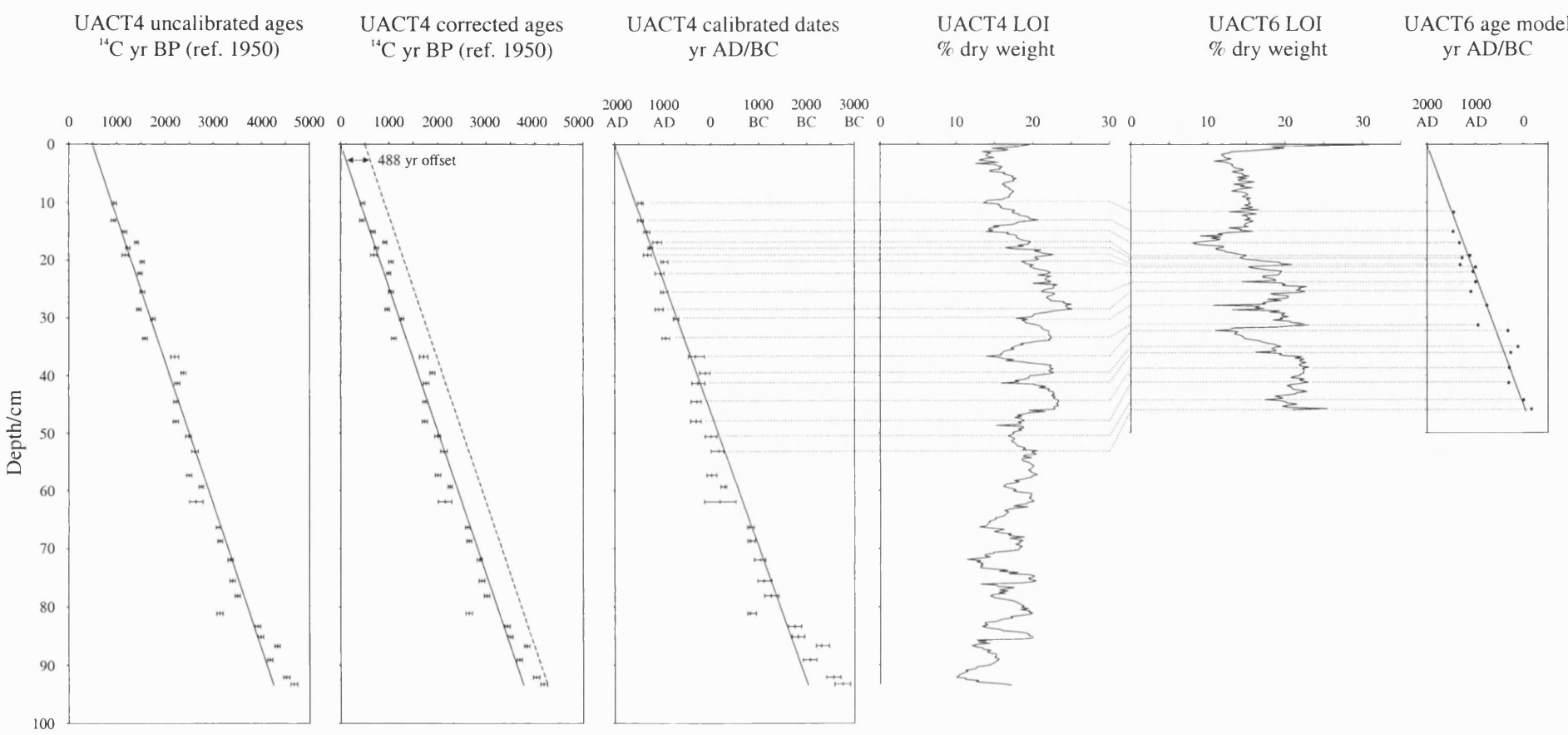


Figure 3.15 Construction of depth-age model for UACT6 based on radiocarbon dating of UACT4. The top two dated samples (5.8-6.0 and 8.0-8.2 cm depth) were excluded from the analysis and are not shown.

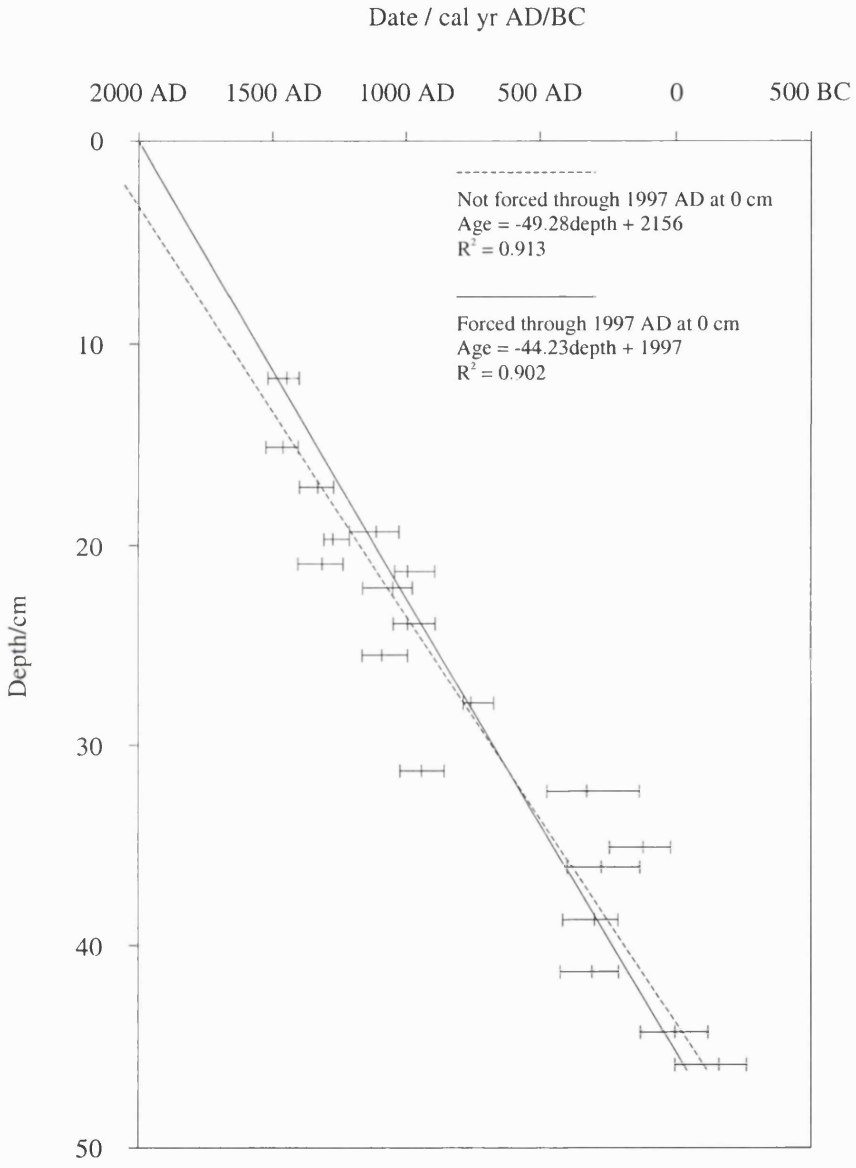


Figure 3.16 Dating of core UACT6. Best estimate calibrated radiocarbon dates (488 yr old carbon correction, forced through 1997 AD at 0 cm) were transferred from UACT4 to UACT6 by correlation of LOI maxima and minima. Median dates are shown, as are the most probable 2 σ error ranges.

Figure 3.16 shows the UACT6 depth-age model constructed following the procedure given in Figure 3.15 and described above. At 46.2 cm long, core UACT6 is significantly shorter than UACT4. Only nineteen of the thirty-four calibrated radiocarbon ages used to date UACT4 can be transferred from UACT4 to UACT6. As is found with the dating of UACT4, the best fit linear regression through the UACT6 dates does not fall through the present day (*i.e.* 1997 AD) at the surface. Although the upper sediments of UACT6 are not dated by ^{210}Pb, it is reasonable to assume that the surface sediment represents the present day. UACT6 was recovered from the same area of Lochan Uaine as UACT4, and in a similar depth of water. It is unlikely that a hiatus would be present in UACT6 but not in UACT4. For this reason, the linear regression of the UACT6 calibrated radiocarbon dates is forced through 1997 AD at the surface. This reduces the R^2-value of the regression from 0.913 to 0.902. Both of these values are significant at above the 99.5% level. Using this model, the base of UACT6 at 46.2 cm is dated to *c.* 50 BC. The average sediment accumulation rate for the core is 0.226 mm yr^{-1}, slightly lower than the 0.232 mm yr^{-1} accumulation rate for the preferred dating model of UACT4. As with UACT4 a significant error will be associated with the dating of UACT6. Based on the 2σ ranges of the calibrated radiocarbon dates and the differences between the various possible dating models of the cores, this error is estimated to be as large as 500 years at the base of UACT6. This is mostly due to the need to correct for the possible *c.* 500 yr old carbon effect in the construction of a dating model for UACT4. In all dating models the error should decrease upcore as the surface sediment almost certainly represents the present day.

3.6 Summary

The first section of this chapter describes the lithostratigraphy of cores recovered from Lochan Uaine. Downcore dry weight and LOI profiles are presented for UACT3 and UACT4 (analysed by Battarbee *et al.*, 1996; Barber *et al.*, 1999; Battarbee *et al.*, in press), UACT2 (recovered as part of the TIGGER IIa project, but analysed as part of this study), and UACT6, UACT8 and UACT11 (recovered and analysed as part of this study). All cores exhibit prominent downcore variations in dry weight and LOI,

with the exception of UACT2 which is thought to have been cored at an angle. Core UACT6 is chosen as the master core for this study. Correlations between the LOI profiles of UACT6 and UACT3/UACT4 are presented.

The second section of this chapter describes the construction of a core chronology for UACT6. As no radiocarbon dates are available for UACT6, it is necessary first to construct a calibrated chronology for UACT4, and then to transfer this to UACT6 on the basis of the correlation between the UACT4 and UACT6 LOI profiles. The radiometric dating of UACT4 is discussed. An attempt is made to use tephrochronology as a means of dating UACT4 and UACT6, but this is unsuccessful due to a number of reasons. Tephra is present in low concentrations compared to other mineral particles, and locating and identifying tephra shards within this mineral matrix is problematical. It is possible to remove the mineral matrix by density separation (Turney, 1998). However, the tephra peaks identified in UACT4 by Battarbee *et al.* (1996) are stratigraphically diffuse, and as such are of little use in validating the radiocarbon chronology. No major peaks are seen in UACT6, and a poor correlation between the tephra profiles of UACT4 and UACT6 is evident.

The final section describes the calibration of the UACT4 radiocarbon chronology, and the transfer of this chronology to UACT6. The steps followed in this process may be summarised as follows:

1) ^{210}Pb analysis of the top of UACT4 shows that the surface corresponds to the present day (*i.e.* 1993 AD, when the core was taken).

2) Thirty-six AMS radiocarbon ages of bulk sediment are available for UACT4, of which the top two are excluded from all analyses due to possible contamination with industrial-age carbon.

3) A linear regression through the uncalibrated ^{14}C ages indicates an intercept with the surface at 488 ^{14}C yr BP (ref. 1950). This suggests contamination by old carbon (Oldfield *et al.*, 1997b; Björck *et al.*, 1998).

4) The uncalibrated ^{14}C ages are corrected for old carbon by subtracting 488 ^{14}C yr, so that the linear regression passes through 0 ^{14}C yr BP (ref. 1950) at the surface.

5) The corrected ^{14}C ages are calibrated using the program CALIB version 4.1 (Stuiver and Reimer, 1986, 1993) and the atmospheric sample dataset INTCAL98.14C (Stuiver *et al.*, 1998a,b). 'Calculation Method B' is used.

6) Of the thirty-four calibrated dates, nineteen are transferred to UACT6 using the LOI correlation between UACT4 and UACT6.

7) A linear regression is plotted through the nineteen calibrated dates which were transferred to UACT6. This is forced to intercept the surface at 1997 AD when the core was taken. The linear regression forms the preferred dating model for UACT6, which has the following equation:

$$\text{Date AD/BC} = -44.23x(\text{depth in centimetres}) + 1997 \qquad [3.1]$$

Using this model, the base of UACT6 at 46.2 cm is dated to about 50 BC. The sediment accumulation rate of the core is about 0.0226 cm yr^{-1}, slightly lower than that seen in UACT4.

Chapter 4

Bulk Sediment Analyses

4.1 Introduction

The previous chapter described lithostratigraphic analysis of cores recovered from Lochan Uaine. In all cores, dry weight and LOI show major fluctuations downcore. Correlation between these fluctuations was used to date the main core used in this study, UACT6, by transferring a ^{210}Pb and ^{14}C-based chronology from core UACT4. The LOI variations indicate changes in the ratio of organic to mineral matter in the sediment. They do not indicate which of these fractions drives the changes. For example, a switch from high to low LOI could indicate a decrease in total organic input, an increase in total mineral input, or a combination of both. Without knowing the precise nature of the variation, it is often difficult to place a palaeoenvironmental interpretation on LOI variations.

The difficulty of interpreting LOI variations alone is demonstrated by considering the possible sources of organic and mineral matter to the sediment, as shown by Table 4.1. Both organic and mineral matter could originate in the lake, in the catchment, and outside the catchment. At Lochan Uaine siliceous diatom remains are very abundant in the sediment mineral fraction (Battarbee *et al.*, 1996), yet diatoms will also contribute organic matter to the sediment. Thus, it is not known whether an increase in diatom productivity would be associated with a relative increase in mineral content (*i.e.* a decrease in LOI) or an increase in organic content (*i.e.* an increase in LOI).

Table 4.1 Indication of the potential sources of organic and mineral matter to lake sediments.

Type of material (organic/mineral)	Source (lake/catchment/outside catchment)	Sediment fractions
Organic	Lake	Algae, aquatic macrophytes, bryophytes, chironomids, bacteria, aquatic animals
Mineral	Lake	Biogenic silica (diatoms, chrysophytes), carbonate
Organic	Catchment	Vascular plants, bryophytes, soils, peats, pollen, animals
Mineral	Catchment	Clastic material, phytoliths, carbonate
Organic	Outside catchment	Pollen, animals, organic pollutants (*eg.* PAHs)
Mineral	Outside catchment	Aeolian dust, tephra, carbonaceous particles

Analyses of certain properties of the mineral fraction of the Lochan Uaine sedimentary record are described by Battarbee *et al.* (1996). Contiguous magnetic measurements

from throughout UACT3 show that the magnetic properties are derived almost exclusively from lithogenic catchment materials. Downcore shifts in some of these properties are seen, notably in the 'hard' IRM component, but the variations in different components do not appear to be strongly related to each other or to the LOI profile. It is suggested that the magnetic fluctuations may reflect particle size variations, differing importances of catchment sources of magnetic minerals, or shifts in the relative proportion of lithogenic inputs compared to other sediment fractions. The lack of close coherence between magnetic measurements and LOI is perhaps surprising, although Battarbee *et al.* (1996) note that the measurements are close to the noise level of the method used. Particle grain size analysis of a 15 cm section of core UACT4 shows a close relationship between increased LOI and increased grain size. However, the sediment is dominated by diatom remains, and particle size variations are thought to reflect systematic changes in diatom cell size or diatom breakage, rather than size variations in the catchment-derived clastic material. Finally, determination of metal contents in UACT3 (lead, iron, copper, nickel, manganese, cobalt, zinc, magnesium, calcium, aluminium) does not reveal any coherent variations in concentration (unpublished data).

Given the inconclusive results of these analyses of the sediment mineral fraction, it was decided in this study to focus on the sediment organic fraction. This chapter describes the measurement of bulk sediment parameters, including total organic carbon (TOC), chlorin content and bulk organic $\delta^{13}C$. Although all organic matter in lake sediments is susceptible to diagenesis, it is thought that palaeoenvironmental information contained in bulk measurements may be less susceptible to influence by diagenetic alteration than that found in minor sediment constituents (Meyers and Lallier-Vergès, 1999). Diagenetic problems in minor sediment constituents are discussed in Chapter 5 in relation to lipid analysis.

4.2 Dry Weight and Loss-on-Ignition

Dry weight and LOI for core UACT6 were measured using the methods described in Chapter 2, and downcore profiles of these values have been presented previously in

Chapter 3 (Figure 3.4). Significant variations in both parameters are seen, and a strong correlation exists between higher dry weight values and lower LOI values. This was expected as inorganic matter has a greater density, and correspondingly has a lower water content, than organic matter. In non-calcareous sediments such as those in Lochan Uaine, LOI may generally be used as a proxy for sediment organic content (Allen *et al.*, 1974).

4.3 Carbon, Nitrogen, Hydrogen, Carbonate

Bulk carbon, nitrogen, hydrogen and carbonate were measured by the Microanalytical Section, School of Chemistry, University of Bristol. Bulk carbon and carbonate measurements, and the associated organic carbon content, are dealt with together. Nitrogen and hydrogen will be examined separately. Finally, the C/N and C/H ratios will be discussed.

4.3.1 Bulk carbon, carbonate, and organic carbon

Given the base-poor geology of Lochan Uaine, and knowledge of the physical, chemical and biological systems which typically operate in remote mountain lakes and their catchments, it is expected that most of the carbon in the sediment of Lochan Uaine will be in the form of organic compounds. Very little is expected to be present as inorganic carbon. LOI analysis of the sediment supports this hypothesis. The mass loss upon ashing at 550°C is in the region of 10-20% of dry weight (Section 3.2). This mass loss is caused by oxidation of organic compounds to release CO_2. A few samples were ashed at 925°C following the method of Bengtsson and Enell (1986) to calculate carbonate content. The resulting values are all below 0.1% of dry weight. Carbonate values obtained by this method are thought likely to be prone to significant measurement errors and the decision was made not to proceed with the analysis for the whole core. Subsequent analysis by the Microanalytical Section, School of Chemistry, University Of Bristol, confirms the low carbonate content throughout UACT6.

The bulk carbon content of UACT6 is shown in Figure 4.1. Both LOI and bulk carbon content exhibit similar downcore profiles. This supports the hypothesis that the majority of the carbon found in the sediment is in the form of organic molecules, as mentioned above with regard to LOI analysis. The hypothesis is confirmed by the very low carbonate content measured (Figure 4.1). Carbonate is present at below 0.2% of dry weight throughout almost the entire core.

By subtracting the mass of carbonate from the mass of bulk carbon content, the organic carbon content of the core can be calculated. As the carbonate content is very low throughout the core, bulk carbon content and organic carbon content are practically identical.

4.3.2 The relationship between LOI and organic carbon

It has been suggested that under certain conditions LOI and organic carbon content of non-calcareous sediments are related by a simple conversion factor, allowing organic carbon content to be calculated from the LOI value, and *vice versa*. Other studies find a more complex relationship between LOI and organic carbon. Mackereth (1966) found that the LOI/TOC ratio is relatively constant at around 2 in lake sediments with TOC contents greater than *c.* 10%. At progressively lower carbon contents, an increase in the ratio is seen. For example, LOI/TOC ratios of around 3 are recorded in sediments with an organic carbon content of 3%. A near-identical relationship was seen by Håkanson and Jansson (1983) in sediments from different areas of Lake Mälaren, Sweden, who suggest that the relationship TOC = (LOI/2) only holds for LOI values above 10%. It may thus be inappropriate to use a single constant to convert LOI values to organic carbon contents (Cato, 1977), especially at low concentrations or where large magnitude differences in concentration are seen. Bengtsson and Enell (1986) urge caution in using conversion factors even within different parts of the same core, while noting that in most cases organic carbon represents 40-60% of the LOI value.

The assumption that LOI is a direct proxy measure of sediment organic content does not hold true in all circumstances. In highly inorganic sediments, ashing at 550°C may

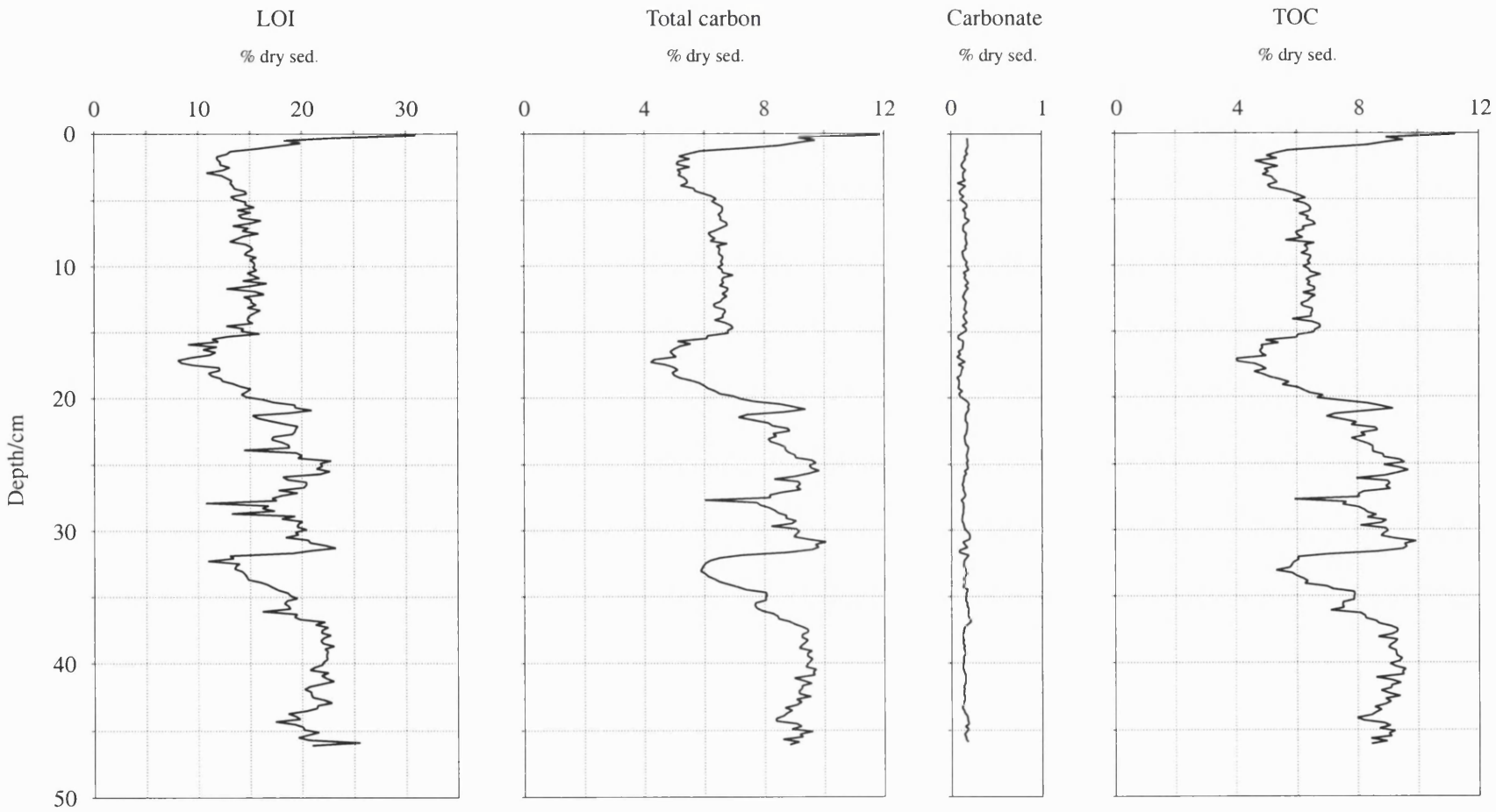


Figure 4.1 LOI, total carbon, carbonate, and TOC, core UACT6. Horizontal scale varies.

remove not just organic matter, but also water chemically bound to the mineral matrix and not removed during the previous drying at 105°C (Mackereth, 1966; Håkanson and Jansson, 1983; Bengtsson and Enell, 1986; Sutherland, 1998). This is particularly true in sediments with a high clay content, in which case samples with a comparatively high organic content may be affected. Sutherland (1998) notes that while LOI/TOC ratios in soils are generally in the range 1.7 to 2.2, similar to the values for lake sediments observed by Mackereth (1966) and Håkanson and Jansson (1983), in fluvial bed sediments ratios from 6.2 to 27.4 are recorded. This is attributed to water loss by dehydration of iron, aluminium and manganese oxides at 450°C. The extent of this problem in the analysis of Lochan Uaine sediment is not known, although it is thought to be minimal owing to the comparatively high organic content (*c.* 10-20%) and the predominance of silt-sized siliceous diatom remains in the mineral matrix (Battarbee *et al.*, 1996).

It was noted previously that LOI and total carbon, and hence also TOC, show similar downcore variations in UACT6. This correlation is shown in Figure 4.2. The R^2-value of 0.865 is significant at above the 99% level. The best fit linear regression is given by the following equation:

$$\%TOC = 0.381(\%LOI) + 1.061 \quad [4.1]$$

The fact that the regression line does not pass exactly through the origin may suggest that the correlation is not perfectly linear, as suggested by Mackereth's (1966) and Håkanson and Jansson's (1983) data. Non-linear regression curves only give marginally higher R^2-values when fitted to the data in Figure 4.2. By comparison, the linear regression measured by Håkanson and Jansson (1983) is given below:

$$\%TOC = 0.48(\%LOI) - 0.73 \quad [4.2]$$

A further indication of whether the relationship between LOI and TOC is linear may be seen by comparing TOC with the ratio of LOI/TOC (Figure 4.3). The LOI/TOC ratio remains relatively constant at *c.* 2.5 (*i.e.* approximately 1/0.381, from Equation

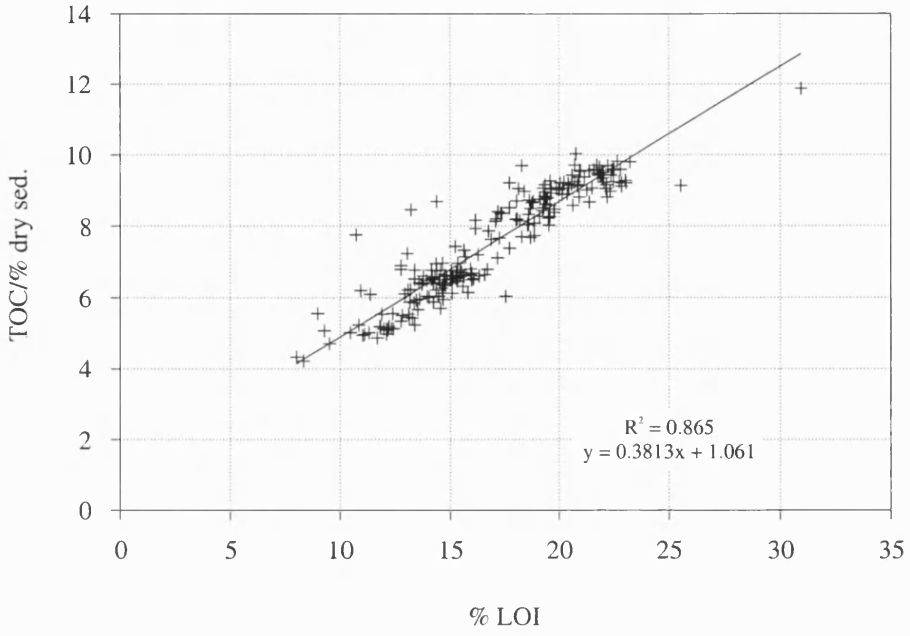


Figure 4.2 LOI *vs* TOC content (expressed as a percentage of dry sediment), core UACT6. The correlation is significant at the 99% level.

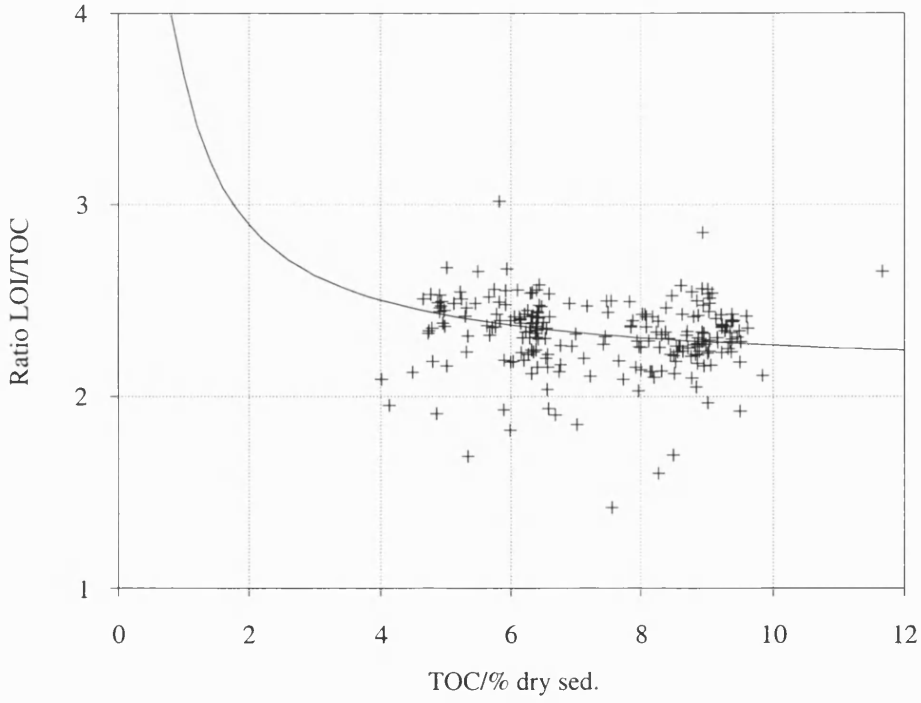


Figure 4.3 Comparison of LOI/TOC ratio with TOC content of sediment, core UACT6. The line represents the relationship found by Håkanson and Jansson (1983, page 77) for surface sediment from three bays in Lake Mälaren, Sweden.

4.1) across the whole range of TOC values, reflecting the linear regression seen in Figure 4.2. Figure 4.3 also shows the relationship seen by Håkanson and Jansson (1983) for Lake Mälaren, Sweden. A similar relationship was seen by Mackereth (1966). At lower TOC values an increase in the LOI/TOC ratio is seen. Thus it appears that the ratio between LOI and TOC is only constant at higher concentrations such as those found in UACT6. At lower concentrations the linear relationship breaks down, and it becomes progressively more difficult to infer TOC from LOI values.

4.3.3 Nitrogen and hydrogen

Total nitrogen and hydrogen concentrations in core UACT6 are shown in Figure 4.4 alongside the TOC content. All three variables show similar downcore variations, although the hydrogen measurements exhibit more noise than either TOC or nitrogen. When the concentrations of nitrogen and hydrogen are compared with those of TOC, strong linear relationships are seen which are significant at above the 99% level (Figures 4.5 and 4.6). As with the regression of LOI and TOC discussed above, marginally higher R^2-values are obtained when a non-linear (quadratic) regression curve is fitted. The differences are not large enough to justify using the non-linear regression curves in preference to the linear regression curves. Given the strong correlations of both nitrogen and hydrogen with TOC, it seems likely that organic matter forms the main input of these elements to the sediment of Lochan Uaine, rather than inorganic sources.

Carbon and hydrogen are present in approximately similar concentrations in all of the three main types of organic matter; carbohydrates, lipids and proteins (Table 4.2). By contrast nitrogen is not present in carbohydrates, is present only in low quantities in lipids, but forms a large component of proteins. Plants contain the lowest concentrations of protein and invertebrates the highest, hence nitrogen tends to accumulate through the food chain (Goodell, 1972). The concentration of nitrogen in the sediment may be used as an indicator of organic matter sources in sediments, and the most commonly used method of doing this is through the carbon/nitrogen (C/N) ratio.

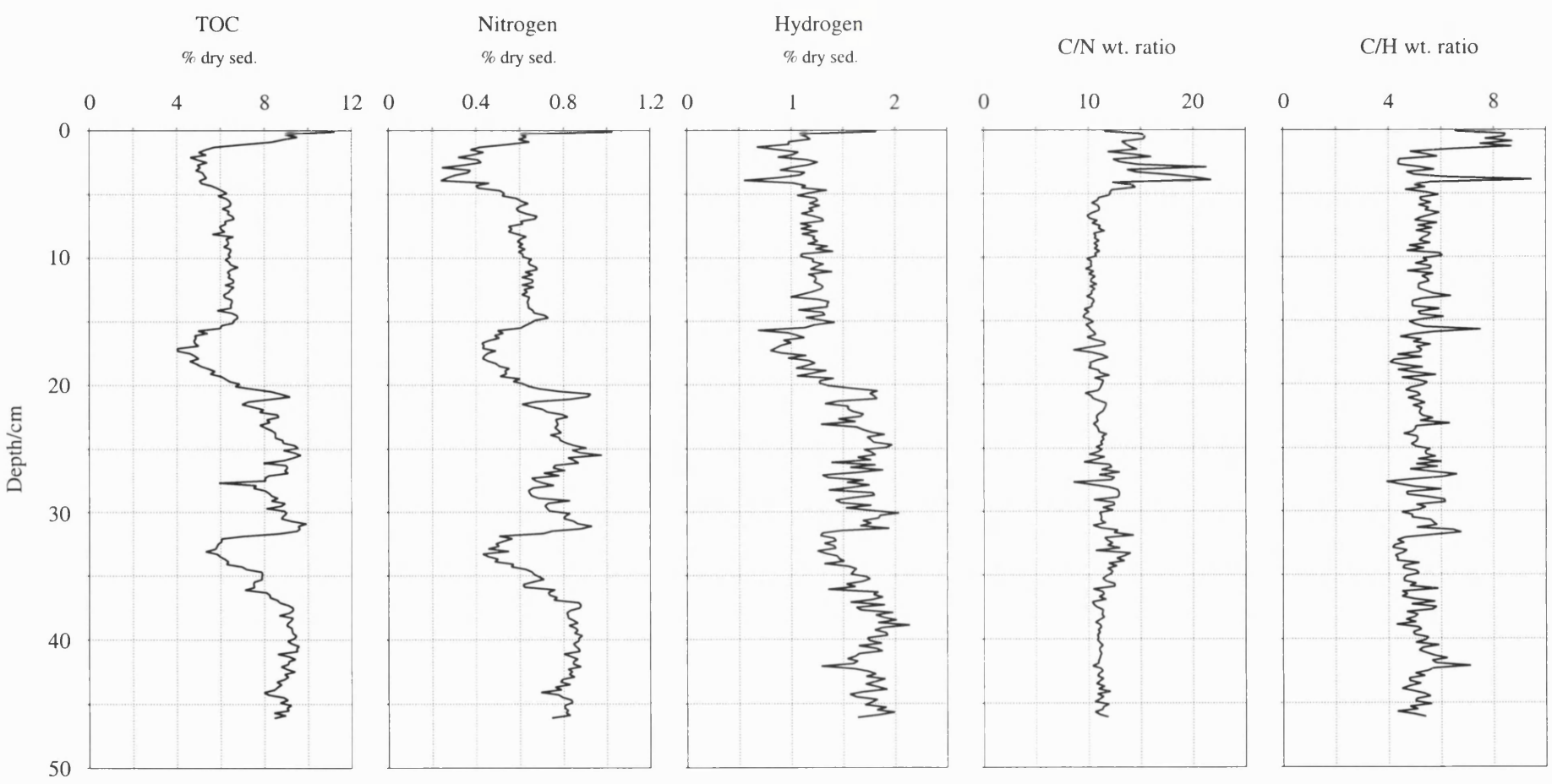


Figure 4.4 Bulk geochemical analyses, core UACT6.

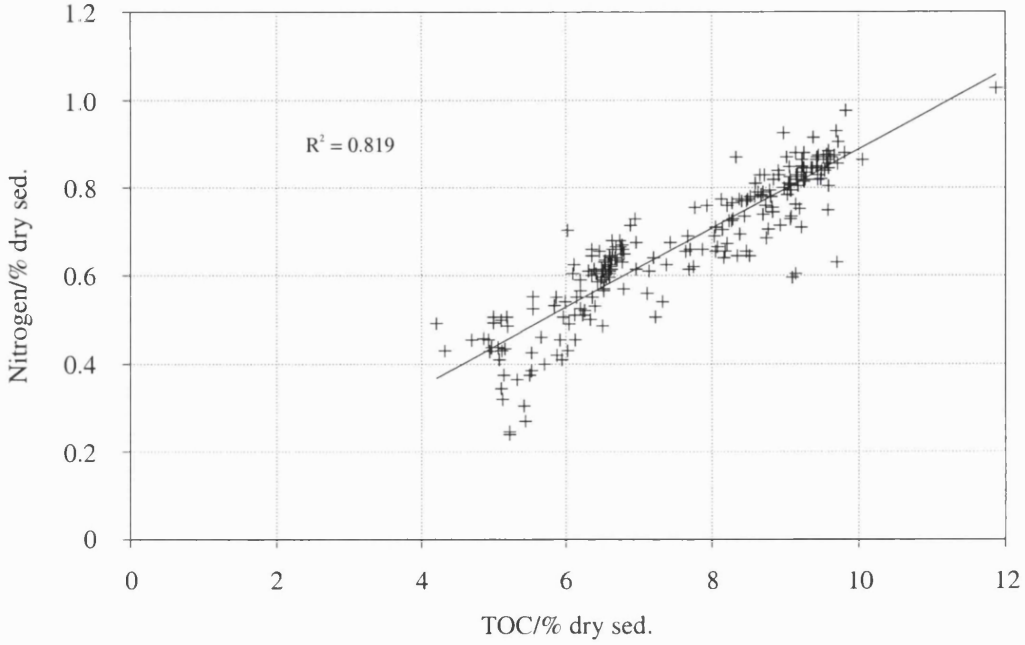


Figure 4.5 TOC *vs* nitrogen, core UACT6.

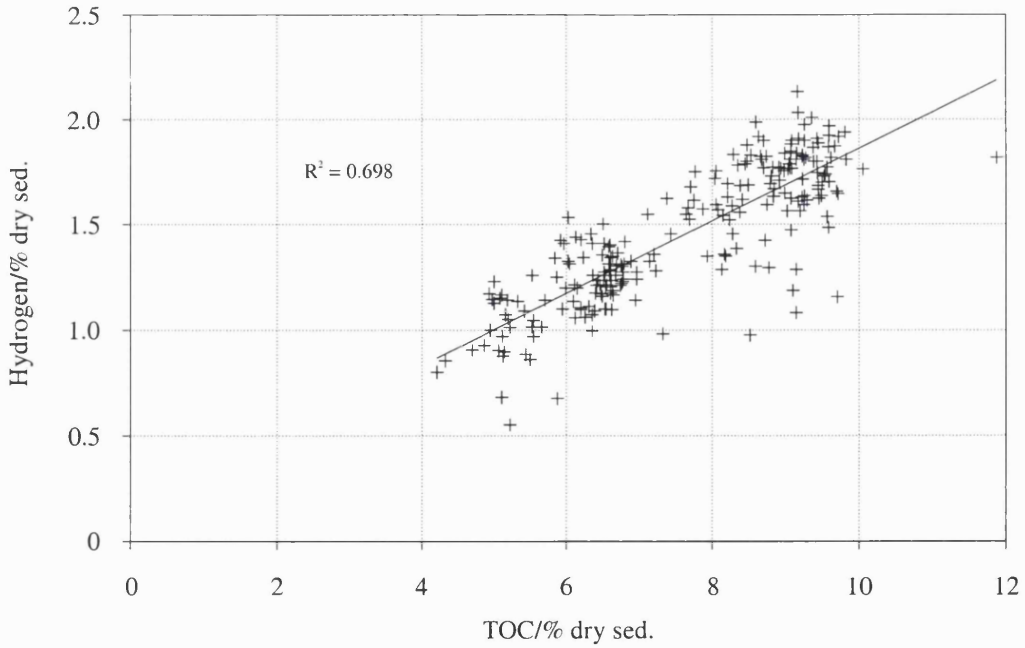


Figure 4.6 TOC *vs* hydrogen, core UACT6.

Table 4.2 Elemental composition of the main components of organic matter (from Goodell, 1972, page 136).

Element	Carbohydrate %	Lipid %	Protein %
O	49.38	17.90	22.40
C	44.44	69.05	51.30
H	6.18	10.05	6.90
P		2.13	0.70
N		0.61	17.80
C/N		113.2	2.9

4.3.4 C/N ratio

4.3.4.1 Organic sources and the C/N ratio

The C/N ratio is frequently used as an indicator of the source of the organic material in lake sediments. Organisms typically found in lakes, such as algae and plankton, contain high concentrations of protein and hence have a high nitrogen content (Table 4.2). By contrast, terrestrial plants are dominated by low-nitrogen components such as cellulose and lignin (Meyers *et al.*, 1984b). These differences are reflected in the ratio of carbon to nitrogen which is much higher in terrestrially-derived organic matter (Krishnamurthy *et al.*, 1986; Tyson, 1995). Redfield (1958) suggests that the relative proportions of C/N/P in marine plankton are roughly constant at 106:16:1, giving a C/N ratio by weight of 5.7. More recent studies confirm that C/N ratios may be used to help identify organic matter sources. There is general agreement that C/N ratios less than *c.* 10 are typical of nonvascular aquatic organisms, while ratios of *c.* 20 and above are restricted to vascular terrestrial plants (Håkanson and Jansson, 1983; Hedges *et al.*, 1985; Meyers, 1990, 1994; Meyers and Ishiwatari, 1993; Tyson, 1995; Meyers and Lallier-Vergès, 1999; Bianchi *et al.*, 1999). Values in between these ranges may indicate inputs from both aquatic and terrestrial sources. C/N ratios may be affected by diagenesis due to the mobility of nitrogen in biological systems (Meyers and Benson, 1988; Tyson, 1995), although Meyers and Ishiwatari (1993) suggest that burial of organic matter in lake sediments has the effect of stabilising C/N ratios. In the following section C/N weight ratios will be quoted throughout as these are most commonly used in the literature (Tyson, 1995). In cases where the C/N atomic ratio has been published, this has been converted to C/N weight ratio by multiplying by

$^{12}/_{14}$. If the form of ratio was not specified, it was assumed that the C/N weight ratio was used.

4.3.4.2 The C/N ratio in lake sediments

Measured values of C/N in lake surface sediments include: 6 in Lake Biwa, Japan (Koyama, 1972; Meyers and Horie, 1993); 9.19 in Lake Motuso, 8.56 in Lake Haruna, and 8.36 in Lake Suwa, Japan (Kawamura and Ishiwatari, 1985); 16 in Lake Vättern and 18 in Lake Vänern, Sweden (Håkanson and Jansson, 1983); 8 in Walker Lake, Nevada (Meyers and Benson, 1988); 9 in Pyramid Lake, Nevada (Tenzer *et al.*, 1997); 8 in Lake Michigan (Rea *et al.*, 1980; Meyers *et al.*, 1984b; Meyers and Eadie, 1993); 12 in Coburn Mountain Pond, Maine (Ho and Meyers, 1994); 11 in Lake Baikal, Siberia (Qiu *et al.*, 1993); and 14 in Lake Bosumtwi, Ghana (Talbot and Johannessen, 1992). These C/N ratios are mostly low and indicate either an algal input, or a mixture of algal and terrestrial inputs. Studies of 51 lakes by Hecky *et al.* (1993) show arctic and subarctic lakes to have lower C/N ratios (*c.* 8-10) than lakes in temperate and tropical regions (*c.* 10-20). Also, small lakes are more deficient in nitrogen than large lakes and have correspondingly higher C/N ratios.

Downcore changes in the C/N ratio are used to reconstruct past changes in lake sediment inputs. Such studies have been undertaken at Upton Broad, England (Cranwell, 1984b), Lake Steisslingen, Germany (Mayer and Schwark, 1999), Lago Paione Superiore, Italy (Guilizzoni *et al.*, 1996), Lake Michigan (Meyers and Eadie, 1993), Coburn Mountain Pond (Ho and Meyers, 1994), Swan Lake, Nebraska (Hassan *et al.*, 1997), Lake Pleasant, Massachusetts (Kaushal and Binford, 1999), Mono Lake, California (Jellison *et al.*, 1996), Austin Lake, Michigan (Krishnamurthy *et al.*, 1995), Lakes Parker, Hollingsworth and Griffin, and Clear Lake, Florida (Brenner *et al.*, 1999), Lake Baikal (Qiu *et al.*, 1993), Lake Biwa (Ishiwatari and Uzaki, 1987; Meyers and Takemura, 1997), Lake Haruna (Ishiwatari *et al.*, 1980), Karewa lake sediments, India (Krishnamurthy *et al.*, 1986), Lake Nkunga, Kenya (Ficken *et al.*, 1998), Sacred Lake, Kenya (Huang *et al.*, 1999), Lake Bosumtwi, Ghana (Talbot and Johannessen, 1992), and Lake Carajas, Brazil (Sifeddine *et al.*, 1994). In all cases low C/N ratios were interpreted as representing autochthonous

sources, high ratios as representing allochthonous (terrestrial plant) sources, and intermediate values as representing a mixture of sources.

4.3.4.3 C/N ratio of UACT6

The C/N profile of UACT6 was given in Figure 4.4. Unlike many of the studies mentioned above, no major changes in C/N are visible in the core, with the exception of the upper 5 cm. From 5 cm depth to the core base the C/N values lie almost entirely within the range 10-13, and the extreme values recorded for this section are 8.6 and 14.3. These values indicate inputs from both autochthonous and allochthonous sources. Slightly elevated values are found from 32-34 cm depth, coinciding with a period of low TOC and low nitrogen in the sediment. This would be interpreted as an increase in the input of terrestrial plant material to the sediment relative to the input from aquatic organisms. Significantly, no such increase in C/N is seen between 15 and 20 cm depth where a similar decrease in sedimentary TOC and nitrogen is found.

The section from 0-5 cm depth differs from the rest of the core in that much higher C/N values are seen, with some values exceeding 20. The conventional interpretation of these values indicates a significant increase in the proportion of terrestrial plant material reaching the sediment. There are, however, several indications that this interpretation may not be correct. Firstly, the high C/N values from 0-5 cm depth coincide with a period of low TOC and nitrogen in the sedimentary record. The other two such periods seen in UACT6 were discussed above; that from 32-34 cm shows slightly elevated C/N ratios, while no change in the C/N profile is seen from 15-20 cm. If these three events are the result of identical processes, such as a reduction of within-lake primary productivity as suggested by the chlorin and lipid records (discussed in later sections), identical changes in the C/N profile would be expected. The lack of consistent changes in C/N would thus suggest that the three major periods of low TOC and low N are caused by different sets of environmental processes, rather than a recurrence of a single set of environmental processes.

The second possibility is that the C/N profile reflects processes occurring in the active sediment near the mud-water interface. Specifically, nitrogen is known to be mobile in sediments through both biological and non-biological diagenesis (Meyers and Benson, 1988; Tyson, 1995). Non-aromatic carbon-to-nitrogen bonds are weaker than carbon-to-carbon bonds, hence nitrogen will be released more rapidly than carbon during diagenesis of organic compounds (Toth and Lerman, 1977). Prahl *et al.* (1980) note that this nitrogen may be remineralized more rapidly than organic carbon, resulting in higher C/N ratios in the top few centimetres of sediment. Burial within sediments has the effect of stabilising C/N ratios (Meyers and Ishiwatari, 1993), thus the high C/N ratios in the top of UACT6, and the lower values through the rest of the core, may be explained in terms of nitrogen mobility.

One problem with the above explanation is that the C/N values from 0-5 cm in UACT6 are not consistently high, as would be expected, but show large variability between contiguous samples. The topmost sample (0.0-0.2 cm) has a C/N ratio of 12, comparable to that seen in the rest of the core below 5 cm depth. Hence, the third possibility in explaining the observed C/N profile is that of measurement error. A comparison of nitrogen concentration with C/N ratio (Figure 4.7) shows that the five highest C/N values recorded occur in the five core samples with the lowest nitrogen content. It may be that periods with a low sedimentary nitrogen content reflect a decrease in lake productivity, a higher relative input of terrestrial organic matter, and a corresponding increase in C/N ratio, as discussed above. However, the strong inverse relationship between nitrogen content and C/N ratio in these five samples is not seen in the rest of the core. The possibility of measurement errors at low concentrations of nitrogen cannot be ruled out. Notably, the five samples with the lowest nitrogen and highest C/N values do not also have the lowest TOC contents (Figure 4.8). The importance of this is not known. Mackereth (1966) also finds no correlation between C/N and TOC content across the range of values seen in UACT6, although TOC values below 4% are associated with lower C/N ratios. This is attributed to the release of NH_4^+ ions from glacial clays by the Kjeldahl digestion method used by Mackereth. This effect is unlikely to be apparent in UACT6 due to the higher TOC contents and the different nitrogen analysis method employed. The

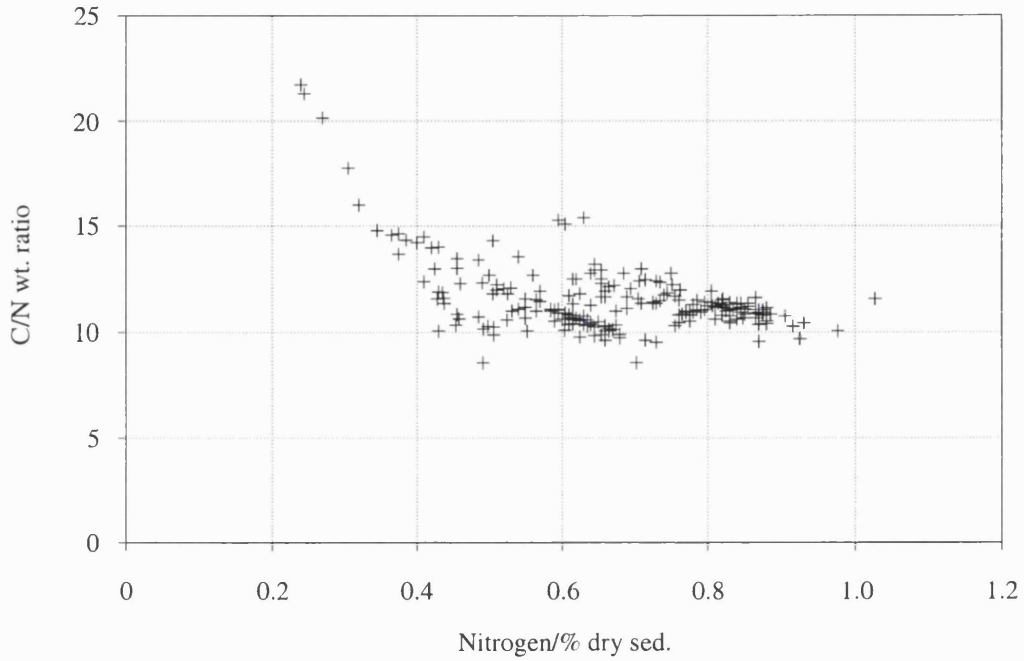


Figure 4.7 Nitrogen *vs* C/N ratio, core UACT6.

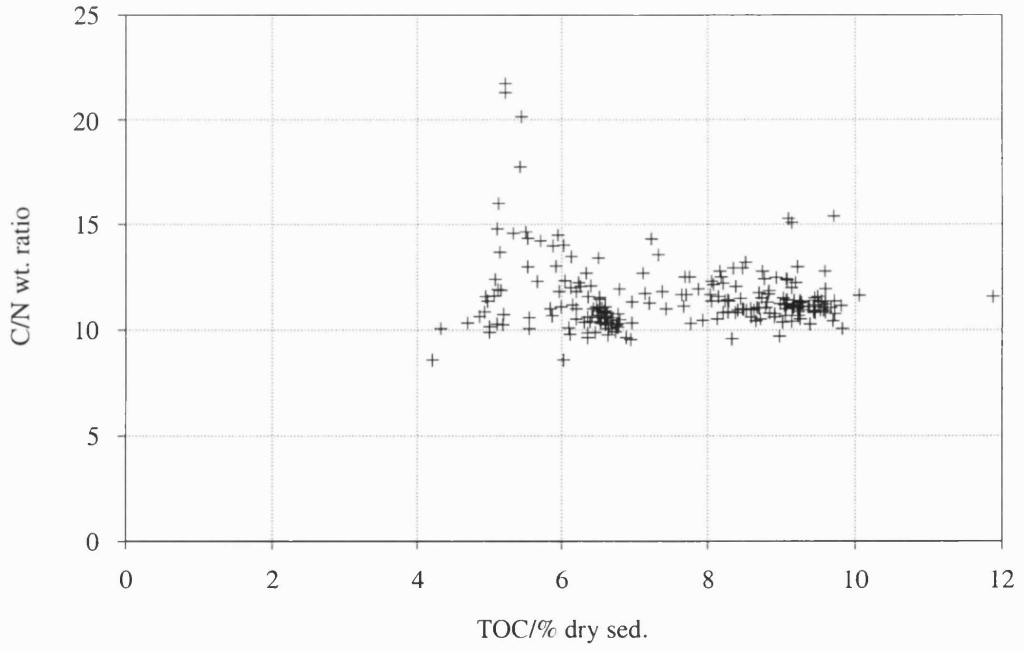


Figure 4.8 TOC *vs* C/N ratio, core UACT6.

difficulty in measuring and interpreting C/N ratios is summed up by Tyson (1995, page 390), "...the biological and diagenetic mobility of nitrogen means that the use of C/N ratios as an indicator of the source of organic matter must be carried out with caution, even in modern sediments".

4.3.5 C/H ratio

The ratio between carbon and hydrogen is sometimes used to indicate organic matter source as it reflects differences in the degree of saturation of organic compounds in different organisms. In ancient sediments, the C/H ratio may also be employed along with the oxygen/carbon ratio to determine the degree of diagenesis of kerogens. Over long time periods, hydrogen is lost as aromatization of organic compounds occurs, and the C/H ratio rises accordingly (Killops and Killops, 1993; Hunt, 1996). As with C/N ratios, C/H ratios may be expressed either as weight ratios or as atomic ratios. Given the greater weight difference between carbon and hydrogen compared to that between carbon and nitrogen it is important to stress which ratio is being used. In the following discussion the C/H weight ratio will be used unless specified otherwise. This can be converted to the atomic C/H ratio by multiplying by $^{1}/_{12}$. Literature on petroleum geochemistry tends to use the atomic H/C ratio, which is simply the inverse of the atomic C/H ratio.

Table 4.3 Atomic H/C and C/H ratios for different organic matter groups (adapted from Talbot and Livingstone, 1989, page 122).

Atomic H/C ratio	C/H weight ratio	Source material
<0.8	>15.0	Altered plant material - mainly wood and coal
0.8-1.3	9.2-15.0	Terrestrial plants - woody and other ligno-cellulosic tissue
1.3-1.7	7.1-9.2	Higher plants - cuticle, spores, pollen, resin, amorphous matter
>1.7	<7.1	Phytoplankton - algae, bacteria, amorphous matter

Talbot and Livingstone (1989) list atomic H/C ratios for the main organic matter groups (Table 4.3). They explain the differences in ratios between the main groups thus, "Because of their relatively high content of saturated organic compounds, algal and amorphous remains tend to be more hydrogen-rich than the other three groups. Herbaceous remains are richer in aromatics and so have a lower hydrogen content,

while woody material is dominated by polycyclic aromatic compounds that are even poorer in hydrogen" (Talbot and Livingstone, 1989, page 123). They note that the boundaries in C/H ratio between the different groups are diffuse, hence the values reproduced in Table 4.3 should be used as a guide only.

Figure 4.4 shows the downcore variations in C/H weight ratio in UACT6. This shows similarities to the C/N profile. The highest C/H values all occur in the top 5 cm of sediment and remain relatively constant throughout the rest of the core. The highest recorded value, 9.5 at 3.8-4.0 cm depth, coincides with the lowest hydrogen content. The C/H ratio is consistently above 6.5 in the top 1.6 cm, compared to a mean throughout the core of only 5.3. The figures in Table 4.3 suggest that C/H ratios below *c.* 7.1 are indicative of phytoplankton whereas those between 7.1 and 9.2 tend to be more indicative of higher plants. However, it was noted that these boundaries should be used as a rough guide only, hence it is hard to interpret the elevated C/H ratios in the top 5 cm of UACT6 as being indicative of a change in organic matter source. Also, the coincidence of the highest C/H ratio and the lowest hydrogen content suggests that there may be increased measurement errors associated with low values of hydrogen, as suggested previously with regard to the high C/N ratios at low nitrogen contents.

Below 5 cm depth the C/H weight ratio is remarkably constant and varies little outside the range of 4 to 6. No downcore increase in the ratio is apparent which could be attributed to aromatization of compounds, although such a process is likely to become apparent in the C/H ratio only over much longer time periods (Killops and Killops, 1993; Hunt, 1996). According to Table 4.3, the C/H ratios below 5 cm in UACT6 are consistent with a phytoplankton source. More noise is apparent in this section compared to the C/N ratio profile. This is due to the greater noise in the downcore hydrogen content by comparison with the TOC and nitrogen contents. As with the top 5 cm, the maximum C/H ratio within this part of the core, 7.5 at 15.6-15.8 cm, coincides with the lowest measured hydrogen content, again suggesting that there is an error involved at the lowest hydrogen contents. Alternatively, there is a suggestion that C/H ratio throughout the whole core may be directly correlated with

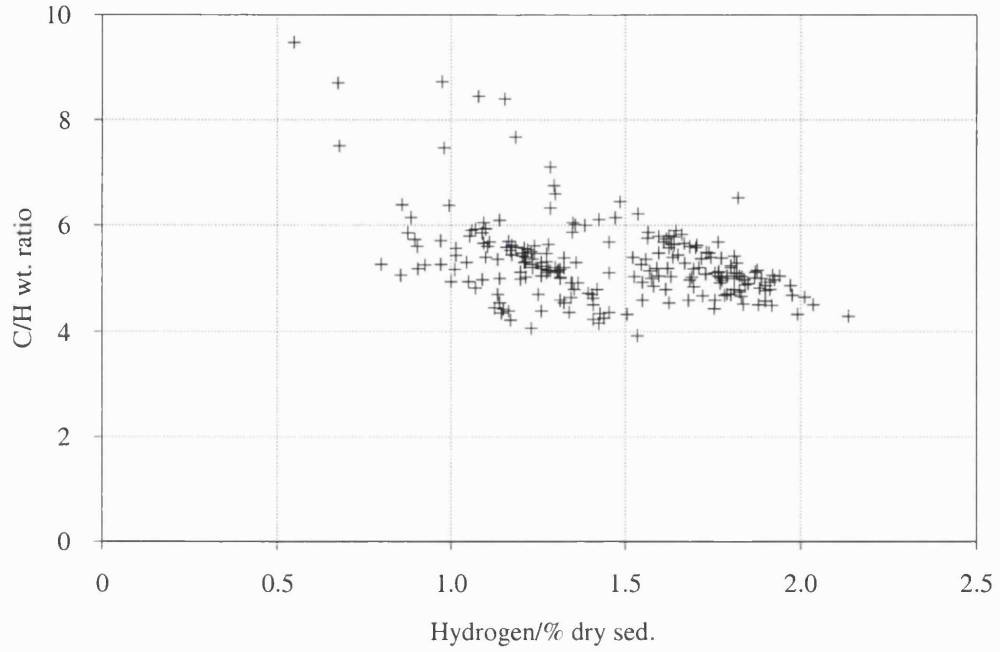


Figure 4.9 Hydrogen *vs* C/H ratio, core UACT6.

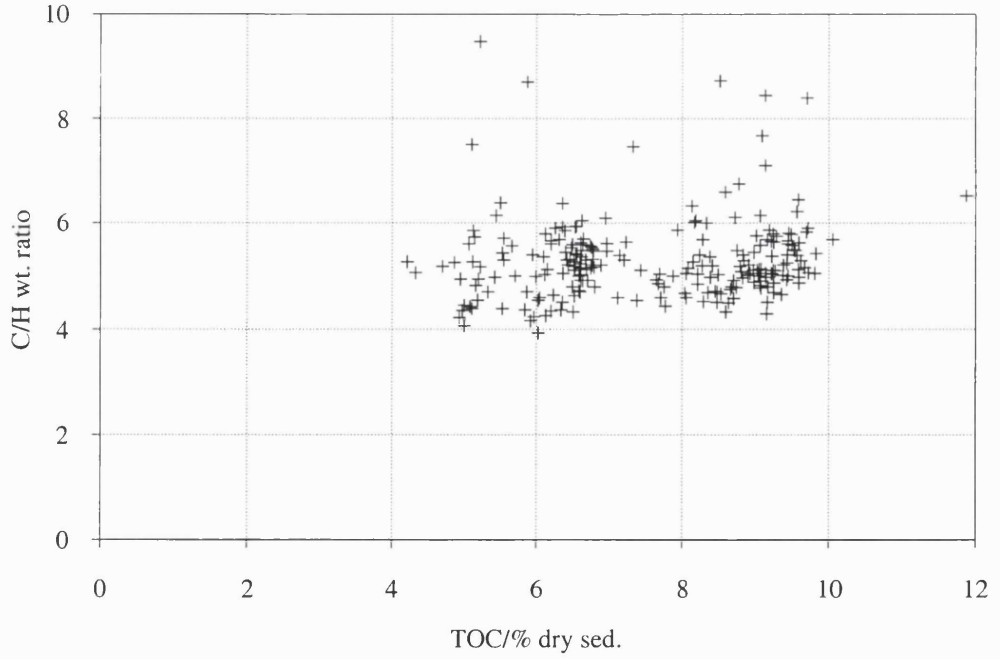


Figure 4.10 TOC *vs* C/H ratio, core UACT6.

hydrogen content. This is seen in Figure 4.9. The negative correlation between C/H ratio and hydrogen content is significant at the 99% level (R^2=0.18, N=231). A slight positive correlation exists between C/H ratio and carbon content, although this is only significant at the 95% and not the 99% level (R^2=0.13, N=231). A much stronger positive relationship between C/H ratio and carbon content is seen by Mackereth (1966, Figure 3, page 174) in his study of three lakes in the English Lake District. Mackereth attributes this relationship to the release of inorganic hydrogen from water bound to the mineral matrix of the sediment. The same effect is responsible for the inverse relationship between TOC content and the LOI/TOC ratio discussed previously (Figure 4.3). Interestingly, although release of bound water only affected the LOI/TOC ratio at TOC concentrations below *c.* 4%, it appears to affect the C/H ratio at all carbon contents up to 16%. We would thus expect a much stronger positive correlation between C/H and carbon content in UACT6 than that seen in Figure 4.10. Mackereth (1966, page 173) does point out that the presence of this inorganic hydrogen source has implications for the interpretation of C/H ratio profiles; "The large variation in C/H ratio brought about [by the release of tightly bound water] masks any small variation in this ratio which may exist in the organic material of different age or origin".

4.4 Chlorins

Chlorins are early degradation products of chlorophyll (Harris *et al.*, 1996). They are found in practically all sediments, both marine and lacustrine (Harradine *et al.*, 1996b). Chlorins may be present as free compounds, or bound to other molecules such as steroids or hopanoids to form chlorin esters. Of the former, Keely and Maxwell (1991) identified two chlorin structures, phaeophytin *a* and pyrophaeophytin *a*, in sediments from Priest Pot, English Lake District. Of the latter, Pearce *et al.* (1993) and Harradine *et al.* (1996a) identified various steryl, hopanyl and tetrahymanyl chlorin esters in sediments of Lake Valencia, Venezuela. Although individual chlorins and chlorin esters were not identified in the sediment of Lochan Uaine, techniques for doing so are described by Eckardt *et al.* (1991), Keely and Maxwell (1991), King and Repeta (1991, 1994), Prowse and Maxwell (1991), Pearce

et al. (1993), Harradine *et al.* (1996a,b), Goericke *et al.* (1999), Talbot *et al.* (1999a,b), and Sachs and Repeta (2000). Identification of chlorins at a similar lake to Lochan Uaine, Lochnagar in the eastern Cairngorms, is currently in progress (Dalton *et al.*, 2000).

4.4.1 Origin of chlorins

There is general agreement in the literature that chlorins derive from phytoplankton chlorophyll *a* (Harradine *et al.*, 1996a; Harris *et al.*, 1996) and chlorophyll *b* (Talbot *et al.*, 1999b). Presumably, therefore, chlorins also derive from the chlorophyll of benthic organisms, although this has yet to be confirmed. The transformation of chlorophyll to chlorins and chlorin esters is thought to proceed via several pathways. Eckardt *et al.* (1992) suggest that the transformation may occur as a response to algal senescence at the conclusion of a bloom, although Harradine *et al.* (1996b) report that studies designed to recreate this process have been unsuccessful in producing steryl chlorin esters. Another pathway for chlorin formation appears to be through zooplankton herbivory of algae, and chlorin esters have been found in zooplankton faecal pellets (Harradine *et al.*, 1996b; Goericke *et al.*, 1999; Talbot *et al.*, 1999a,b). The significance of this pathway in Lochan Uaine is not known as no studies have yet been carried out on the Lochan Uaine zooplankton community. However, the predominance of benthic diatoms in the sediment record, and the almost complete absence of planktonic taxa, suggests that zooplankton herbivory may be relatively unimportant at Lochan Uaine. Grazing of the epilithic flora by benthic invertebrates may be a more significant route for chlorin formation. Identification of the chlorins present may indicate the method of formation. In particular, the steroid component of steryl chlorin esters is thought to represent the sterol content of the source (Harradine *et al.*, 1996b), although Talbot *et al.* (1999a,b) report slight changes in distribution associated with zooplankton herbivory. The derivation of chlorins from higher plant chlorophyll, rather than algal chlorophyll, is not thought to occur at Lochan Uaine. Neither chlorophyll nor chlorins are likely to survive in catchment soils due to the rapid degradation that occurs in these environments. Confirmation of the absence of a higher plant source for chlorins in montane lake sediments awaits further analysis, including the identification of sedimentary chlorins (Dalton *et al.*, 2000).

As chlorins are produced from the chlorophyll of lake biota, their sedimentary concentration is thought to provide a direct proxy for lake productivity. Harris *et al.* (1996) demonstrate how chlorin concentration in a marine core from off the coast of northwest Africa provides a potentially more reliable measure of palaeoproductivity than other proxies, such as biogenic silica which derives mainly from marine diatoms and as such does not represent the entire phytoplankton community. They also note the strong positive correlation between chlorin content and organic matter content of the sediment. They conclude that chlorin content reflects changes in total primary productivity, although they point out that the response may not be linear. Without evidence to the contrary, it seems reasonable to apply this chlorin content-primary productivity interpretation to the analysis of chlorin content in UACT6.

4.4.2 Chlorin content of UACT6

The downcore variation in total sedimentary solvent-extractable chlorins is shown in Figure 4.11. Regions of the core containing low chlorin concentrations are extremely well defined, and occur at depths of approximately 1-5, 17-20 and 32-35 cm. These correspond very well with the periods of low TOC in the core (also shown on Figure 4.11). The main difference between the chlorin and TOC profiles is in the core section from 5-15 cm depth. The relative chlorin concentration compared to the rest of the core is much greater than that seen in the TOC curve. The differences across this section account for the comparatively low R^2-value (0.226) seen for the correlation between chlorin and TOC content (Figure 4.12) compared to that between, for example, TOC and LOI (Figure 4.2). Nonetheless, the correlation is still significant at above the 99% level.

As the chlorin concentrations in Figure 4.11 are expressed as a proportion of TOC, the observed downcore variations should be independent of variations in LOI. This is important, as it was not known whether the LOI variations were caused by changes in the organic input to the sediment, changes in the mineral input, or a combination of both. A variation in mineral input to Lochan Uaine, for example due to catchment erosion and the subsequent inwash of pulses of clastic material, would not have affected the concentration of chlorins relative to TOC mentioned above. The chlorin and TOC data thus provide strong evidence that at least part of the LOI profile of

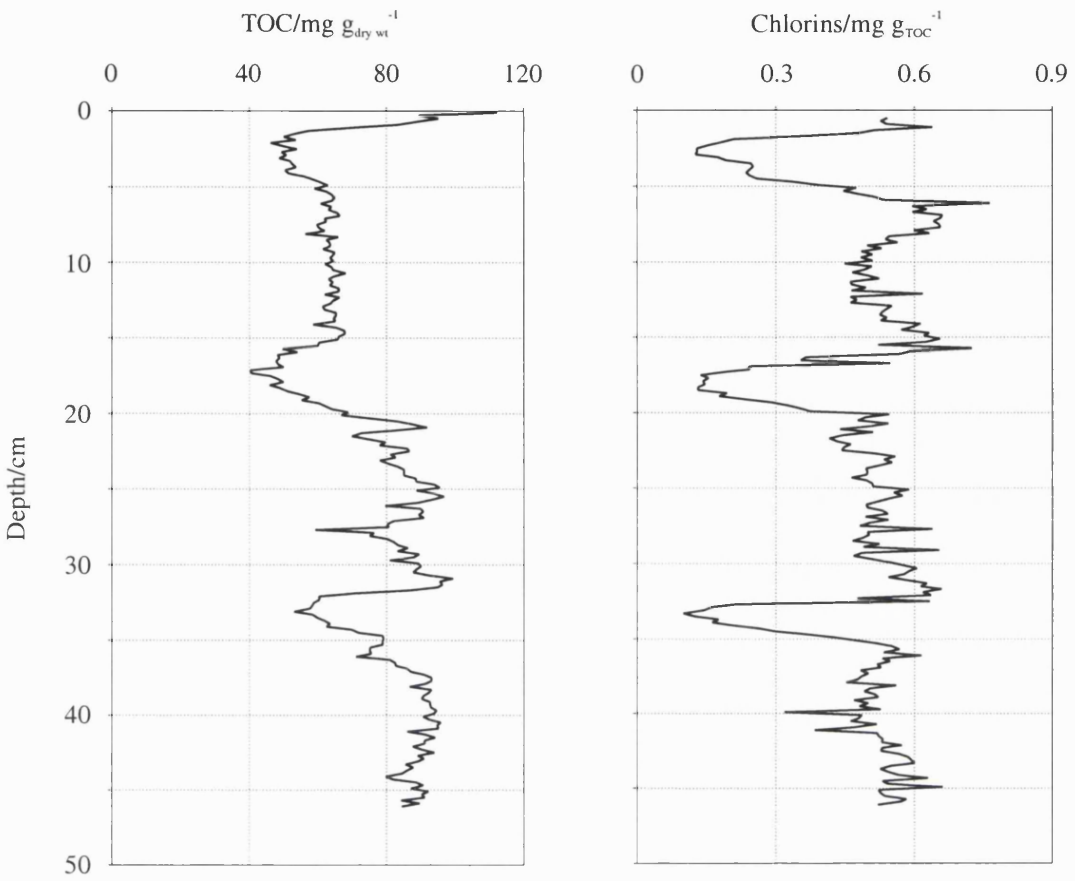


Figure 4.11 TOC and chlorin concentrations, core UACT6.

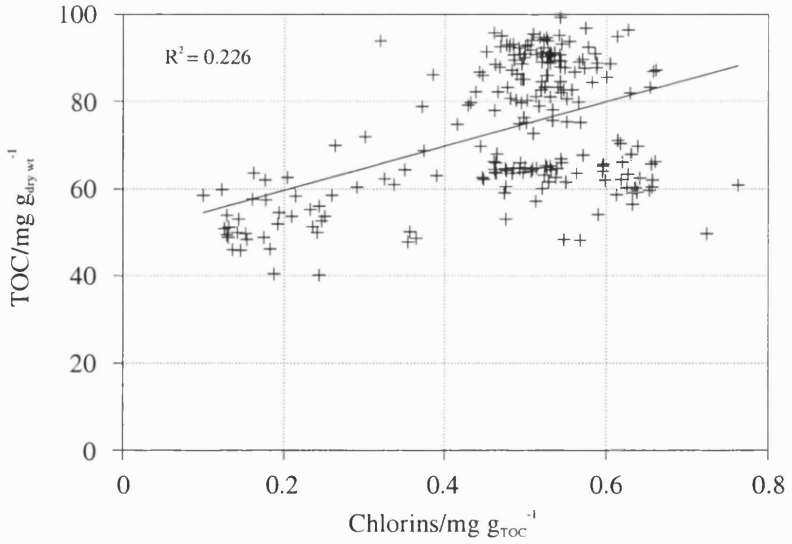


Figure 4.12 Chlorin *vs* TOC concentrations, core UACT6. The regression line is shown, and is significant at above the 99% level.

UACT6 may be explained by variations in the input of organic matter, and specifically chlorins, to the lake sediment record. Further evidence to corroborate this hypothesis is discussed with reference to lipid concentrations in Chapter 5. The nature of the chlorin curve is also interesting, in light of the conclusions of Harris *et al.* (1996) who note that it is not known whether the response of chlorin content to productivity changes is linear. The chlorin minima appear to be much better defined than the corresponding minima in LOI and TOC. The onset of each minimum occurs rapidly, and the terminations occur even more rapidly. During the minima, chlorin concentrations are only *c.* 25% of those seen throughout the rest of the core, a much greater difference than is seen in LOI and TOC. These responses are similar to those expected of a system in which a threshold value is being crossed, rather than one in which the response is linear. Without further data it is difficult to speculate as to the nature of such a threshold. The chlorin signal seen in Figure 4.11 could also reflect differential preservation of chlorins during periods of differing sediment organic content. The mechanisms by which this could occur are not known.

4.5 Bulk organic stable carbon isotope analysis

While the ratio of ^{13}C to ^{12}C ($\delta^{13}C$: Equation 2.1) is one of the most frequently used bulk measurements in marine and lacustrine sediments, the factors influencing $\delta^{13}C$ are complicated. The *c.* 8% mass difference between ^{12}C and ^{13}C means that reactions, be they physical, chemical or biological, tend to discriminate between the two isotopes. In particular, photosynthesis discriminates quite strongly against the heavier isotope, ^{13}C. Photosynthesis is the pathway by which most organisms assimilate carbon (with the exception of *e.g.* chemosynthetic bacteria, or heterotrophs which feed on other organisms), hence organisms exhibit ^{13}C depletion and have lower, more negative $\delta^{13}C$ values. A corresponding enrichment in ^{13}C, with higher, less negative $\delta^{13}C$ values, will be seen in the carbon source. All $\delta^{13}C$ values in the following review are quoted relative to the PDB standard.

4.5.1 Carbon sources in terrestrial and lacustrine environments

The $\delta^{13}C$ value of any organic carbon deposited in a lake sediment will reflect a variety of sources and influences. Allochthonous organic sources mainly take the form of terrestrial plant remains and eroded soils. Terrestrial plants and many soil micro-organisms obtain CO_2 directly from the atmosphere, hence the isotopic fractionation occurring in these organisms will be determined in part by the $\delta^{13}C$ value of atmospheric CO_2. This value can vary over a variety of different timescales, from short (daily to annual) variations caused by changing biomass productivity (Farquhar *et al.*, 1989), to longer (decadal to centennial) variations caused by factors such as volcanism (Kump and Arthur, 1999) and fossil fuel burning (Keeling *et al.*, 1979; see also Section 4.5.2). Ultimately, variations occur on geological timescales, associated with ice ages, global vegetation changes, and so on (Hayes *et al.*, 1999). Nonetheless, for the puposes of the study of the late Holocene, the $\delta^{13}C$ value of atmospheric CO_2 is generally taken to be about -7‰ ± *c.*1‰. This range is small and can probably be disregarded as a factor influencing $\delta^{13}C$ values observed in lake sediments, especially given the large isotopic fractionations associated with CO_2 assimilation and utilisation by organisms. Isotopic fractionation in higher plants is discussed in greater detail in Section 4.5.3.

In soils there can be a significant utilisation of CO_2 released by decomposition of organic detritus. This CO_2 will have an isotopic composition similar to that of the decaying organic matter, and hence can be substantially more depleted in ^{13}C than 'normal' atmospheric CO_2 (Schleser and Jayasekera, 1985; Farquhar *et al.*, 1989). However, it is assumed that reassimilation of this CO_2 is unlikely to have a major influence on terrestrial plants at Lochan Uaine, due to the low biomass present in the catchment. This low biomass prevents the retention of depleted CO_2 beneath a vegetation canopy, and limits the subsequent utilisation of that CO_2 in photosynthesis.

It is worth mentioning that methane may sometimes be used as a carbon source by soil micro-organisms. This process requires anaerobic conditions for methane production by methanogens, but also aerobic conditions for methane utilisation by methylotrophs. Such conditions may be found in waterlogged soils, such as peat bogs, with the

methane moving upwards from an anaerobic environment into an aerobic environment. The extent of this process is not known at Lochan Uaine, but given the skeletal nature of the catchment soils, and the absence of well-developed peat bogs, it is assumed to be minimal.

Sources of carbon incorporated by aquatic organisms are potentially rather more complex than for terrestrial organisms. With the exception of some emergent macrophytes, which are not present at Lochan Uaine, aquatic organisms are unable to use atmospheric CO_2 directly. Several carbon sources may be utilised for photosynthesis by aquatic organisms. CO_2 may be present in water either as a gaseous (CO_2) or dissolved (H_2CO_3) species. Pearson and Coplen (1978) suggest that dissolved CO_2 is around 1‰ lighter than gaseous CO_2 across the normal temperature range of lakes. By contrast, where bicarbonate (HCO_3^-) is present and in isotopic equilibrium with the atmosphere, $\delta^{13}C$ values for bicarbonate are generally around +1‰, compared to -7‰ for atmospheric CO_2 (Pearson and Coplen, 1978). Thus, bicarbonate may be 8-9‰ less depleted in ^{13}C than dissolved CO_2. These differences in the isotopic compositions of the carbon sources will influence the corresponding $\delta^{13}C$ values of organisms which assimilate carbon from the different sources.

Other possible carbon sources for aquatic organisms include dissolved and mineral carbonate, carbon monoxide, and methane. Carbonate is most important as a carbon source in high-pH lake waters, as discussed in Section 4.5.2, but is generally not significant in acidic lakes. Carbon monoxide is not considered an important source of carbon in any lacustrine environments, due to the ease with which it is either reduced to methane or oxidised to CO_2 (Wetzel, 1983). However, where anaerobic conditions exist, methane may be produced by methanogenic bacteria. This was discussed above with respect to soils. Methane produced within a lake may be significantly depleted in ^{13}C by comparison with dissolved atmospheric CO_2 (Håkansson, 1985). Anaerobic conditions are most likely to be found within the sediment column, or at depth within the water column, especially in productive lakes or during periods of high aquatic productivity. The importance of methane as a carbon source will be greatly reduced in lakes with limited anaerobic conditions, such as well mixed, oligotrophic lakes.

Finally, carbon may be present in lake waters in the form of dissolved CO_2 released by respiration. As this carbon has previously been assimilated by the organism via the usual photosynthetic route, it will have a $\delta^{13}C$ value similar to that of the plant as a whole. O'Leary (1981) gives examples of $\delta^{13}C$ values for respired CO_2 from plants. These values are from 2‰ to 12‰ less depleted in ^{13}C than the whole plant, with the difference appearing greatest for CO_2 released during respiration in the light. O'Leary also notes that the source of CO_2 for respiration is important, as lipids are more depleted in ^{13}C than carbohydrates (see Chapter 6). As with methane, the importance of respired CO_2 in assimilation by aquatic organisms is likely to be lowest in well mixed, oligotrophic lakes.

4.5.2 Sources of carbon in Lochan Uaine

Bulk $\delta^{13}C$ measurements in sediments have traditionally focused on two carbon types: organic carbon and inorganic carbon (carbonate). Lochan Uaine is an acidic, ultra-oligotrophic lake lying on an entirely granitic catchment, and as a result there is likely to be only a minimal contribution of bicarbonate to the lake system from dissolution of catchment bedrock (Håkansson, 1985). Almost all carbon in Lochan Uaine and its catchment derives ultimately from the atmosphere. Catchment vegetation will assimilate CO_2 directly from the atmosphere, while aquatic organisms will mainly utilise carbon dissolved in lake water. The present day acidity of the water (pH 5.8) means that most inorganic carbon will be in the form of CO_2 or H_2CO_3 (known collectively as $H_2CO_3^*$) with only a small contribution possible from HCO_3^- (Figure 4.13). A diatom-inferred pH reconstruction of a core from Lochan Uaine confirms that the lake has been no less acidic than at present for the last *c.* 2000 yr, which is the approximate age of core UACT6 (Battarbee *et al.*, 1996). No carbonate precipitation occurs in the lake, or is likely to have occurred at any stage during the lake's history. This is due in part to the low pH and to the lack of carbonate input from catchment erosion. Additionally, the low nutrient status of Lochan Uaine makes depletion of CO_2 in surface waters during algal blooms less likely, thus preventing calcite supersaturation and the subsequent precipitation of carbonates (Kelts and Hsü, 1978). Consequently, the carbon in the lake sediment exists almost entirely as organic carbon

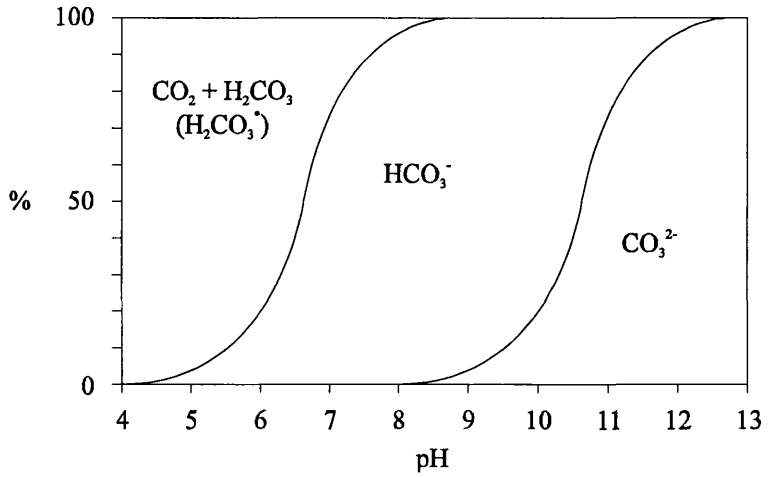


Figure 4.13 Relative proportions of dissolved carbonate species at different pH values (from Kelts and Hsü, 1978, page 299).

(Figure 4.1). Bulk $\delta^{13}C$ measurements in core UACT6 were made only on the organic carbon fraction.

Studies of more specific carbon fractions in the sediment have been undertaken by various authors. Analysis of $\delta^{13}C$ in carbonate tests of aquatic organisms is common, but these are not found in acidic lakes such as Lochan Uaine. In other cases, parts of the organic fraction have been separated for individual analysis, such as humic compounds or the lignin and cellulose components. Most recently, stable carbon isotope analysis of individual organic compounds has become possible. Such measurements were undertaken on sediment from Lochan Uaine and are discussed in Chapter 6.

Interpretation of the bulk organic carbon isotope record contained in any sedimentary sequence requires an understanding of the pathways by which that carbon became incorporated into the sediment, and of the processes affecting that incorporation. Specifically, the isotope fractionation encountered at each stage in the process must be examined.

Given the lack of carbonate inputs from the Lochan Uaine catchment outlined in the previous section, it is fairly safe to assume that the majority of the carbon in Lochan

Uaine and its catchment originated as atmospheric CO_2. The $\delta^{13}C$ of the atmosphere is about -7‰ (Descolas-Gros and Fontugne, 1990; Killops and Killops, 1993), hence organisms which utilise atmospheric CO_2 exclusively will have comparatively lighter isotope ratios. The atmospheric carbon fractionation is not constant, but has been found to vary by small amounts temporally and spatially. The increase in biomass during summer can cause $\delta^{13}C$ values up to 1‰ heavier than in winter, due mainly to the decreased amount of isotopic discrimination at warm temperatures (Wilson and Grinsted, 1977; Schleser, 1995). Schleser has also shown that lower $\delta^{13}C$ values are sometimes found in industrialised areas as fossil fuel combustion releases isotopically light CO_2 at *c.* -25‰. This is not thought to be significant at Lochan Uaine due to the remote nature of the catchment relative to major industrial centres. In future years, 'contamination' by ^{13}C-depleted CO_2 will continue to increase as fossil fuel burning continues at a high rate.

4.5.3 Carbon isotope fractionation in land plants

Atmospheric CO_2 is incorporated into terrestrial plants directly through the photosynthetic reaction. Isotopic fractionation during photosynthesis is the main process controlling the $\delta^{13}C$ of plants, and it is worth examining in more detail. During carbon assimilation by photosynthesis, fractionation occurs by a variety of physical and chemical processes such as diffusion, dissolution, and the carboxylation reaction (Schleser, 1995). It has been suggested that the major process controlling the $\delta^{13}C$ of C_3 plants is the first reaction of CO_2 during photosynthesis, namely the Rubisco-catalysed enzymatic fixation of CO_2 to produce 3-phosphoglycerate, or PGA (Park and Epstein, 1960). The depletion associated with this process is potentially as high as 17‰ (Degens, 1969). Other biochemical reactions occurring during and after photosynthesis, such as the biosynthesis of amino acids and lipids, also have a high potential for carbon fractionation (respectively 15‰ and 18‰ maximum; Degens, 1969). The actual fractionation that occurs during these reactions is likely to be much lower as the carbon has already been significantly depleted in ^{13}C during PGA synthesis.

The $\delta^{13}C$ of any single organism is not consistent amongst all of its component parts. This is a result of the varying fractionations associated with different biochemical reactions, as mentioned above. Leavitt and Long (1982) found that cellulose in trees was *c.* 1‰ lighter than the corresponding whole-tissue samples. A further difference of 3‰ is seen between cellulose extracted from leaves and that from bark. Sachs *et al.* (1999) report a small difference in $\delta^{13}C$ (*c.* 0.3‰) between chlorophyll *a* and bulk samples. Much larger differences are seen with lipids. Isotopic fractionation occurs during the oxidation of pyruvate to acetyl-CoA and during subsequent lipid biosynthesis, and ^{13}C depletion of up to 15‰ relative to bulk plant tissue is recorded in lipids (Park and Epstein, 1960; Degens, 1969). $\delta^{13}C$ variations between components of the same organism can have implications for lake sediment studies, as differential preservation of these components can significantly influence the bulk $\delta^{13}C$ values measured. Carbon isotope ratios of lipids will be discussed more fully in Chapter 6.

Although the $\delta^{13}C$ of an organism is determined mainly by the biochemical reactions occurring within that organism, a variety of environmental factors can influence the degree of fractionation to varying extents. Foremost of these is the temperature during carbon assimilation. Schleser (1995) and Mayer and Schwark (1999) state that warm temperatures tend to produce less negative $\delta^{13}C$ than cold temperatures. This is probably due to the effects of temperature on biochemical reactions, particularly the Rubisco stage of photosynthesis whereby carbon from CO_2 is incorporated into the plant. The Rubisco enzyme shows increased activity at lower temperatures, resulting in greater isotope discrimination and more negative $\delta^{13}C$ values (Wilson and Grinsted, 1977; Descolas-Gros and Fontugne, 1990). The temperature effect on isotopic fractionation was also seen by Stuiver and Braziunas (1987) who report that trees at lower, warmer latitudes exhibit less negative $\delta^{13}C$ values than those at higher latitudes. However, they also note that some studies find an opposite correlation between $\delta^{13}C$ and temperature. Similar results are recorded in tree ring studies, some of which find clear variations in $\delta^{13}C$ associated with annual temperature variations (Wilson and Grinsted, 1977; Pilcher, 1995; Trimborn *et al.*, 1995), while others report only limited success in making this correlation (O'Leary, 1981; Schleser, 1995).

Other environmental factors thought to influence plant $\delta^{13}C$ include humidity, precipitation, physiology, light intensity, soil moisture, nutrient availability, and pollution (Stuiver and Braziunas, 1987; Schleser, 1995; Trimborn *et al.*, 1995). High humidity and precipitation are associated with increased discrimination and more negative $\delta^{13}C$ values (Schleser, 1995; Trimborn *et al.*, 1995). Studies of leaf lipids by Lockheart *et al.* (1997) found that fractionation increased throughout the growing season, and was greater for shaded leaves than leaves in direct sunlight. This illustrates the complexity of the system, and explains why strong relationships between $\delta^{13}C$ and temperature are not always seen (Stuiver and Braziunas, 1987).

4.5.4 $\delta^{13}C$ range in land plants

Despite the many factors influencing fractionation, land plants tend to exhibit $\delta^{13}C$ values within a certain well-defined range of values. Although the values given by different authors vary, there is general consensus that C_3 plants, which use only the Calvin cycle during photosynthesis, have $\delta^{13}C$ values of around -35 to -20‰, with a mean of around -29 to -26‰ (Bender, 1971; Smith and Epstein, 1971; Nakai, 1972; Pearson and Coplen, 1978; Schidlowski, 1988; Descolas-Gros and Fontugne, 1990; Martinelli *et al.*, 1991; Proctor *et al.*, 1992; Killops and Killops, 1993; Meyers and Eadie, 1993; Schleser, 1995; Tyson, 1995; Waichman, 1996; Meyers and Takemura, 1997; Meyers and Lallier-Vergès, 1999). Only C_3 plants have been identified in the Lochan Uaine catchment. Plants which use the Crassulacean Acid Metabolism (CAM) photosynthetic pathway are only rarely found in subarctic sites such as Lochan Uaine, while C_4 plants are generally confined to lower latitudes. The lack of these plants is significant, as the different biochemical reactions involved in photosynthesis create different carbon isotope fractionations. C_4 plants typically have heavier $\delta^{13}C$ values than C_3 plants at -20 to -6‰, while CAM plants can have a much larger range which overlaps with those of both C_3 and C_4 plants (Bender, 1971; Smith and Epstein, 1971; Pearson and Coplen, 1978; Schidlowski, 1988; Martinelli *et al.*, 1991; Schleser, 1995; Waichman, 1996; Meyers and Takemura, 1997; Meyers and Lallier-Vergès, 1999).

4.5.5 Carbon isotope fractionation in aquatic organisms

The high content of diatom frustules in the Lochan Uaine sediment (Battarbee *et al.*, 1996) suggests that there is an important contribution to the total organic matter from lake biota. Almost all phytoplankton are believed to be C_3 photosynthesisers (Meyers and Lallier-Vergès, 1999). However, this does not necessarily mean that they will exhibit identical $\delta^{13}C$ values to the terrestrial plants as given above. A variety of extra factors are important in determining the isotopic fractionation of organisms living within a water body.

The most important difference lies in the source of CO_2 for photosynthesis. Whereas terrestrial plants utilise CO_2 directly from the atmosphere, aquatic organisms cannot do so and must instead use other carbon sources. A water column may contain carbon in a variety of forms. The form of inorganic carbon present is strongly dependent on lake water pH. Acid waters below pH 6 are dominated by gaseous CO_2 and carbonic acid (H_2CO_3), whereas in less acidic lakes and in oceans (average pH *c.* 8.5) the majority of carbon is present as bicarbonate (Figure 4.13). This has important implications for organisms which use these different carbon sources. In a well mixed water body, molecular CO_2 will be in isotopic equilibrium with atmospheric CO_2 (Keeling, 1961), although Pearson and Coplen (1978) suggest that dissolved CO_2 in most lake waters is about 1‰ lighter than atmospheric CO_2. Fractionation occurs during the hydration of molecular CO_2 to form the bicarbonate ion HCO_3^-, so that bicarbonate is relatively enriched in ^{13}C. The magnitude of this fractionation is dependent on temperature and is greater at low temperatures, but bicarbonate typically has a $\delta^{13}C$ of +1‰, compared to -7‰ for atmospheric $\delta^{13}C$ (Degens, 1969; Pearson and Coplen, 1978).

Because of the differences in $\delta^{13}C$ between dissolved CO_2 and bicarbonate, the proportion of each assimilated by an organism will affect that organism's $\delta^{13}C$ value (Nakai, 1972; Krishnamurthy *et al.*, 1986). In an acidic freshwater lake such as Lochan Uaine, inorganic carbon will be present principally as dissolved CO_2, with at most a few percent of bicarbonate. Dissolved CO_2 is used preferentially by primary producers (Hayes *et al.*, 1999). Diatoms, which constitute a large part of the sediment

of Lochan Uaine, are believed to use only dissolved CO_2 as a carbon source (Nakai, 1972). It is likely that there is an adequate supply of dissolved CO_2 in the lake water throughout the year. Lochan Uaine is ultra-oligotrophic, and the total CO_2 requirements of primary producers will be much lower than for a lake with high productivity. Also, the lake is well mixed throughout the year, except possibly during the period of winter ice cover, and there will be an adequate supply of CO_2 throughout the growing season. It is thus unlikely that dissolved CO_2 will ever become limited, and use of bicarbonate as a carbon source will not become necessary.

For these reasons we can be confident that dissolved CO_2, rather than bicarbonate, has provided the carbon source for aquatic organisms in Lochan Uaine throughout the Holocene. Nonetheless, variations in $\delta^{13}C$ are possible through a variety of other mechanisms. Some of these have been mentioned previously with respect to terrestrial vegetation, especially the effect of temperature variations on isotopic composition. Studies of marine and freshwater phytoplankton show that, as for terrestrial plants, isotopic discrimination is enhanced at lower temperatures leading to more negative $\delta^{13}C$ values (Degens, 1969; Håkansson, 1985; Rau *et al.*, 1989; Descolas-Gros and Fontugne, 1990; Ariztegui and McKenzie, 1995; Mayer and Schwark, 1999; Hayes *et al.*, 1999). There are two principle reasons for this. Firstly, the increased activity of the Rubisco reaction at lower temperatures causes greater isotopic fractionation (Descolas-Gros and Fontugne, 1990). Secondly, CO_2 is more soluble in cold water. Organisms in cold water thus have a larger carbon pool from which to take their carbon, resulting in greater discrimination and more negative $\delta^{13}C$ values than in warmer water (Håkansson, 1985; Mayer and Schwark, 1999; Burkhardt *et al.*, 1999; Hayes *et al.*, 1999).

Fractionation in aquatic organisms is also influenced by the slower rate of CO_2 diffusion in water compared to gaseous CO_2 diffusion in the atmosphere. Degens (1969) suggests that this will result in reduced isotopic discrimination in aquatic organisms compared to terrestrial plants, whilst pointing out that this effect may be negligible compared to the fractionation associated with other influences such as temperature or carbon source. This process is also described by O'Leary (1981),

Håkansson (1985), and France (1995). As CO_2 is assimilated by aquatic plants and algae, dissolved CO_2 becomes limited resulting in reduced ^{13}C discrimination. As discussed previously, productivity in Lochan Uaine is not thought to have ever been sufficient to deplete CO_2 concentrations to the extent that bicarbonate utilisation by plants is necessary. However, it is possible that photosynthesis by primary producers could reduce CO_2 concentrations enough to increase discrimination. The importance of this process in an acid, well mixed, oligotrophic lake such as Lochan Uaine is unknown. Further work in mountain lakes is required to resolve these problems.

Various factors other than carbon source and temperature have been reported to affect $\delta^{13}C$ of aquatic organisms. pH is especially important as it determines the species of inorganic carbon present in the lake water (Figure 4.13). It is generally recognised that high acidity is associated with more negative $\delta^{13}C$ values (Degens, 1969; Meyers and Benson, 1988). Growth rate of organisms may be important, and can account for large $\delta^{13}C$ variations between members of the same species (Sachs *et al.*, 1999). The effect of light intensity on fractionation is examined by Burkhardt *et al.* (1999) who describe how $\delta^{13}C$ in three diatom species is related to the length of daylight, providing an aquatic analogue for the studies of Lockheart *et al.* (1997) on terrestrial vegetation. Precipitation is also linked with $\delta^{13}C$, as inwash of soil nutrients under a wetter climate could increase algal productivity and reduce ^{13}C discrimination (Meyers and Lallier-Vergès, 1999). Finally, the role of organic matter reworking must not be overlooked. Although this review has focused on primary producers, the aquatic ecosystem contains numerous other organisms. Primary producers are grazed by heterotrophs, while dead material is used by decomposers and detritivores. Additionally, non-biological diagenesis of organic matter can occur under varying physical and chemical conditions. Isotopic fractionation can occur during any of these processes, and must be born in mind when interpreting sedimentary $\delta^{13}C$ values.

4.5.6 $\delta^{13}C$ range in aquatic organisms

The factors outlined above are all important in influencing the $\delta^{13}C$ of aquatic organisms. This may explain the wide range of $\delta^{13}C$ values quoted for lake-derived organic matter in the literature. These include: -23 to -12‰ for algae (Smith and

Epstein, 1971); -41 to -15‰ for photosynthesisers in Fayetteville Green Lake, New York (Fry, 1986); -35 to -14‰ for phytoplankton (Descolas-Gras and Fontugne, 1990); -31 to -27‰ for mixed plankton (Meyers and Lallier-Vergès, 1999); -30‰ for freshwater plankton (Degens, 1969); -29 to -27‰ for plankton tow matter in Lake Michigan (Meyers and Eadie, 1993); -22 to -20‰ for autochthonous material from Walker Lake, Nevada (Meyers and Benson, 1988); -34.5 to -26.4‰ for freshwater plankton (Nakai, 1972); -35 to -8‰ for eukaryotic algae, and -27 to -3‰ for cyanobacteria (Schidlowski, 1988); -18‰ for algae in arctic, soft water environments (Michel *et al.*, 1989). Examples from marine environments include -15‰ (Burkhardt *et al.*, 1999; Sachs *et al.*, 1999) and -21‰ (Meyers and Benson, 1988) for phytoplankton samples. Tyson (1995) lists published $\delta^{13}C$ values for bacteria and plankton in marine and freshwater environments, all of which show a large range in isotopic fractionation.

Numerous authors suggest that $\delta^{13}C$ values of plankton are the same as for terrestrial C_3 plants as long as only dissolved CO_2 in isotopic equilibrium with the atmosphere is utilised in photosynthesis (Stuiver, 1975; Krishnamurthy *et al.*, 1986; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993; Meyers and Takemura, 1997). When this CO_2 supply becomes limited, and especially when bicarbonate must be used as a carbon source, a significant decrease in ^{13}C discrimination occurs (Håkansson, 1985; Meyers and Lallier-Vergès, 1999). However, this mechanism does not explain those cases where plankton are observed to have more negative $\delta^{13}C$ values than terrestrial C_3 plants (Degens, 1969; Mayer and Schwark, 1999). In one extreme example plankton from Findley Lake, an oligotrophic subalpine lake in the Cascade Mountains, has a measured $\delta^{13}C$ of -47 to -44‰ (Rau, 1978). This is lighter than the hypothetical maximum fractionation for C_3 plants of -37‰ noted by Proctor *et al.* (1992). The discrepancy is attributed to the reprocessing of CO_2 which had already been used in biological processes, and hence was already substantially depleted in ^{13}C.

4.5.7 Bulk organic $\delta^{13}C$ of UACT6

Having discussed the factors affecting carbon isotope fractionation in terrestrial and aquatic organisms, it is possible to attempt an interpretation of the bulk organic $\delta^{13}C$

record of core UACT6 from Lochan Uaine. This is given in Figure 4.14. $\delta^{13}C$ was not determined in contiguous levels but from 112 of the 231 levels in the core. The resolution in the top 15 cm is lower than for the rest of the core as some measurements had to be discounted due to possible instrumental error. The $\delta^{13}C$ values span a range of 3.3‰, with a minimum of -22.6‰ at 18.8-19.0 cm depth and a maximum of -19.3‰ at 13.6-13.8 cm depth (Appendix A). This range of values is greater than the estimated instrumental error (Section 2.2.6). It was noted previously that terrestrial C_3 plants are generally considered to have $\delta^{13}C$ values in the range -35 to -20‰, with a mean of around -29 to -26‰. The bulk $\delta^{13}C$ of Lochan Uaine sediment is thus at the very heaviest end of this range, suggesting that inputs of organic carbon to the sediment may not be solely from terrestrial sources.

The major feature visible in the core is the large shift to lighter isotope values from *c.* 16-20 cm depth. This event appears to take place very rapidly, with $\delta^{13}C$ decreasing from -20.4 to -22.6‰ across less than 2 cm depth of sediment. Likewise, $\delta^{13}C$ then increases from -22.6 to -19.3‰ across 3 cm depth of sediment. These values represent the maximum and minimum fractionations recorded. According to the chronology (Chapter 3), the duration of this event is in the region of several hundred years. Decreases in many of the other bulk parameters occur between 15-20 cm depth, including LOI, TOC and chlorin content. In each case the minimum concentration occurs slightly after the lightest $\delta^{13}C$ value.

Below 20 cm depth the $\delta^{13}C$ curve appears to show greater variability than more recent parts of the core, although this may be due in part to the greater sample resolution compared with the uppermost 15 cm. From 20 cm to the core base $\delta^{13}C$ values generally lie within the range -21 to -20‰. Three events with more negative $\delta^{13}C$ are seen at depths of around 25 cm, 35-37 cm and 46 cm. None of these shows the consistently low values seen in the larger event at 16-20 cm depth. $\delta^{13}C$ values for each level were based on the mean of two or three replicate measurements. Comparison of the duplicate measurements made for the 25, 35-37 and 46 cm levels shows that they are all associated with larger inter-sample differences in $\delta^{13}C$ than

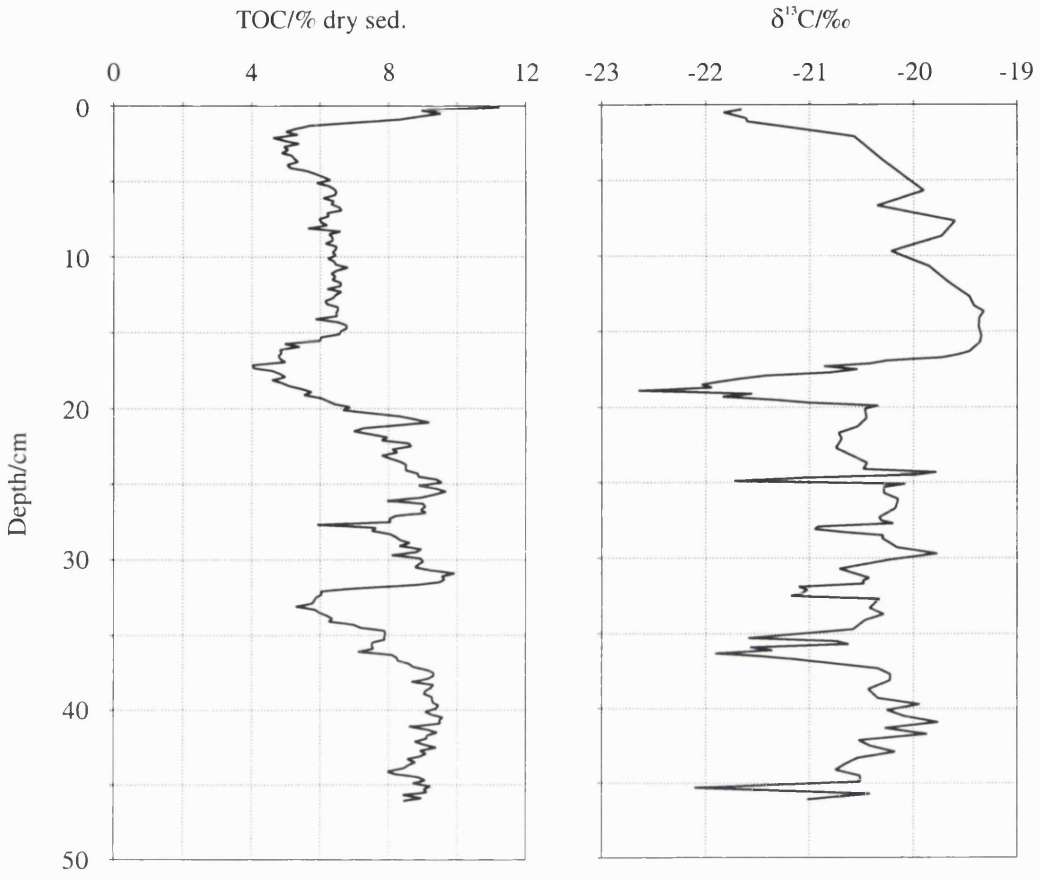


Figure 4.14 TOC and bulk organic $\delta^{13}C$, core UACT6.

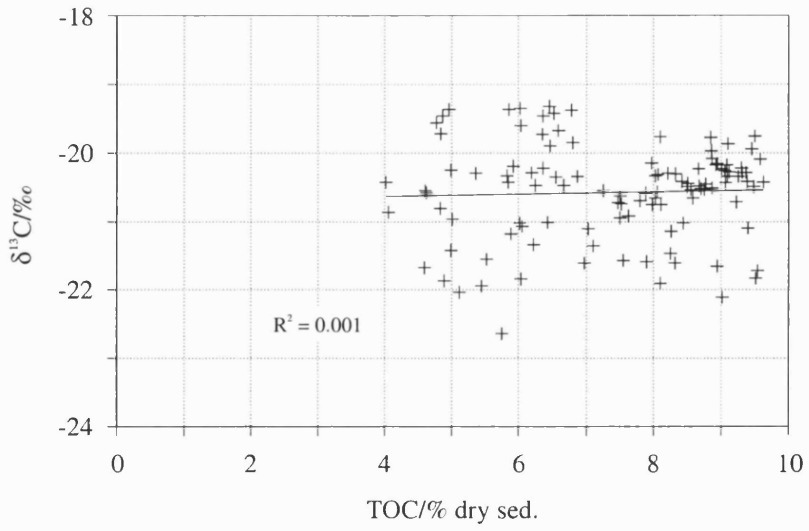


Figure 4.15 TOC *vs* bulk organic $\delta^{13}C$, core UACT6. The correlation is not significant at the 95% level.

other parts of the core. It is thought that this may reflect the presence of terrestrial plant fragments in one of the duplicates for each sample.

Plant macrofossils were clearly visible during extrusion and subsampling of the core (Chapter 3), although it is not known whether they originated in terrestrial or aquatic organisms. Given the small amount of material used for each analysis (<0.002 g) the presence of plant macrofossils can have a significant influence on the bulk $\delta^{13}C$ measurement, as they contribute lighter $\delta^{13}C$ values than are seen in the bulk matrix of fine organic detrital material. An erroneous determination of $\delta^{13}C$ in one duplicate will produce an erroneous bulk $\delta^{13}C$ measurement when the mean of the duplicates is calculated. It was not possible to exclude these duplicates from the analysis as across the whole core the variation between duplicates spanned a continuum of variability from <0.1‰ to >2‰ per sample, and there was no obvious boundary value to differentiate 'accurate' and 'inaccurate' $\delta^{13}C$ measurements. However, the problem of variability between duplicates due to contamination by macrofossils is not thought to be significant throughout most of the core, for two reasons. Firstly, great care was taken when extracting material for analysis to avoid inclusion of any visible macrofossils. The presence or absence of terrestrial material is important in terms of reconstructing changes in organic matter inputs to the lake, but it was felt that such changes should show up in the $\delta^{13}C$ record regardless of whether or not macrofossils were included in the sample to be analysed. Secondly, although the variability between duplicates is as large as 2‰, the majority of samples show much lower variability (±0.3‰ around the mean). Given that the event from 16-20 cm consists of light $\delta^{13}C$ values in ten contiguous samples, it is unlikely that the observed values are due to macrofossil contamination. Hence although the events at 25, 35-37 and 46 cm depth may be artefacts of macrofossil contamination, we can be much more confident that the main 16-20 cm event is real.

Analysis of $\delta^{13}C$ in sediment deposited after the 16-20 cm event is slightly limited by the lower sample resolution. We can say that the heaviest values (>-19.5‰) are found in the 5 cm immediately following the event, and that there follows a gradual increase in fractionation to almost -22‰ at the surface. By comparison, most published values

of $\delta^{13}C$ in lake surface sediments are more depleted, such as the -25.3‰ in Lake Biwa (Meyers and Horie, 1993), -26.3‰ in Lake Michigan (Rea *et al.*, 1980), -24.2‰ in Walker Lake (Meyers, 1990), -26.9‰ in Pyramid Lake (Tenzer *et al.*, 1997), -29.9‰ in Lake Baikal (Qiu *et al.*, 1993), -28.4‰ in Coburn Mountain Pond (Ho and Meyers, 1994), and -26.4‰ in Lake Bosumtwi (Talbot and Johannessen, 1972). The values at the top of UACT6 are difficult to interpret. As with the 16-20 cm event, the low $\delta^{13}C$ values seen in all four samples from the top 1 cm suggest that this isotopic excursion is real. Yet whereas the light values at 16-20 cm were associated with low TOC concentrations, the light values at the surface coincide with the highest TOC concentrations in the core. Indeed, throughout the core as a whole there is no significant correlation between $\delta^{13}C$ and TOC (Figure 4.15). It is especially noticeable that unlike the section from 16-20 cm, the low TOC contents from 1-5 cm and 32-34 cm are not correlated with a major lightening of $\delta^{13}C$ values. This contrasts with the analysis of a section of core UACT4, in which a much stronger correlation between $\delta^{13}C$ and LOI is apparent (Figure 1.1). The reasons for this are not known, although it is interesting to note that although a *c.* 10% LOI fluctuation is recorded in both the 16-20 cm section of UACT6 and in the section of UACT4, the $\delta^{13}C$ shift in UACT4 of >3‰ is several times larger than the 0.8‰ fluctuation observed in UACT4.

4.5.8 Interpretation of bulk organic $\delta^{13}C$ variations

4.5.8.1 Previous studies

Given the wide range of factors affecting carbon fractionation of living organisms, it is not surprising that many different interpretations of $\delta^{13}C_{TOC}$ profiles in Holocene lake sediments are given. Some authors interpret periods of ^{13}C enrichment as indicating an increase in lake productivity, as at Lake Bosumtwi, Ghana (Talbot and Johannessen, 1972), Lakes Ontario and Erie (Schelske and Hodell, 1991, 1995; Hodell and Schelske, 1998), Elk Lake, Minnesota (Dean and Stuiver, 1993), Lakes Suwa and Kizaki, Japan (Nishimura, 1978), Lake Illisarvik, Canada (Michel *et al.*, 1989), and in sections of cores from Lake Biwa (Nakai, 1972; Ishiwatari and Uzaki, 1987; Meyers and Takemura, 1997). In the cases of Lake Bosumtwi, Lake Biwa, and Elk Lake, the

shift in productivity, and hence in $\delta^{13}C$, is thought to be climatically driven either through temperature or precipitation changes.

The opposite relationship between productivity and $\delta^{13}C$ is inferred by some authors, whereby an increase in lake productivity causes increased discrimination and lighter $\delta^{13}C$ values. Examples include Lake Steisslingen, Germany (Mayer and Schwark, 1999), Lake Baikal (Qiu *et al.*, 1993), Coburn Mountain Pond (Ho and Meyers, 1994), and Karewa lake sediments, India (Krishnamurthy *et al.*, 1986). In the case of the Karewa lake, low productivity during cold, dry periods was thought to prevent CO_2 limitation and allow for maximum assimilation of ^{12}C by organisms. A similar trend towards more negative $\delta^{13}C$ during cold periods is seen in the twelve lakes studied by Stuiver (1975): Lake Quassapaug, Connecticut; Linsley Pond, Connecticut; Queechy Lake, New York; Jacobson Lake, Minnesota; Lake of the Clouds, Minnesota; Rutz Lake, Minnesota; Horseshoe Lake, Minnesota; Hall Lake, Washington; Lake Hule, Israel; Lake Jih Tan, Taiwan; Lake Yueh Tan, Taiwan; Lake Victoria, Uganda. Conversely, $\delta^{13}C$ in Walker Lake, Nevada is less negative during dry periods (Benson *et al.*, 1991), while Sifeddine *et al.* (1994) find a different situation again in Lake Carajas, Brazil. Although the switch from mainly terrestrial plant input during wet periods to algal input during dry periods shows up clearly in the TOC and C/N profiles, no variation in $\delta^{13}C$ is seen as algal productivity was never high enough to limit CO_2.

Climatically-induced shifts from C_4 to C_3 plant domination in the catchment of Lake Baikal affect $\delta^{13}C$ (Qiu *et al.*, 1993), but such an effect can be ruled out at Lochan Uaine as C_3 plants have dominated throughout the Holocene. The work of Meyers and Takemura on a Lake Biwa core is interesting to compare with the record at Lochan Uaine, as high TOC content during warm periods (identified from the pollen record) coincides with high $\delta^{13}C$ during certain episodes, but low $\delta^{13}C$ during others. This is similar to the UACT6 record, where the TOC concentration minimum at 15-20 cm depth is associated with a major $\delta^{13}C$ excursion, but no such variation in $\delta^{13}C$ is associated with the other two main TOC minima. Finally, it is worth noting the results of two studies which examine lakes in similar climatic environments, and with similar nutrient status, to Lochan Uaine. Michel *et al.* (1989) recorded a $\delta^{13}C$ value of -18‰

for algae in a soft water lake in arctic Canada. By contrast, Rau (1978) found the plankton of an oligotrophic, subalpine lake (Findley Lake, Cascade Mountains) to have $\delta^{13}C$ values in the range -47 to -44‰, attributed to the assimilation of biogenic CO_2. This demonstrates the difficulties involved in interpreting sedimentary $\delta^{13}C$ records.

4.5.8.2 Lochan Uaine

Interpretation of the bulk organic $\delta^{13}C$ record at Lochan Uaine must obviously focus on the major event in the record - the large fluctuation towards more negative $\delta^{13}C$ between 15 and 20 cm depth. Certain processes can be ruled out. For instance, C_4 plants are not present in the catchment and are unlikely to have been present at any time during the Holocene, hence $\delta^{13}C$ does not reflect shifting dominance between C_3 and C_4 plants in the catchment. Likewise, carbon limitation is not thought to be significant. Lochan Uaine is a relatively well-mixed lake. The lack of prolonged stratification means that there will be a constant supply of dissolved CO_2 to all parts of the water column, including the bottom waters. The lake is also ultra-oligotrophic, as a result of which there is a low demand for CO_2 to be used in photosynthesis. Thus, CO_2 will not become limited even during periods of relatively high productivity for the lake. Finally, there are no carbonate inputs to the lake which could alter the $\delta^{13}C$ of dissolved carbon in the lake water.

Previous studies of bulk organic $\delta^{13}C$ in lakes as discussed above are divided as to whether an increase in lake productivity causes a shift to heavier or lighter isotope values. Given the well-mixed, oligotrophic nature of Lochan Uaine it is hard to see how changes in lake productivity alone could account for the >3‰ variation seen in core UACT6. A more likely cause of this variation is changes in the relative amounts of organic input from different sources. At Lochan Uaine, the two main organic matter sources are C_3 plants, which are almost exclusively found in the catchment rather than the lake and are thus an allochthonous indicator, and algae and bacteria, which are used as an autochthonous indicator. The $\delta^{13}C$ ranges of C_3 plants are generally well known, but a wide selection of ranges are given for aquatic micro-organisms. Bulk $\delta^{13}C$ values of aquatic organisms were not measured at Lochan

Uaine due to the lack of material collected. However, there is evidence from compound-specific isotope analysis of sedimentary lipids (Chapter 6) that autochthonous organic matter in Lochan Uaine is enriched in ^{13}C relative to allochthonous organic matter. The depletion event between 15-20 cm depth in UACT6 may represent a decreased input of autochthonous material to the sediment relative to allochthonous material. Such an interpretation agrees with the chlorin record which also suggests a decrease in lake productivity at the same depth. However, no depletion in $\delta^{13}C$ is seen to match the other two minima in the chlorin record.

Variations in $\delta^{13}C$ related to temperature changes are another possibility at Lochan Uaine. Depletion of ^{13}C is generally increased at lower temperatures (Schleser, 1995; Mayer and Schwark, 1999). Over the course of the Holocene, average temperature variations are thought to be small at less than 1°C. A change of this magnitude would be unlikely to result in a variation in the $\delta^{13}C$ of organic matter of over 3‰ as seen in UACT6. However, the average temperature is probably not as important as the temperature during certain parts of the year. In particular, the temperature during the growing season may be significant as this affects fractionation during the period of maximum primary productivity, and it is this signal that is likely to dominate the sedimentary record. Hence, it is possible that climatic variation is displayed in the organic $\delta^{13}C$ record as changes in fractionation related to growing season temperature, with increased fractionation reflecting colder temperatures.

4.6 Summary

This chapter has examined a range of bulk determinations made on Lochan Uaine core UACT6. These were dry weight and LOI, concentrations of total carbon, TOC, carbonate, nitrogen, hydrogen, and chlorins, C/N and C/H ratios, and bulk organic $\delta^{13}C$. All of these variables are potentially related to the amount and source of organic matter deposited in the sediment, and hence all are potential indicators of past productivity in the lake and its catchment.

4.6.1 LOI, total carbon, carbonate, TOC, nitrogen and hydrogen

Percentage LOI, total carbon, TOC, nitrogen and hydrogen contents all exhibit similar downcore profiles. The main features of these profiles include three periods of low values at *c.* 1-6, 15-20 and 32-36 cm depth, and periods of increased values at *c.* 0-1, 6-15, 20-32 and 36-46 cm depth. These periods of increased values are slightly different in nature. From 6-15 cm depth values remain stable but at a comparatively low level, although not as low as during the periods of minimum values. Higher values are seen from 20-32 and 36-46 cm depth, with greater variability being apparent during the former period. LOI and TOC are found to be very closely correlated (Equation 4.1), suggesting that in lakes such as Lochan Uaine one can be calculated from the other. This linear relationship may break down in sediments with LOI values less than 2-3% (Mackereth, 1966; Håkanson and Jansson, 1983). The similarities between LOI, which measures the amount of organic matter in the sediment, and TOC, nitrogen and hydrogen, suggest that organic matter is the main source of C, H and N in the sediment. Carbonate is present in negligible concentrations only.

4.6.2 C/N and C/H ratios

Although LOI, TOC, nitrogen and hydrogen profiles all reflect the total concentration of organic matter in the sediment, downcore variability in these parameters does not imply a change in the amount of organic matter input, as a change in mineral matter input could have the same effect. As such, LOI, TOC, N and H profiles are not a direct proxy for organic matter productivity in Lochan Uaine and its catchment. C/N and C/H ratios may potentially be used to infer relative changes in organic matter source, if not changes in total productivity. These profiles and their interpretation are given in Figure 4.16. However, neither C/N nor C/H ratios show any major downcore variability to match that seen in LOI and TOC. These ratios, and the C/H ratio in particular, are thought to be insensitive to small shifts in organic matter source. From 5 cm depth to the core base the C/N ratio varies between *c.* 10-13. These values suggest a mixed contribution of algal/bacterial and higher plant-derived organic matter. Higher C/N ratios are seen in the top 5 cm of core. Two possible explanations are suggested for this: 1) diagenetic changes occurring near the mud-water interface,

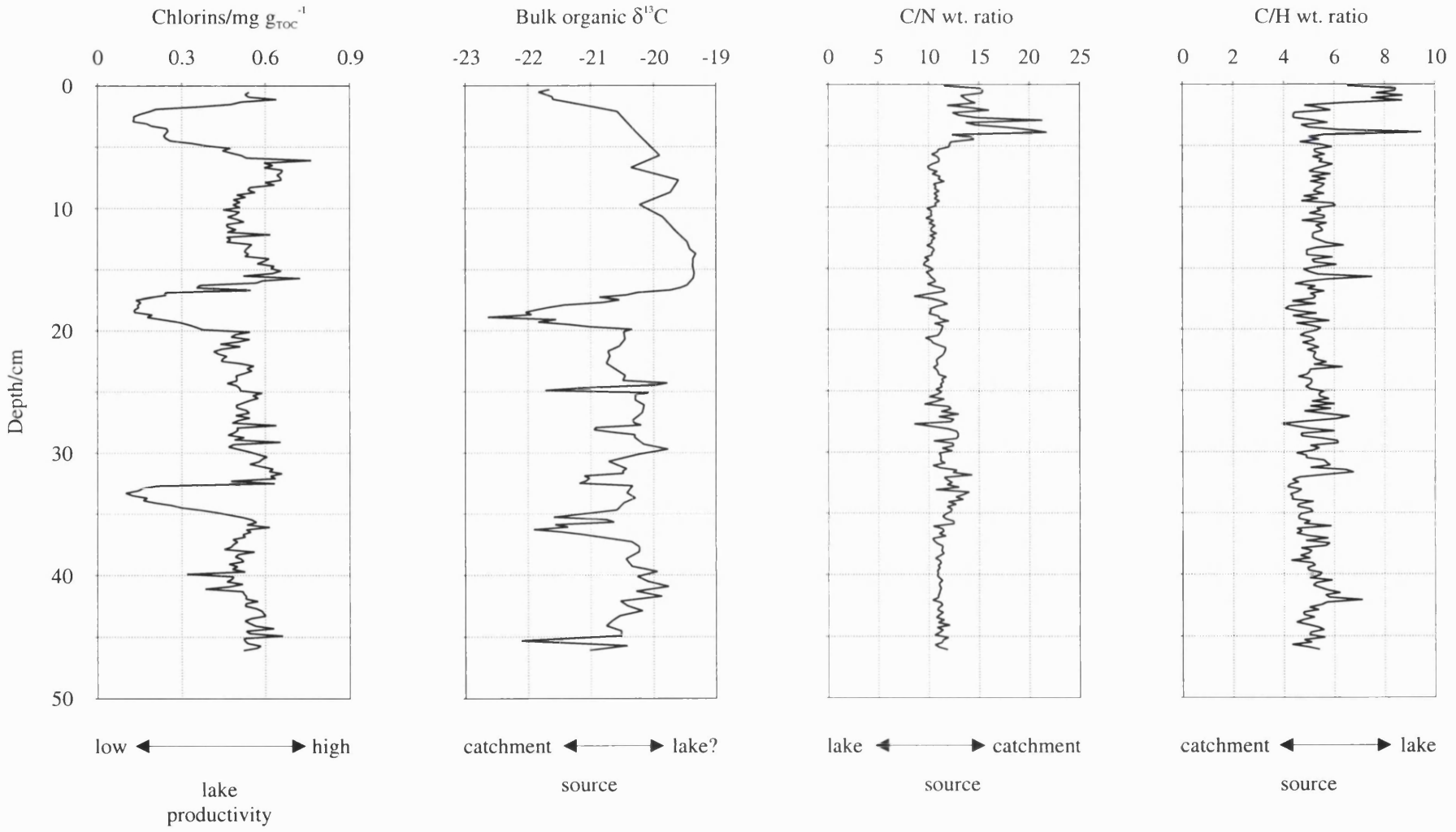


Figure 4.16 Potential bulk indicators of palaeoproductivity, core UACT6.

rather than an increased relative input of higher plant organic matter; 2) instrumental errors in nitrogen determination at low concentrations.

4.6.3 Chlorins

Chlorin concentration is perhaps the most useful proxy measure of palaeoproductivity. By expressing chlorin values as a proportion of TOC, rather than as a proportion of sediment dry weight, the resulting chlorin profile is independent of variations in sediment mineral content. Chlorins are thought to be a product of the degradation of algal chlorophyll, hence high chlorin concentrations are interpreted as reflecting periods of high lake productivity (Figure 4.16). The chlorin profile shows similar features to the LOI, TOC, nitrogen and hydrogen profiles, with two main differences. Firstly, the concentration minima at *c.* 1-6, 15-20 and 32-36 cm depth are much more clearly defined than in the other bulk parameters, and the concentrations during these minima are far lower relative to concentrations during the intervening periods. This suggest that chlorin concentration may not respond in a linear fashion to productivity. Secondly, the periods between the minima show greater similarities in the chlorin record. Notably, the section from 6-15 cm depth displays similar chlorin concentrations to those from 0-1, 20-32 and 36-46 cm depth, whereas in the LOI, TOC, N and H profiles this section was characterised by relatively low values. It is possible that the coincidence of chlorin minima with the LOI minima reflects decreased preservation of chlorins during periods of low sedimentary organic content, but it has not been possible to test this hypothesis.

4.6.4 Bulk organic $\delta^{13}C$

As with C/N and C/H ratios, the potential of bulk organic $\delta^{13}C$ analysis lies in the ability to infer changes in relative contributions of organic matter sources, rather than to reconstruct an absolute measure of palaeoproductivity. Of the several hypotheses proposed to explain the downcore $\delta^{13}C$ variations in UACT6, it is thought that the most likely explanation is that the variations reflect changes in the relative inputs from different organic matter sources. C_3 plants typically have $\delta^{13}C$ values more depleted than those seen in UACT6. Compound-specific isotope analysis of lipids (Chapter 6) suggests that lake primary producers have $\delta^{13}C$ values less depleted than those seen in

UACT6. Greater fractionation is thus interpreted as reflecting an increased relative importance of allochthonous contributions to the sediment, and less negative $\delta^{13}C$ values reflect greater autochthonous input. The possible influence of temperature variations on the $\delta^{13}C$ profile are not known.

Chapter 5

Lipid Analysis

5.1 Introduction

The preceding chapter examined downcore variations in bulk organic parameters in UACT6. The variation in some of these parameters suggests a variation in the origin of the organic material between higher plant and algal/bacterial sources. For instance, the greater heavy isotope depletion seen in the bulk organic $\delta^{13}C$ profile from 15-20 cm depth suggests a relative increase in the importance of higher plant inputs to the sediment. Such changes can be better investigated by studying smaller fractions of the organic matter. The lipid fraction was used for this analysis. Lipids typically account for only a few percent of total sedimentary organic matter, with the rest being composed of humic acids, lignin, cellulose, and so on. However, lipids have an important advantage in that they can be used as biomarkers - in other words, certain components can be related to a particular source organism or group of organisms. Analysis of these biomarkers can be used to indicate variations in relative organic matter sources in the lipid fraction, which in turn indicates the sources contributing to the whole organic fraction. This chapter describes the analysis of lipids from Lochan Uaine. The first section examines lipids extracted from eight reference vegetation types collected from the Lochan Uaine catchment. Along with previously published studies, these analyses are used to indicate the most likely sources of lipids found in the sediment. The second section describes the analysis of lipids extracted from twenty-eight levels in core UACT6, covering the last 2000 yr of sediment accumulation. These results are discussed in relation to the modern reference material, and interpreted in terms of changes in organic matter sources. A summary of the findings is provided at the end of the chapter.

5.2 Modern reference specimens

5.2.1 Total lipid extracts

The eight vegetation specimens chosen for analysis were all prepared in exactly the same way as for sediment samples (Section 2.2.7), except that due to the higher lipid content smaller masses of reference vegetation specimens were required. The specimens had been chosen to reflect the major vegetation types found in Lochan

Uaine and its catchment which could be contributing organic material to the lake sediment. The mass of lipids extracted as a proportion of dry weight is consistently higher than for sediment samples (Table 5.1). No sediment samples have a total lipid extract (TLE) greater than 5 mg $g_{dry\ wt}^{-1}$ (Figure 5.8a), whereas all reference vegetation specimens have concentrations of above 10 mg $g_{dry\ wt}^{-1}$. Within the eight reference vegetation specimens the TLE varies by more than one order of magnitude. The liverwort and *Sphagnum* have extracts of 11-12 mg $g_{dry\ wt}^{-1}$, while the fern sample contains >200 mg $g_{dry\ wt}^{-1}$. This represents more than one fifth of the total fern dry weight. *Juniperus* also displays a high lipid content.

Table 5.1 Masses of total lipid extracts (TLEs) from reference specimens.

Vegetation specimen	TLE / mg $g_{dry\ wt}^{-1}$
Algal scrape*	23.6
Aquatic bryophyte	20.2
Lichen (*Cladonia* sp.)	31.0
Fern	204.9
Grass	54.7
Dwarf shrub (*Juniperus*)	108.1
Liverwort	11.4
Moss (*Sphagnum*)	11.9

* collected from lowland lake

5.2.2 Hydrocarbons

Most of the modern reference specimens contain a similar distribution of hydrocarbon components to those seen in the lake sediment. All specimens are dominated by *n*-alkanes, and only grass contains a significant proportion of other hydrocarbons. Histogram distributions of *n*-alkanes from the eight reference specimens are given in Figure 5.1. In all cases a strong odd-over-even chain-length predominance is apparent.

Although the greatest TLEs are seen in the fern and in *Juniperus*, by far the greatest concentration of *n*-alkanes is seen in grass where *n*-C_{31} is present at almost 600 μg $g_{dry\ wt}^{-1}$. The dominant component in the fern, the C_{29} *n*-alkane, has a concentration of 130 μg $g_{dry\ wt}^{-1}$, whereas *n*-C_{27} in *Juniperus* is present at <11 μg $g_{dry\ wt}^{-1}$. Of the other specimens, the most abundant *n*-alkanes in *Cladonia* and the liverwort have concentrations similar to those of *Juniperus*, whilst *n*-C_{21} in *Sphagnum* is higher at

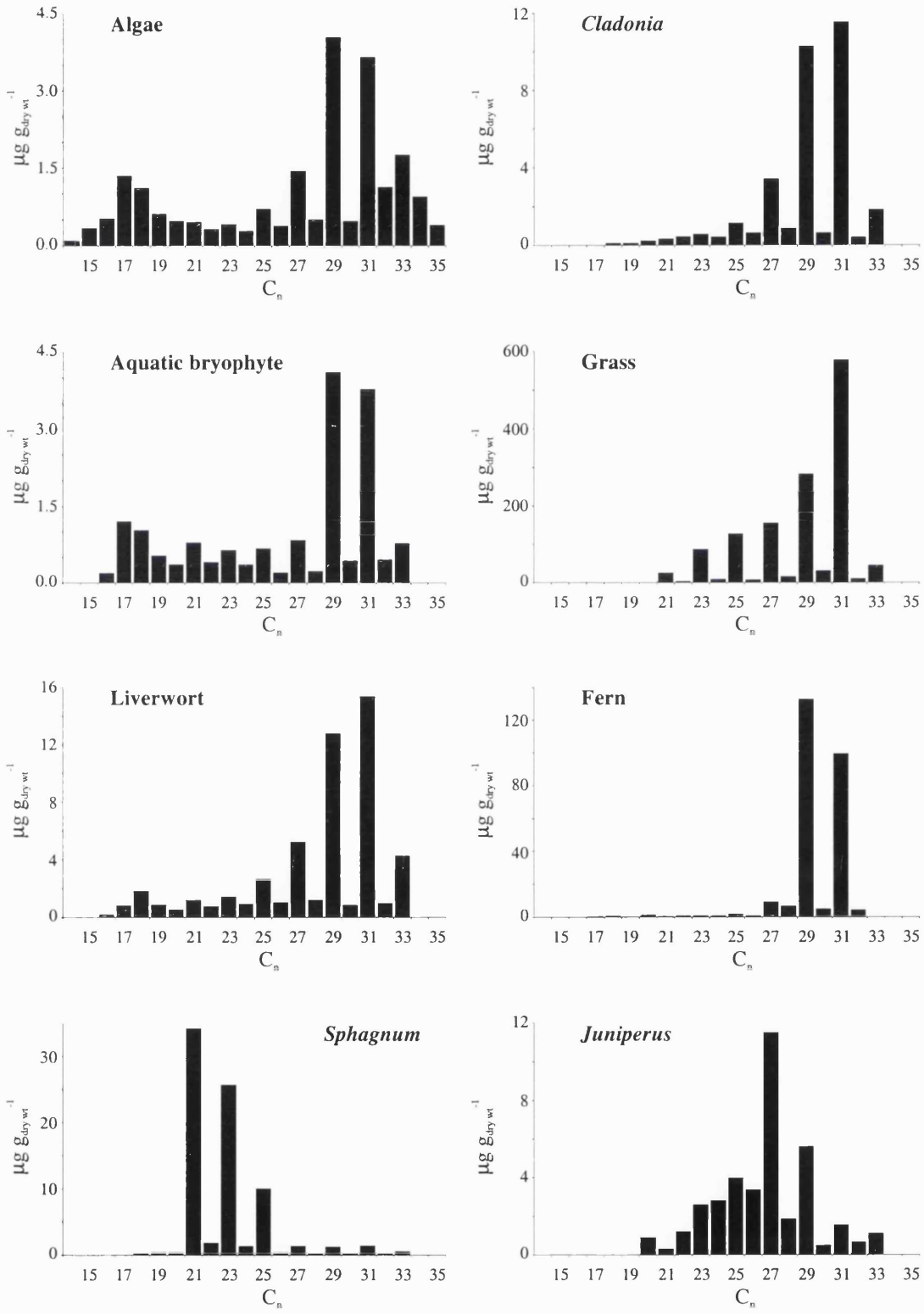


Figure 5.1 Distributions of *n*-alkanes in modern vegetation from the Lochan Uaine catchment (except for the algal specimen, which is taken from a lowland lake).

>30 μg $g_{dry\ wt}^{-1}$. The lowest values are seen in the algal and aquatic bryophyte specimens, where hydrocarbons are present at <4.5 μg $g_{dry\ wt}^{-1}$.

Similar *n*-alkane distributions are seen in the algal, aquatic bryophyte and liverwort specimens (Figure 5.1). These distributions are bimodal, the maxima occurring at *n*-C_{17} to *n*-C_{18}, and at *n*-C_{29} to *n*-C_{31}. In each case the longer chain-length *n*-alkanes are the more abundant. These components also show a stronger odd-over-even chain-length predominance than for the less abundant short chain-length components. In liverwort, *n*-C_{18} is more abundant than *n*-C_{17}. It is thought that all three distributions represent contamination from organisms other than those under study. The algal sample was obtained by scraping submerged rocks from around the shoreline of a lowland lake in southern England, as similar material collected from Lochan Uaine did not provide a sufficient concentration of lipids for analysis. Rock scraping removes attached algae such as epilithic diatoms, but will also remove any sedimented detrital organic material. When algal scraping was undertaken, the rocks were seen to be covered by a layer of fine organic detritus, thought to originate mainly from catchment soil erosion. As it was not possible to separate algae from this detritus, the *n*-alkane distribution shown in Figure 5.1 almost certainly represents a contribution from both algal and higher plant sources. Conversely, the aquatic bryophyte and liverwort specimens from Lochan Uaine are contaminated with algal material. In both cases, microscopic inspection of the specimens reveals large numbers of attached diatoms. The extent and significance of this contamination is not known. Comparison with the literature suggests that the true algal *n*-alkane signal consists solely of short chain-length components, whilst the true aquatic bryophyte and liverwort signals consist of mid and longer chain-length components. The other reference vegetation specimens, which are not from submerged or semi-submerged environments and hence are less likely to be affected by algal or organic detrital contamination, show no short/long chain-length bimodality in their *n*-alkane distributions.

The *Sphagnum* specimen contains *n*-alkanes ranging from C_{18} to C_{33}, but is entirely dominated by, in order of decreasing concentration, *n*-C_{21}, *n*-C_{23}, and *n*-C_{25} (Figure 5.2) A strong odd-over-even predominance is evident. This predominance of mid

chain-length *n*-alkanes in *Sphagnum* agrees closely with observations by Cranwell (1973b) and Quirk (1978), although *n*-C_{23} is found to be the dominant homologue in those cases. Nott *et al.* (2000) also find *n*-C_{23} to predominate in *Sphagnum recurvum*, although a smaller *n*-C_{31} peak is seen in *S. palustre* and *S. papillosum*, and this component is dominant in *S. magellanicum*, *S. capillifolium* and *S. cuspidatum* (Figure 5.3).

In the *Cladonia* specimen, *n*-C_{31} is slightly more dominant than *n*-C_{29}, with lower concentrations of *n*-C_{27} and *n*-C_{33}. Lichens are a symbiotic organism formed from fungi and algae. Barnes and Barnes (1978) identified *n*-C_{29} as predominating in many fungi, which agrees fairly well with the *Cladonia* results. No major peak in short chain-length *n*-alkanes is seen which could have derived from the algal component of *Cladonia*, although the algal biomass in lichens is very small compared to that of the fungi. Both C_{18} and C_{19} *n*-alkanes are present in low concentrations, as are other odd chain-length *n*-alkanes up to *n*-C_{33}. The grass is dominated by *n*-C_{31}, with *n*-C_{29} less abundant and shorter chain-lengths more abundant than in *Cladonia*. A similar dominance was seen by Cranwell *et al.* (1987), although in that case the grasses studied are C_4 grasses, whereas all grasses in the Lochan Uaine catchment utilise the C_3 photosynthetic pathway. In the fern, the concentration of the *n*-C_{29} homologue is slightly greater than *n*-C_{31}, but other hydrocarbons are almost completely absent. Barnes and Barnes (1978) note that ferns, which lie below flowering plants phylogenetically, exhibit bimodal *n*-alkane distributions maximising at C_{17}/C_{18} and $C_{25}/C_{27}/C_{29}$. In all of the above cases, a strong odd-over-even chain-length predominance is apparent. *Juniperus* differs from *Cladonia*, grass and fern in that *n*-C_{27} is dominant, and that the expected odd-over-even predominance is barely noticeable at shorter chain-lengths.

The only modern reference specimen to contain a significant hydrocarbon component other than *n*-alkanes is grass (Figure 5.4). Three homologous series of components are visible, eluting before the C_{23} to C_{29} *n*-alkanes. These components have yet to be identified, but it is thought that they may be *n*-alkenes, the three series representing differing positions of the double carbon bond, or branched hydrocarbons.

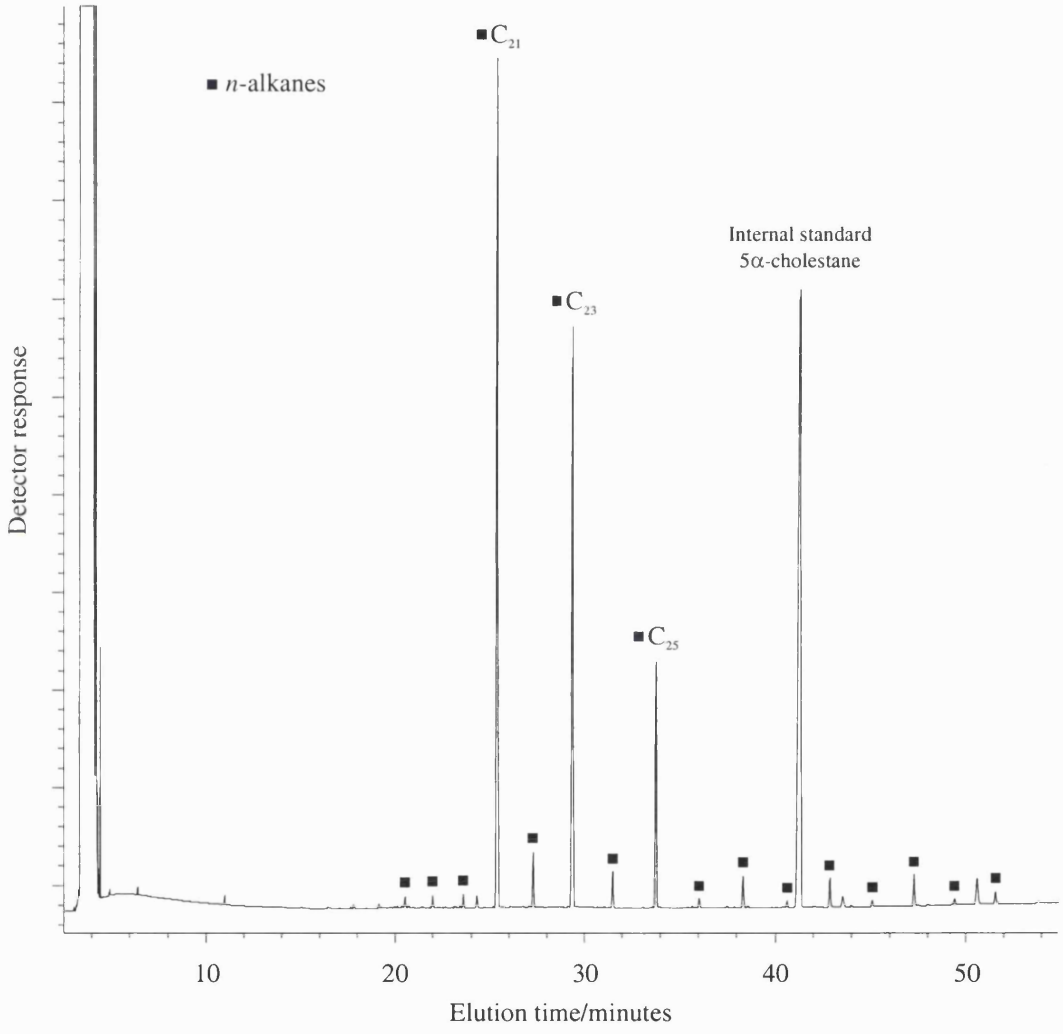


Figure 5.2 GC profile of *Sphagnum* hydrocarbon extract from the Lochan Uaine catchment.

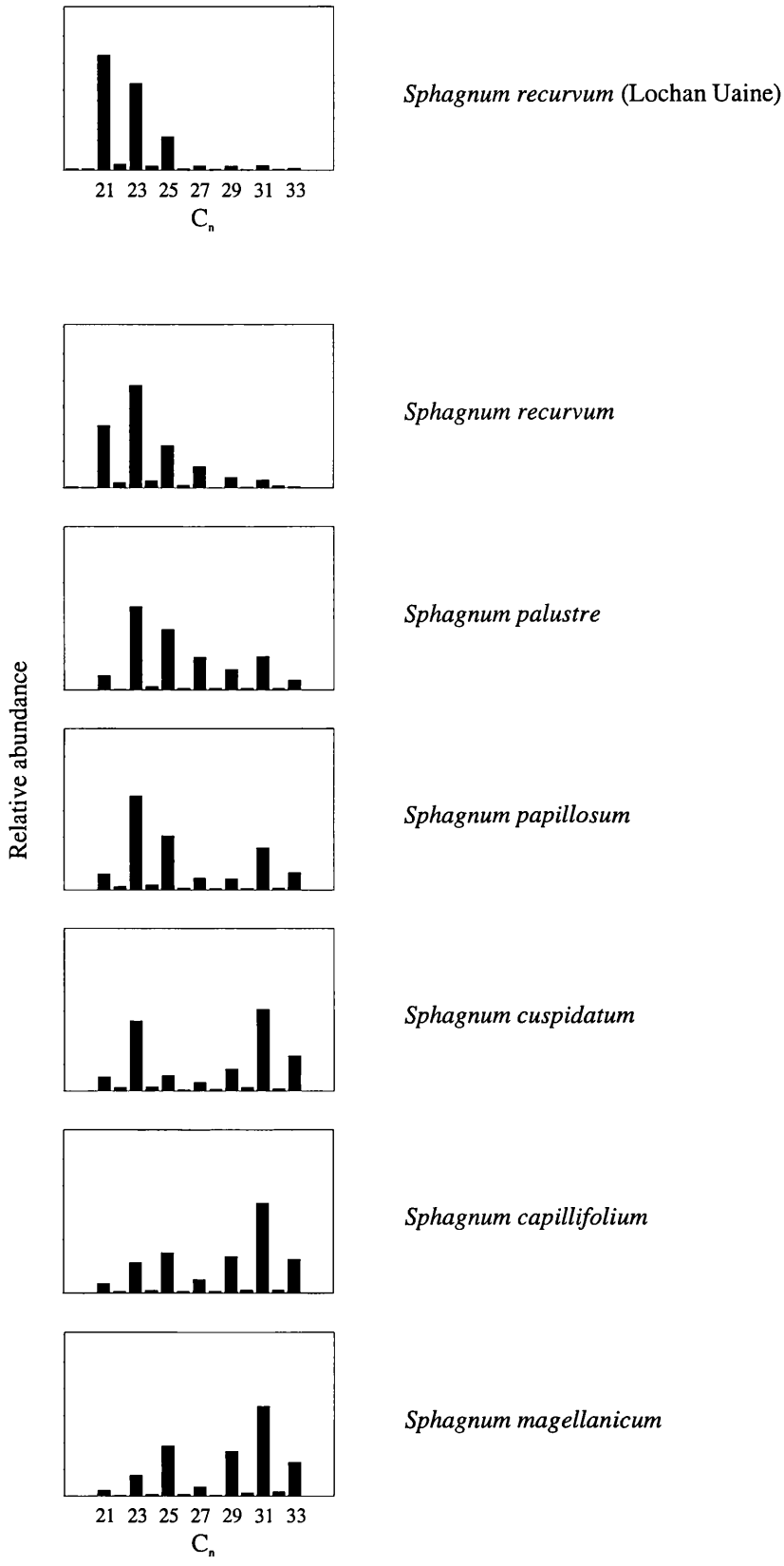


Figure 5.3 Comparison of *n*-alkane histogram distribution of *Sphagnum recurvum* collected from the Lochan Uaine catchment with *n*-alkane distributions of six species of *Sphagnum* analysed by Nott *et al.* (2000).

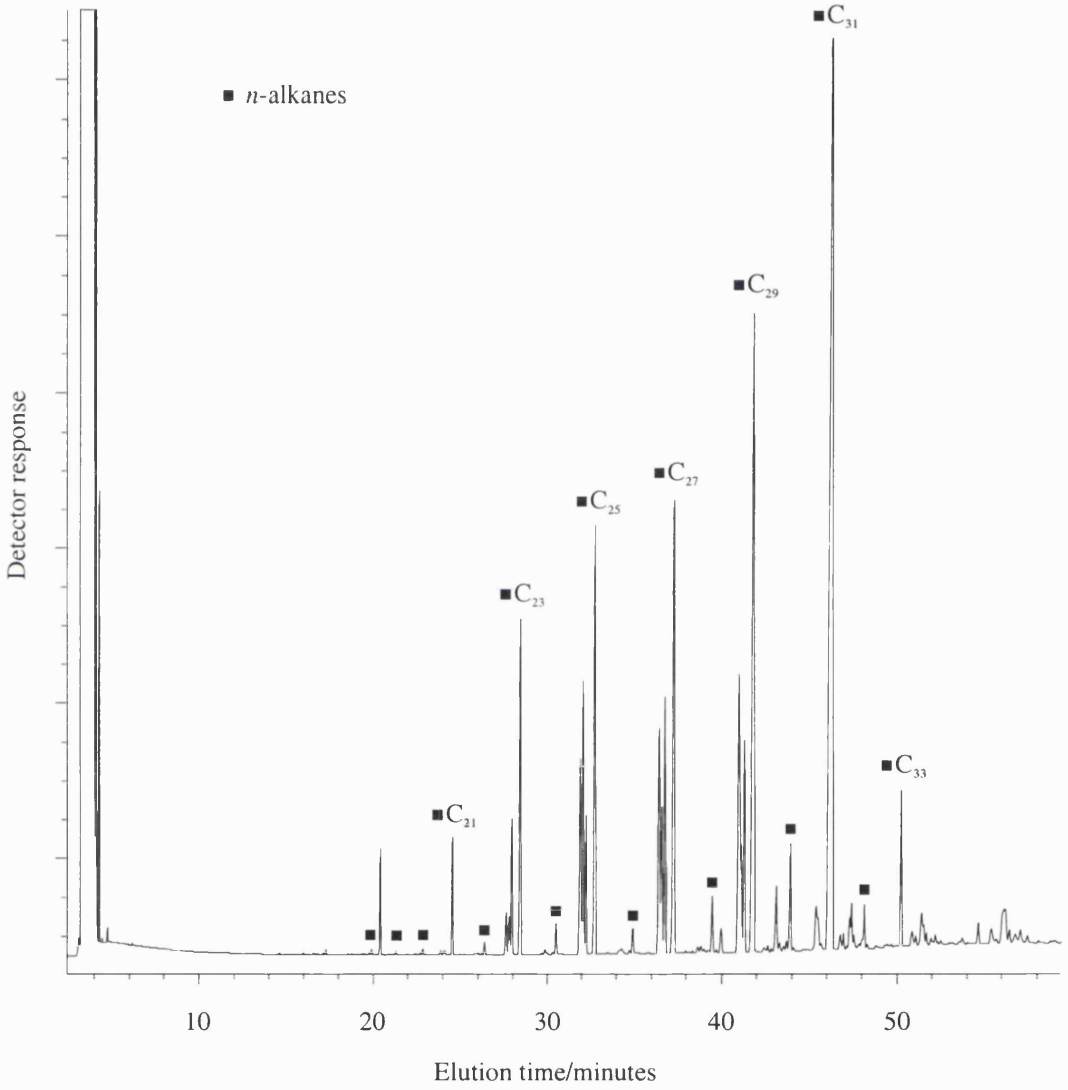


Figure 5.4 GC profile of grass hydrocarbon extract from the Lochan Uaine catchment.

Identification of these components is not thought to be of great importance to the interpretation of the UACT6 lipid record as there is no evidence for their presence in the sediment, including in the surface sample. This suggests either that they form a very minor or no input, or that they are lost through degradation prior to deposition in the sediment column.

5.2.3 Alcohols and sterols

Of all the fractions studied, the alcohol and sterol fraction shows the greatest differences between catchment reference material and the sediment. Whereas the sediment of core UACT6 is dominated by *n*-alkanols, reference specimens are dominated by sterols. These comprise both unsaturated (stenol) and saturated (stanol) forms. Sterols are identified by mass spectral analysis and by comparison with published data (Brooks *et al.*, 1968; Steel and Henderson, 1972; Gaskell and Eglinton, 1976; Nishimura and Koyama, 1976, 1977; Huang and Meinschein, 1978; Combaut, 1986). Sterols as TMS ethers are identified on the basis of a range of ions, such as $[M]^+$, $[M-15]^+$, $[M-90]^+$ and $[M-105]^+$. In particular, peaks at *M/z* 129 and $[M-129]^+$ are diagnostic of Δ^5-stenol TMS ethers, whilst peaks at *M/z* 215, 216, 217, 230 and 305 are diagnostic of stanol TMS ethers.

Despite the vast number of possible sterols which could be formed by varying the number of carbons in the side chain, the amount and positions of unsaturation, stereoisomeric configuration and so on, living organisms are dominated by relatively few sterols (Huang and Meinschein, 1979). The common and systematic names of the most common sterols are given in Table 5.2. Common names will be used throughout the text for clarity.

5.2.3.1 Sterol distributions in living organisms

The distributions of sterols in organisms has been the subject of much discussion in the literature, particularly the question of whether certain sterols or groups of sterols may be used as biomarkers for precursor organisms. Higher plants are generally dominated by C_{29} sterols such as β-sitosterol, stigmasterol and stigmastanol (Tomita *et al.*, 1969; Bennett *et al.*, 1969; Bae and Mercer, 1970; Pryce, 1971; Willuhn and

Köstens, 1975). Lesser amounts of C_{28} sterols such as campesterol and ergostanol are often found (Nishimura and Koyama, 1977; Rieley *et al.*, 1991a). Although no C_{27} sterols were identified in leaf wax samples from six tree species in the catchment of Ellesmere Lake, Shropshire (Rieley *et al.*, 1991a), other studies have found both cholesterol and cholestanol in higher plants (Gaskell and Eglinton, 1976; Nishimura and Koyama, 1977). Huang and Meinschein (1979) state that after C_{29} sterols, C_{27} sterols have the greatest predominance in higher plants. Hence, while there is general agreement that C_{29} sterols predominate in higher plants, it is also evident that they provide a source of both C_{27} and C_{28} sterols.

Table 5.2 Common sterols in living organisms.

Common name	Systematic name	Carbon number	Structure (Appendix F)
Stenols			
Cholesterol	cholest-5-en-3β-ol	C_{27}	I
Campesterol	24α-methylcholest-5-en-3β-ol	C_{28}	II
Brassicasterol	24β-methylcholest-5,22E-dien-3β-ol	C_{28}	III
Ergosterol	24β-methylcholest-5,7,22E-trien-3β-ol	C_{28}	IV
β-Sitosterol	24α-ethylcholest-5-en-3β-ol	C_{29}	V
Stigmasterol	24α-ethylcholest-5,22E-dien-3β-ol	C_{29}	VI
Dinosterol	4α,23,24R-trimethyl-5α-cholest-22E-en-3β-ol	C_{30}	VII
Stanols			
Cholestanol	5α-cholestan-3β-ol	C_{27}	VIII
Ergostanol	24β-methyl-5α-cholestan-3β-ol	C_{28}	IX
Stigmastanol	24α-ethyl-5α-cholestan-3β-ol	C_{29}	X

Accounts of sterol distributions in other organisms are similarly conflicting. According to Huang and Meinschein (1979), C_{27} and C_{28} sterols are most abundant in marine plankton and invertebrates. They propose that different ecosystems may be identified by the relative proportions of C_{27}-C_{29} sterols (Figure 5.5). However, this scheme appears to be overly simplistic. Nishimura and Koyama (1977) found that certain species of phytoplankton and zooplankton (the cyanobacteria *Microcystis aeruginosa* and the rotifer *Brachionus calyciflorus*) were dominated by cholesterol (C_{27}), campesterol (C_{28}) and their saturated analogues, in accordance with Huang and Meinschein's proposal. By contrast, a rotifer population analysed by Robinson *et al.* (1984a) contained, in addition to C_{27} and C_{28} sterols, significant quantities of C_{29} (24-ethylcholest-5,7,22-trien-3β-ol and β-sitosterol) and C_{30} (dinosterol) sterols. In

ciliated protozoa, C_{29} sterols (stigmasterol and β-sitosterol) were dominant. Similarly, all but one species of cyanobacteria analysed by Murata and Nishida (1987) were dominated by C_{29} sterols, and these are also seen to be a significant component of *Chlorobium* sp. (Robinson *et al.*, 1984a) and eustigmatophyte microalgae (Volkman *et al.*, 1999). Given that C_{27}-C_{29} sterols are found in both higher plants and other organisms (algae, bacteria, zooplankton, invertebrates *etc.*), it is problematic to use sterol carbon number distributions as indicators of specific organic sources (Volkman, 1986).

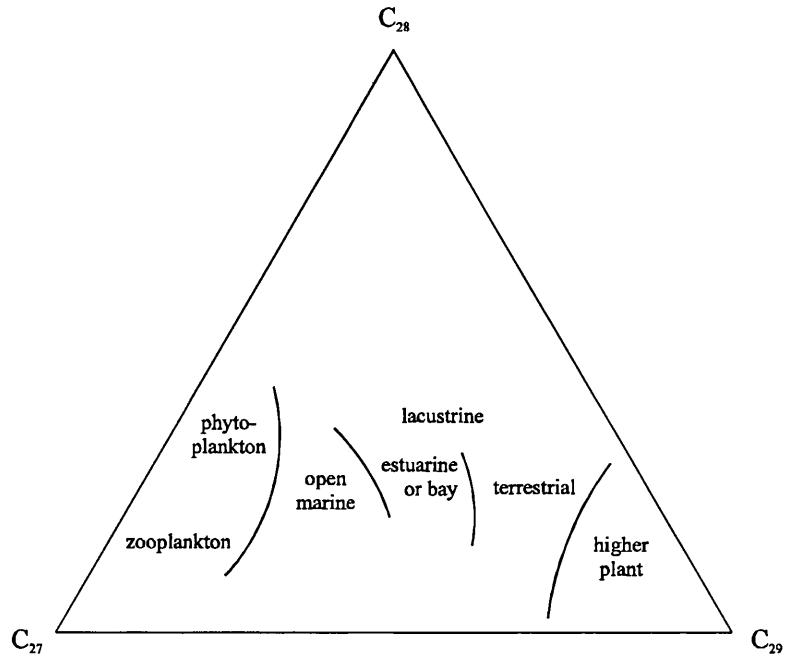


Figure 5.5 Carbon number distribution of sterols in varying ecological systems (after Huang and Meinschein, 1979, page 742).

In a few cases, specific sterols have been linked to specific groups of organisms. For a long time dinosterol was thought to originate solely from dinoflagellates (Robinson *et al.*, 1984b; Volkman *et al.*, 1993). A similar relationship existed between brassicasterol and diatoms (Volkman *et al.*, 1998). This latter component may be particularly important to find at Lochan Uaine, as diatom remains form a major part of the sediment. However, both dinosterol and brassicasterol have been found to occur in organisms other than those mentioned. For example, dinosterol is present in a marine diatom species of *Navicula* (Volkman *et al.*, 1993) and rotifers (Robinson *et*

al., 1984a), and brassicasterol is present in non-diatom microalgae (Goad *et al.*, 1983), in *Sphagnum* (Gaskell and Eglinton, 1976) and in ciliated protozoa (Robinson *et al.*, 1984a). The predominance of sterols in diatoms varies greatly, with some dominated by C_{28} sterols, and others by C_{27} or C_{29} sterols (Kanazawa *et al.*, 1971; Rubinstein and Goad, 1974; Orcutt and Patterson, 1975; Nishimura and Koyama, 1976; Huang and Meinschein, 1979; Barrett *et al.*, 1995). As Volkman *et al.* (1998, page 1163) state, "Diatoms show a great variety of sterol compositions and no sterol appears to be either unique or representative".

5.2.3.2 Sterol distributions in modern reference specimens

A summary of the major sterols identified in reference material from the Lochan Uaine catchment is given in Table 5.3. The algal scrape is dominated by cholesterol, but also contains all of the other major sterols. This specimen was obtained by scraping submerged rocks in the littoral zone of a lowland lake, and was seen to contain both diatoms and other algal groups. The diversity of the sterol composition is thus in keeping with the results reported in the literature. It should be remembered that the algal scrape is thought to have been contaminated with eroded soil and other higher plant detritus, as discussed previously in relation to *n*-alkanes. Some of the sterols may thus have originated in higher plants, although this effect may be minimised by the apparent rapid loss of sterols from detrital material, as seen by the low sterol concentrations in the Lochan Uaine sediment profile (Section 5.3.4).

Problems of algal and bacterial contamination are thought to occur in the submerged aquatic bryophyte and liverwort specimens. C_{29} sterols (stigmasterol and β-sitosterol) are most abundant in the aquatic bryophyte, and campesterol (C_{28}) is also a major component, with lower concentrations of other sterols. The liverwort is dominated by C_{29} sterols, with only trace amounts of lower carbon number sterols. Given the diverse nature of sterols in algae and bacteria, the degree of contamination of the aquatic bryophyte and liverwort by different sterols is not known. Concentrations of the major sterols in bryophytes and liverworts are higher than for the algae scrape.

Table 5.3 Sterols found in Lochan Uaine catchment reference vegetation specimens. All values are expressed as μg $g_{dry\ wt}^{-1}$.

	Algae	Bryophyte	*Cladonia*	Fern	Grass	Liverwort	*Juniperus*	*Sphagnum*
Cholesterol	79	21	16	89	67	-	4	9
Campesterol	15	208	10	87	68	trace	91	145
Brassicasterol	12	44	-	56	26	trace	45	17
β-sitosterol	32	156	75	1066	689	194	30	216
Stigmasterol	9	330	22	44	96	235	77	169

The *Cladonia*, fern and grass all show similar sterol distributions, although in very different concentrations. All are dominated by β-sitosterol with minor amounts of the other major sterols, except for *Cladonia* in which no brassicasterol is identified. The results for fern and grass are in keeping with published data which show C_{29} sterols to dominate in higher plants (Tomita *et al.*, 1969; Bennett *et al.*, 1969; Bae and Mercer, 1970; Pryce, 1971; Willuhn and Köstens, 1975). β-sitosterol was also found to dominate in a fern species, *Dryopteris dilatata*, from the catchment of Rostherne Mere, while campesterol and stigmasterol were minor components (Gaskell and Eglinton, 1976). No trace of ergosterol is found in *Cladonia*, even though this sterol predominates in many fungi (Killops and Killops, 1993). The concentrations of β-sitosterol in fern and grass are higher than those in *Cladonia* by an order of magnitude, and in the case of the fern the concentration exceeds 1 mg $g_{dry\ wt}^{-1}$. This is the highest concentration of any individual component identified in any of the reference specimens, and compares with concentrations of 600 μg $g_{dry\ wt}^{-1}$ for the C_{31} *n*-alkane in grass, and <200 μg $g_{dry\ wt}^{-1}$ for the C_{16} *n*-alkanoic acids in fern and grass (Figures 5.1 and 5.7). It should be remembered that the fern contains the greatest amount of lipid of all the reference specimens analysed (Table 5.1).

Both *Juniperus* and *Sphagnum* contain all the major sterols. In both cases C_{28} and C_{29} sterols predominate, with much lower concentrations of cholesterol (C_{27}). The order of sterol predominance in *Sphagnum* (β-sitosterol; stigmasterol; campesterol; brassicasterol; cholesterol) is slightly different to that seen in *Sphagnum* from Rostherne Mere (stigmasterol; β-sitosterol; campesterol; cholesterol; brassicasterol) (Gaskell and Eglinton, 1976). In both cases the highest concentrations are found in C_{29} sterols. It is also interesting to note that the *Sphagnum* samples from Lochan

Uaine and Rostherne Mere are both seen to contain brassicasterol, which was formerly thought of as a diatom-specific biomarker (Volkman *et al.*, 1998), but has since been identified in numerous higher plants, including other modern reference specimens from the Lochan Uaine catchment (Table 5.3).

By contrast to the concentrations of sterols in the reference material, other alcohols are present in only low abundances. In particular, *n*-alkanols are scarce, despite the fact that homologous series of *n*-alkanols dominate the alcohol/sterol fraction of the lake sediment (Section 5.3.5).

5.2.3.3 *n*-Alkanol distributions in living organisms

n-Alkanols are commonly found as esterified components of more complex acyl lipids, most notably waxes. Waxes are abundant in most higher plants, but are much less common in algae and bacteria (Albro, 1976; Weete, 1976). As *n*-alkanols and *n*-alkanoic acids are biosynthetically related, they will tend to exhibit similar carbon chain-length distributions, although Robinson *et al.* (1986) suggest that wax esters from bacteria have comparatively short alkyl chains, and correspondingly longer acyl chains. This results in the strong even-over-odd predominance in carbon chain-length distribution observed in *n*-alkanols.

There is general agreement that long ($>C_{20}$) *n*-alkanol carbon chain-lengths originate from higher plant sources, whilst shorter chain-lengths are associated with algae, bacteria and other micro-organisms (Wünsche *et al.*, 1988; Farr *et al.*, 1990; Volkman *et al.*, 1998). Rieley *et al.* (1991a) found that trees from the Ellesmere Lake catchment were dominated by C_{22}-C_{28} *n*-alkanols, apart from a sycamore specimen which was contaminated with mould spores and had a substantial C_{14} to C_{18} *n*-alkanol component. Eglinton and Hamilton (1967) demonstrate how *n*-alkanol predominance varies within different parts of the same organism, with the C_{26} *n*-alkanol predominating in the stem and fruit of a sultana plant, and the C_{28} *n*-alkanol in the leaves. In a few cases, long chain-length *n*-alkanols are found in micro-organisms, such as the C_{22}-C_{28} even numbered *n*-alkanols present in *Anabaena cylindrica* (Abreu-Grobois *et al.*, 1977). Likewise, analysis of *Chlorobium* by Robinson *et al.*

(1984a) revealed a bimodal distribution, with the main components being the C_{16} *n*-alkanol and the less abundant C_{26} *n*-alkanol. Similar bimodal distributions are seen in *n*-alkanols from rotifers and ciliated protozoa.

5.2.3.4 *n*-Alkanol distributions in modern reference specimens

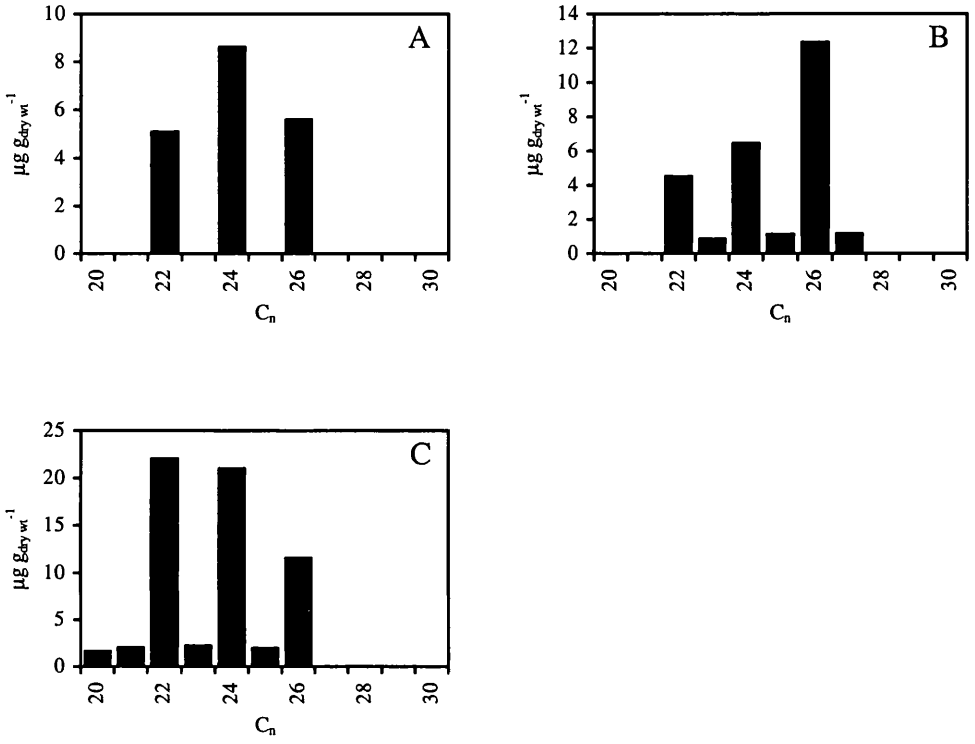


Figure 5.6 **(a)** Aquatic bryophyte, **(b)** liverwort and **(c)** *Sphagnum* *n*-alkanol carbon chain-length distributions. Vertical scales differ.

Series of *n*-alkanols in concentrations above trace quantities are only detected in three of the eight reference specimens; the bryophyte, liverwort and *Sphagnum* (Figure 5.6). In all three specimens the C_{22}, C_{24} and C_{26} *n*-alkanols are most abundant, though the predominant *n*-alkanol varies between the specimens. Alkanols longer than the C_{26} *n*-alkanol are difficult to identify and quantify as they elute close to, and in some cases co-elute with, the more abundant sterols. A strong even-over-odd chain-length predominance is present in the three specimens, as might be expected given the source organisms. A major C_{26} *n*-alkanol component is observed in grass, with a concentration of 409 µg $g_{dry\ wt}^{-1}$. This compares to the concentration of 689 µg $g_{dry\ wt}^{-1}$ for β-sitosterol, the most abundant sterol in grass. A similar predominance of the C_{26}

homologue in Gramineae was observed by Tulloch (1976). The low concentrations of *n*-alkanols in the reference material may be because they are bound in wax esters, whereas in the sediment these waxes often hydrolyse rapidly into their constituent alcohols and acids (Cranwell and Volkman, 1981).

Other alcohols identified in the reference material include 1-mono-C_{16}-glycerol and 1-mono-C_{18}-glycerol. These are present in the bryophyte, liverwort and *Sphagnum*, but in low concentrations only (<5 $\mu g\ g_{dry\ wt}^{-1}$). These components are present in sediment samples only in very low concentrations, and no further effort is made to assess their use as organic source biomarkers.

5.2.4 Carboxylic acids

Carboxylic ('fatty') acids form a major lipid component of many organisms. Numerous types of acid may be present, including straight chain saturated (*n*-alkanoic), mono-unsaturated (*n*-alkenoic) and poly-unsaturated forms, as well as branched chain acids, cyclic acids, and hydroxy acids. Straight chain carboxylic acids in living organisms almost always exhibit a strong preference for even carbon chain-lengths, due to their biosynthesis from C_2 acetyl units. This in turn gives rise to the even chain-length predominance of straight chain alcohols and the odd chain-length predominance of straight chain hydrocarbons. As the sediment analysed in this study is dominated by *n*-alkanoic acids, the bulk of this section will be devoted to an examination of the distribution of these components and their precursors in living organisms.

5.2.4.1 *n*-Alkanoic acid distributions in living organisms

As with *n*-alkanes and *n*-alkanols, it is frequently suggested that short chain-length *n*-alkanoic acids originate in algae and bacteria, while longer chain lengths are typical of higher plants (Barnes and Barnes, 1978). In fact, this is only partly true. The confusion is partly due to the several different modes in which acids are found in living organisms. While free *n*-alkanoic acids are found in many biota (Tulloch, 1976),

they are more commonly bound as sub-units of larger molecules. In particular, acids are important constituents of glycerides and waxes.

Glycerides from plants tend to contain mostly mono-unsaturated and poly-unsaturated acids, especially $C_{18:1}$, $C_{18:2}$ and $C_{18:3}$, and algae are thought to contain greater proportions of poly-unsaturated acids than higher plants (Killops and Killops, 1993). Saturated and unsaturated C_{16} acids may also be important (Cranwell, 1978, 1982), though unsaturated acids are more abundant in organisms than saturated acids (Meyers and Benson, 1988). In waxes, both short and long chain-length acids can be present, esterified to an alcohol. Longer chain-lengths tend to predominate, especially the C_{24}, C_{26} and C_{28} *n*-alkanoic acids (Eglinton and Hamilton, 1967; Cranwell, 1978, 1982). As waxes are generally confined to higher plants where they form protective coatings on leaves, it follows that long chain-length acids are found almost exclusively in higher plants. A few algae and bacteria do produce waxes, however, and there is increasing evidence that some algae and bacteria can produce long chain-length acids (Volkman *et al.*, 1998).

It thus follows that the association of short chain-length acids with algae and bacteria, and long chain-lengths with higher plants, does not hold true when both free and bound acids are included. Some acids, notably $C_{16:0}$ (palmitic acid) and $C_{18:0}$ (stearic acid) are ubiquitous in bacteria, algae and higher plants (Cranwell, 1982; Meyers and Eadie, 1993; Volkman *et al.*, 1998). This creates problems using these components as biomarkers. As Rieley *et al.* (1991a, page 907) state, "Since *n*-hexadecanoic acid occurs in many different organisms...it is difficult to assign the C_{16} acid observed to any specific source". Long chain-lengths, however, are almost entirely associated with a higher plant origin, and hence are of greater use as biomarkers.

5.2.4.2 *n*-Alkanoic acid distributions in modern reference specimens

Analysis of the acid fractions of seven modern reference specimens reveals similar *n*-alkanoic acid chain-length distributions (no adequate chromatogram was obtained for *Cladonia*). All are dominated by the $C_{16:0}$ acid, and all show an approximately bimodal distribution with major components at $C_{16:0}$ to $C_{18:0}$ and in the mid to long chain-

length range (Figure 5.7). Most specimens also contain acids in the C_{20} to C_{30} range in varying concentrations, and all exhibit a strong predominance of even-over-odd chain-lengths.

The algal scrape contains low concentrations of longer chain-length *n*-alkanoic acids with strong even-over-odd predominance. For example, the C_{24} homologue has a concentration of 5 $\mu g\ g_{dry\ wt}^{-1}$, compared to 55 $\mu g\ g_{dry\ wt}^{-1}$ and 35 $\mu g\ g_{dry\ wt}^{-1}$ for the $C_{16:0}$ and $C_{18:0}$ acids respectively. Although longer chain-lengths are seen in a few species (Volkman *et al.*, 1998), most studies find only shorter chain-lengths in algal and bacterial material (Parker, 1969; Barnes and Barnes, 1978; Cranwell, 1978; Cranwell *et al.*, 1987). Matsuda and Koyama (1977b) report that diatoms and cyanobacteria contain high concentrations of $C_{14:0}$ and $C_{16:0}$ acids, but low concentrations of $C_{18:0}$. The presence of long chain-length *n*-alkanoic acids in the algal scrape almost certainly represents contamination by higher plant detrital material, evidence for which is also seen in the hydrocarbon and alcohol fractions. It is thus also possible that higher plants contribute to the $C_{16:0}$ and $C_{18:0}$ *n*-alkanoic acids.

In the aquatic bryophyte, fern and grass, acids longer than C_{18} are present only in low concentrations. As a proportion of the shorter chain-length ($C_{16:0}$ and $C_{18:0}$) acids these concentrations are comparable to those in the algal scrape, although the absolute concentrations are slightly lower in the aquatic bryophyte than in the fern and grass. The predominant long chain-length acid is variously C_{24} (fern), C_{26} (grass), or C_{28} (aquatic bryophyte). These components probably reflect an input from wax esters or from free acids in leaf surface waxes. As with all the reference specimens analysed, it is not possible to determine what fraction of the long chain-length *n*-alkanoic acids existed as free acids, and what fraction was released by the autolysis of wax esters in the period between collection and analysis. A similar predominance of short chain-length acids in higher plants is seen by several studies (Jamieson and Reid, 1972; Matsuda and Koyama, 1977b; Rieley *et al.*, 1991a). In all cases longer chain-lengths are also detected in low concentrations.

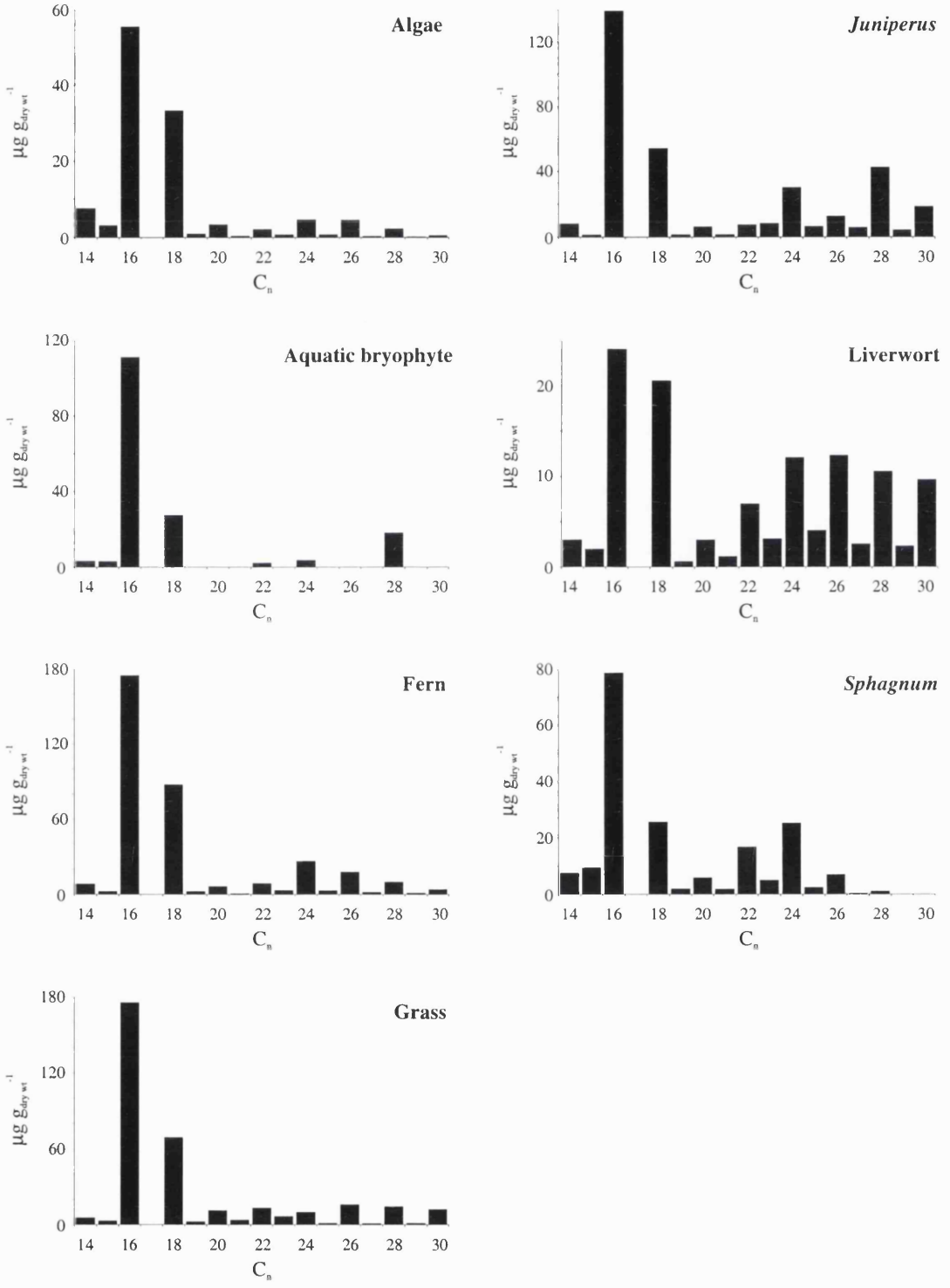


Figure 5.7 Distributions of *n*-alkanoic acids in modern catchment reference specimens. No adequate results were obtained for the *Cladonia* sample. The C_{17} acid used as the internal standard is not shown.

Mid and long chain-length *n*-alkanoic acids are present in greater abundances in the remaining reference specimens, with C_{28} predominating in *Juniperus*, and C_{26} predominating in the liverwort. In the latter case, concentrations of all the C_{24} to C_{30} even chain-length *n*-alkanoic acids are comparable. Although the liverwort and aquatic bryophyte specimens are visibly contaminated with diatoms, it is not thought that these will contribute any long chain-length acids. Diatoms will certainly contribute various short chain-length acids, but the most abundant of these, such as $C_{16:0}$, are ubiquitous, and such that exogenous contributions cannot easily be separated from those components already present in the specimens. Excluding the short chain-length acids, *Sphagnum* is dominated by the C_{24} and C_{22} acids. Of note, these mid chain-length acids are far more abundant than longer chain-lengths. A predominance of mid over long chain-length components is also seen in *Sphagnum n*-alkanes, thus reinforcing the idea that they are biosynthetically related. Finally, although no adequate chromatogram was obtained for the *Cladonia* sample, previous work has established that fungi, and presumably therefore lichens, are dominated by short chain-length acids (Weete, 1974; Matsuda and Koyama, 1977b).

Of the other acids present, $C_{16:1}$ and $C_{18:1}$ are identified in the algal scrape and aquatic bryophyte, although in lower concentrations than the corresponding $C_{16:0}$ and $C_{18:0}$ acids. It is possible that these are also present in other samples, but bound in glycerides or waxes rather than present as free acids. These mono-unsaturated acids are present in the uppermost sample of UACT6 but disappear rapidly in older samples. This is attributed to degradational processes. The rapid loss of short chain-length mono-unsaturated acids, and their reported widespread occurrence in algae/bacteria and higher plants, precludes their use as an organic source biomarker. Thus, no further analysis of these components is undertaken.

5.2.5 Ketones and wax esters

Gas chromatographic analysis of the ketone and wax ester fraction was performed for the eight reference vegetation specimens, all of which are found to contain a large number of these components. However, these analyses are excluded from the study of Lochan Uaine sediments, for a variety of reasons. Chromatographic resolution of the

ketone and wax ester fraction from both modern reference specimens and from sediment samples (Section 5.3.5) is poor. This is due to the complexity of the mixture, which prevents accurate determination of component concentrations in modern reference material. A similar problem is found with the ketone and wax ester fraction of samples from UACT6. This prevents analysis of downcore changes in concentration of the components present. Co-elution of components makes mass-spectrometric identification problematic. Also, phthalate contamination seems particularly high in the ketone and wax ester fraction, presumably from the plastic core tube in which the core was recovered, or from the plastic sample bags in which the samples were stored wet prior to dry weight and LOI analysis.

Nonetheless, analysis of the ketone and wax ester fraction in future studies could prove useful. Wax esters are thought to originate mainly from higher plants, so their presence in lake sediments could be used as a higher plant biomarker - although, as noted above by Volkman *et al.* (1998), waxes are produced by certain algae and bacteria, and some of these waxes include long chain-length acids and alcohols. Also, long chain-length *n*-alkanols and *n*-alkanoic acids in modern plant specimens are present in low abundances by comparison with the sediment record where they predominate (Section 5.3). This suggests that long chain-length *n*-alkanols and *n*-alkanoic acids in the sediment are produced mainly by the autolysis of larger units such as waxes, hence the potential interest in studying these precursor components in modern reference material.

5.3 UACT6 sediment samples

5.3.1 Total lipid extracts

The concentrations of the total lipid extracts (TLEs) for samples from core UACT6 vary considerably, but all within a single order of magnitude (Figure 5.8a). As would be expected, the TLE shows a strong positive correlation with total organic carbon (TOC) values for the corresponding combined samples, and an R^2-value of 0.702 is recorded (Figure 5.8c). This is significant at the 99% level. At higher TOC values, the relative proportion of carbon contained in the lipids is found to increase. The reasons for this are unknown, although it suggests that during periods of high organic matter input to the sediment the relative input of lipids increases. Alternatively, preservation of lipids may be lower during periods of reduced organic input to the lake sediment. When TLE is plotted as a percentage of TOC ($TLE_{\%TOC}$) the resulting curve (Figure 5.8b) appears similar to that of TLE mg $g_{dry\ wt}^{-1}$ (Figure 5.8a). However, regression analysis shows that the relationship between TOC and $TLE_{\%TOC}$ is weaker, although still significant at the 99% level (Figure 5.8d).

5.3.2 GC and GC-MS analysis: total lipid extracts and neutral fractions

The TLEs of four samples were derivatised and analysed by high temperature-gas chromatography (HT-GC) to test whether further fractionation was necessary. A typical HT-GC profile is given in Figure 5.9, which shows that this approach is unsuitable for detailed assessment of variations in lipid composition downcore. Most importantly, the complexity of the mixture means that chromatographic separation of components is poor. This factor increases the likelihood that two or more components will co-elute, thereby making integration of peak areas unreliable. As peak areas are used to quantify the concentrations of the components present, the errors inherent in the TLE chromatograms are deemed unacceptable. Four TLE samples were separated by aminopropyl Bond Elut into acid and neutral fractions, and the neutral fractions were derivatised and analysed as for the TLE samples above. Similar problems are experienced with chromatographic separation due to the complexity of the mixtures, although not to the same extent as with the TLE samples. It was thus necessary to further fractionate the neutral components into hydrocarbons, aromatics, ketones and

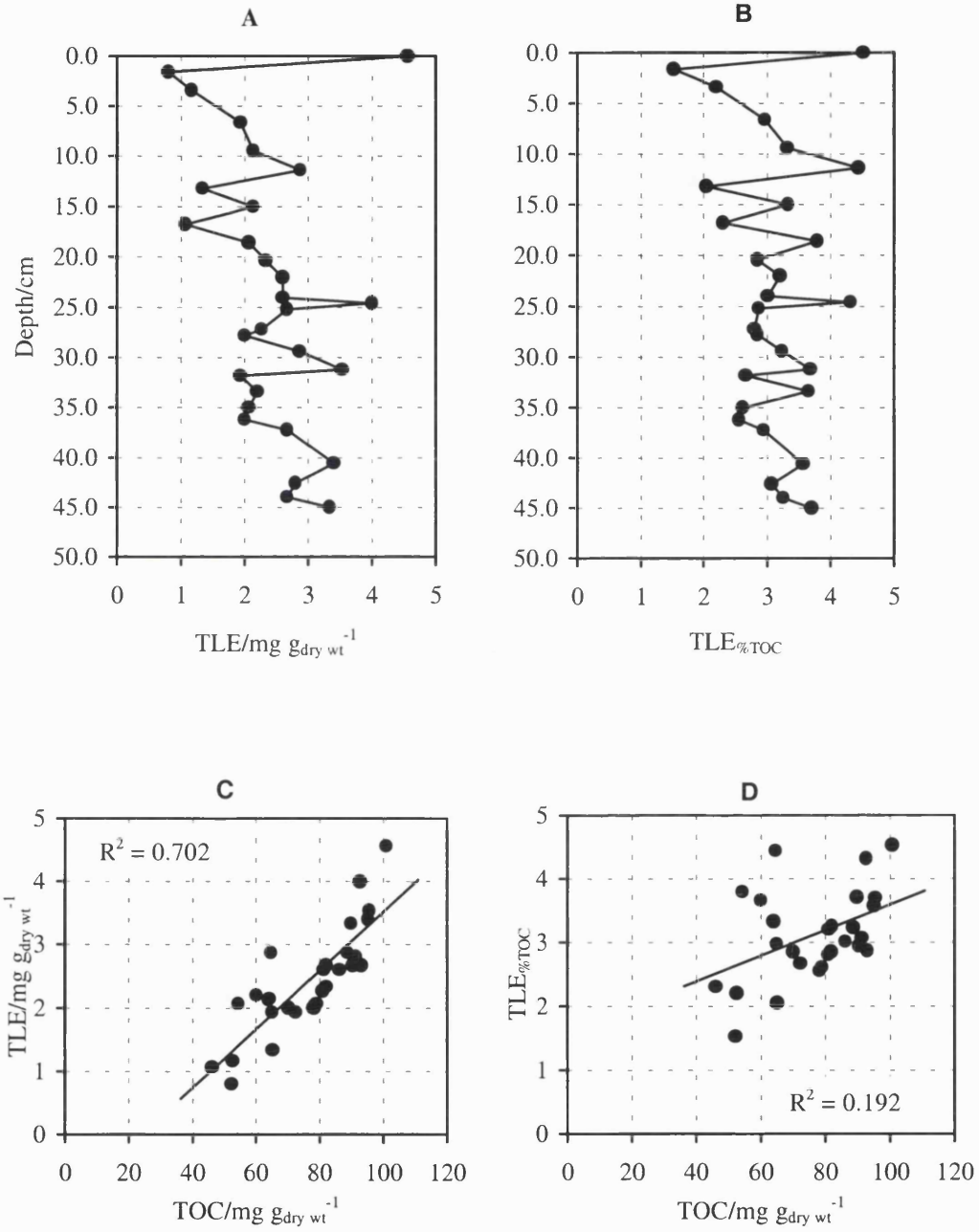


Figure 5.8 TLE **(a)** concentration expressed as mg $g_{dry\ wt}^{-1}$ **(b)** concentration expressed as $TLE_{\%TOC}$ **(c)** correlation between TOC (mg $g_{dry\ wt}^{-1}$) and TLE (mg $g_{dry\ wt}^{-1}$) **(d)** correlation between TOC (mg $g_{dry\ wt}^{-1}$) and $TLE_{\%TOC}$.

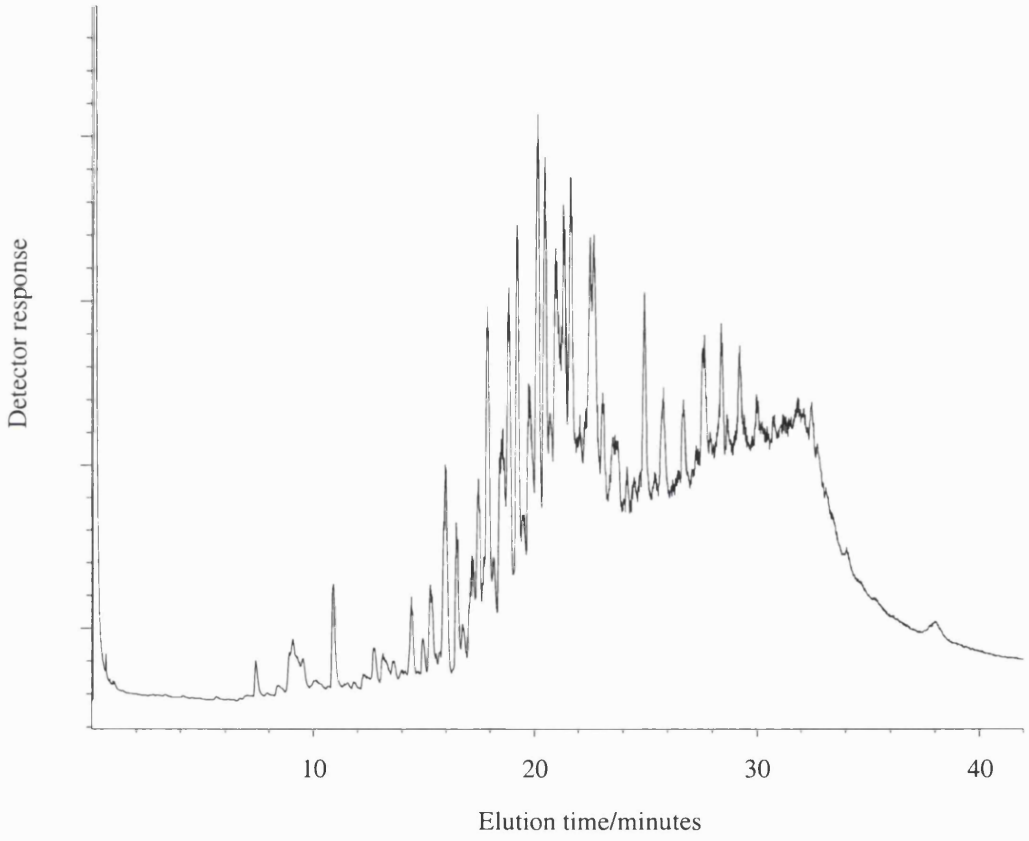


Figure 5.9 HT-GC profile of the trimethylsilyated TLE of sample 25.2-25.8 cm, showing poor chromatographic resolution and peak co-elution due to the large number of components present.

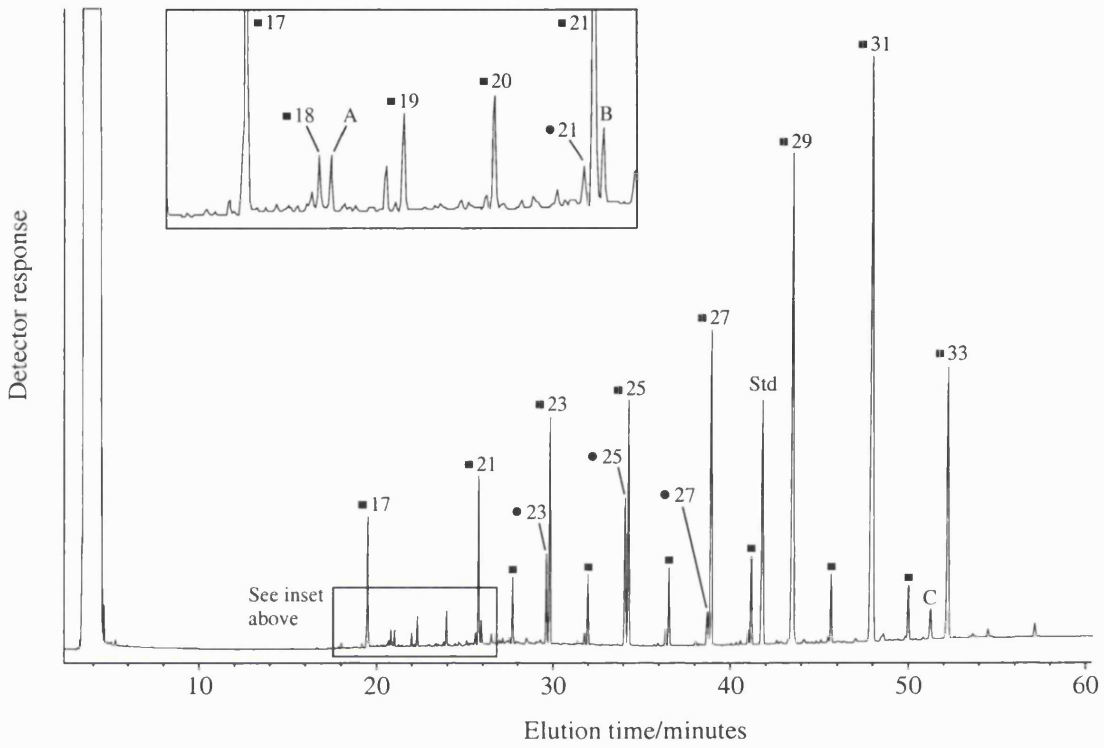
wax esters, alcohols and sterols, and polar compounds, by column chromatography. This process was described in Chapter 2.

5.3.3 Hydrocarbons

The distribution of hydrocarbon components in the twenty-eight samples taken from core UACT6 shows a strong overall consistency. The fraction is dominated by *n*-alkanes having carbon chain-lengths in the range C_{16} to C_{35} and exhibiting a strong preference for odd-over-even chain-lengths (Figures 5.10 and 5.11). This is seen in numerous similar studies (Bray and Evans, 1961; Meinschein, 1969; Cranwell, 1973b, 1978, 1990; Thompson and Eglinton, 1978; Meyers *et al.*, 1980a,b; Wünsche *et al.*, 1988; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993; Ho and Meyers, 1994; Farrimond and Flanagan, 1996; Nott *et al.*, 2000). The C_{31} *n*-alkane predominates throughout UACT6, followed by the C_{29} *n*-alkane, and approximately equal amounts of C_{33} and C_{27}. In most of the samples, the C_{17} component was present in low abundance. Bimodality in *n*-alkane chain-length distribution is common in Holocene lake sediments (Cranwell, 1978; Ho and Meyers, 1994; Kawamura and Ishiwatari, 1985; Meyers *et al.*, 1980b, 1984a). In addition to the *n*-alkanes, odd chain-length primary *n*-alkenes are present in the range C_{21}-C_{29}, as seen in sediments at Priest Pot, northern England (Cranwell *et al.*, 1987). These are dominated by the C_{25} and C_{23} *n*-alkenes. A C_{30} hopanoid component, identified as hopan-22-ene (diploptene), is detected eluting between the C_{32} and C_{33} *n*-alkanes, and in many samples phytane is detected in low concentrations, eluting just after the C_{18} *n*-alkane. A C_{25} highly branched isoprenoid (HBI) monoene is also seen. Several other hydrocarbon components are present, but in concentrations too low to allow mass spectrometric identification.

5.3.3.1 Total *n*-alkane content of UACT6 sediment

When the sum total of C_{16} to C_{35} *n*-alkanes is plotted downcore as a proportion of dry sediment (Figure 5.12a), a significant positive correlation with TOC is seen (Figure 5.13a). This almost certainly reflects primarily the downcore variations in the organic to mineral matter ratio (LOI), rather than variations in the content of the organic



■ *n*-Alkanes (selected carbon numbers shown)

● Primary *n*-alkenes

Std Internal standard (5α-cholestane)

A Phytane (2,6,10,14-tetramethylhexadecane) [**XI**]

B C_{25} monoene highly branched isoprenoid (HBI) [**XII**]

C Diploptene [**XIII**]

Figure 5.10 Typical GC profile of a hydrocarbon fraction (25.2-25.8 cm depth), core UACT6.

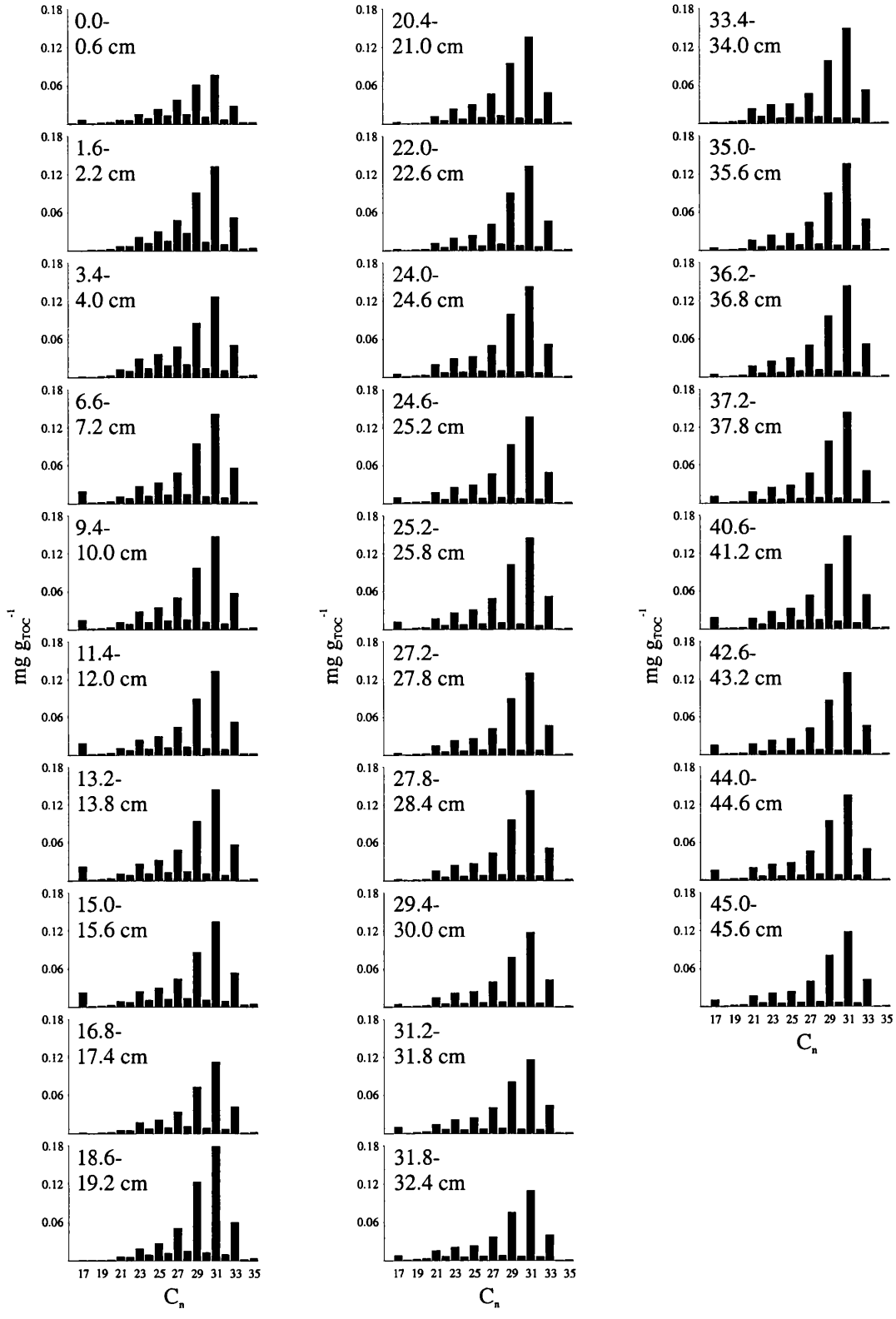


Figure 5.11 Histogram distributions of *n*-alkanes in core UACT6.

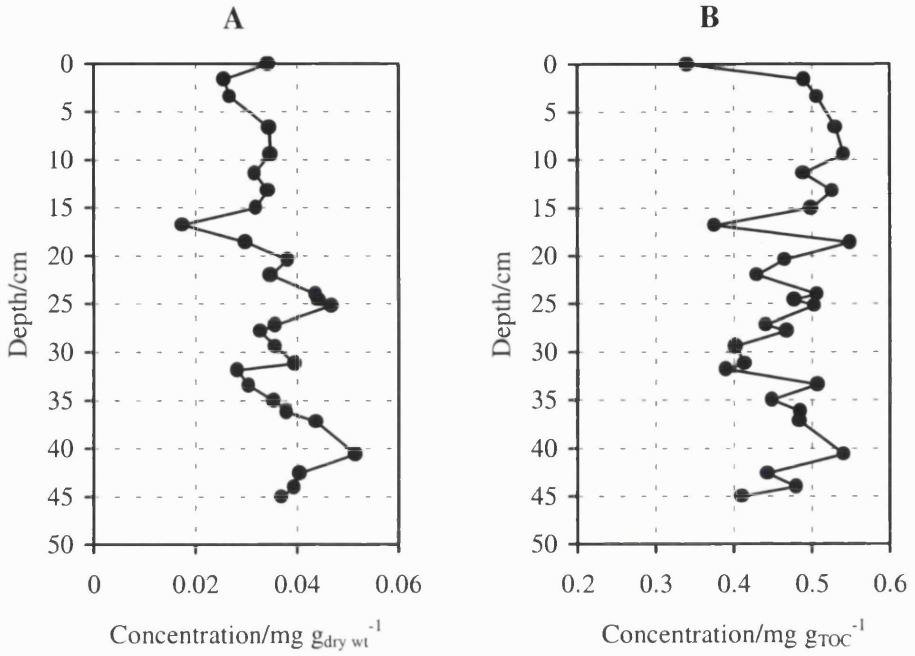


Figure 5.12 Downcore concentration of sum total of C_{15} to C_{35} *n*-alkanes, core UACT6, **(a)** expressed as a proportion of dry sediment, and **(b)** expressed as a proportion of TOC.

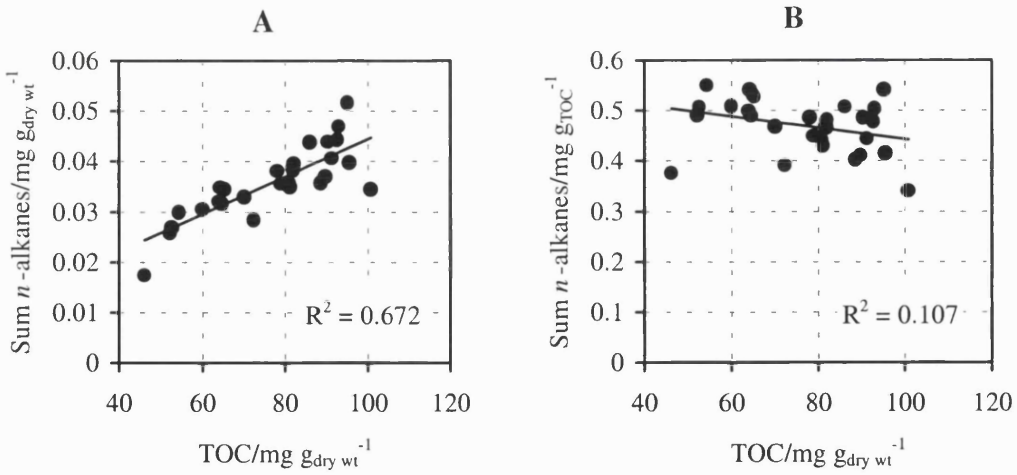


Figure 5.13 Correlations between **(a)** TOC and the sum of *n*-alkanes expressed as a proportion of dry sediment, and **(b)** TOC and the sum of *n*-alkanes expressed as a proportion of TOC.

fraction. By plotting the total concentration of *n*-alkanes downcore as a percentage of TOC, a measure is obtained which is independent of any potential changes in sediment inorganic content (Figure 5.12b). Although downcore variations are seen, the correlation with the downcore variation in TOC is not as strong, although it is just significant at the 95% level, and is also a negative correlation (Figure 5.13b). This is the opposite to the relationship seen between TOC and $TLE_{\%TOC}$ (Figure 5.8d), and suggests either that the relative input of *n*-alkanes to the sediment is lower when total sedimentary organic content is higher, or that preservation of *n*-alkanes is reduced during such periods.

5.3.3.2 Carbon preference index of *n*-alkanes

A measure of the predominance of odd carbon chain-lengths over even, or vice versa, may be calculated using the Carbon Preference Index (CPI) (Bray and Evans, 1961). Other methods of comparing chain-length distributions have been developed, such as the Odd-Even Predominance (OEP) ratio of Scalan and Smith (1970). It was decided to use the CPI method as it is the most widely used method in the literature, thus allowing comparison between the results from Lochan Uaine and other published works. CPI analysis of *n*-alkanes in core UACT6 confirms the obvious predominance of odd-numbered chain-lengths seen in Figure 5.11. Of greater interest is the strong downcore decrease in CPI, from values of less than 4 at the surface to around 8 near the base (Figure 5.14). This varying chain-length ratio can also be observed when histograms of *n*-alkanes for the entire core are compared. The abundance of even chain-length *n*-alkanes shows a marked downcore decrease by comparison with the dominant odd chain-length *n*-alkanes. In most higher plants and algae, the majority of *n*-alkanes are of odd chain-lengths on account of their biosynthesis involving decarboxylation of fatty acids (Killops and Killops, 1993). The presence of even chain-length *n*-alkanes can not be explained by this process, and their origin is not known for certain. Even chain-length *n*-alkanes were identified in all of the modern reference specimens analysed, suggesting that they are produced naturally in low quantities. They may also be a product of chemical alteration of odd chain-length *n*-alkanes, although this is unlikely in relatively modern samples such as those from UACT6. It is unlikely that the downcore decrease in abundance of even chain-lengths

is due to ongoing removal by microbial processes, as odd chain-length components are not similarly affected.

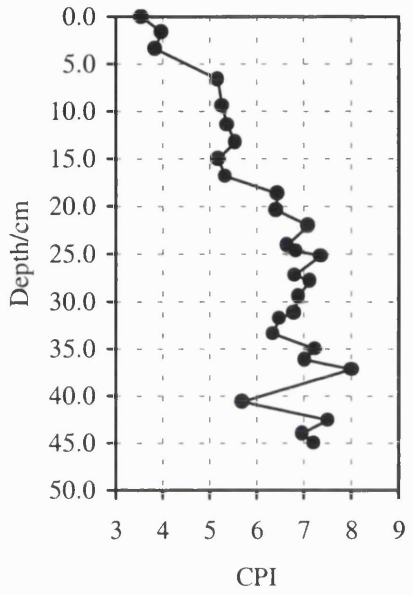


Figure 5.14 Downcore variation in CPI of C_{16}-C_{35} *n*-alkanes (after Bray and Evans, 1961). A value of 1 indicates no odd-over-even chain-length predominance. The mean CPI is 6.48.

One other possible source of even chain-length *n*-alkanes is from fossil fuels, which have a roughly even distribution of chain-lengths due to degradation over geological timescales (Meinschein, 1969; Brassell *et al.*, 1978). Products of fossil fuel combustion may have been introduced to the sediment by atmospheric pollution during the industrial age, as seen in the surficial sediments of Lake Huron (Cranwell, 1982). However, due to the low sediment accumulation rate at Lochan Uaine, such pollution is likely to be important only in the uppermost two or three samples analysed for lipids. This may explain the low CPI values in these samples. The reasons for the gradual increase in CPI below 5 cm depth cannot be explained by this process. In lakes such as Huron direct pollution may be possible from boats, industrial waste, spillages *etc.*, but such processes can be ruled out at Lochan Uaine due to the remoteness of the catchment.

5.3.3.3 *n*-Alkane chain-lengths and organic matter sources

Perhaps the most frequently used interpretation of *n*-alkane chain-length distributions is the identification of organic matter sources. In general, long chain-lengths $>n\text{-}C_{20}$ come from allochthonous sources, and shorter chain-lengths $<n\text{-}C_{20}$ are from autochthonous sources. Numerous studies of modern day organisms, from catchments or from laboratory cultures, have confirmed that short chain-length *n*-alkanes are associated almost entirely with algae (Oró *et al.*, 1967; Meinschein, 1969; Gelpi *et al.*, 1970; Blumer *et al.*, 1971; Weete, 1976; Giger and Schaffner, 1977; Barnes and Barnes, 1978; Cranwell, 1982; Meyers *et al.*, 1984b) and bacteria (Barnes and Barnes, 1978; Cranwell *et al.*, 1987; Murata and Nishida, 1987). The main source of both organisms will be from within the lake, although in some catchments inwash of bacteria in eroded soil or peat may be significant.

By comparison, longer chain-length *n*-alkanes are always associated with higher plants, where the alkanes are commonly, but not exclusively, found in leaf waxes (Eglinton *et al.*, 1962; Eglinton and Hamilton, 1967; Meinschein, 1969; Brassell *et al.*, 1978; Cranwell, 1973a, 1982, 1990; Rieley *et al.*, 1991a). Such components are not restricted only to vascular plants, but have been found in non-woody plants such as bryophytes and fungi. While long chain-length *n*-alkanes are often interpreted as representing allochthonous sources, there will be an autochthonous component in lakes which contain submerged vegetation. At Lochan Uaine the input of long chain-length *n*-alkanes from autochthonous sources is thought to be minimal, as macrophytic vegetation in the lake is restricted to a sparse population of an aquatic bryophyte with a low lipid content. Thus, we can be reasonably confident that long chain-length *n*-alkanes in the sediment of Lochan Uaine are an allochthonous indicator, as higher plants are almost entirely confined to the catchment rather than the lake. Likewise, short chain-length *n*-alkanes can be used as an indicator of aquatic organisms. Algae and bacteria are likely to derive mostly from within the lake, as evidenced by the large component of diatom silica in the Lochan Uaine sediment mineral matter. Numerous published studies use the interpretation of long/short *n*-alkane chain-lengths to reconstruct palaeoenvironmental histories from lake sediments (Cranwell, 1973b, 1978, 1981, 1982, 1990; Ishiwatari *et al.*, 1980; Meyers *et al.*,

1980a,b, 1984a; Kawamura and Ishiwatari, 1985; Cranwell *et al.*, 1987; Meyers and Benson, 1988; Wünsche *et al.*, 1988; Rieley *et al.*, 1991a; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993; Ho and Meyers, 1994; Ficken *et al.*, 1998; Wilkes *et al.*, 1999).

5.3.3.4 Individual *n*-alkane concentrations in UACT6

Long chain-length n-*alkanes:* n-C_{27} *to* n-C_{33}

The predominance of odd chain-length components from C_{27} to C_{33} in the *n*-alkane fraction is strongly indicative of a higher plant origin. Straight chain components (*n*-alkanes, *n*-alkanols, *n*-acids) produced by algae and bacteria generally contain fewer than 20 carbon atoms (*e.g.* Oró *et al.*, 1967; Gelpi *et al.*, 1970; Barnes and Barnes, 1978; Cranwell, 1982). Hence, the predominance of long chain-length *n*-alkanes suggests two possibilities: 1. Sedimentary lipids are dominated by an input of higher plant-derived biomarkers, or 2. Other major lipid components, such as short chain-length hydrocarbons, are being removed preferentially before, during, or after deposition. A combination of both factors may be occurring.

Several methods are used to analyse sedimentary hydrocarbon distributions. The simplest is to plot downcore changes in each component expressed as a proportion of sediment dry weight, as mentioned previously. The method does not, however, take into account possible variations in the TOC content of the sediment, which will bias results. This is seen in the analyses of TLE and total *n*-alkanes above, both of which show strong positive correlations with TOC when expressed as a proportion of sediment dry weight. A more useful method is to calculate the concentration of components as a proportion of TOC, a measure which should be independent of changes in sedimentary mineral content. Finally, the ratios between different components or groups of components may be compared to assess relative changes in concentration.

Selected results from the analysis of component concentrations are given in Table 5.4. In general, mid and long chain-length hydrocarbons show a good correlation with TOC when expressed as a percentage of sediment dry weight, but little or no

correlation when expressed as a percentage of TOC itself. This suggests that while these components form a relatively constant fraction of the sediment organic content, their signal in the sediment as a whole may be distorted by variations in the input of minerogenic matter. The short chain-length, C_{17} *n*-alkane shows the least significant relationship with TOC when expressed as proportion of sediment dry weight, yet this is still significant at the 95% confidence level. R^2-values invariably increase when the surface sediment sample (0.0-0.6 cm depth) is excluded from the analysis. As this sample contains the mud-water interface it is not thought to be representative of sediment from deeper levels in the core. Although this sample has the highest TOC, and a correspondingly high TLE, concentrations of hydrocarbons, acids, and alcohols are no greater than for other samples, and in many cases are smaller. The reasons for this are not known, although it possibly reflects the presence of organic components such as polysaccharides in the surface sediment. These degrade rapidly, and may not be present in older, deeper sediments.

Table 5.4 Correlation coefficients (R^2-values) between selected hydrocarbon components and TOC (* represents an inverse relationship). Bold type indicates significance at the 95% confidence limit; underlining represents significance at the 99% confidence limit. Due to the large sample size (N=28), correlations are often given as being significant even when the visible correlation is not good. Most R^2-values below 0.3 fall into this category.

Component	Component ($g_{dry\ wt}^{-1}$) *vs* TOC ($g_{dry\ wt}^{-1}$)	Component ($g_{dry\ wt}^{-1}$) *vs* TOC ($g_{dry\ wt}^{-1}$), excluding top sample (0.0-0.6 cm)	Component (g_{TOC}^{-1}) *vs* TOC ($g_{dry\ wt}^{-1}$)
C_{17} *n*-alkane	**0.157**	**0.179**	0.030
C_{21} *n*-alkane	**0.577**	**0.774**	**0.228**
C_{23} *n*-alkane	**0.601**	**0.744**	0.004
C_{25} *n*-alkane	**0.630**	**0.656**	0.080*
C_{27} *n*-alkane	**0.767**	**0.794**	0.012*
C_{29} *n*-alkane	**0.656**	**0.786**	0.036*
C_{31} *n*-alkane	**0.568**	**0.787**	0.092*
C_{33} *n*-alkane	**0.549**	**0.772**	**0.202***
C_{23} *n*-alkene	**0.477**	**0.813**	**0.241**
C_{25} *n*-alkene	**0.464**	**0.697**	**0.318**
Sum of C_{16} to C_{35} *n*-alkanes	**0.672**	**0.767**	**0.107***

The abundances of the C_{29} and C_{31} *n*-alkanes in Lochan Uaine are calculated as ratios of the sum of all odd chain-length *n*-alkanes (Figure 5.15a). No major changes are visible downcore, except for a peak between 15-20 cm depth representing an increase

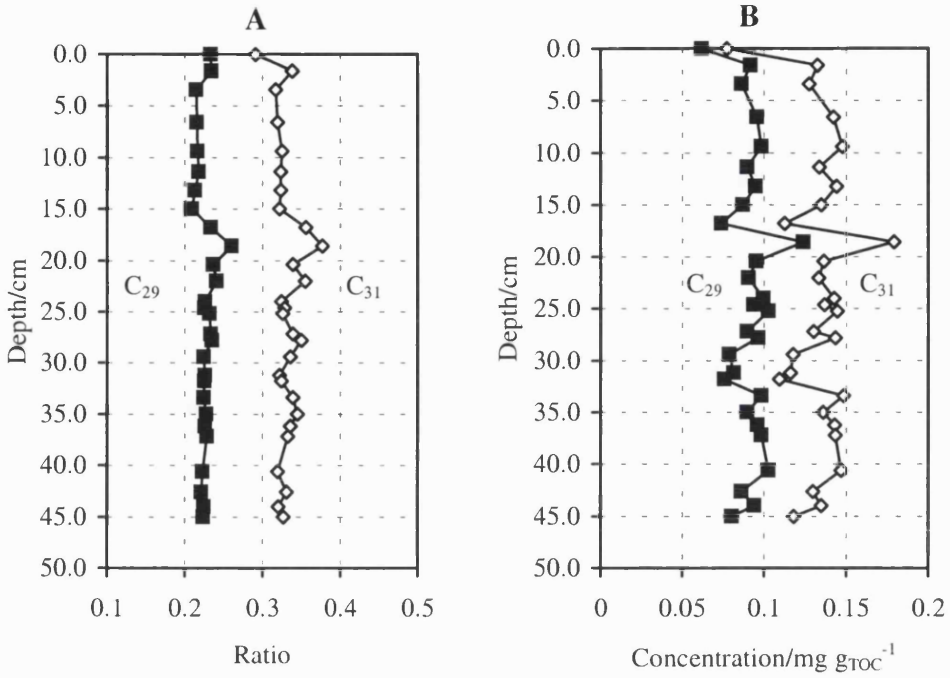


Figure 5.15 (a) Ratio of C_{29} and C_{31} *n*-alkanes to the sum of all odd chain-length *n*-alkanes, and **(b)** downcore changes in concentration of C_{29} and C_{31} *n*-alkanes. See also Table 5.X.

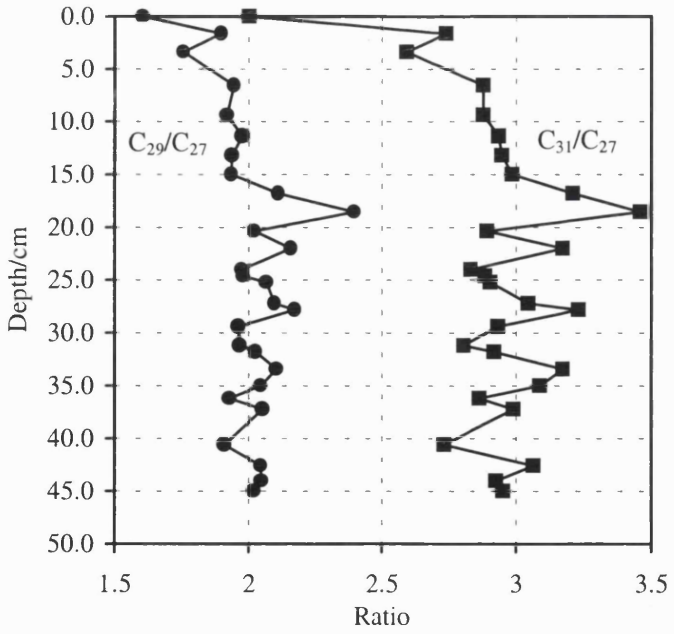


Figure 5.16 Change in ratios of selected long chain-length *n*-alkanes.

in the relative contributions of each of the two components. A feature at this depth is visible in many of the variables studied, including LOI, TOC, chlorins, and bulk organic $\delta^{13}C$, and it obviously represents a major event in the depositional history of Lochan Uaine. When C_{29} and C_{31} *n*-alkanes are plotted as a proportion of TOC, greater variability is apparent, again including the event occurring betwen 15 amd 20 cm depth (Figure 5.15b). However, as with the TLE discussed previously, the correlation between component abundance expressed as a proportion of TOC, and TOC itself is weak (Table 5.4). Thus, the concentrations of C_{29} and C_{31} *n*-alkanes as a proportion of TOC do not change as TOC varies downcore. Similar results are seen by Ho and Meyers (1994).

In some studies the C_{31} *n*-alkane is associated with peat-dominated catchments, while the *n*-C_{27} and *n*-C_{29} homologues are thought to be more typical of forested catchments (Cranwell, 1973b). Ho and Meyers (1994) used the ratios of C_{31}/C_{27} and C_{29}/C_{27} *n*-alkanes to show a post-1950 increase in catchment tree cover at Coburn Mountain Pond, Maine, USA. At Lochan Uaine, both ratios show similar trends (Figure 5.16). Below 20 cm depth the ratios are relatively constant. A peak at 15-20 cm depth is followed by a decrease in both ratios from 15 cm to the surface. By Ho and Meyer's (1994) interpretation this suggests a recent increase in catchment tree cover. However, Lochan Uaine lies well above the tree-line. The curves may suggest an increasing importance of woody plants, as opposed to peat-forming species. As ever the possible influence of imperfect preservation of lipids should not be overlooked. There are good reasons for thinking that the concentrations of long chain-length *n*-alkanes have not been significantly affected by degradation, as discussed below in relation to the C_{17} *n*-alkane.

Short chain-length n-*alkanes:* n-C_{17}

Although present in much lower concentrations than longer chain-length *n*-alkanes, the C_{17} *n*-alkane (*n*-heptadecane) shows significant variation downcore. When plotted as a proportion of the longer odd chain-length components in the range C_{27}-C_{33}, a variation of more than one order of magnitude is seen (Figure 5.17a). The relative proportion of the short chain-length component is especially high between 5 and 15

cm depth, with smaller (but still well-defined) peaks at the surface, 24-26 cm, 30-32 cm, and from 37 cm to the core base. It is widely accepted that short chain-length *n*-alkanes are indicative of an algal or bacterial origin, while longer chain length *n*-alkanes are a product of higher plants. The analysis of reference plant specimens from Lochan Uaine and its catchment generally supports these findings, although contamination of several specimens with organic material from other sources is a problem (Section 5.2). This suggests that the relative contributions of algal/bacterial and higher plant sources to the sediment have varied during the period of time represented by core UACT6.

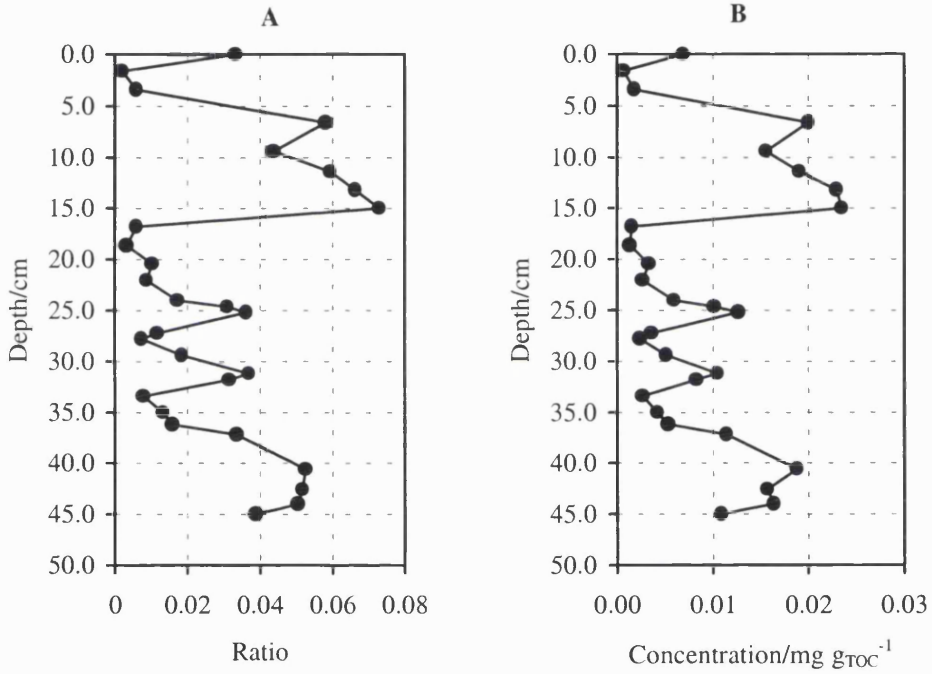


Figure 5.17 (a) Variation in the ratio of C_{17} *n*-alkane to long chain-length *n*-alkanes (C_{27}-C_{33} odd carbon numbers), and **(b)** concentration of C_{17} *n*-alkane as a proportion of TOC.

Preservation of short chain-length n-*alkanes*

The downcore variation of the C_{17} *n*-alkane is also important in indicating the degree of degradation which has affected the record. It was previously suggested that the predominance of longer chain-length *n*-alkanes in the sediment of Lochan Uaine may reflect preferential degradation of shorter chain-length components. Such degradation may occur before, during, or after deposition. Short chain-length components are generally more susceptible to microbial degradation than longer chain-length

components (Brassell *et al.*, 1978; Giger *et al.*, 1980; Cranwell, 1978). If significant degradation of the C_{17} *n*-alkane has occurred, a consistent downcore decrease in concentration may be expected, as seen at Voua de la Motte, France (Wünsche *et al.*, 1988), Coburn Mountain Pond, Maine (Ho and Meyers, 1994), and Upton Broad (Cranwell, 1984b). Such a decrease is not seen at Lochan Uaine, and the C_{17} *n*-alkane shows fluctuations throughout the core. It is thus reasonable to infer that degradation is not the only process affecting the distribution of this component, although it cannot entirely be ruled out. If degradation of shorter chain-length *n*-alkanes is minimal, it follows that degradation of longer chain-length *n*-alkanes should be even less likely, as stability increases with increasing chain-length. Hydrocarbons have a lower susceptibility to degradation than other lipid classes (Cranwell, 1981; Meyers and Ishiwatari, 1993).

As with the longer chain-length *n*-alkanes, addition of an internal standard during extraction allows the concentration of the C_{17} *n*-alkane in the sediment to be calculated. The downcore change in concentration, expressed as a proportion of TOC, is given in Figure 5.17b. Unlike longer chain-length *n*-alkanes, significant variation is seen. Following the assumption that short and long chain-length *n*-alkanes originate, respectively, from algal/bacterial and higher plant sources, it follows that these results indicate variation in lake primary productivity, during a period in which allochthonous input remained relatively constant. Due to the poor chronological control on core UACT6 it is not possible to calculate influx rates of lipids with any degree of accuracy, although in future studies it would be worthwhile to attempt such analyses on well-dated cores, especially annually-laminated sequences.

Mid chain-length n-*alkanes:* n-C_{21} *to* n-C_{25}

In addition to the short and long chain-length *n*-alkanes, which indicate algal/bacterial and higher plant input, mid chain-length *n*-alkanes are used as an indicator of *Sphagnum* species, in particular *n*-C_{23} (Cranwell, 1973b; Quirk, 1978). Analysis of *Sphagnum* from the Lochan Uaine catchment supports these findings (Section 5.2.2), as do recent studies of peat bogs in northern England (Nott *et al.*, 2000). In the study of Nott *et al.*, the C_{23} *n*-alkane is identified as the main indicator of certain *Sphagnum*

species, although in the Lochan Uaine catchment *Sphagnum* specimen it is slightly less dominant than the n-C_{21} homologue. None of the other reference specimens analysed have comparable concentrations of mid chain-length hydrocarbons, with the exception of grass (although longer chain-lengths dominate in grass). The C_{23} n-alkane is more abundant than n-C_{21} in all sediment samples analysed. In certain east African lakes, such as Lake Nkunga, Mt Kenya, C_{23} and C_{25} n-alkanes are found to be indicative of submerged/floating aquatic macrophyte input to the sediment (Ficken *et al.*, 1998, 2000). No aquatic macrophytes are present in Lochan Uaine. Aquatic bryophytes are found in low densities around the margins of the lake. The hydrocarbon sample extracted from these bryophytes is found to be dominated by C_{29} and C_{31} n-alkanes, with much lower abundances of n-C_{23} and n-C_{25}. Furthermore, the total lipid concentration in this sample is far lower than in other reference specimens analysed. It is not thought that there is a significant input to the sediment of C_{23} and C_{25} n-alkanes from aquatic sources. As a result, the use of C_{21} and C_{23} n-alkanes as indicators of *Sphagnum* is thought to be more reliable than if aquatic macrophytes had been present in Lochan Uaine.

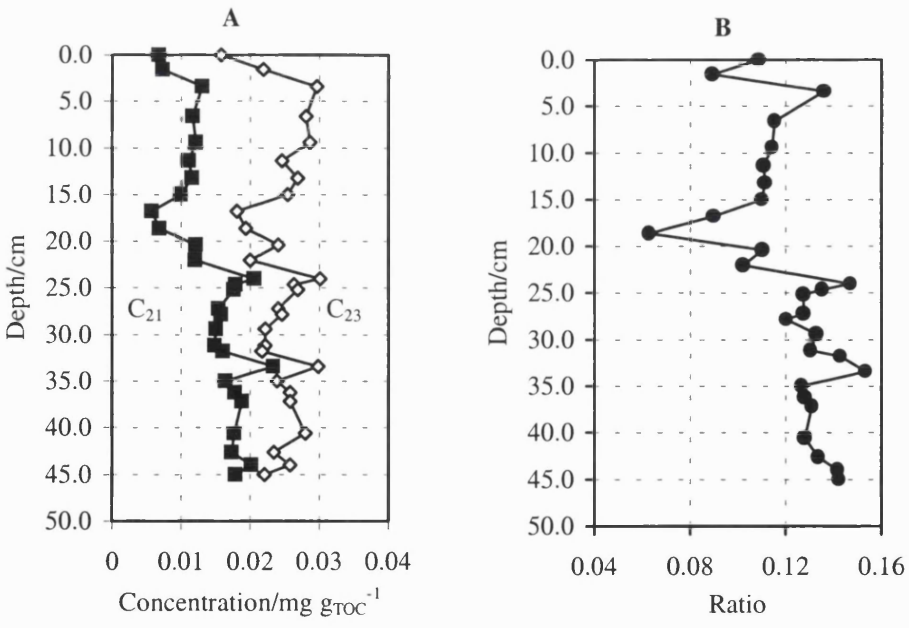


Figure 5.18 (a) Variation in concentration of C_{21} and C_{23} n-alkanes, and **(b)** ratio of mid chain-length to long chain-length n-alkanes, calculated as $(C_{21}+C_{23})/(\Sigma C_{27\text{-}33odds})$.

Other non-*Sphagnum* sources of mid chain-length *n*-alkanes have been proposed, as in Laguna Leija, Chile, where *n*-C_{23} is found to dominate the algal mat (Simoneit *et al.*, 1980). Again, this is not thought to affect the signal at Lochan Uaine. Algal mats do not form due to the ultra-oligotrophic status of the lake, and analysis of modern reference specimens of algae have found only low concentrations of *n*-C_{23} (*cf.* Wilkes *et al.*, 1999), although it is possible that this comes from the detrital higher plant material which contaminated the algal scrape. *Sphagnum* thus appears to be an important source of medium chain-length *n*-alkanes in the sediment of Lochan Uaine.

Although mid chain-length *n*-alkanes generally show only a poor relationship with TOC when expressed as a proportion of TOC (Table 5.4), significant changes are nonetheless visible in the downcore profile (Figure 5.18a). This contrasts with the C_{27} to C_{33} long chain-length *n*-alkanes which show minimal downcore variation. In particular, low concentrations of these components occur at the surface and between 15-20 cm depth, while peaks in concentration are found at 4-10 cm, 24 cm, and 33 cm depth. These changes are seen more clearly when the ratio of mid to long chain-length *n*-alkanes is calculated (Figure 5.18b). This ratio should provide an estimate of the relative influx of *Sphagnum* to the sediment, by comparison with vascular plants. Quirk (1978) reports that as *Sphagnum* decays the *n*-C_{23} alkane is preferentially removed until the *n*-C_{31} alkane becomes dominant. A similar increase in chain-length of the dominant homologue is seen as *Sphagnum* peats humify (Lehtonen and Ketola, 1993). The downcore variations, and overall increase, in the ratio of mid to long chain-length *n*-alkanes, suggests that the sediment at Lochan Uaine does not contain a simple degradation signal. It is also interesting to note that Cranwell (1973b) identifies the C_{31} *n*-alkane as predominating in peat catchments, whereas in forested catchments *n*-C_{29} is more abundant. The C_{31} *n*-alkane predominates throughout core UACT6. At an minimum elevation of 910 m, the Lochan Uaine catchment lies well above the present day tree-line (Pears, 1967, 1968). The catchment vegetation assemblage near the lake margin contains large numbers of peat-forming species, although no well-developed peat sequences are found in the catchment. Some lake catchments at lower elevations in the Cairngorms contain evidence of tree growth during the Holocene, despite lying above the present day tree-line (Bennett, 1996). These include

Lochnagar at an elevation of 780 m. No such evidence for past tree growth is seen at Lochan Uaine, and it is unlikely that Holocene temperatures were ever high enough to allow tree development in the catchment. This may explain the predominance of the C_{31} *n*-alkane throughout core UACT6, in agreement with Cranwell's (1973b) findings.

5.3.3.5 *n*-Alkenes

The C_{21}-C_{29} odd chain-length primary *n*-alkenes are dominated by the C_{25} and C_{23} components. From 0-19 cm depth, both components are present in roughly equal abundances, whether expressed as a proportion of the sum of all *n*-alkanes, or as a proportion of TOC (Figure 5.19). There are large increases in concentration below 17-24 cm depth, with C_{25} becoming roughly twice as abundant by comparison with C_{23}. The significance of these two components is not well known, and they are not seen in any of the modern day reference specimens. Only grass contains significant quantities of hydrocarbons other than *n*-alkanes, and primary *n*-alkenes are not identified amongst them.

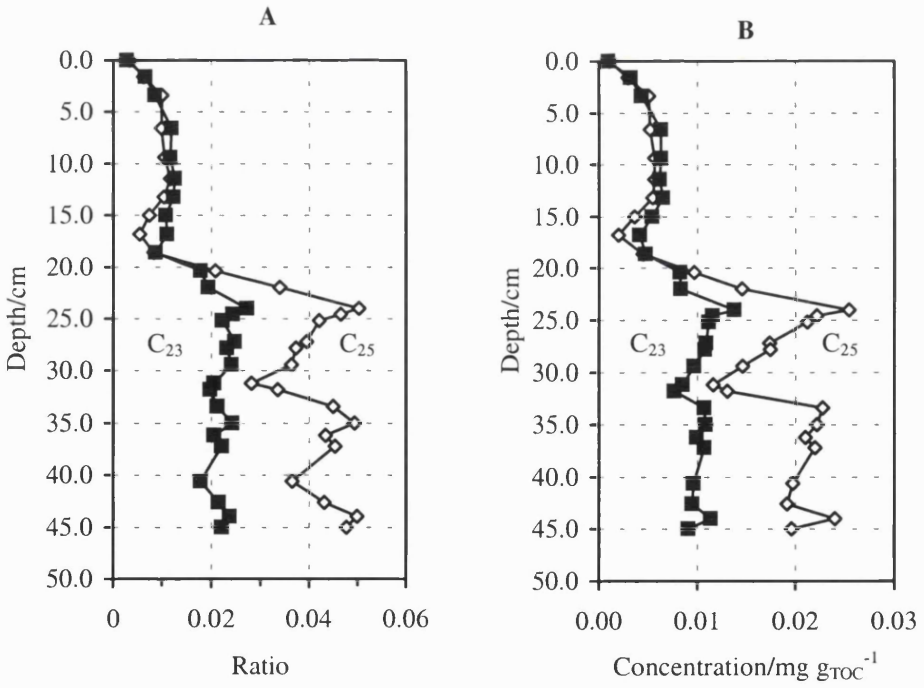


Figure 5.19 (a) Downcore variation in the ratio of C_{23} and C_{25} primary *n*-alkenes to the sum of all *n*-alkanes, and **(b)** concentration of C_{23} and C_{25} *n*-alkenes.

5.3.3.6 Other hydrocarbons

Hopan-22-ene (diploptene)

The component eluting between the C_{32} and C_{33} *n*-alkanes is a C_{30} hopanoid (Figure 5.10). Although the precise structure could not be determined, it is tentatively identified as hopan-22-ene (diploptene) (Appendix F, structure **XIII**). The molecular ion $[M]^+$ 410 and $[M-15]^+$ 395 are both present and indicate a C_{30} component, and ions at *M/z* 191 and *M/z* 189 correspond to cleavage of ring C of the hopanoid skeleton (Rodier *et al.*, 1999). Hopanoids have previously been found in the sediments of numerous Euopean lakes, including Baldeggersee and Vitznau Basin in Switzerland, Lake Constance in Germany/Switzerland/Austria, Lago di Mezzano in Italy, Marsworth Reservoir and Lake of Menteith in Britain, and Kalandsvatenet and Lake Pollen in Norway (Buchholz *et al.*, 1993; Innes *et al.*, 1997, 1998; Rodier *et al.*, 1999; Wilkes *et al.*, 1999). In some cases these hopanoids have been identified, and most are found to be variations on bacteriohopanetetrol (bacteriohopane-32,33,34,35-tetrol: Appendix F, structure **XIV**). Precise identification of hopanoids is difficult, often relying on comparisons between the mass spectrum of the component under study and the mass spectra of a range of standards. As Rodier *et al.* (1999, page 713) comment, "Complex biohopanoids are generally not amenable to the routine analytical techniques applied in conventional organic geochemical studies". Hopanoids, and diploptene in particular, are thought to originate in various types of bacteria, where they are used to reinforce membranes (Rohmer *et al.*, 1984; Ourisson *et al.*, 1991; Ourisson and Rohmer, 1992).

Hopanoids are also found in Holocene peat deposits, where they have been correlated with an increasing *Sphagnum* content (Van Dorssalaer, 1977; Quirk *et al.*, 1984; Farrimond and Flanagan, 1996). Farrimond and Flanagan state that the hopanoids appeared to be formed during the decay of *Sphagnum* moss, although whether the source organism was the *Sphagnum* or bacteria is unclear. In UACT6, the concentration of diploptene is consistently low (Figure 5.20a). This low concentration, and associated errors in integrating GC peak areas, may account for the large downcore variations. Overall, a trend of increasing concentration with increasing sediment age is apparent.

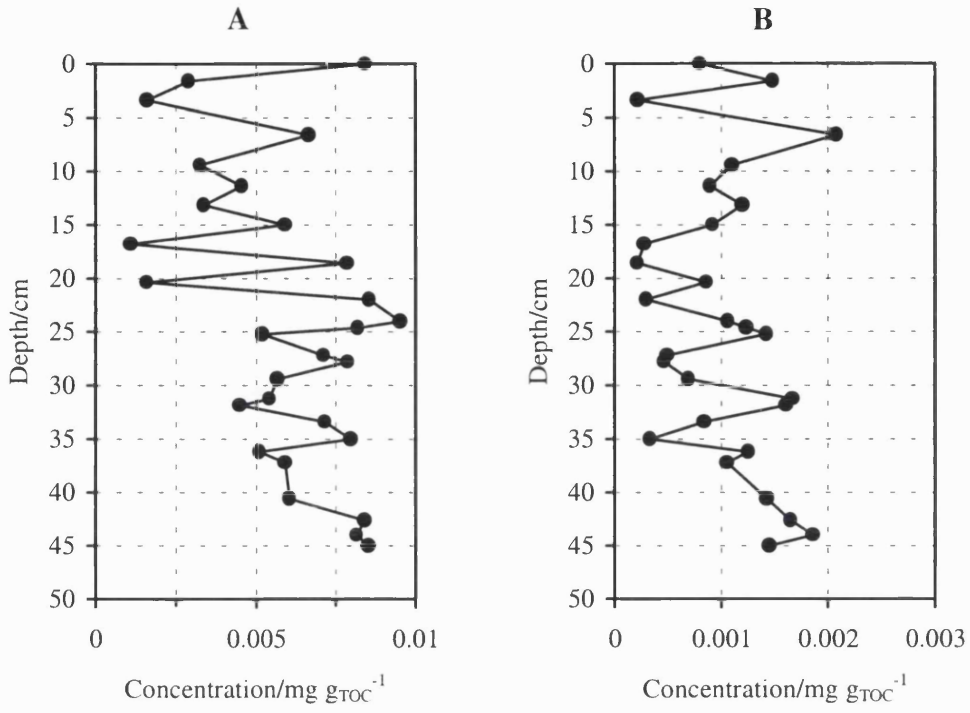


Figure 5.20 Downcore variations in **(a)** diploptene, and **(b)** phytane.

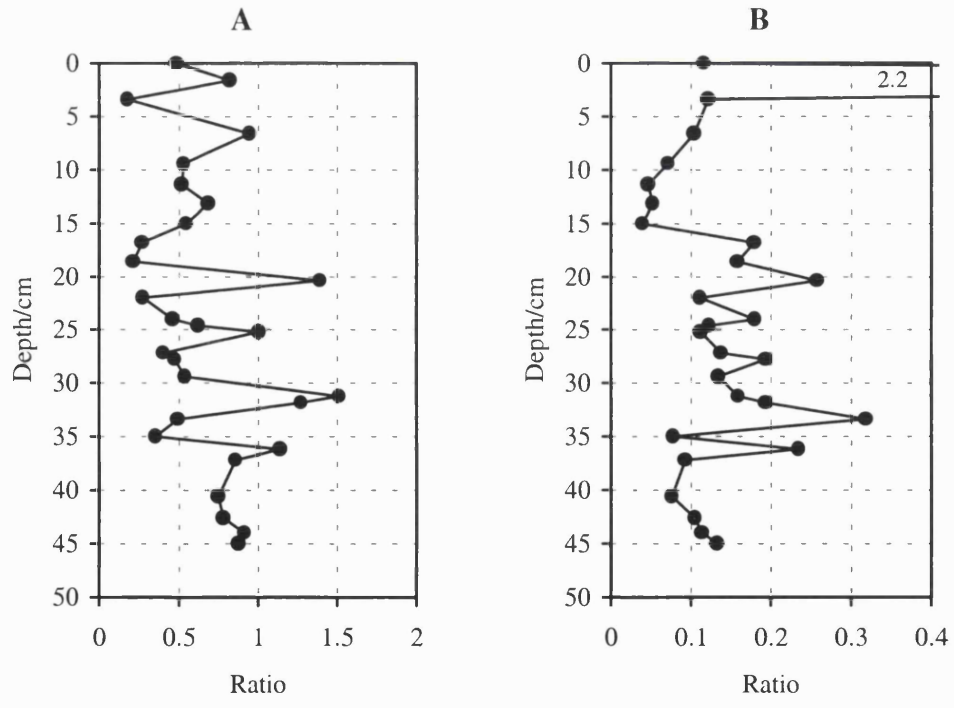


Figure 5.21 **(a)** Phytane/*n*-C_{18} alkane ratio, and **(b)** phytane/*n*-C_{17} alkane ratio.

Phytane

In many samples, the isoprenoid C_{20} hydrocarbon phytane (2,6,10,14-tetramethylhexadecane: Appendix F, structure **XI**) is detected eluting just after the C_{18} *n*-alkane, and in a roughly equal concentration (ten Haven *et al.*, 1987). As with diploptene, the concentration of phytane is very low and shows large downcore fluctuations (Figure 5.20b). As such, long term trends are hard to distinguish from the noise, but phytane seems to show a decrease from the base of the core to *c.*18 cm depth, and an increase from 18 cm to the surface. Phytane is thought to be produced mainly by methanogenic bacteria (Risatti *et al.*, 1984), although eukaryotic algae are also listed as a possible biological precursor (Sinninghe Damsté *et al.*, 1995). Meyers and Eadie (1993, page 52) state that, "Phytane is produced by anaerobic microbial reprocessing of phytol". The main source of phytol used in this microbial activity is probably from degradation of chlorophyll (Cranwell, 1978). Numerous types of chlorophyll contain the phytyl sidechain, including chlorophylls-*a*, *b*, *d*, and bacteriochlorophylls-*a* and *b*. Ho and Meyers (1994) used the ratio of phytane to the C_{18} *n*-alkane as an indicator of the input from methanogen *vs.* algal sources in Coburn Mountain Pond, Maine, USA. They interpreted this in terms of past bioturbation and seasonal water column anoxia. At Lochan Uaine, as at Coburn Mountain Pond, considerable downcore fluctuations are seen in the ratio (Figure 5.21a). This may be a record of past anoxia, or it may merely be due to noise, as the concentrations of both components are low and subject to larger measurement errors than more abundant components. The current pattern of seasonal oxic/anoxic conditions in Lochan Uaine is not known, although given the ultra-oligotrophic status of the lake and the amount of water column mixing, it is reasonable to assume that the bottom waters are well oxygenated. Ho and Meyers (1994) do not discuss their reasons for comparing phytane to the C_{18} *n*-alkane specifically. At Coburn Mountain Pond, as at Lochan Uaine, the C_{17} *n*-alkane is much more abundant, and is thought to originate from the same sources as *n*-C_{18}. The phytane to *n*-C_{17} ratio for core UACT6 is shown (Figure 5.21b). The large peak at 2 cm depth is due to an abnormally low *n*-C_{17} value. Otherwise, the observed changes in ratio merely reflect variation in *n*-C_{17} as phytane remains relatively constant. High concentrations of *n*-C_{17} from 5-15 cm and 37-46 cm are matched by low values in the phytane/*n*-C_{17} ratio, and *vice versa*. It must be

remembered that Ho and Meyers (1994) use *n*-C_{18} as an indicator solely of algal sources, whereas others find short chain-length *n*-alkanes to originate also in bacterial sources (Barnes and Barnes, 1978; Murata and Nishida, 1987; Cranwell *et al.*, 1987). Hence, the phytane/*n*-C_{17} and phytane/*n*-C_{18} ratios may not be exclusive indicators of methanogen *vs.* algal input, and are more likely to represent methanogen *vs.* algal *and bacterial* sources.

Several other hydrocarbon components are present in the sediment, as seen in GC profiles (Figure 5.10). Concentrations of some components are too low to allow mass spectrometric identification. Pristane is not seen, although it is commonly identified in recent sediments and is thought to be indicative of diagenesis of the phytol sidechain of chlorophyll *a*, possibly during reprocessing by planktonic herbivores (Blumer *et al.*, 1963). Both pristane and phytane are more resistant to degradation than *n*-alkanes (Didyk *et al.*, 1978), hence their respective low concentration and absence at Lochan Uaine are not thought to be a product of post-depositional diagenesis.

C_{25} highly branched isoprenoid alkene

A hydrocarbon component eluting just after the C_{21} *n*-alkane is identified as a C_{25} highly branched isoprenoid (C_{25} HBI) monoene. Recent studies have found C_{25} HBIs in both freshwater and marine environments (Rowland and Robson, 1990; Hird *et al.*, 1992; Summons *et al.*, 1993; Cooke *et al.*, 1998; Johns *et al.*, 1999). Nichols *et al.* (1988, 1989) and Johns *et al.* (1999) found C_{25} HBIs in collections of Antarctic sea ice diatoms, and this was confirmed by analysis of laboratory-cultured diatoms such as *Haslea ostrearia* and *Rhizosolenia setigera* (Volkman *et al.*, 1994; Belt *et al.*, 1996; Wraige *et al.*, 1997, 1998, 1999; Johns *et al.*, 1999; Sinninghe Damsté *et al.*, 1999a,b). It is not known whether diatoms are the exclusive biological precursors of these components, but Sinninghe Damsté *et al.* (1995) were sufficiently confident of the origin of C_{25} HBIs to state that they "...may be considered as a proxy for contributions from diatoms" (page 478). It should be noted that *Haslea ostrearia* and *Rhizosolenia setigera* are both marine diatoms, and no corresponding studies of freshwater diatoms are known.

The precise identification of the component, including its structure, requires the use of additional techniques to standard GC-MS, such as nuclear magnetic resonance (NMR) spectroscopy (Belt *et al.*, 1994; Wraige *et al.*, 1997, 1998, 1999; Volkman *et al.*, 1998). Sinninghe Damsté *et al.* (1995) found the alkane 2,6,10,14-tetramethyl-7-(3-methylpentyl)pentadecane (Appendix F, structure **XII**) eluting in the same position as the C_{25} HBI at Lochan Uaine, while other studies have identified monoene (Dunlop and Jefferies, 1985), diene (Nichols *et al.*, 1988; Johns *et al.*, 1999) and other more highly unsaturated C_{25} HBI hydrocarbons (Volkman *et al.*, 1994, 1998; Belt *et al.*, 1996; Sinninghe Damsté *et al.*, 1999b). The molecular ion value of the component present in UACT6, [M^+] 350, suggests a monoenic C_{25} HBI. The ion at *M/z* 266 corresponds to cleavage of the methylpentyl branch, and suggests that the unsaturated bond is not found on this branch. Overall, the mass spectrum agrees well with that given for similar components in other studies (Johns *et al.*, 1999; Rowland and Robson, 1990). Other than this, little can be said of the structure of this component without further analysis.

The downcore concentration of the C_{25} HBI monoene in UACT6 is given in Figure 5.22. Strong similarities are seen with the LOI and TOC profiles and with the C_{17} *n*-alkane profile, in particular the periods of low concentration at around 2-4, 15-20, 26-28 and 33-35 cm depth, and the higher concentrations at the surface and from 5-15, 24-27, 30-32 and 37-45 cm depth. The correlation between C_{25} HBI monoene and TOC is significant at the 95% level (R^2=0.344), as is that between C_{25} HBI monoene and C_{17} *n*-alkane (R^2=0.265). The importance of these correlations will be discussed in a later section (Section 5.4).

Although comparisons of concentrations of short *vs* long chain-length *n*-alkanes suggest a low algal input to the lake sediment, the sediment mineral matter contains a large component of diatom biogenic silica, with diatom valve concentrations of up to $5x10^8$ $g_{wet\ sed}^{-1}$ (Battarbee *et al.*, 1996). A diatom biomarker would allow a direct comparison to be made between inputs to the organic and mineral fractions of the sediment. The downcore concentration of the C_{25} HBI monoene shows negligible concentrations at 3 cm and 17-20 cm depth, but a large decrease from the base of the

core towards 20 cm depth. Diatom valve concentrations for core UACT4 show a similar overall downcore increase, though a lot of variability is apparent in the diatom data and the specific maxima and minima seen in the C_{25} HBI monoene signal are not present (Battarbee *et al.*, 1996). It is possible that the diatom productivity signal as determined from diatom concentrations is obscured by any small changes in sediment accumulation rate occurring concurrently with the changes in LOI, TOC or C_{25} HBI monoene concentration (Battarbee *et al.*, in press). Also, the apparent low input of algal lipids to the sediment may merely reflect low lipid concentrations in the source organisms, by comparison with many higher plants which display high lipid concentrations (Table 5.1).

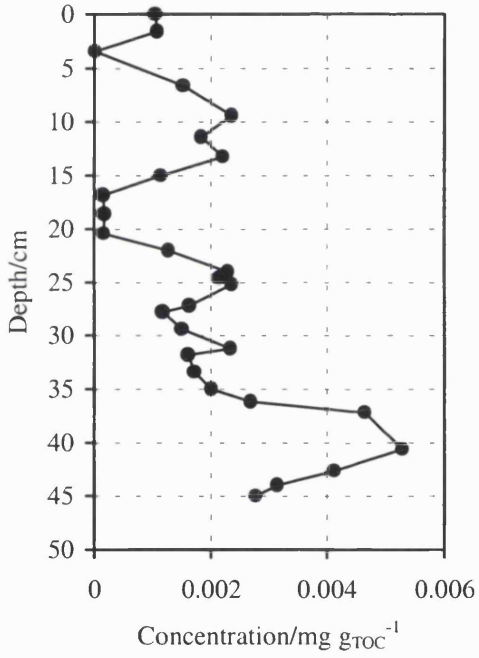


Figure 5.22 Downcore concentration of the C_{25} HBI monoene.

5.3.4 Acids

n-Alkanoic acids are found in organic sediments of all ages (Cranwell, 1982). Their ubiquity means that they are used widely in organic geochemical studies of lake sediments, as are unsaturated, branched-chain, cyclic, and hydroxy acids. The sediment record at Lochan Uaine is dominated throughout by *n*-alkanoic acids (Figures 5.23 and 5.24), and only in the surface sample are there significant amounts

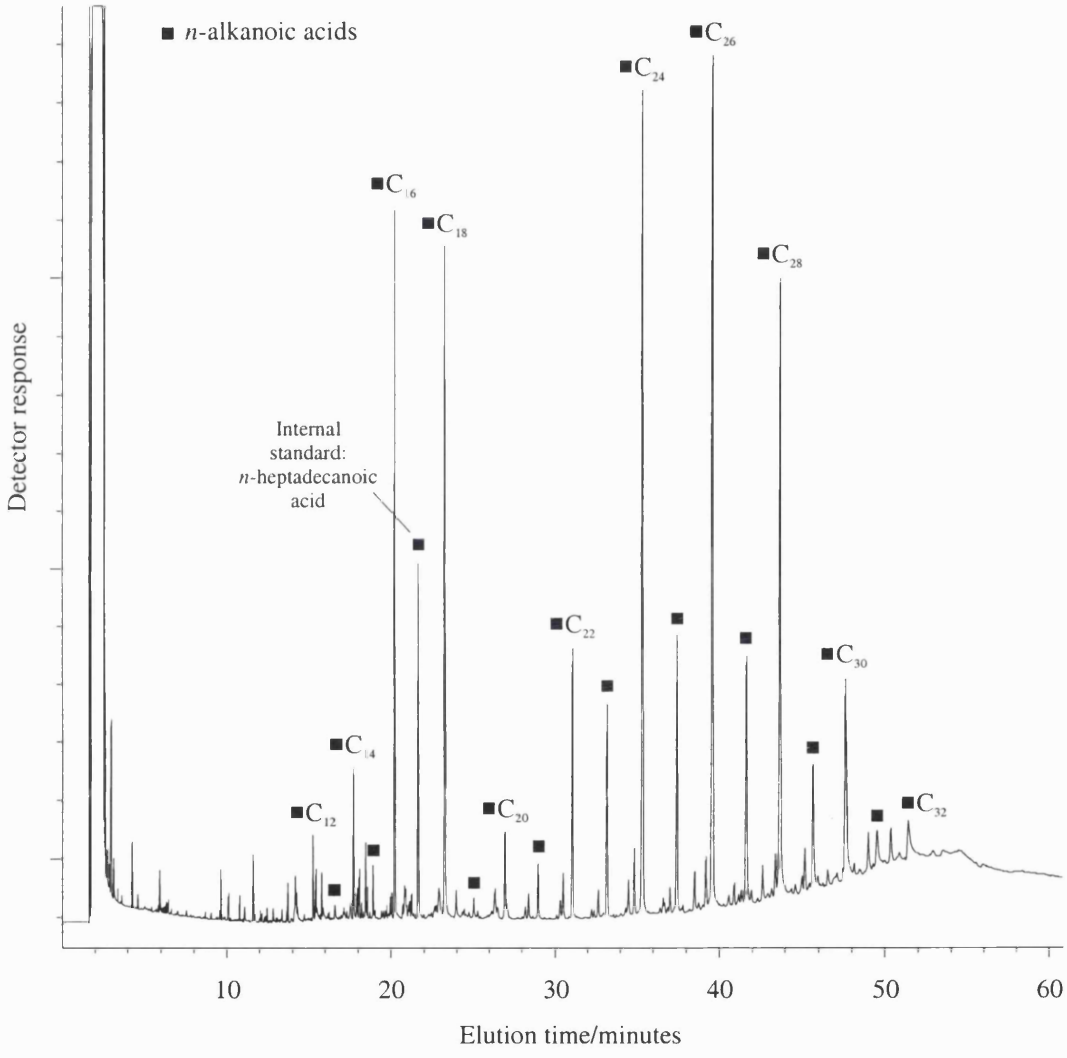


Figure 5.23 Typical GC profile of an acid fraction (1.6-2.2 cm), core UACT6.

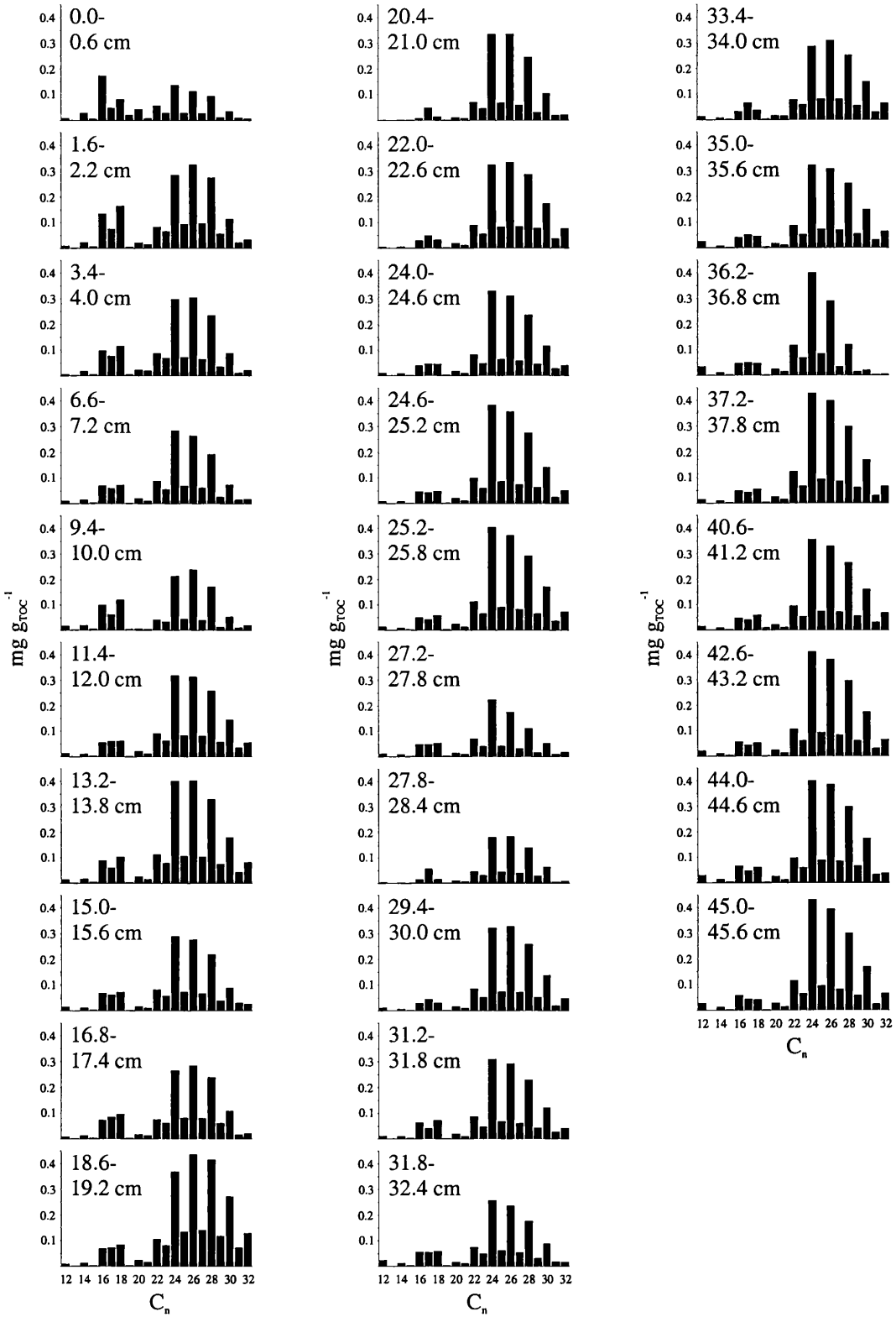


Figure 5.24 Histogram distributions of *n*-alkanoic acids in core UACT6. Heptadecanoic acid (n-C_{17}) is the internal standard.

of any other acids, namely short chain-length *n*-alkenoic acids. It is likely that these components are lost rapidly through degradation processes. Hence, this section will be restricted to the analysis of *n*-alkanoic acids and their use as palaeoindicators in lake sediment studies.

5.3.4.1 Total *n*-alkanoic acid content of UACT6 sediment

The total concentration of all acids in UACT6 ranges from 0.9-2.5 mg g_{TOC}^{-1} (0.09-0.25% of TOC), representing roughly 0.1-0.2 mg $g_{dry\ wt}^{-1}$ (0.01-0.02% of sediment dry weight). The bulk of these acids are *n*-alkanoic acids. This range is similar to that of 0.2-0.8 mg $g_{dry\ wt}^{-1}$ which Cranwell (1974) gives for small oligotrophic temperate lakes, of which Lochan Uaine is a good example, and lower than the 1 mg $g_{dry\ wt}^{-1}$ suggested by Eglinton *et al.* (1968) for productive lakes. Other published figures for total monocarboxylic acid concentrations (converted to mg $g_{dry\ wt}^{-1}$ and mg g_{TOC}^{-1} where necessary) include: 0.03 mg $g_{dry\ wt}^{-1}$ or 4 mg g_{TOC}^{-1} in Walker Lake (Meyers and Benson, 1988); from 2-16 mg g_{TOC}^{-1} at Lago di Mezzano (Wilkes *et al.*, 1999); 0.46 mg $g_{dry\ wt}^{-1}$ at Loch Affric (Cranwell, 1990); from 0.02-0.11 mg $g_{dry\ wt}^{-1}$ or 0.35-0.58 mg g_{TOC}^{-1} at Lake Biwa (Kawamura and Ishiwatari, 1984); *c.* 0.7-2.8 mg g_{TOC}^{-1} at Lake Haruna (Ishiwatari *et al.*, 1980); 0.01-0.13 mg $g_{dry\ wt}^{-1}$ at Lake Huron (Meyers and Takeuchi, 1979; Meyers *et al.*, 1980a); 0.05-0.5 mg $g_{dry\ wt}^{-1}$ at Lake Suwa (Nishimura and Koyama, 1977a); *c.* 1-3 mg g_{TOC}^{-1} at Heart Lake (Meyers *et al.*, 1984a). Total acid concentrations vary greatly between lakes, but the concentrations measured at Lochan Uaine are not atypical.

5.3.4.2 Carbon preference index of *n*-alkanoic acids

n-Alkanoic acids in sediments are found mainly in the chain-length range C_{10} to C_{34} (Cranwell, 1982), with those at Lochan Uaine lying in the range C_{12} to C_{32} (Figure 5.23). Almost invariably in Holocene sediments a strong even-over-odd chain-length predominance is apparent, reflecting the origin of these components in living organisms where they are biosynthesised from C_2 acetyl units. In core UACT6, the CPI of C_{21}-C_{31} *n*-alkanoic acids varies from 3 to 5 downcore, with a mean value of 4.03 (Figure 5.25). This compares with a mean CPI of 6.48 for *n*-alkanes (Section

5.3.3.2). No major trends are seen in the CPI of *n*-alkanoic acids, whereas *n*-alkanes showed a significant downcore increase.

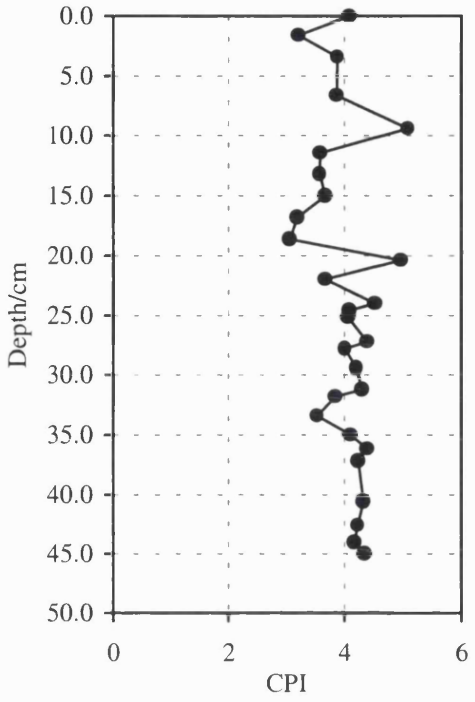


Figure 5.25 Downcore variation in CPI of mid and long chain-length *n*-alkanoic acids (C_{21}-C_{31}), indicating an even-over-odd predominance, core UACT6. Short chain-length *n*-alkanoic acids are excluded from the analysis due to the use of the C_{17} *n*-alkanoic acid as an internal standard.

Published values of CPI for free *n*-alkanoic acids show considerable variation. These include values of 7.7 at Crose Mere (Cranwell, 1978), 5.0-9.5 at Rostherne Mere (Thompson and Eglinton, 1978), 5.3±6 at Lake Haruna (Ishiwatari *et al.*, 1980), 4.5-4.8 at Loch Clair (Cranwell, 1981), 6.4-9.7 at Upton Broad (Cranwell, 1982), 5.0-11.4 at Coniston Water (Cranwell, 1984a), 6-7 at Ellesmere (Rieley *et al.*, 1991a), 1-8 in Coburn Mountain Pond (Ho and Meyers, 1994), and 5-21 in Lake Nkunga (Ficken *et al.*, 1998). Meyers and Eadie (1993) record even/odd chain-length ratios from 8 to 28 in settling matter within the water column of Lake Michigan, while CPI values of 6.0-7.5 are seen in a marine sediment by Madureira *et al.* (1995). It should be noted that not all of these published values cover the same chain-length range as is used at Lochan Uaine (C_{21}-C_{31}), and some include short chain-length acids in the CPI determination. Nonetheless, it can be seen that the CPI values recorded in Lochan Uaine are not uncommon.

5.3.4.3 Individual *n*-alkanoic acid concentrations in UACT6

As with the *n*-alkane distribution, no major downcore variations in *n*-alkanoic acids are apparent. Chain-length distributions of *n*-alkanoic acids exhibit a consistent bimodal distribution, with maxima at C_{16}-C_{18} and C_{24}-C_{28} (Figure 5.24). The C_{16} acid dominates in the uppermost sample (0.0-0.6 cm depth), but longer chain-lengths dominate in all other samples. Of these, sixteen samples are dominated by the C_{24} acid and eleven by the C_{26} acid. In most cases the abundances of C_{24} and C_{26} acids are very similar, and have values within 10% of each other in twenty-two of the twenty-eight core samples.

The correlations between abundances of *n*-alkanoic acids and TOC are given in Table 5.5. Similar results are seen as for hydrocarbons (Table 5.4). When acids are measured as a proportion of dry sediment weight, several show strong correlations with TOC. This is especially true of the most abundant longer chain-length C_{24}, C_{26} and C_{28} *n*-alkanoic acids. The R^2-values are found to increase considerably when the surface sediment sample (0.0-0.6 cm depth) is excluded from the statistical analysis. Reasons for excluding this sample have been discussed previously in relation to hydrocarbons. No correlation is seen between TOC and the short chain-length C_{16} and C_{18} *n*-alkanoic acids. To remove the influence of potential downcore changes in sediment mineral content, the analyses are repeated with acids expressed as a proportion of TOC, rather than as a proportion of dry sediment. Few significant correlations are seen for the *n*-alkanoic acids, and the C_{16} and C_{18} components both show a slight negative relationship.

Both C_{16} and C_{18} *n*-alkanoic acids show similar downcore decreases in concentration, from over 0.15 mg g_{TOC}^{-1} in the upper core to around 0.05 mg g_{TOC}^{-1} at lower depths (Figure 5.26). In both cases the lowest values occur at 20.4-21.0 and 27.8-28.4 cm depth. The most noticeable difference occurs in the surface sample (0.0-0.6 cm depth), where the concentrations are 0.17 and 0.08 mg g_{TOC}^{-1} for C_{16} and C_{18} *n*-alkanoic acids respectively, a difference of 111%. In other samples, the concentrations of the two components are in general within 20% of each other.

n-Alkanoic acid	Acid ($g_{dry\ wt}^{-1}$) *vs* TOC ($g_{dry\ wt}^{-1}$)	Acid ($g_{dry\ wt}^{-1}$) *vs* TOC ($g_{dry\ wt}^{-1}$), minus top sample	Acid (g_{TOC}^{-1}) *vs* TOC ($g_{dry\ wt}^{-1}$)	Acid (g_{TOC}^{-1}) *vs* TOC ($g_{dry\ wt}^{-1}$), minus top sample
C_{16}	0.064	0.000*	0.035*	**0.279***
C_{18}	0.001*	0.030*	**0.285***	**0.358***
C_{20}	**0.466**	**0.464**	0.097	0.025
C_{22}	**0.535**	**0.641**	0.049	**0.119**
C_{24}	**0.497**	**0.719**	0.063	**0.231**
C_{26}	**0.380**	**0.622**	0.000	0.045
C_{28}	**0.270**	**0.436**	0.009*	0.001
C_{30}	**0.214**	**0.350**	0.001	0.024
C_{32}	**0.137**	**0.235**	0.003	0.022

Table 5.5 Correlation coefficients (R^2-values) between selected *n*-alkanoic acid components and TOC (* represents an inverse relationship). Bold type indicates significance at the 95% confidence limit; underlining represents significance at the 99% confidence limit. Values are shown with and without inclusion of the surface sample in the statistical analysis (0.0-0.6 cm).

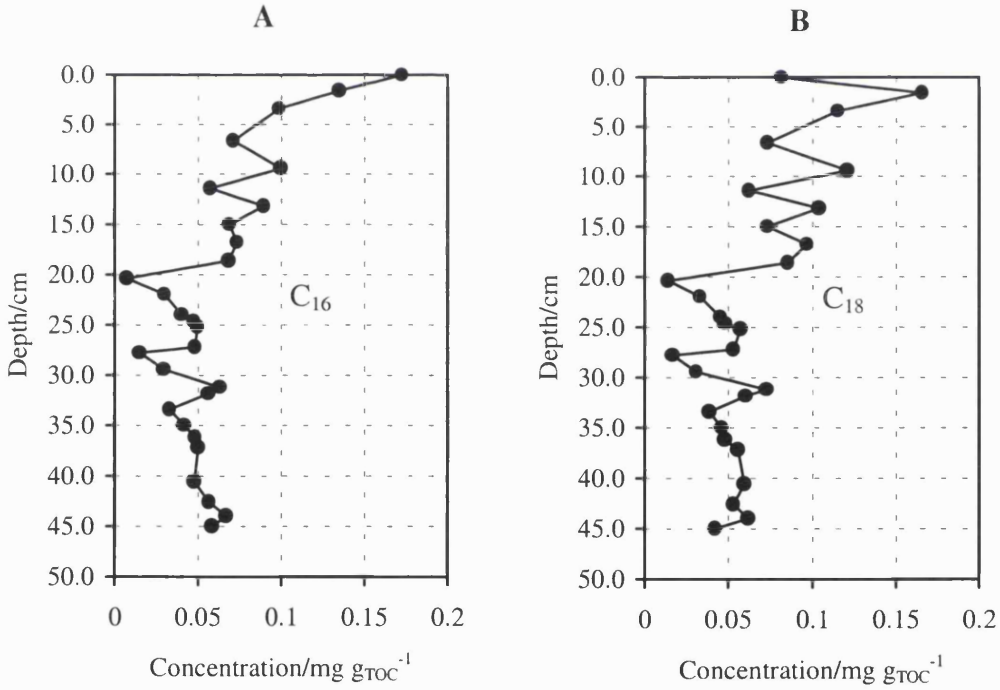


Figure 5.26 Downcore concentrations of **(a)** the C_{16} *n*-alkanoic acid, and **(b)** the C_{18} *n*-alkanoic acid, core UACT6.

Concentrations of longer chain-length acids show no downcore decrease (Figure 5.27). Both the C_{24} and C_{26} *n*-alkanoic acids vary considerably, mostly between values of 0.2 and 0.4 mg g_{TOC}^{-1}. If anything, a slight downcore increase in concentration is apparent. Of note, the lowest concentrations of these two components are recorded at 0.0-0.6 cm depth, despite the high TOC content and the high concentrations of shorter chain-length *n*-alkanoic acids. As with *n*-alkanes and the shorter chain-length acids discussed above, this may reflect differences between deeper core sediment and that at the mud-water interface. It may also reflect degradation processes - if, as suggested by analysis of modern reference specimens, *n*-alkanoic acids tend to be found in organisms as parts of larger structures such as waxes rather than as free lipids, then an increase in these acids might be expected with increasing depth as they are freed from their parent compounds. The large increase in C_{24} and C_{26} *n*-alkanoic acids from the surface down to 1.6 cm depth suggests that this process occurs rapidly in the sediments of Lochan Uaine.

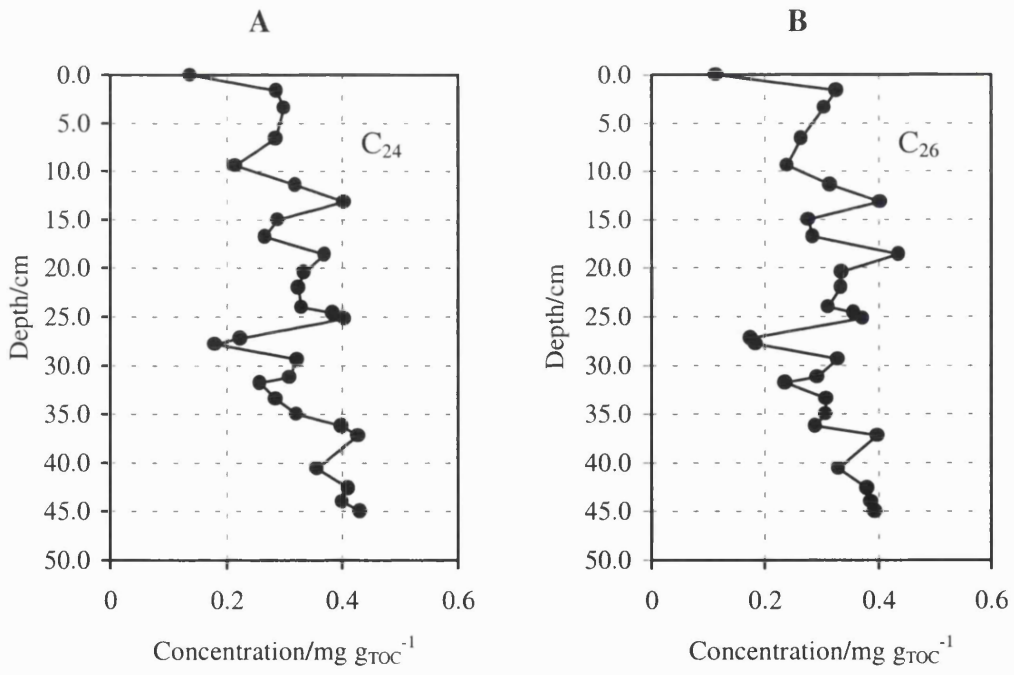


Figure 5.27 Downcore concentrations of **(a)** the C_{24} *n*-alkanoic acid, and **(b)** the C_{26} *n*-alkanoic acid, core UACT6.

Distributions of *n*-alkanoic acids similar to those seen in UACT6 are common in lake sediments worldwide. Bimodal distributions with maxima in the short (C_{16}-C_{18}) and

long (C_{22}-C_{30}) chain-length ranges, as seen in the UACT6 0.0-0.6 cm sample, were found at Blelham Tarn, Ennerdale Water, Seathwaite Tarn, Cam Loch and Esthwaite Water (Cranwell, 1974), Lake Suwa (Matsuda and Koyama, 1977a), Crose Mere (Cranwell, 1978), Lake Haruna (Ishiwatari *et al.*, 1980), Pyramid Lake (Meyers *et al.*, 1980b), Coniston Water (Cranwell, 1984a), Lakes Biwa, Suwa and Motosu (Kawamura and Ishiwatari, 1984, 1985), Voua de la Motte (Wünsche *et al.*, 1988), Ellesmere Lake (Farr *et al.*, 1990; Rieley *et al.*, 1991a), Coburn Mountain Pond (Ho and Meyers, 1994), and Lago di Mezzano (Wilkes *et al.*, 1999). Long chain-length predominance was seen at Grasmere (Cranwell, 1974), Loch Clair (Cranwell, 1981), Loch Affric (Cranwell, 1990), and Lake Nkunga (Ficken *et al.*, 1998). Short chain-length predominance was seen at Lake Huron (Meyers and Takeuchi, 1979; Meyers *et al.*, 1980a), Lake Haruna (Kawamura and Ishiwatari, 1985), Lake Kinneret (Robinson *et al.*, 1986), and Priest Pot (Cranwell *et al.*, 1987), and in settling particulate matter in Lake Michigan (Meyers *et al.*, 1984b; Meyers and Eadie, 1993) and Skjervatjern Lake (Berdié *et al.*, 1995). Often the chain-length predominance changes downcore. In some instances this has been associated with catchment changes, as at Pyramid Lake where a switch from short chain-length predominance to a bimodal distribution was attributed to increased sediment accumulation rate, and corresponding enhanced preservation of *n*-alkanoic acids (Meyers *et al.*, 1980b). More commonly, a downcore decrease in short chain-length components is seen. This is usually due to degradation processes.

Preservation of short chain-length n-*alkanoic acids*

It is widely recognised that short chain-length components degrade more rapidly than long chain-length components, and *n*-alkanoic acids follow this pattern (Matsuda and Koyama, 1977a; Barnes and Barnes, 1978; Meyers and Takeuchi, 1979; Cranwell and Volkman, 1981; Cranwell, 1982; Kawamura and Ishiwatari, 1984; Meyers and Benson, 1988; Wünsche *et al.*, 1988; Meyers and Eadie, 1993). A possible degradation route of *n*-alkanoic acids is given by Parker (1969), whereby CO_2 is lost from the acid to form an unstable radical. This in turn reacts to form an acid or an *n*-alkane with one carbon atom less than the original component. Degradation of short chain-length components can be rapid and may begin prior to deposition in the

sediment, during the settling of organic matter (Meyers *et al.*, 1984b). Following deposition, degradation of *n*-alkanoic acids will be greatest in the uppermost, biologically active zone of the sediment (Cranwell, 1982). Meyers *et al.* (1980a) suggest that below this zone, degradation will be relatively limited over Holocene timescales. This view is corroborated by Matsuda and Koyama (1977a), who found that short chain-length acids in sediment from Lake Suwa decrease by more than 90% within the top 25 cm of core. Concentrations of these acids then vary little between 25 cm and the core base at 150 cm. Meyers and Eadie (1993) attempted to quantify the relative degradation rates of different chain-length acids, using data from sediment traps in Lake Michigan (Figure 5.28). They showed that the C_{16} *n*-alkanoic acid degraded roughly 10 times as fast as the C_{30} *n*-alkanoic acid. A corresponding rate of 6-7 times was calculated for coastal marine sediments by Haddad *et al.* (1992).

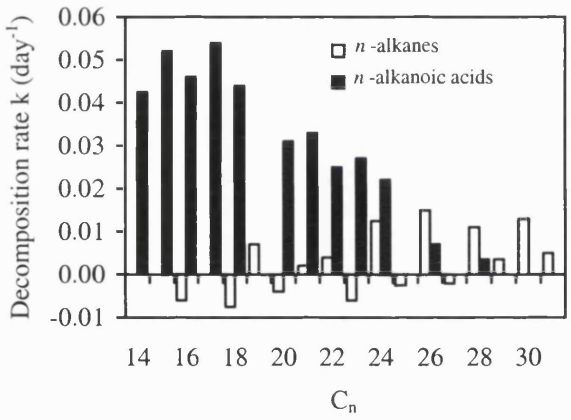


Figure 5.28 Decomposition rates of C_{14}-C_{31} *n*-alkanoic acids and *n*-alkanes from sediment trap data in Lake Michigan, expressed as a constant *k*. Negative values for some *n*-alkanes reflect inputs to the sediment traps from sources other than sinking particulate matter. Redrawn from Meyers and Eadie (1993, page 54, Figure 4).

In some cases there are indications that bound or esterified short chain-length *n*-alkanoic acids display enhanced preservation compared to free acids (Cranwell, 1978, 1981, 1990; Cranwell and Volkman, 1981). At Crose Mere, the free, esterified and bound *n*-alkanoic acids have CPIs of 7.7, 9.3, and 13.7, respectively (Cranwell, 1978). The lower value for free acids compared to the bound components suggests that more rapid conversion of even to odd chain-lengths may occur in this fraction, possibly via the mechanism described by Parker (1969) and mentioned above. In

others cases, the free, bound and esterified acid fractions all show similar chain-length distributions (Ishiwatari *et* al., 1980; Meyers *et al.*, 1984b; Cranwell *et al.*, 1987). Other factors thought to enhance the preservation of short chain-length acids include high sediment accumulation rates and anoxia at the mud-water interface (Meyers *et al.*, 1980b; Meyers and Ishiwatari, 1993), while unsaturated acids are more sensitive to degradation (Cranwell, 1974; Meyers and Takeuchi, 1979; Meyers *et al.*, 1980a; Ho and Meyers, 1994).

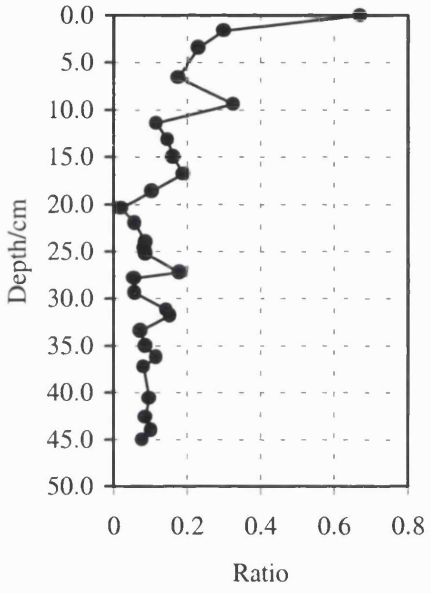


Figure 5.29 Ratio of short to long chain-length *n*-alkanoic acids in core UACT6, calculated as $(C_{16}+C_{18})/(C_{24}+C_{26}+C_{28}+C_{30})$.

Degradation of short chain-length n-*alkanoic acids in UACT6*

At Lochan Uaine a marked increase in shorter chain-length *n*-alkanoic acids is seen up the core. This is visible in the downcore profiles of the C_{16} and C_{18} acids (Figures 5.26), and in the ratio between long and short chain-length acids (Figure 5.29). The latter decreases from 0.7 at the surface, to consistently below 0.2 from 10 cm depth to the core base. The decrease is not as smooth as those seen by Matsuda and Koyama (1977a), the fluctuations arising from variations in the concentrations of the short chain-length acids rather than the longer chain-lengths, as seen in Figure 5.24. The environment at Lochan Uaine is not conducive to the preservation of short chain-length *n*-alkanoic acids. The sediment accumulation rate is very low (*c.* 0.25 mm yr^{-1}),

hence acids will remain in the biologically active zone for longer periods of time than if the sediment accumulation rate had been high. Likewise, it is unlikely that anoxia plays a significant role at the mud-water interface. The altitude, climate, and relatively shallow depth of Lochan Uaine mean that the water will generally be well mixed and hence well oxygenated, although it is possible that stratification occurs during the period of winter ice cover. The ultra-oligotrophic nature of the lake means that algal blooms which could potentially deplete oxygen are absent. The resulting oxic conditions at the mud-water interface create a reactive environment in which rapid degradation of short chain-length acids can occur. It is almost certainly a combination of low sediment accumulation rate and lack of bottom water anoxia which cause the loss of short chain-length *n*-alkanoic acids from the sediment record of Lochan Uaine. This also accounts for the loss of the less stable $C_{16:1}$ and $C_{18:1}$ components which are detected only in the surface sample.

5.3.4.4 *n*-Alkanoic acid chain-lengths and organic matter sources

It was seen with *n*-alkanes that short chain-length components are associated with algal and bacterial origin, and longer chain-length components with a higher plant origin. In Lochan Uaine these are thought to be equivalent to autochthonous and allochthonous inputs, respectively. Numerous studies apply a similar interpretation to *n*-alkanoic acid chain-length distributions (Cranwell, 1974, 1978, 1981, 1982, 1990; Barnes and Barnes, 1978; Meyers and Takeuchi, 1979; Ishiwatari *et al.*, 1980; Meyers *et al.*, 1980a,b; Kawamura and Ishiwatari, 1984, 1985; Cranwell *et al.*, 1987; Wünsche *et al.*, 1988; Ho and Meyers, 1994; Wilkes *et al.*, 1999). However, as is seen in the case of modern reference specimens (Section 5.2), this interpretation does not always hold true for *n*-alkanoic acids due to the ubiquity of certain short chain-length acids. In particular, the C_{16} *n*-alkanoic acid is a common constituent of bacteria, algae and higher plants (Meyers and Eadie, 1993). Much, if not all, of the short chain-length component of higher plants may be degraded prior to deposition in the sediment (Cranwell, 1982). By contrast, long chain-length *n*-alkanoic acids are only rarely found in organisms other than higher plants. Meyers *et al.* (1984a, page 730) summarise the situation thus: "Although shorter chain length *n*-alkanoic acids...are not accurate indicators of biotic source due to their ubiquity, the longer

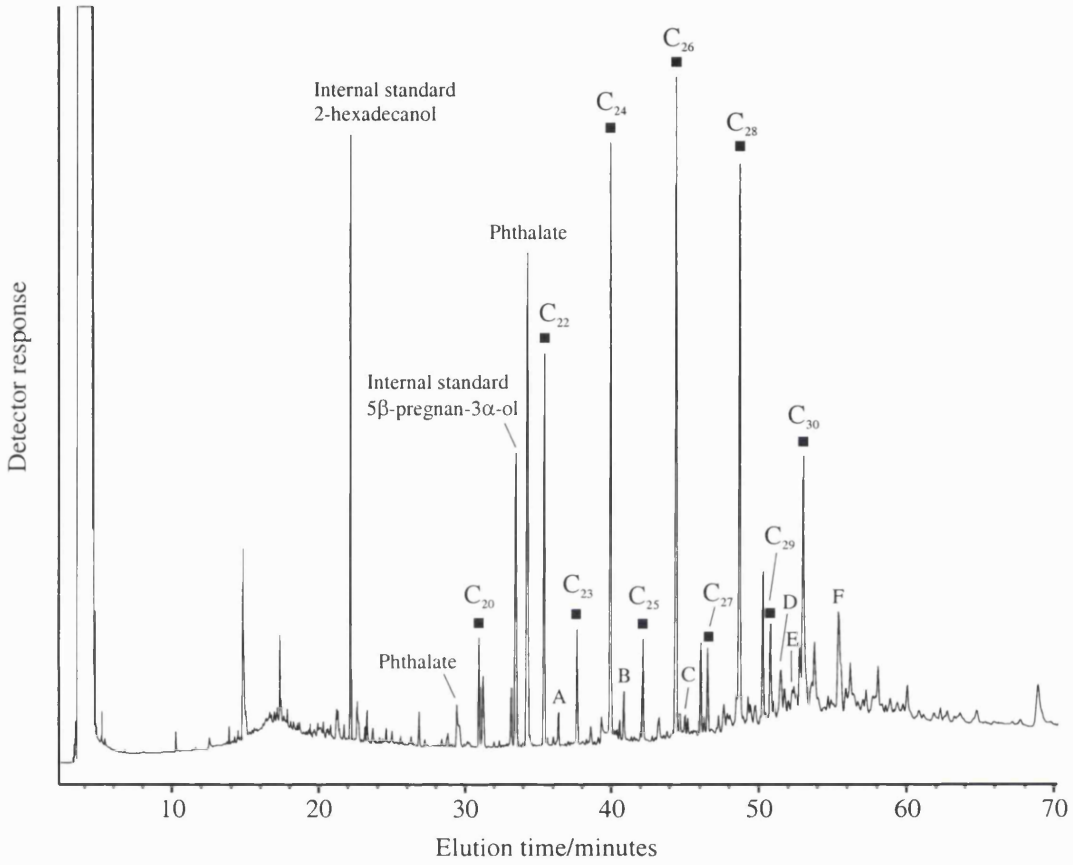
chain length homologues would seem [to be] valid land-plant indicators". The predominance of long chain-length *n*-alkanoic acids in all but the uppermost sample of core UACT6 suggests a significant higher plant input. No significance can be attached to the shorter chain-length acids seen in minor quantities throughout the core, except to show that degradation processes are an important consideration at Lochan Uaine.

5.3.5 Alcohols and sterols

The sedimentary alcohol and sterol fraction is dominated by straight chain *n*-alkanols in the range C_{20} to C_{30} (Figure 5.30). In nearly all samples the C_{26} component predominates, although the C_{28} and C_{24} components are also present in comparable concentrations (Figure 5.31). This predominance of the C_{24} to C_{28} components was expected, as a similar distribution is seen in the biosynthetically-related long chain-length *n*-alkanoic acids. In addition to *n*-alkanols, numerous other alcohols are present in lower concentrations, most notably sterols. This section will first examine *n*-alkanol distributions in UACT6, followed by sterol distributions.

5.3.5.1 Carbon preference index of *n*-alkanols

As with *n*-alkanoic acids, *n*-alkanols exhibit a strong even-over-odd predominance in carbon chain-length (Figure 5.32). Mean CPI for *n*-alkanols in the range C_{21} to C_{29} is 6.90. The highest CPI recorded is 8.3 for the 0.0-0.6 cm surface sample. Below this the CPI drops to *c.* 6, and thereafter shows a general downcore increase. A similar downcore increase is seen in the *n*-alkane CPI, although in that case the surface sample is not so anomalous. Published values of CPI for free sedimentary *n*-alkanols include 9.6 in Crose Mere (Cranwell, 1978), 8.6 and 10.6 in Loch Clair (Cranwell, 1981), and from 3-20 in Lake Nkunga, Kenya (Ficken *et al.*, 1998).Values from 6.5-10 are also observed in marine sediments (Madureira *et al.*, 1995). The CPI of *n*-alkanols generally appears to be greater than that of *n*-alkanes.



■ C_{xx} *n*-alkanols

A 1-mono-C_{16}-glycerol

B 1-mono-C_{18}-glycerol

C Brassicasterol [**III**]

D β-Sitosterol [**V**]

E Stigmastanol [**X**]

F 4-methylstanol

Figure 5.30 Typical GC profile of an alcohol and sterol fraction (11.4-12.0 cm), core UACT6.

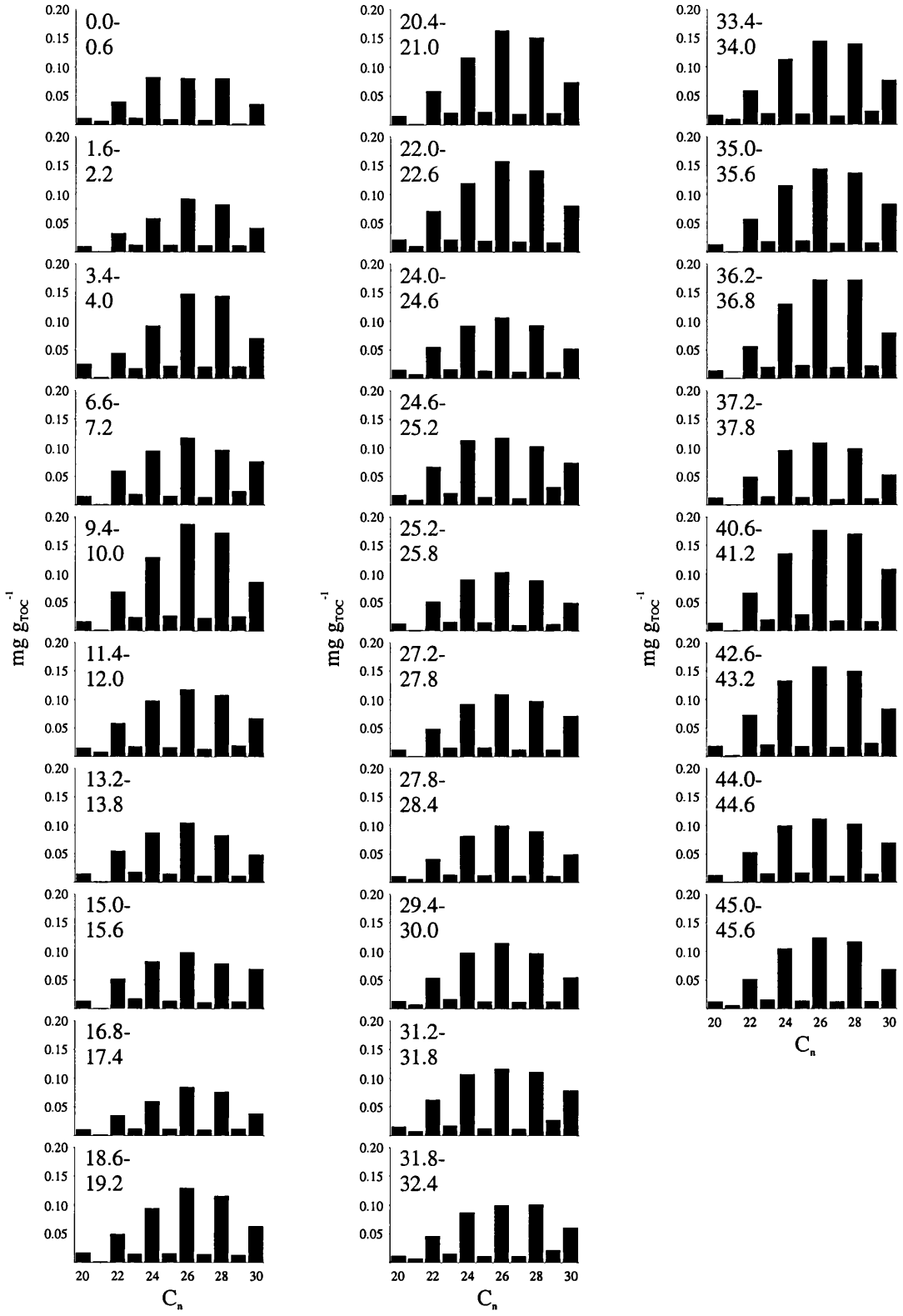


Figure 5.31 Histogram distributions of *n*-alkanols in core UACT6.

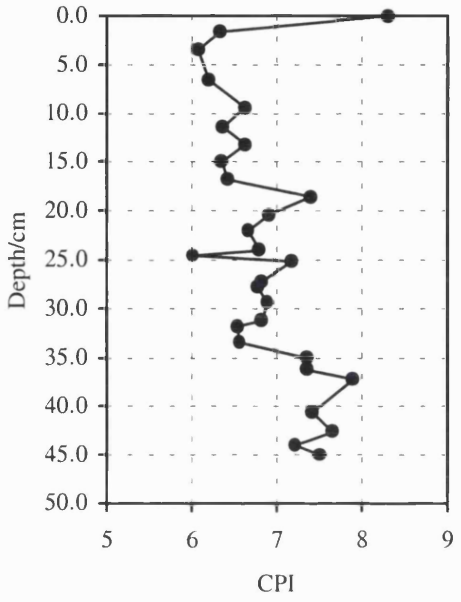


Figure 5.32 CPI of *n*-alkanols in core UACT6, calculated using the C_{21} to C_{29} chain-length range (Bray and Evans, 1961). The mean value is 6.90.

5.3.5.2 Individual *n*-alkanol concentrations in UACT6

Downcore variations in concentration of the five main *n*-alkanols are given in Figure 5.33. All show similar trends, especially the three most abundant components (C_{24}, C_{26}, C_{28}). Lowest values occur at the surface and at around 17 cm depth, whilst maxima are seen at 10 cm, 20-22 cm, 36 cm, and 40 cm. Overall, a slight downcore increase in concentration is apparent. Although these results seem broadly consistent with the downcore variations in TOC, only the C_{22} and C_{24} components are correlated significantly with TOC when expressed as a proportion of TOC (Table 5.6). As before, the relationship is generally improved when the surface sample with an abnormally high TOC is excluded from the analysis.

The distribution of *n*-alkanols in Lochan Uaine sediment is similar to that seen in numerous other lakes. The predominance of long chain-length *n*-alkanols ($>C_{20}$) has been observed in Loch Clair (Cranwell, 1981; Cranwell and Volkman, 1981), Lake Motosu (Kawamura and Ishiwatari, 1985), Voua de la Motte (Wünsche *et al.*, 1988), Lake Nkunga (Ficken *et al.*, 1998), and Lago di Mezzano (Wilkes *et al*, 1999). Additionally, shorter chain-length *n*-alkanols ($<C_{20}$) are present in many lakes, such as

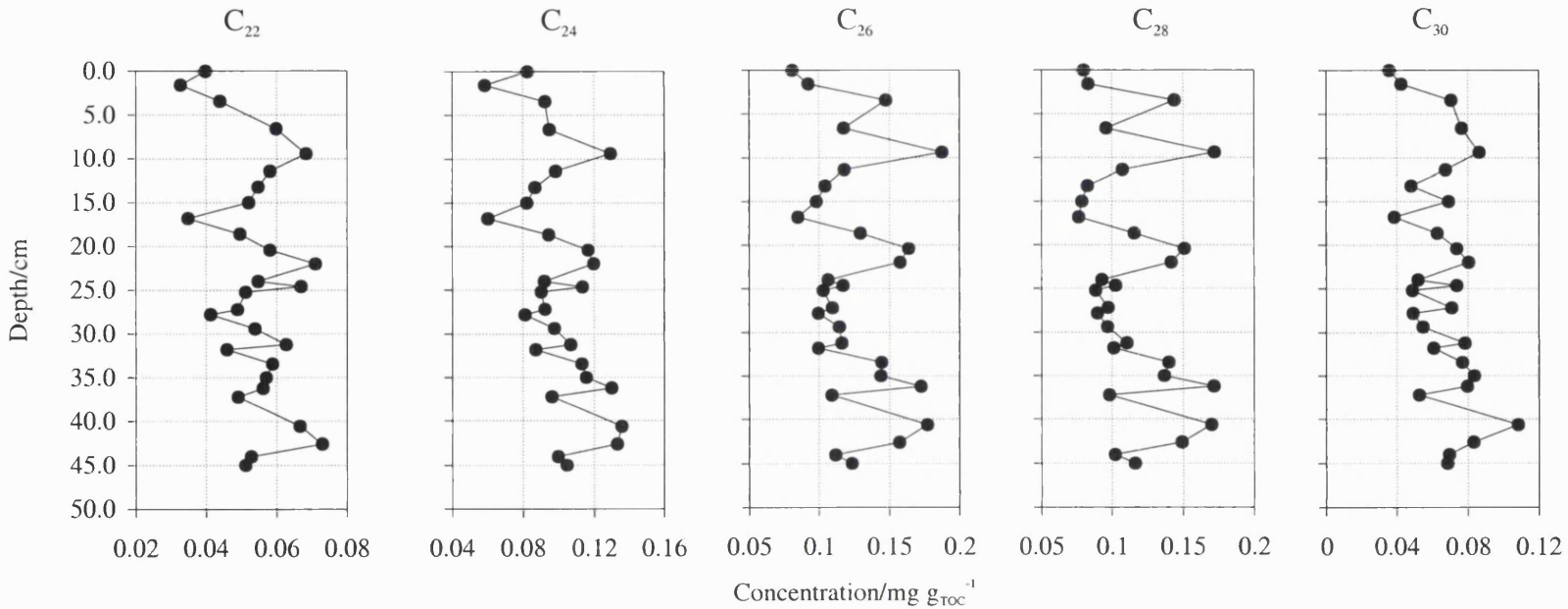


Figure 5.33 Downcore concentration in C_{22}-C_{30} even chain-length *n*-alkanols, core UACT6.

Crose Mere (Cranwell, 1978), Heart Lake (Meyers *et al.*, 1984a), Priest Pot (Robinson *et al.*, 1984a; Cranwell *et al.*, 1987), Lakes Suwa, Biwa and Haruna (Kawamura and Ishiwatari, 1985), Lake Kinneret (Robinson *et al.*, 1986), Ellesmere (Farr *et al.*, 1990; Rieley *et al.*, 1991a), and Coburn Mountain Pond (Ho and Meyers, 1994). In some of these lakes the shorter chain-length components are more abundant than longer chain-length components. No *n*-alkanols with a chain-length shorter than C_{20} have been identified in UACT6.

Table 5.6 Correlation coefficients (R^2-values) between *n*-alkanol components and TOC (* represents an inverse relationship). Values are shown with and without inclusion of the anomalous surface sample (0.0-0.6 cm). Bold type indicates significance at the 95% confidence limit; underlining represents significance at the 99% confidence limit.

n-Alkanol	Alkanol ($g_{dry\ wt}^{-1}$) *vs* TOC ($g_{dry\ wt}^{-1}$)	Alkanol ($g_{dry\ wt}^{-1}$) *vs* TOC ($g_{dry\ wt}^{-1}$), minus top sample	Alkanol (g_{TOC}^{-1}) *vs* TOC ($g_{dry\ wt}^{-1}$)	Alkanol (g_{TOC}^{-1}) *vs* TOC ($g_{dry\ wt}^{-1}$), minus top sample
C_{20}	**0.449**	**0.488**	0.006*	0.001*
C_{22}	**0.683**	**0.773**	**0.155**	**0.276**
C_{24}	**0.706**	**0.759**	**0.196**	**0.284**
C_{26}	**0.424**	**0.517**	0.004	0.030
C_{28}	**0.389**	**0.452**	0.007	0.029
C_{30}	**0.424**	**0.564**	0.034	**0.113**

5.3.5.3 *n*-Alkanol chain-lengths and organic matter sources

Prior to the last few decades, studies of *n*-alkanols in lacustrine sediments have been neglected in favour of other lipid classes (Parker, 1969; Barnes and Barnes, 1978). Since then, the use of *n*-alkanols as source-specific biomarkers has become more common. These studies have generally relied on the interpretation of chain-length distributions obtained by studies of modern vegetation; namely, that long chain-length components originate in higher plants, and shorter chain-length components come from aquatic sources. This in turn indicates the relative inputs to the sediment of allochthonous and autochthonous sources. Published works which use this interpretation include those of Cranwell (1978, 1981, 1982), Cranwell and Volkman (1981), Robinson *et al.* (1984a, 1986), Cranwell *et al.* (1987), Wünsche *et al.* (1988), Farr *et al.* (1990), Rieley *et al.* (1991a), and Wilkes *et al.* (1999). Kawamura and Ishiwatari (1985) demonstrate that short chain-lengths predominate in highly productive lakes where the principal sources of organic material for the sediment are

autochthonous, and long chain-lengths predominate in oligotrophic lakes with mainly allochthonous sources. The link between chain-length and source is not always as clear. Ho and Meyers (1994) state that the predominant C_{22} component in Coburn Mountain Pond could originate in either microbial or higher plant sources, while Ficken *et al.* (1998) show that in Lake Nkunga the C_{26} component could come from either higher plants in the catchment or from aquatic macrophytes within the lake. Meyers *et al.* (1984a) suggest that short chain-lengths do not necessarily indicate autochthonous origin as they appear to be ubiquitous in both higher plants and algae/bacteria, although longer chain length *n*-alkanols seem to originate solely from higher plants. However, this interpretation of short-chain *n*-alkanols has little bearing on the studies at Lochan Uaine, as no chain-lengths shorter than C_{20} were identified in any sediment samples. The input of the C_{26} *n*-alkanol from aquatic macrophytes seen by Ficken *et al.* (1998) would not seem to be a problem as none are found at Lochan Uaine. It thus seems likely that all the *n*-alkanols found at Lochan Uaine, having chain-lengths $>C_{20}$, originate from higher plant sources in the lake catchment.

5.3.5.4 Preservation of *n*-alkanols

One potential problem in any sediment is the loss of short chain-length *n*-alkanols through degradation processes. Not only are alkanols more susceptible to degradation than alkanes and alkanoic acids (Cranwell, 1981), but short chain-length *n*-alkanols are preferentially degraded over long chain-length *n*-alkanols (Robinson *et al.*, 1984a; Meyers and Benson, 1988; Wünsche *et al.*, 1988; Ho and Meyers, 1994). It is possible that the lack of short chain-length components in the sediment reflects this rapid loss through degradation, rather than an absence in the first place. If short chain-length *n*-alkanols were ever present in the sediment, they would most likely be found in the youngest sample, 0.0-0.6 cm, in the same way that *n*-alkanoic acids are most abundant at the surface and decrease in concentration downcore. As *n*-alkanols shorter than C_{20} are not seen anywhere in the core, including the surface sample, it seems that either these components are lost from the sediment very rapidly, or that there is negligible input of these components to the sediment.

Madureira *et al.* (1995) describe a method for measuring the degree of preservation of *n*-alkanols, known as the alcohol preservation index (API: Equation 5.1). In theory, *n*-alkanes are more stable, and hence less susceptible to degradation, than *n*-alkanols. A decrease in the abundance of *n*-alkanols relative to *n*-alkanes may indicate degradation of the more reactive alcohols. The API measures the relative changes in concentration of the most common terrestrial *n*-alkanes and *n*-alkanols to give a value between 0 and 1. Assuming that degradation of *n*-alkanes occurs more slowly than for *n*-alkanols, a decrease in the API should suggest degradational loss of *n*-alkanols.

$$API = \frac{\sum(C_{24}OH + C_{26}OH + C_{28}OH)}{\sum(C_{24}OH + C_{26}OH + C_{28}OH) + \sum(C_{27}alk + C_{29}alk + C_{31}alk)} \quad [5.1]$$

where: $C_{XX}OH$ are *n*-alkanols

$C_{XX}alk$ are *n*-alkanes

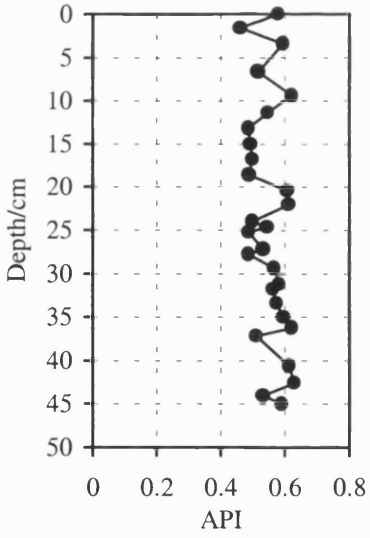


Figure 5.34 Variations in the alcohol preservation index (API) of UACT6 downcore.

The API profile of core UACT6 is given in Figure 5.34. Values generally lie within the range 0.5 to 0.6, similar to those of a core from the Biscay Abyssal Plain (Madureira *et al.*, 1995). Although fluctuations are seen throughout the core, no consistent downcore trend in API is apparent. This suggests that there is no preferential loss of *n*-alkanols relative to *n*-alkanes during the period represented by core UACT6. It should be noted that possible degradation of components prior to deposition is not known. Furthermore, the API only takes into account long chain-

length higher plant components, and not the potentially more reactive short chain-length autochthonous components.

In addition to the free *n*-alkanols discussed above, *n*-alkanols may also be found in sediments as esterified components of waxes or as bound lipids. Several studies find that free *n*-alkanols predominate in sediments, forming 79% and 69% of the total sedimentary *n*-alkanols in Crose Mere and Loch Clair respectively (Cranwell, 1978, 1981). Likewise, free *n*-alkanols are rougly ten times as abundant as bound components throughout a core from Walker Lake, Nevada (Meyers and Benson, 1988). By contrast, esterified and bound *n*-alkanols are present only at levels of 14% and 7% in Crose Mere, respectively, and 14% and 17% in Loch Clair (Cranwell, 1978, 1981). At the latter site, Cranwell and Volkman (1981) show the esterified components to have a near-identical chain-length distribution to the free components. They state that, "...the ester bond may survive intact for several hundred years in lacustrine sediments" (page 29), and that this may provide esterified lipids with greater protection from microbial degradation than free lipids. As with free *n*-alkanols, short chain-length esterified *n*-alkanols are attributed to aquatic sources, and long chain-lengths to terrestrial sources (Fukushima and Ishiwatari, 1984). Only free *n*-alkanols are analysed for this study, although the HT-GC profile presented in Figure 5.9 suggests that bound components are present in the form of wax esters. Future analyses could investigate the presence and composition of esterified and bound alcohols.

5.3.5.5 Sterols and organic matter sources

Numerous studies of lake sediments have attempted to use sterols as organism-specific biomarkers. In particular, C_{27} sterols are often used as indicators of an algal or bacterial origin, and C_{29} sterols as indicators of a higher plant origin (Gaskell and Eglinton, 1975; Nishimura, 1977a; Cranwell, 1978, 1981, 1982, 1990; Huang and Meinschein, 1979; Ishiwatari *et al.*, 1980; Meyers *et al.*, 1984b; Rieley *et al.*, 1991a). As with *n*-alkanes, the differentiation between algal/bacterial and higher plant sterols can be thought of as representing the relative inputs of autochthonous and allochthonous matter. Wünsche *et al.* (1988, page 1136) state that, "...The $C_{27}/(C_{27}$ +

C_{29}) ratio is a reliable autochthonous versus allochthonous input indicator provided that only side chain saturated sterols are taken into account". A similar ratio was used by Wilkes *et al.* (1999), but using dinosterol and 5-dehydrodinosterol (both C_{30}) as aquatic indicators, and β-sitosterol and stigmastanol (both C_{29}) as terrestrial indicators. However, studies of modern day vegetation show that many organisms contain a diverse sterol composition (Section 5.2.3). Algae, bacteria and higher plants may all contain C_{27}, C_{28} and C_{29} stenols and stanols. These include β-sitosterol, which is often used as a higher plant biomarker (Volkman, 1986), and brassicasterol, which has been used as a diatom biomarker (*e.g.* Volkman *et al.*, 1998) but is also found in other organisms, such as the fern, grass, *Juniperus* and *Sphagnum* specimens collected from the Lochan Uaine catchment (Table 5.3). It may thus be problematic to use sterols alone to identify organic matter sources (Volkman, 1986).

5.3.5.6 Distribution of sterols in UACT6

At Lochan Uaine the alcohol and sterol fraction of the sediment lipid extract is dominated by *n*-alkanols, with only minor sterol components. The exception is the uppermost sample (0.0-0.6 cm depth) which displays higher concentrations of sterols, and which is found to contain the following sterols in the concentrations indicated: cholesterol (0.040 mg g_{TOC}^{-1}), brassicasterol (0.022 mg g_{TOC}^{-1}), campesterol (0.036 mg g_{TOC}^{-1}), stigmasterol (0.051 mg g_{TOC}^{-1}), and β-sitosterol (0.077 mg g_{TOC}^{-1}). The only stanol identified was stigmastanol (0.009 mg g_{TOC}^{-1}). These concentrations compare with 0.080 to 0.083 mg g_{TOC}^{-1} for the most abundant alcohols, the C_{24}, C_{26} and C_{28} *n*-alkanols. Huang and Meinschein (1979) also found that C_{29} sterols, and especially β-sitosterol, dominate in lake and river sediments.

Below this surface layer most sterols exhibit a sharp decrease in concentration. Cholesterol, campesterol and stigmasterol virtually disappear from the sediment record and are only seen in trace amounts throughout the rest of core UACT6. Brassicasterol and β-sitosterol are present throughout the core in low concentrations, and exhibit substantial variation between samples (Figure 5.35). In the case of brassicasterol, the downcore concentration profile resembles that of several other variables, including LOI, TOC, the C_{17} *n*-alkane, and the C_{25} HBI monoene

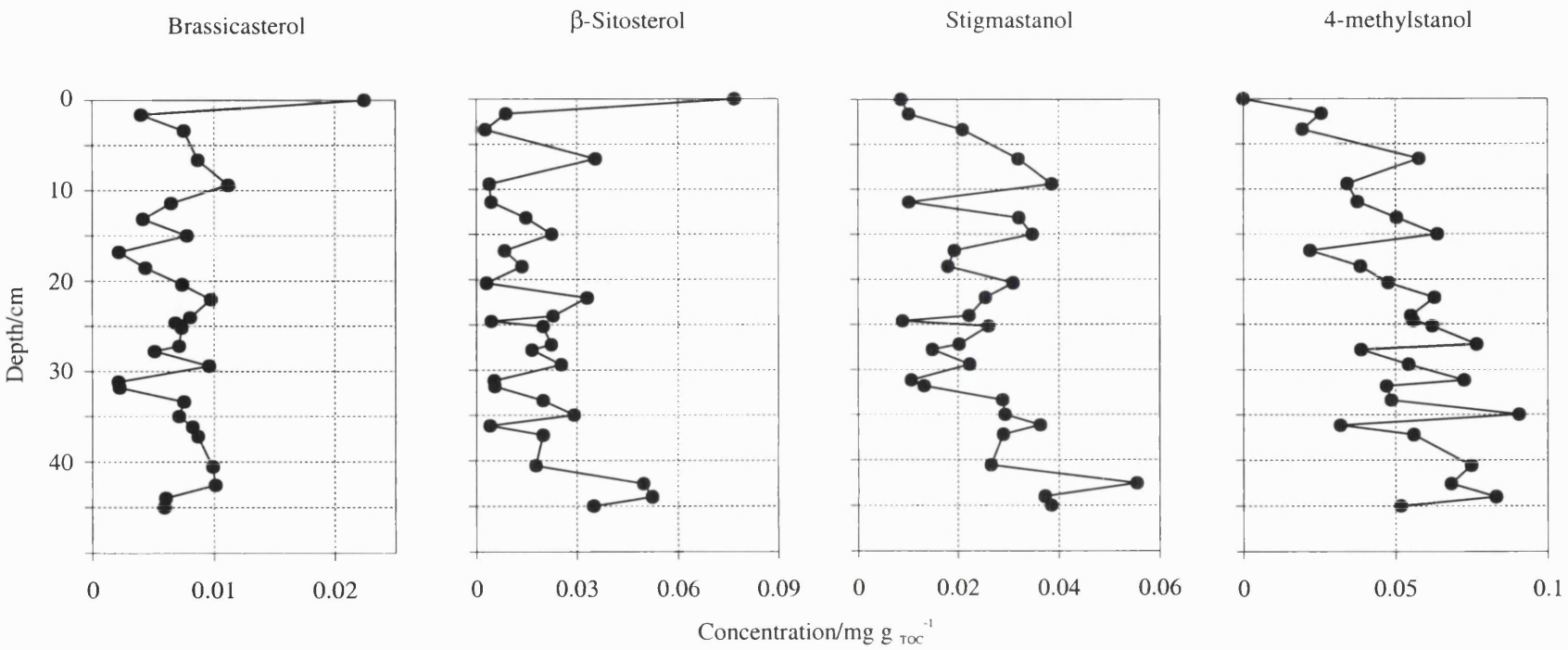


Figure 5.35 Downcore concentrations of four sterols, core UACT6.

hydrocarbon. The correlation between TOC and brassicasterol is found to be significant at the 99% confidence level (R^2=0.194, N=28). Brassicasterol is an important sterol in diatoms, and the C_{25} HBI hydrocarbon is thought to be an exclusive product of diatoms. A downcore covariation of the two components would strengthen the argument that they are proxies of diatom productivity. However, brassicasterol is also found in numerous plants in the Lochan Uaine catchment, suggesting that diatoms are not an exclusive source of this sterol in the sediment. The correlation between brassicasterol and the C_{25} HBI monoene hydrocarbon is found to be significant at the 95% confidence level only when the 0.0-0.6 cm sample is excluded, as the high concentration of brassicasterol in this sample biases the least squares regression fit.

5.3.5.7 Preservation of sterols

Rapid decreases in sterol concentration below the top few centimetres of sediment, similar to those seen at Lochan Uaine, have been recorded previously (*e.g.* Nishimura and Koyama, 1976, 1977; Nishimura, 1978; Farr *et al.*, 1990). These are often accompanied by a decrease in the stenol to stanol ratio. In many cases this process is attributed to microbially-mediated hydrogenation of stenols to form stanols (Gaskell and Eglinton, 1975, 1976; Nishimura and Koyama, 1976, 1977; Nishimura, 1977a,b, 1978; Cranwell, 1981; Robinson *et al.*, 1984a; Meyers and Ishiwatari, 1993). This is aided by the fact that stenols, by virtue of their unsaturation, are naturally less stable than stanols (Farr *et al.*, 1990). Similar hydrogenation processes are inferred in peats (Lehtonen and Ketola, 1993) and in marine sediments (Huang and Meinschein, 1978; Madureira *et al.*, 1995). Nishimura and Koyama (1977) propose a model describing how stenol and stanol concentrations vary with sediment depth (Figure 5.36). Oxidative conditions exist at the sediment surface, suggesting that most of the stanols found there originate in living organisms. The microbiologically active layer below this results in reducing conditions, where overall sterol degradation is decreased but rapid hydrogenation of stenols to form stanols occurs. Below this, hydrogenation and degradation processes continue more slowly. It is thought that the rate of stenol to stanol conversion in the high reduction zone is increased when there is a high input of

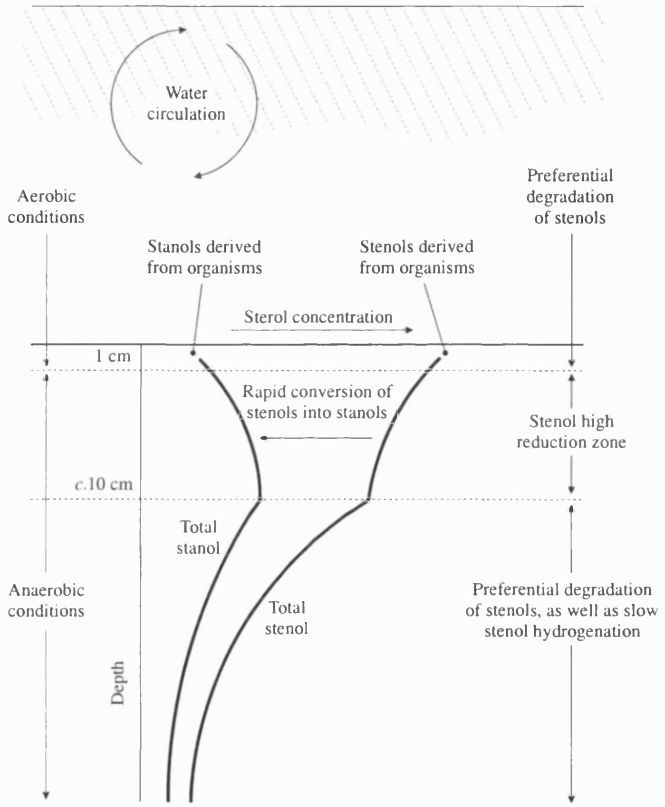


Figure 5.36 Downcore variation in stanols and stenols in a lake sediment (from Nishimura and Koyama, 1977; Fig. 1, page 383).

autochthonous organic matter, as stenols from terrestrial sources are less sensitive to hydrogenation than those from aquatic sources (Nishimura, 1978).

Two stanols, stigmastanol and a 4-methylstanol, are present throughout core UACT6. Both show overall downcore increases in concentration, although the profiles are noisy (Figure 5.35). The fact that both of these components are saturated suggests that they may be produced by the hydrogenation of unsaturated precursor components as discussed above. If this is the case, the likely precursors of stigmastanol would be either β-sitosterol or stigmasterol. The precursor of the 4-methylstanol is not known as no 4-methylstenols were identified in the sediment, although it is possible that dinosterol is the precursor. Alternatively, the stanols may not originate from stenol hydrogenation at all. Stanols can occur naturally in living organisms (Nishimura and Koyama, 1977; Rieley *et al.*, 1991a), although they are not identified in the modern reference specimens collected from the Lochan Uaine catchment.

5.3.6 Ketones and wax esters

Although HT-GC analysis was performed for the ketone and wax ester fraction from all twenty-eight samples throughout UACT6, the chromatography suffers from the same problems as described previously in relation to modern reference material (Section 5.2.5). Chromatographic separation is poor, and co-elution of components is evident. This prevents accurate determination of component concentrations, and the analysis of downcore changes in these concentrations as described previously with respect to the hydrocarbon, acid, and alcohol/sterol fractions. Phthalate contamination also appeared to be a significant problem in the ketone and wax ester fraction. Nonetheless, future studies of ketones and wax esters in lake sediments would be of interest. In particular, wax esters provide a potential source of shorter straight chain components including alkanoic acids and alkanols. The low abundances of these components in modern vegetation specimens compared to their predominance in UACT6 suggests that the autolysis of higher plant waxes may be an important process at Lochan Uaine.

5.3.7 Aromatic and polar fractions

Several sediment samples were chosen for analysis of aromatic and polar fractions by GC and HT-GC, respectively (Appendix C). No aromatic components are observed in any of the eight samples run. The only components seen represent contamination by very low concentrations of hydrocarbons which were incompletely eluted during 'flash' column chromatography. Of note, the topmost sediment samples contain no aromatic components which could have come from industrial-age pollution. No components are seen in either of the polar fractions run, and no vegetation specimens are analysed for aromatic or polar components. It is possible that aromatic and polar components are present in the sediment of Lochan Uaine, but in concentrations too low to allow detection by the method used.

5.4 Summary of lipid analyses

5.4.1 Modern reference specimens

Lipids were extracted from eight modern reference vegetation specimens in the catchment of Lochan Uaine. The specimens were chosen to reflect the variety of different vegetation types in the catchment and the lake, rather than merely the most abundant species overall. The eight specimens were: an aquatic bryophyte from the littoral zone of Lochan Uaine, a scrape of epilithic algae from a submerged rock, a liverwort from the lake edge, and a moss, lichen, grass, fern and shrub from the catchment around the lake perimeter. The sample size of the algal scrape from Lochan Uaine proved insufficient for analysis, and a larger sample was retrieved from a lake in southern England. It was felt that the types of organism present (algae and bacteria) would be reasonably similar at both sites, and hence give similar organic geochemical signals.

Total lipid extract

The modern reference specimens vary greatly in the concentrations of lipids they contain. The lowest TLEs are recorded in the liverwort (11.4 mg $g_{dry\ wt}^{-1}$) and the *Sphagnum* moss (11.9 mg $g_{dry\ wt}^{-1}$), and the highest are in the fern (205 mg $g_{dry\ wt}^{-1}$)

and the dwarf *Juniperus* (108 mg $g_{dry\ wt}^{-1}$). This variation in concentration of more than one order of magnitude has implications in the analysis of the sedimentary lipid record. The different lipid contents of the source organisms, along with possible degradation of these lipids, prevent quantification of their overall inputs of organic matter to the sediment based on lipid biomarker concentrations.

Hydrocarbons

The hydrocarbon content of all the reference specimens is dominated by *n*-alkanes, with the exception of grass in which numerous other components are present, possibly unsaturated or branched hydrocarbons. The *n*-alkane distribution varies between samples. The lichen (*Cladonia* sp.), grass, fern and *Juniperus* are dominated solely by long chain-length odd carbon numbered *n*-alkanes. The algal sample, aquatic bryophyte and liverwort are also dominated by long chain-length *n*-alkanes, but with a smaller secondary peak in short chain-length *n*-alkanes. The algal scrape is thought to contain organic detritus from higher plants, which could have contributed longer chain-length *n*-alkanes. There is general agreement in the literature that short chain-length *n*-alkanes predominate in algae and bacteria (*e.g.* Barnes and Barnes, 1978; Meyers *et al.*, 1984b; Murata and Nishida, 1987; Cranwell *et al.*, 1987). Likewise, the aquatic bryophyte and liverwort are contaminated with algal material, as diatoms were observed growing attached to these specimens. The algae could contribute shorter chain-length *n*-alkanes. These contamination problems prevent the unambiguous attribution of short chain-length *n*-alkanes to algae and longer chain-length *n*-alkanes to higher plants, although given the strong agreement in the literature it seems reasonable to use this chain-length/source organism relationship in the interpretation of sedimentary hydrocarbon distributions. The *Sphagnum* is dominated by mid chain-length odd carbon numbered *n*-alkanes, as seen by Nott *et al.* (2000). These components are present in low concentrations in other reference specimens, but they may potentially be used as a *Sphagnum* biomarker.

Alcohols and sterols

The alcohol and sterol fraction is dominated by sterols, in contrast to the equivalent fraction in the sediment record which is dominated by *n*-alkanols. Sterols present in

the reference vegetation specimens include cholesterol, campesterol, brassicasterol, β-sitosterol and stigmasterol. As before, contamination problems are likely to have affected the algal scrape, the aquatic bryophyte and the liverwort. Sterol carbon number distributions are not considered reliable indicators of organic source (*cf.* Huang and Meinschein, 1979). Such analysis is in any event prevented by the low concentration of sterols in the UACT6 sediment record, and the relatively poor chromatographic resolution during the period of sterol elution (Figure 5.30). The low concentrations of *n*-alkanols observed in reference specimens indicate that they are uncommon as free lipids, and homologous series of *n*-alkanols are only detectable in the aquatic bryophyte, liverwort and *Sphagnum*. *n*-Alkanols may be present in reference specimens mainly as constituents of more complex acyl lipids, in particular leaf surface waxes of higher plants (Eglinton and Hamilton, 1967), where longer chain-length *n*-alkanols are considered indicative of a higher plant input. However, due to poor chromatographic separation the ketone and wax ester fraction was not analysed.

Acids

n-Alkanoic acids are recorded in seven of the eight reference vegetation specimens, the exception being *Cladonia* where no adequate GC profile was obtained. In all cases C_{16} and C_{18} *n*-alkanoic acids predominate. These components are thought to be ubiquitous in plants, either as free lipids or as constituents of more complex lipids such as waxes and glycerides (Meyers and Eadie, 1993; Volkman *et al.*, 1998). As such they are of no use as biomarkers of organic source. By contrast, longer chain-length *n*-alkanoic acids are thought to originate solely in higher plants. These components are detected in small quantities in all the modern reference specimens analysed. Their presence in the algal scrape may be the result of contamination, and hence does not necessarily invalidate the hypothesis that they are a higher plant biomarker. The highest concentrations of longer chain-length *n*-alkanoic acids are seen in the liverwort, *Juniperus* and *Sphagnum*. In *Sphagnum*, mid chain-length acids are more common than long chain-length acids. A similar distribution is seen in the *Sphagnum* *n*-alkanes, and may reflect the biosynthetic association between these components.

5.4.2 UACT6 sediment samples

Lipids are analysed from twenty-eight non-contiguous sediment samples from throughout core UACT6. The samples are approximately evenly spaced, although a deliberate effort was made to choose samples from extremes in LOI and bulk organic $\delta^{13}C$ in an attempt to accentuate any differences giving rise to these variations.

Total lipid extract

When expressed as a proportion of dry sediment, TLE shows a strong positive correlation with TOC. To remove the possible effects of variations in sediment mineral content, the analysis is repeated with TLE expressed as a proportion of TOC. The resulting correlation is not as strong, but is still significant. This suggests either that lipids constitute a greater proportion of organic matter during periods of high total organic matter input to the sediment, or that lipid preservation is influenced by the sedimentary organic matter content.

Hydrocarbons

The hydrocarbon fraction is dominated by long chain-length odd numbered *n*-alkanes, although throughout the core a secondary peak is seen of the *n*-C_{17} component. The CPI shows an increase in odd-over-even predominance with increasing depth, from 3.5 at the surface to over 7 at the core base. The reasons for this trend are not known.

Long chain-length *n*-alkanes are interpreted as being indicative of a higher plant source, and short chain-length *n*-alkanes are indicative of an algal/bacterial source. At Lochan Uaine, higher plants are almost entirely confined to the catchment. The sole exception is the aquatic bryophyte, which is present in low quantities in littoral regions of the lake. The sparse presence of this bryophyte, and its low lipid content compared to other catchment plants, suggests that it is not a major source of organic material to the sediment. Assuming higher plant inputs to the sediment originate mainly in the catchment, it follows that long chain-length *n*-alkane higher plant biomarkers can be used as an indicator of catchment productivity. Conversely, short chain length *n*-alkane algal/bacterial biomarkers are used as an indicator of within-lake productivity.

Minimal downcore change in long chain-length C_{29} and C_{31} *n*-alkanes is seen, whether they are expressed as a proportion of TOC or as a ratio to the total *n*-alkane content. This suggests that the contribution of higher plant allochthonous material to the sedimentary organic matter has remained relatively constant throughout the deposition history of UACT6. Degradation of these components is not thought to be significant as hydrocarbons are generally very stable, and long chain-lengths are more stable than short chain-lengths. The short chain-length C_{17} *n*-alkane shows large downcore variations, the major shifts of which match well with those seen in bulk parameters including LOI, TOC and chlorin content. The large variations in the autochthonous biomarker, coupled with the lack of variation of allochthonous biomarkers, suggests that lake productivity may have a large influence in driving the downcore variations in sedimentary organic content. Given its short chain-length, the C_{17} *n*-alkane is more susceptible to degradation than longer chain-lengths. However, no consistent downcore decrease in concentration is seen which may indicate ongoing degradation of this component. If degradation has occurred, it appears to have been insufficient to obscure the lake primary productivity signal - although, as with TLE, it is possible that preservation is somehow related to the sediment organic matter content.

C_{21} and C_{23} *n*-alkanes are potential indicators of *Sphagnum* input. Although downcore variations of these are not strongly correlated with LOI and TOC, it is noticeable that synchronous decreases in all of these parameters occur at 15-20 cm depth. This event is more pronounced when the ratio of mid to long chain-length *n*-alkanes is plotted. A large decrease at this time is also seen in the concentrations of C_{23} and C_{25} primary *n*-alkanes, although the significance of these components as biomarkers is not known.

Of the other hydrocarbons present, the profile of the C_{25} HBI monoene closely matches that of the C_{17} *n*-alkane, and hence also the LOI and TOC profiles. The C_{25} HBI monoene is regarded as a diatom biomarker. Its close correlation with the downcore C_{17} *n*-alkane concentration increases the confidence that these are synchronous signals of lake primary productivity. Diatom remains form a major proportion of the mineral fraction in the sediment of Lochan Uaine, hence the

identification of a diatom biomarker in the organic sediment fraction is a significant result.

Acids

The acid fraction of UACT6 is dominated by *n*-alkanoic acids with an even carbon number preference. Fluctuations in CPI are visible downcore, although no long term trends are apparent. The values are typical of those seen in other lake sediment studies.

A bimodal distribution in *n*-alkanoic acids is seen throughout core UACT6, maximising at C_{16} to C_{18} and C_{24} to C_{28}. The short chain-length acids show a marked decrease downcore, with concentrations of both dropping from >0.15 mg g_{TOC}^{-1} at the surface to <0.05 mg g_{TOC}^{-1} at the core base. This is attributed to preferential degradation of short chain-length acids, as recorded by Meyers and Eadie (1993). Longer chain-length *n*-alkanoic acids exhibit no such downcore decrease. If anything a slight overall increase is seen downcore in the *n*-C_{24} and *n*-C_{26} acids, although the signals contain much greater variability than was seen in the corresponding long chain-length *n*-alkanes. This downcore increase could reflect the ongoing autolysis of components such as waxes, and the subsequent release of free *n*-alkanoic acids into the sediment. Slight downcore increases are also seen in *n*-alkanols, which along with alkanoic acids form the main constituents of wax esters. The apparent lack of consistent large variations in the long chain-length *n*-alkanoic acid record of UACT6 is interpreted as reflecting minimal changes in the relative input of higher plant material to the sediment organic fraction. This agrees with the interpretation applied to the lack of downcore change of long chain-length *n*-alkanes, as described above.

Alcohols and sterols

The alcohol and sterol fraction of UACT6 is dominated by long chain-length *n*-alkanols, although numerous other components are present, including low concentrations of sterols and other unidentified components. As with *n*-alkanoic acids a strong even-over-odd chain-length predominance is seen in the *n*-alkanols. The highest CPI is recorded in the topmost sample, below which values drop sharply

before increasing steadily towards the base of the core. A similar downcore increase in CPI was seen for *n*-alkanes. The significance of these increases is not known.

The most abundant *n*-alkanols in the sediment are the C_{24}, C_{26} and C_{28} *n*-alkanols. No alkanols shorter than C_{20} are recorded in any of the twenty-eight sediment samples, suggesting either that there has been no input of them to the sediment during the course of deposition of UACT6, or that they have been removed through the preferential degradation of short chain-length components. Any such degradation would have to be rapid to account for the absence of short chain-lengths from even the surface sediment. Comparison of long chain-length *n*-alkanol abundances to those of *n*-alkanes using the alcohol preservation index of Madureira *et al.* (1995) indicates that degradation of long chain-length *n*-alkanols has been minimal.

The downcore variations in concentration of *n*-alkanols are similar to those seen for long chain-length *n*-alkanoic acids. There is no strong correlation with the variations seen in LOI and TOC, although all *n*-alkanols show a period of low concentration from 15-20 cm depth, coinciding with one of the three pronounced minima in the LOI, TOC and chlorin profiles. Overall, the major even chain-length *n*-alkanols show slight downcore increases in concentration. These are similar to the increases seen in long chain-length *n*-alkanoic acids, possibly indicating a common origin as products of leaf wax degradation. The long chain-length *n*-alkanols are interpreted as indicating an allochthonous, higher plant input to the sediment.

The surface sediment sample (0.0-0.6 cm depth) contains numerous sterols in comparatively high concentrations, including cholesterol, brassicasterol, campesterol, stigmasterol and β-sitosterol. Below the surface a marked decrease in sterol concentrations is seen, and cholesterol, campesterol and stigmasterol virtually disappear from the sediment record. This is assumed to be caused by rapid degradation of these components. Brassicasterol and β-sitosterol remain throughout the core in low abundances, along with stigmastanol and 4-methylstanol. Brassicasterol shows a significant correlation with TOC content, similar to the responses of the C_{17} *n*-alkane and the C_{25} HBI monoene hydrocarbon. Brassicasterol

is known to be produced by diatoms and is potentially a diatom biomarker, although it is also found in other organisms including some of the modern vegetation reference specimens collected from the Lochan Uaine catchment. The apparent downcore increases in stigmastanol and 4-methylstanol may reflect a diagenetic origin, being formed by the hydrogenation of unsaturated precursor sterols such as β-sitosterol or stigmasterol (stigmastanol), or dinosterol (4-methylstanol) (Nishimura and Koyama, 1977).

Chapter 6

Compound-Specific Stable Carbon Isotope Analysis

6.1 Introduction

Chapter 4 examined the analysis of bulk stable carbon isotopes in the sediments of Lochan Uaine, and discussed those factors influencing carbon fractionation in living organisms and the preservation of this signal in lacustrine sequences. It was shown that $\delta^{13}C$ can be affected by a large number of variables including temperature, water availability, carbon source, light availability, and the photosynthetic pathway employed. It was also noted that, in the same way that the bulk $\delta^{13}C$ of a lake sediment reflects the individual isotope values of all the carbon inputs to that sediment, so the bulk $\delta^{13}C$ of an organism reflects the $\delta^{13}C$ values of all the individual components of that organism. This chapter examines these ideas more closely through the compound-specific isotope analysis of sedimentary lipids, the distributions of which were presented in Chapter 5.

6.2 Isotopic fractionation of lipids in organisms

It has been known for some time that the lipid fraction of most organisms is depleted in ^{13}C relative to other organic fractions such as carbohydrate, protein, lignin and cellulose (Park and Epstein, 1960; Degens, 1969; O'Leary, 1981). Park and Epstein (1961) found that the depletion relative to a whole tissue sample was between 1.9 and 8.7‰ for a variety of plants, including a value of 5.0‰ for a sample of mixed phytoplankton. Other values reported for the relative depletion of the lipid fraction compared to bulk tissue include 4‰ in *Quercus rubra* leaves (Sharkey *et al.*, 1991), 5.3‰ in a C_3 plant (Benedict, 1978), 4.8‰ in cyanobacteria (Sakata *et al.*, 1997), 7.4‰ in photosynthetic bacteria (Wong *et al.*, 1975), 7‰ in *Escherichia coli* (Monson and Hayes, 1982b), 5‰ in methanotrophic bacteria (Jahnke *et al.*, 1999), and 4 to 15‰ in unspecified plants (Degens, 1969).

The greater ^{13}C depletion of the lipid fraction relative to bulk plant tissue is due to the additional fractionation associated with lipid biosynthesis. Significant fractionation occurs during photosynthetic carbon assimilation, as mentioned previously (Chapter 4). The amount of fractionation depends on several factors. The photosynthetic pathway used is important as greater ^{13}C depletion is found with the C_3 pathway than

with the C_4 pathway, with CAM plants falling between these two extremes. Similarly, differences in $\delta^{13}C$ are seen between plants which utilise atmospheric CO_2, bicarbonate, or methane as the carbon source (Summons *et al.*, 1994; Jahnke *et al.*, 1999). Fractionation tends to be greatest in methanogens and lowest in organisms which use bicarbonate. Additionally, the influence of environmental factors such as temperature and the availability of light, water and nutrients must not be overlooked. Yet while these factors are all important in explaining the bulk $\delta^{13}C$ value of an organism, they do not explain why lipids are more depleted than other organic components. For this a more detailed examination of plant metabolism is required. This will concentrate on processes occurring in C_3 plants, as no C_4 or CAM plants are presently found in Lochan Uaine or its catchment, nor are likely to have grown there during the Holocene.

During C_3 photosynthesis, carbon is taken in by the plant and converted, through a series of enzymatically catalysed stages, to form various carbohydrates (Figure 6.1). The fractionation associated with this process is potentially large and lies in the range 20-40‰, mostly occurring during the Rubisco-catalysed carboxylation of ribulose bisphosphate to give 3-phosphoglycerate (Christeller *et al.*, 1976; Benedict, 1978; O'Leary, 1981; Roeske and O'Leary, 1984; Guy *et al.*, 1993; Leegood, 1999). The carbohydrates produced by this reaction are then used in the biosynthesis of other compounds. In most cases the fractionation associated with this biosynthesis is low, and components such as lignin, cellulose, pectin, complex carbohydrates and protein generally have $\delta^{13}C$ values within a few permil of the bulk plant tissue (Park and Epstein, 1960, 1961; Abelson and Hoering, 1961; Wong *et al.*, 1975; Leavitt and Long, 1982; Hayes, 1993; Sachs *et al.*, 1999). The greater fractionation found in lipids occurs during the formation of the C_2 acetate units from which lipids are formed.

Hayes (1993) discusses isotopic fractionation occurring during lipid biosynthesis. The two main pathways by which this is achieved, in prokaryotic and eukaryotic organisms, are given in Figures 6.2 and 6.3. In both cases, the main depletion occurs at the carbon branchpoint downstream of pyruvate during its conversion to acetyl-

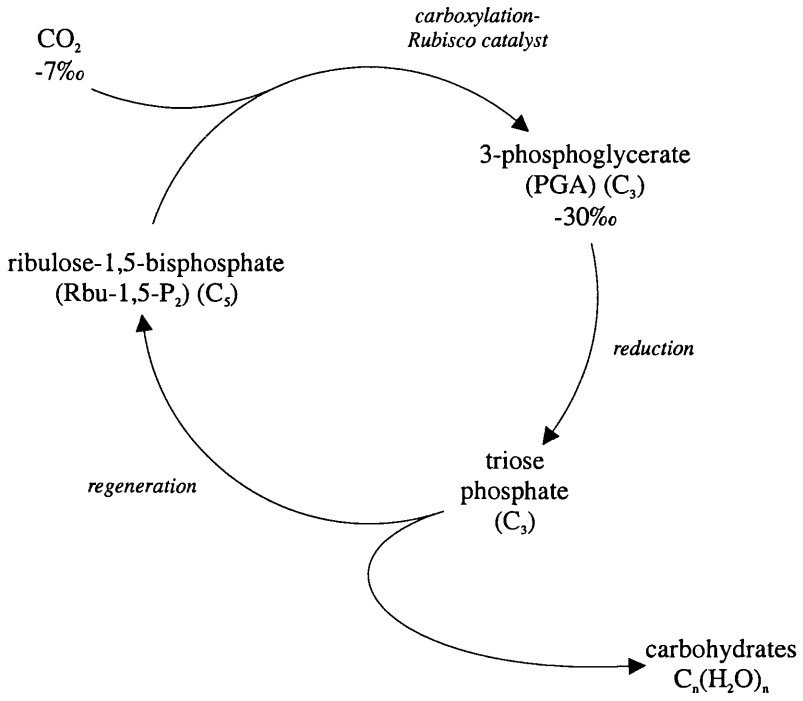


Figure 6.1 Summary of the Benson-Calvin cycle as used in C_3 plants (adapted from Descolas-Gros and Fontugne, 1990; Schleser, 1995; Leegood, 1999). Approximate $\delta^{13}C$ values are from Benedict (1978).

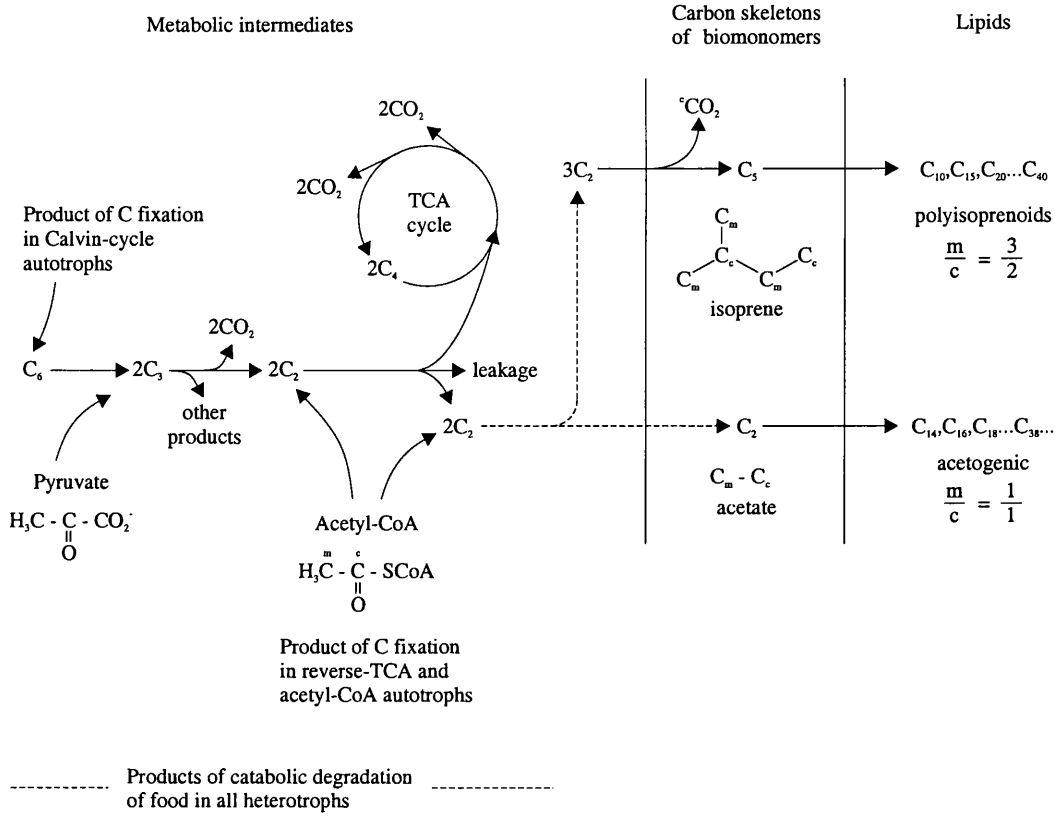


Figure 6.2 Summary of biosynthetic pathways of lipids in prokaryotic organisms (from Hayes, 1993, Figure 8, page 118).

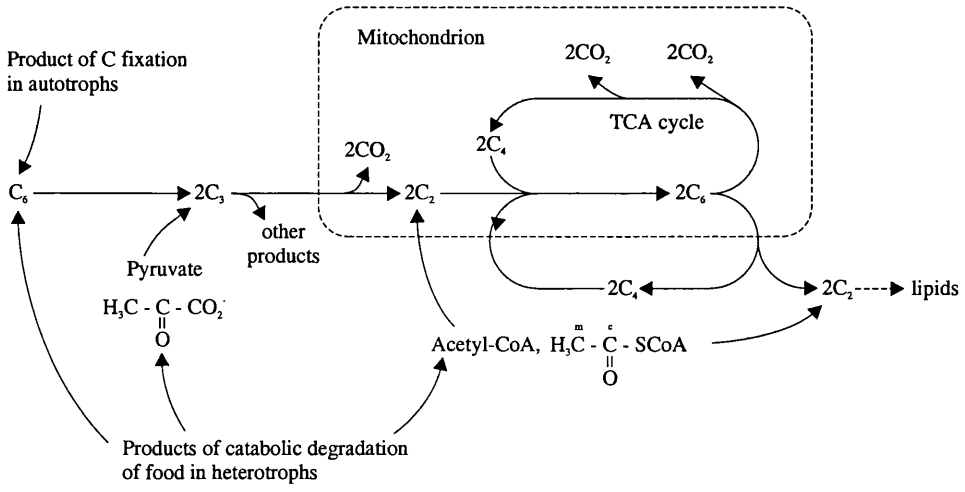


Figure 6.3 Summary of biosynthetic pathways of lipids in eukaryotic organisms (from Hayes, 1993, Figure 9, page 119).

CoA, catalysed by the pyruvate dehydrogenase enzyme (DeNiro and Epstein, 1977; Melzer and Schmidt, 1987; Hayes, 1993).

6.3 $\delta^{13}C$ in lipids from prokaryotic organisms

In prokaryotic organisms, isotopic depletion is found to specifically affect the carboxyl carbon of acetyl-CoA but not the methyl carbon, denoted as C_c and C_m respectively in Figure 6.2 (Abelson and Hoering, 1961; DeNiro and Epstein, 1977; Monson and Hayes, 1982b; Melzer and Schmidt, 1987; Hayes, 1993). The $\delta^{13}C$ value of a lipid depends on the relative numbers of carboxyl and methyl carbons in its structure. This distinction is important as some lipids are synthesised from C_2 acetate units, which contain one carbon originating in the methyl position in acetyl-CoA and one from the carboxyl position. Other lipids are synthesised from C_5 isoprene units which contain a different ratio of methyl to carboxyl carbons. The effect this has on lipid $\delta^{13}C$ will be discussed.

Straight-chain lipids are formed from C_2 acetate units and are known as acetogenic lipids. Fatty acids are formed initially, and other acetogenic lipids such as *n*-alkanes and *n*-alkanols are synthesised from fatty acids. Fatty acids contain an equal number of carbon atoms originating from the methyl and carboxyl positions in acetyl-CoA. Other acetogenic lipids contain an equal or almost equal number of these carbon atoms, depending on whether or not a carbon atom is removed by decarboxylation during formation as is the case with *n*-alkanes. The average fractionation a fatty acid from a prokaryotic organism will exhibit during synthesis from carbohydrate will thus be 50% of that seen in a carboxyl carbon during the pyruvate dehydrogenase reaction. This process also has the effect of creating an alternating pattern of depletion in the carbon atoms of acetogenic lipids, as seen in studies of prokaryotes such as *Escherichia coli* (DeNiro and Epstein, 1977; Monson and Hayes, 1980, 1982b; Melzer and Schmidt, 1987).

Not all lipids are acetogenic. Lipids constructed from C_5 isoprene units are known as polyisoprenoid lipids. These include important terpenoid groups such as the steroids,

hopanoids and carotenoids, although such lipids are less important in prokaryotic organisms than eukaryotes (Hayes, 1993). Although isoprene is itself constructed from C_2 acetate units, the odd number of carbon atoms means that the ratio of carbons originating in the methyl and carboxyl positions of acetyl-CoA cannot be 1:1, and is in fact 3:2 (Figure 6.2). As methyl carbons are not affected by fractionation during the pyruvate dehydrogenase reaction in prokaryotic organisms, the fractionation of isoprene during synthesis from carbohydrate is only 40% of that seen in a carboxyl carbon. The equivalent value for acetate is 50%, hence isoprene exhibits only 80% of the fractionation seen in acetate, and lipids constructed from isoprene are 20% less depleted in ^{13}C than acetogenic lipids (Sharkey *et al.*, 1991; Hayes, 1993). Compound-specific $\delta^{13}C$ measurements of lipids from cyanobacteria by Sakata *et al.* (1997) support this view. They find that acetogenic lipids are depleted by 7.6 to 9.9‰ relative to average biomass, whereas polyisoprenoid lipids show a smaller depletion of 6.4 to 6.9‰. These values are consistent with the 20% less depletion assumed for polyisoprenoid lipids.

6.4 $\delta^{13}C$ in lipids from eukaryotic organisms

The processes described above apply to prokaryotic organisms only. Studies of depletion patterns in lipids from eukaryotic organisms suggest that the depletion pattern is the opposite of that found in prokaryotic organisms, and that the methyl carbon in acetyl-CoA is more depleted in ^{13}C than the carboxyl carbon (Monson and Hayes, 1982a; Melzer and Schmidt, 1987). This may be due to the more complex pathways associated with lipid biosynthesis in eukaryotic organisms. Acetate is formed within the mitochondrion but can only be exported by combining with a C_4 compound to form C_6 citrate (Figure 6.3). Additional fractionation may occur during this process (Hayes, 1993). The net result is that polyisoprenoid lipids from eukaryotes are expected to show greater fractionation than acetogenic lipids as they contain three 'depleted' carbon atoms, rather than the two found in polyisoprenoids from prokaryotes. As yet there is little experimental evidence to confirm this. Summons *et al.* (1994) record greater ^{13}C depletion in polyisoprenoid steroids and hopanoids than in acetogenic fatty acids, but these samples are taken from eukaryotic

methanotrophic bacteria which use different biosynthetic pathways from eukaryotic C_3 organisms. Conversely, Sharkey *et al.* (1991) find that fatty acids from *Quercus rubra* leaves are more depleted in ^{13}C than a polyisoprenoid lipid, β-carotene. They conclude that this is due to the comparative lightness of the carboxyl carbons of acetyl-CoA, as discussed by DeNiro and Epstein (1977) with reference to prokaryotic organisms. This is at odds with Monson and Hayes' (1982a) conclusion that the methyl carbons are lighter in ^{13}C in eukaryotic organisms, of which *Q. rubra* is an example. Hayes (1993) acknowledges that further work is required on carbon isotopic fractionation in lipids from eukaryotes.

A further complication in the analysis of isotopic values of lipids was noted by Rossmann *et al.* (1991). They found that the widely used assumption that all of the carbon atoms in glucose exhibit identical isotopic fractionations is incorrect. Carbon atoms in positions 3 and 4 are found to become enriched in ^{13}C relative to the molecular average during carbohydrate biosynthesis, while carbon atoms in positions 1, 2, 5 and 6 become depleted. Furthermore, during lipid biosynthesis the two enriched carbon atoms are lost as CO_2 while the four depleted carbon atoms form acetyl-CoA. This process may provide another mechanism by which lipids become depleted in ^{13}C relative to bulk plant tissue.

Chapter 4 discussed the factors affecting bulk $\delta^{13}C$ in organisms and sediments. These also affect the $\delta^{13}C$ of lipids within organisms. However, there are several additional factors which may affect fractionation in lipids. Hayes (1993) lists the four main determinants of $\delta^{13}C$ in an organic molecule: 1) $\delta^{13}C$ of carbon source; 2) fractionation during carbon assimilation; 3) fractionation during metabolism and biosynthesis; 4) carbon budgets in reaction networks. These will be discussed in turn.

The $\delta^{13}C$ of the carbon source provides the 'base' value upon which all further fractionation takes place. Organisms which utilise a source such as bicarbonate generally have higher $\delta^{13}C$ values than organisms which utilise a more depleted source such as atmospheric or dissolved atmospheric CO_2. Carbon availability may also play a role, principally in environments such as highly productive lakes and oceans where

carbon becomes limited and less isotopic discrimination is possible by organisms. The factors influencing $\delta^{13}C$ of the carbon source, including temperature and pH, were discussed in Chapter 4 and will not be covered further here.

Fractionation during carbon assimilation also depends to a certain extent on the carbon source and environmental factors such as temperature and humidity, but is mostly controlled by the photosynthetic pathway utilised. Differences in fractionation are seen between C_3 plants, C_4 plants and CAM plants, and other organisms such as chemoautotrophs and methanogens. The main depletion in C_3 plants is associated with the activity of the Rubisco enzyme, and is usually between 20-40‰ (Degens, 1969; O'Leary, 1981; Hayes, 1993). A lesser fractionation is observed to affect the individual carbon atoms of the carbohydrate product (Rossmann *et al.*, 1991).

The main processes by which fractionation during lipid biosynthesis occurs were discussed above, namely the depletion of a carbon atom during the pyruvate to acetyl-CoA conversion, and the subsequent incorporation of these depleted carbon atoms into acetogenic or polyisoprenoid lipids. The influence of temperature on this reaction is poorly known. If, as with the Rubisco reaction, the enzymes catalyzing lipid biosynthesis are more efficient at lower temperatures, a greater ^{13}C depletion of lipids relative to bulk tissue is expected. Jahnke *et al.* (1999) measured $\delta^{13}C$ of total biomass and total lipids from a methanotrophic bacterium at two temperatures. At 15°C the total biomass had a $\delta^{13}C$ of -25‰, and total lipids measured -30‰. At 10°C these figures were -30‰ and -35‰ respectively. Depletion of total lipids and biomass was greater at a lower temperature, but the difference in $\delta^{13}C$ between lipids and biomass remained constant at 5‰. There is thus no evidence for increased fractionation during lipid biosynthesis at low temperatures, and the observed fractionations are likely to be due solely to temperature effects during incorporation of carbon. Although the difference in temperature between the two experiments of Jahnke *et al.* was only 5°C, the maximum likely variation in mean annual temperature at Lochan Uaine during the Holocene is much lower at around 1°C. DeNiro and Epstein (1977) recorded a temperature dependent fractionation of the carboxyl carbon during the pyruvate hydrogenase reaction, but only of around 0.4‰ more

fractionation per 1°C increase. It is thus unlikely that any potential direct temperature effects on isotopic fractionation during lipid biosynthesis will be found in the core UACT6 biomarker record. Direct temperature effects on the Rubisco reaction, and indirect effects due to temperature-related environmental changes, cannot be discounted. Also, Jahnke *et al.* examined methanotrophic bacteria, which are non-photosynthetic and utilise different carbon pathways from C_3 plants. This is demonstrated by Teece *et al.* (1999), who found that fatty acids in a gram negative facultative marine bacterium were more depleted relative to total biomass under anaerobic than aerobic conditions, although the effects of temperature were not explored. An examination of the effect of temperature on lipid biosynthesis in C_3 plants would thus be of use.

The fourth and final factor given by Hayes (1993) to explain isotopic fractionation of organic molecules is in the carbon budgets of reaction networks. Carbon branchpoints are found where a single reactant can lead to multiple products, such as during various enzymatically catalysed reactions. At such points the mass balance of isotopes must be maintained, so a relative depletion in one product must be matched by an enrichment in another product. Related to the idea of carbon budgets is the process of reusing products of reactions, which may themselves be ^{13}C depleted, in further reactions. Lockheart *et al.* (1997) observed a gradual depletion in $\delta^{13}C$ of leaf lipids in *Quercus castaneifolia* and *Fagus sylvatica* throughout the growing season. They hypothesised that this may reflect the ongoing replacement of weathered leaf waxes by depleted internal carbon, although they pointed out that temperature effects on Rubisco activity may also play a role. Park and Epstein (1960) noted how plants with a high lipid content generally exhibit less-depleted $\delta^{13}C$ values, as the high demand for carbon allows for less isotopic discrimination. This was also seen by Summons *et al.* (1994) and Pancost *et al.* (1999) who showed that a specific biomarker from a specific organism may have a wide range of $\delta^{13}C$ values depending on environmental conditions such as substrate, carbon assimilation, and organism growth cycle.

6.5 Compound-specific isotope studies in organisms

The GC-IRMS technique (Matthews and Hayes, 1978) provides a potentially very powerful tool in biogeochemical studies. The ability to measure isotopic fractionation of an individual biomarker, which may itself be associated with a specific precursor organism, allows analysis of palaeoecological and palaeoenvironmental data in sediments which would not be available using conventional bulk isotope analyses. This section describes some of the studies which have employed GC-IRMS of lipids in both modern and fossil samples.

The ^{13}C depletion of lipids in organisms relative to bulk organic material was discussed above. Reported measurements of the magnitude of this depletion vary between different authors and between the different organisms studied. Most studies give values of lipid depletion within 10‰ of the bulk plant tissue (Park and Epstein, 1961; Wong *et al.*, 1975; Benedict, 1978; Monson and Hayes, 1982b; Jasper and Hayes, 1990; Sharkey *et al.*, 1991; Sakata *et al.*, 1997; Jahnke *et al.*, 1999). By contrast, $\delta^{13}C$ variations between different types of organisms such as C_3 plants, C_4 plants, CAM plants and methanogens show much greater variation (Degens, 1969; Bender, 1971; Smith and Epstein, 1971; Nakai, 1972; Pearson and Coplen, 1978; Fry, 1986; Schidlowski, 1988; Meyers and Benson, 1988; Michel *et al.*, 1989; Descolas-Gros and Fontugne, 1990; Martinelli *et al.*, 1991; Proctor *et al.*, 1992; Killops and Killops, 1993; Meyers and Eadie, 1993; Schleser, 1995; Tyson, 1995; Waichman, 1996; Meyers and Takemura, 1997; Meyers and Lallier-Vergès, 1999; Burkhardt *et al.*, 1999; Sachs *et al.*, 1999). In most cases it is possible to infer the type of source organism of a biomarker from the compound-specific $\delta^{13}C$ value, using the assumption that this value will be no more than *c.* 10‰ more depleted than the bulk value of the precursor organism.

Reddy *et al.* (2000) measured isotope ratios of long chain-length *n*-alkanes in four species of *Micromeria.* These lay within the range -38 to -34‰, which the authors state is typical of C_3 plants. The same conclusion was reached by Benedict (1978) who recorded a total lipid $\delta^{13}C$ value of -32‰ in cotton, another C_3 plant. $\delta^{13}C$ values of -37 to -36‰ were seen in *n*-alkanes from *Brassica oleracea* (Evershed *et al.*,

1994), between -39 and -27‰ in lipids of several tree species (Lockheart *et al.*, 1997), and between -39 and -30‰ in leaf wax *n*-alkanes (Rieley *et al.*, 1991b).

6.6 Compound-specific isotope studies in lacustrine sediments

This technique of relating compound-specific $\delta^{13}C$ to particular source organisms is used in some palaeoenvironmental studies. Ficken *et al.* (1998) and Huang *et al.* (1999) used GC-IRMS techniques on sediment records from two Kenyan lakes, Sacred Lake and Lake Nkunga. At both sites large decreases in the $\delta^{13}C$ of terrestrial higher plant lipids were seen between the Last Glacial period and the Holocene, with values at Sacred Lake changing from *c.* -19‰ to *c.* -30‰. These were interpreted as representing a change from C_4 plant dominance during the last glacial period due to the lower atmospheric partial CO_2 pressure (pCO_2), to C_3 plant dominance during the Holocene. At Sacred Lake a concurrent decrease in $\delta^{13}C$ of isoprenoid hydrocarbons was seen, from -5‰ at the Last Glacial Maximum to -30‰ during the early Holocene. Isoprenoid hydrocarbons are used as algal biomarkers. As with the terrestrial plant biomarkers, the decrease in $\delta^{13}C$ was attributed to the effects of changing pCO_2, particularly on freshwater green algae which are known to favour low pCO_2.

In Lake Baikal, as in Sacred Lake and Lake Nkunga, a large decrease in bulk organic $\delta^{13}C$ was recorded at the transition from the Last Glacial period to the Holocene (Brincat *et al.*, 2000). This would conventionally be interpreted as showing a switch from C_4 to C_3 plants, and in the African lakes this interpretation was confirmed by compound-specific isotope analysis of lipids from terrestrial plants. However, at Lake Baikal such analyses on long chain-length *n*-alkanes showed no such switch, and $\delta^{13}C$ remained constant in the C_3 range of -33.5 to -31‰ throughout the period. Brincat *et al.* concluded on the basis of this evidence that there was no expansion of C_4 plants in the catchment during the Last Glacial period, and that some other factor must be influencing the bulk $\delta^{13}C$ record.

Rieley *et al.* (1991b) were able to discriminate between more specific inputs to the sediment of Ellesmere lake, UK. Analysis of $\delta^{13}C$ in *n*-alkanes extracted from catchment trees showed that they lay in the range -38.7 to -30.1‰. The corresponding values for *n*-alkanes from a lake sediment core showed a less negative maximum depletion, with a range of -35.9 to -30.1‰. One tree species, *Aesculus hippocastanum*, was found to exhibit only very depleted *n*-alkane values of -38‰ and below. This species was discounted as a major contributor of organic matter to the lake sediment. Shorter chain-length lipids exhibited less negative $\delta^{13}C$ which lay in the range -24 to -20‰, implying a probable origin from algae rather than C_3 plants.

6.7 Compound-specific isotope studies in marine and ancient sediments

Compound-specific isotope studies of marine sediments are more common than those of lake sediments, although the interpretations are often similar. Goñi *et al.* (1997) showed that lignin phenols in offshore sediments along the eastern US coast originated in C_4 grasslands of the Mississippi Basin, while those in nearshore sediments came from C_3 coastal forests and swamps. This difference was attributed to hydrodynamic sorting. *n*-Alkane $\delta^{13}C$ values in a marine core from the mouth of the Johnstone River, Australia, suggest an increase in C_4 plant abundance during the last 6000 yr, while the record of the last century shows the influence of basin clearance for sugarcane cultivation and pasture (Bird *et al.*, 1995). Naraoka and Ishiwatari (2000) measured a $\delta^{13}C$ of -26.1‰ for long chain-length fatty acids from a North Pacific core. They argued that as this value is typical of bulk values for terrestrial C_3 plants, and as lipids are known to be depleted relative to these bulk values, then the fatty acids must originate from a mixture of C_3 and C_4 plants or marine organisms. Identification of organic matter sources using compound-specific isotope analysis is also described by Pancost *et al.* (1999) for surface waters off the coast of Peru, and by Yamada and Ishiwatari (1999) for a core from the Japan Sea. The technique is also used to analyse ancient sediments such as the Messel Shale (Hayes *et al.*, 1987; Freeman *et al.*, 1990) and various Miocene sequences (Schoell *et al.*, 1994; Schouten *et al.*, 1997; Pagani *et al.*, 2000). Of particular interest is the study by Jasper and Hayes (1990) who measured $\delta^{13}C$ in heptatriaconta-15,22-dien-2-one, a C_{37}

alkadienone deriving specifically from prymnesiophyte algae such as coccolithophorids. By comparing the $\delta^{13}C$ of this highly specific biomarker with that of calcite tests of the planktonic foraminifera *Globigerinoides ruber*, Jasper and Hayes were able to derive a record of dissolved CO_2 concentration over the last *c.* 90 kyr which agrees well with the atmospheric CO_2 changes seen in the Vostok ice core (*e.g.* Barnola *et al.*, 1987; Petit *et al.*, 1999).

6.8 Results of compound-specific isotope analysis of lipids from core UACT6

GC-IRMS analysis was performed on the hydrocarbon, alcohol and acid fractions of the lipid extract from UACT6, using the methods described in Chapter 2. Hydrocarbons were analysed from eighteen samples, and alcohols and acids from sixteen. The results of each of these three fractions are discussed separately, and a final section attempts to bring these results together.

6.8.1 *n*-Alkanes

Downcore variations in $\delta^{13}C$ of the major odd chain-length *n*-alkanes are given in Figure 6.4. No even chain-length *n*-alkanes are shown as they are present in much lower abundances than the odd homologues. This increases the errors involved in measuring $\delta^{13}C$, although the values obtained for the longer even chain-length *n*-alkanes are in a similar range to those found in the odd chain-length *n*-alkanes. The C_{17} *n*-alkane is also present only in low concentrations throughout the core, and the $\delta^{13}C$ values are likely to be subject to significant errors. However, given the importance of this biomarker as an indicator of algal and bacterial sources, it is felt necessary to include the results in the analysis. All samples are run in duplicate or triplicate. Although the ranges of values obtained for each repeat sample are greater for *n*-C_{17} than for longer chain-length *n*-alkanes, the maximum variation is only 2.5‰. This is not great enough to suggest any possible overlap in $\delta^{13}C$ values with longer chain-length homologues. Less variation is seen in the ranges of $\delta^{13}C$ values for longer chain-length homologues. This variation is typically less than 0.5‰, although analysis of standards suggests a 95% significance range of ±1‰ for the hydrocarbon sample. These measurement errors were discussed in greater detail in Chapter 2.

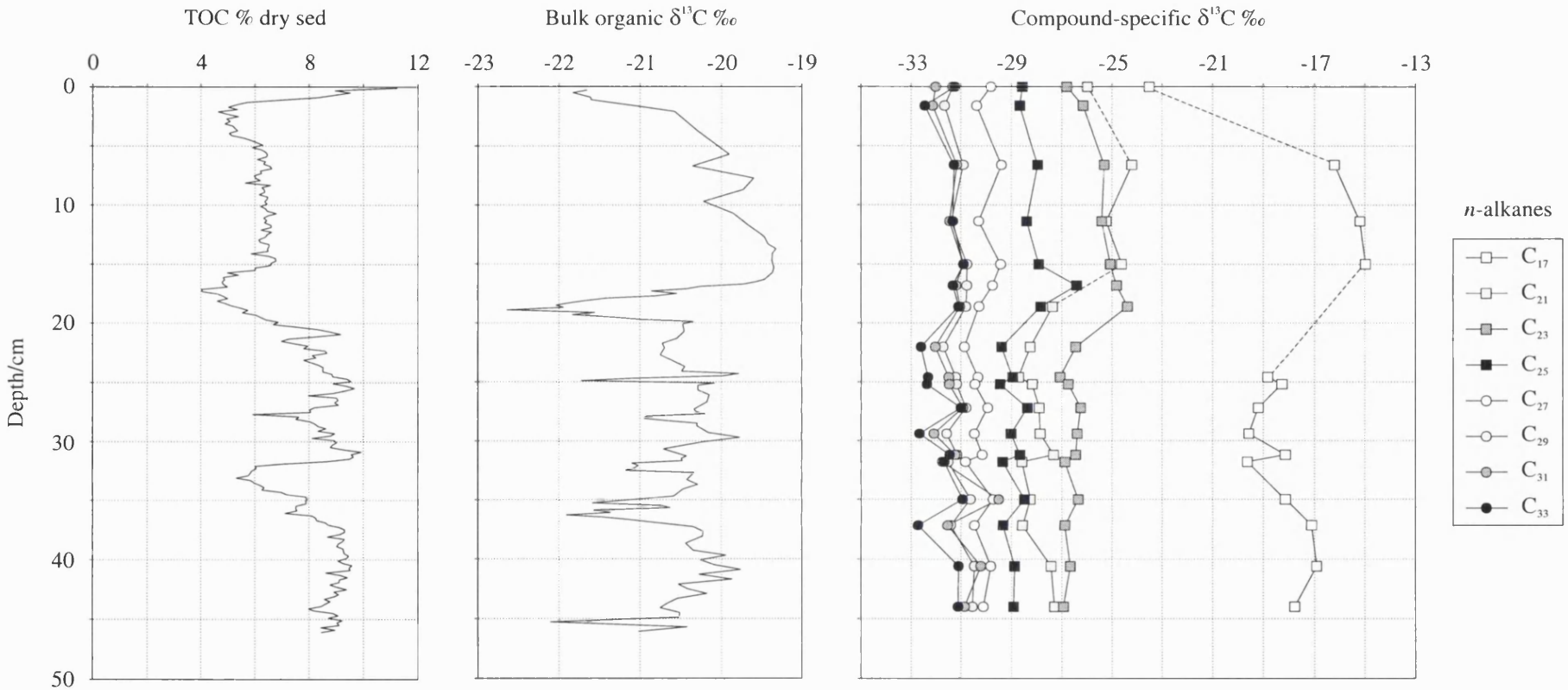


Figure 6.4 Downcore variation of TOC, bulk organic $\delta^{13}C$, and $\delta^{13}C$ of selected *n*-alkanes, core UACT6.

6.8.1.1 *n*-Alkane chain-length and $\delta^{13}C$

A distinct lightening of carbon isotopic values is seen with increasing *n*-alkane chain-length in Figure 6.4. This is more clearly illustrated in Figure 6.5. The *n*-C_{17} homologue exhibits the lowest ^{13}C depletion and the widest spread of values. The range covered lies from -23.5 to -15‰, although only the 0.0-0.6 cm depth sample has a value more depleted than -20‰. At none of the eighteen depths analysed do any of the longer chain-length *n*-alkanes (C_{21} to C_{33}) have a value heavier than -24‰. A small amount of overlap is found between the *n*-C_{21} and *n*-C_{23} homologues, so that *n*-C_{21} is less depleted than *n*-C_{23} in the top 15 cm of UACT6, and more depleted from 15 cm depth to the core base. Very little such overlap is seen for chain-lengths above C_{23}, and at each level the *n*-alkanes almost invariably follow the pattern of increasing ^{13}C discrimination with increasing carbon chain-length.

The greater discrimination against ^{13}C at longer carbon chain-lengths may be related to the process of lipid biosynthesis. Although the main fractionation occurs during the pyruvate dehydrogenase reaction, it is possible that further fractionation occurs during subsequent steps (Degens, 1969). Longer chain-length *n*-alkyl lipids are constructed from a larger number of C_2 acetate units than shorter chain-length homologues. The larger number of biosynthetic steps during the formation of longer carbon chains provides a greater opportunity for isotopic fractionation to occur. Maximum fractionation between individual fatty acids of an organism is measured at 4‰ by Degens (1969), and this value is unlikely to differ much for other classes of aliphatic compound. Evershed *et al.* (1994) report that up to 6‰ variation in $\delta^{13}C$ of long chain-length *n*-alkanes can occur within a single leaf of a C_3 plant, whilst variation of 2‰ was recorded by Reddy *et al.* (2000) in four species of *Micromeria*. Preliminary measurements of the $\delta^{13}C$ of *n*-alkanes in two plants from the Lochan Uaine catchment are presented in Figure 6.6. In both cases the total variation is less than 2‰. An increase in fractionation with chain-length is seen in the *Sphagnum* sample but not in the liverwort sample. Future studies would benefit from a more detailed examination of compound-specific isotope values of modern lake and catchment vegetation.

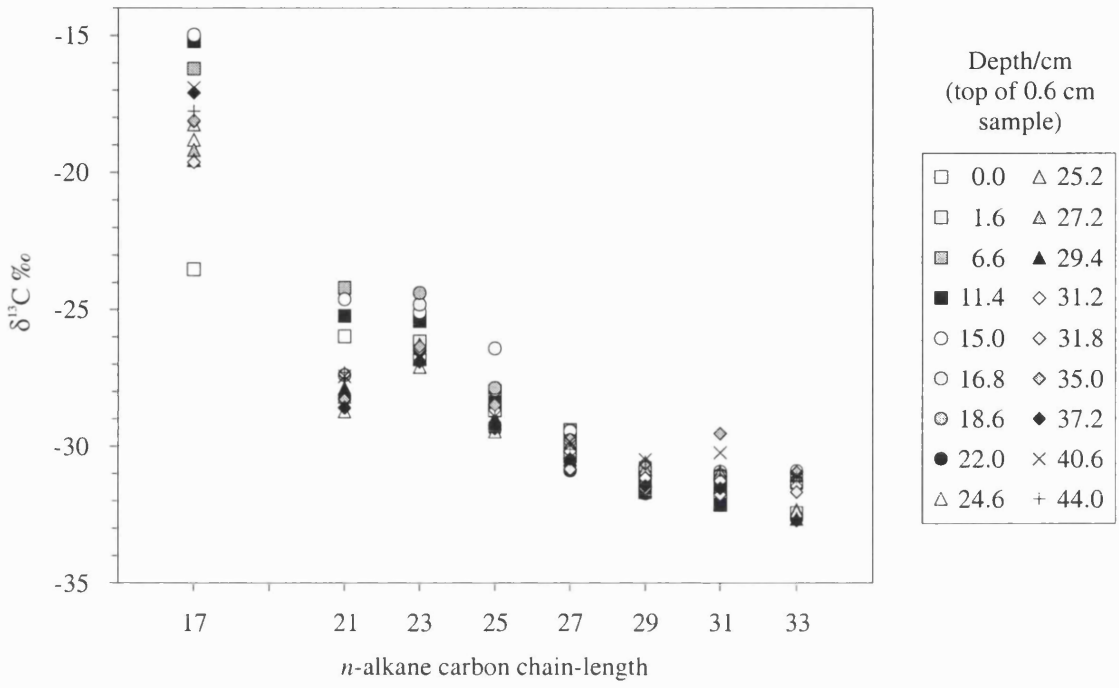


Figure 6.5 Range of $\delta^{13}C$ values exhibited by the major *n*-alkanes in the eighteen depths analysed, core UACT6.

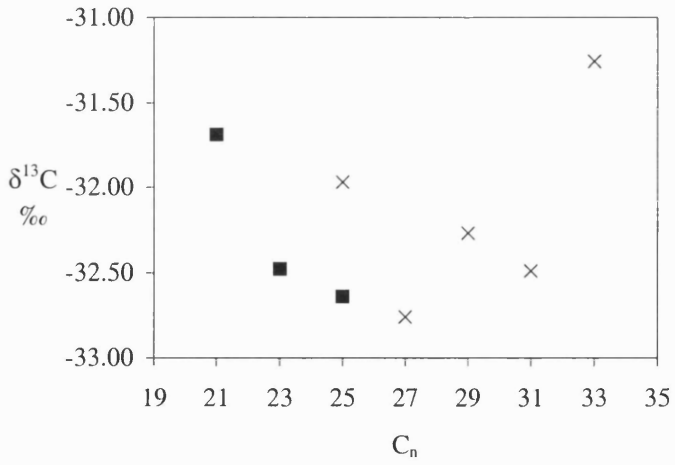


Figure 6.6 Carbon isotopic values of major *n*-alkanes in *Sphagnum* (filled squares) and liverwort (crosses) from the Lochan Uaine catchment.

Although the total range in $\delta^{13}C$ of the C_{17} to C_{33} *n*-alkanes extracted from UACT6 is 18‰, this is mostly due to the heavy values of the *n*-C_{17} homologue. This compound is thought to originate from an autochthonous rather than allochthonous source. Total variation amongst longer chain-length *n*-alkanes from terrestrial plants is much lower, with *n*-C_{27} to *n*-C_{33} being covered by a range of only 4‰. It is thus possible that the strong relationship between $\delta^{13}C$ and *n*-alkane chain-length in UACT6 reflects 1) differences in biomarker source, and 2) an increased fractionation during biosynthesis of longer homologues. The decrease in $\delta^{13}C$ with increasing chain-length is commonly seen in sediments, and is reported from Lake Nkunga (Ficken *et al.*, 1998), Lake Baikal (Brincat *et al.*, 2000) and Ellesmere (Rieley *et al.*, 1991b). It is also seen in a soil sample by Evershed *et al.* (1994). Bird *et al.* (1995) and Yamada and Ishiwatari (1999) identifed the phenomenon in marine samples from around Australia and Japan respectively, although in both cases an inverse relationship was seen at chain-lengths longer than *n*-C_{32}. By contrast, $\delta^{13}C$ showed no response to *n*-alkane chain-length in sediments from Sacred Lake (Huang *et al.*, 1999); nor was any relationship seen in the four species of *Micromeria* analysed by Reddy *et al.* (2000).

In addition to the decrease in $\delta^{13}C$ with increasing chain-length in UACT6, a decrease is also seen in the total downcore range of $\delta^{13}C$ values for each homologue. Hence while the *n*-C_{17} alkane varies by 8.5‰ downcore and the *n*-C_{21} alkane varies by 5‰, none of the *n*-C_{27} to *n*-C_{31} alkanes shows variation of more than 3‰. The closest grouping of $\delta^{13}C$ values is found with the C_{29} *n*-alkane where the total downcore variation is only 1.3‰. There are two possible reasons for this trend. Firstly, the *n*-C_{27} to *n*-C_{31} alkanes are the most abundant in the core. The high concentrations of these compounds allow for more accurate determinations of $\delta^{13}C$ than for compounds such as *n*-C_{17} which are present in much lower concentrations. Secondly, the variations may represent actual downcore changes rather than measurement errors. In this case, little variation in longer chain-length *n*-alkanes from terrestrial sources is seen, but significant variation occurs in lipids from other sources such as algae and bacteria.

6.8.1.2 Downcore variations in $\delta^{13}C$ of the C_{17} *n*-alkane

The downcore profiles of the $\delta^{13}C$ values of individual *n*-alkanes seem to support the view that the larger $\delta^{13}C$ variations seen in shorter chain-length *n*-alkanes reflect real variations rather than measurement errors (Figure 6.4). The main variation is seen in the C_{17} *n*-alkane. This profile shows similarities to that of bulk organic $\delta^{13}C$. The least-depleted values in both curves are found between 3 and 16 cm depth, whilst greater depletion is seen in the top 3 cm and below 16 cm depth. However, several $\delta^{13}C$ values are missing from the *n*-C_{17} alkane profile due to the concentration being too low to allow $\delta^{13}C$ determination. Importantly, these include the samples between 0 and 5 cm, and from *c.* 15-25 cm depth. It is in these sections that the greatest changes in bulk organic $\delta^{13}C$ are seen. A further problem is that due to the low concentration of *n*-C_{17} throughout the core, larger errors in $\delta^{13}C$ measurement are expected than for more abundant components, as described above. However, these errors are thought to be no greater than 2.5‰, much less than the total downcore variation of 8.5‰. This suggests that the fluctuations visible in Figure 6.4 are real, and not merely a product of measurement error. It is also noticeable by comparison with the downcore concentration profile of the C_{17} *n*-alkane (Figure 5.17) that the greatest ^{13}C depletion occurs when the concentration of this compound is lowest, from *c.* 0-5 cm and 16-35 cm depth. Likewise, the heaviest $\delta^{13}C$ values are recorded from *c.* 5-16 cm and 35-46 cm, coinciding with the highest concentrations of *n*-C_{17}. This suggests that greater isotopic fractionation may occur in algae and bacteria during periods of reduced productivity, although the mechanisms controlling such a process are not known.

6.8.1.3 Downcore variations in $\delta^{13}C$ of mid and long chain-length *n*-alkanes

The mid chain-length *n*-alkanes from C_{21} to C_{25} show similar patterns to *n*-C_{17}. A shift to more negative $\delta^{13}C$ values is seen below around 15-20 cm depth. This coincides with a synchronous shift in the *n*-C_{17} curve and with the major depletion event in the bulk $\delta^{13}C$ record. Amongst the mid chain-length *n*-alkanes, the change in $\delta^{13}C$ is greatest in *n*-C_{21} (3-4‰), and between 2-3‰ in *n*-C_{23} and *n*-C_{25}. By contrast, no such changes are seen in the C_{27} to C_{33} long chain-length *n*-alkanes. As mentioned above, these all show low variation throughout core UACT6 of 2-3‰. Attempting to apply a

palaeoenvironmental interpretation to such variations would be ambiguous as they are not much larger than the probable error range of ±1‰ associated with the GC-IRMS technique. Nonetheless, the lack of change in $\delta^{13}C$ of these terrestrial hydrocarbons suggests that any changes in input of these biomarkers to Lochan Uaine during the late Holocene are not detectable. This interpretation is backed up by the lack of change in terrestrial hydrocarbon concentrations in UACT6, as discussed in Chapter 5.

6.8.1.4 $\delta^{13}C$ of mid and long chain-length *n*-alkanes as an indicator of organic source

The general range of $\delta^{13}C$ values exhibited by each biomarker provides additional information on their origin. In Chapter 5 the long chain-length *n*-alkanes are used as indicators of allochthonous input to the lake from terrestrial plants in the catchment. The $\delta^{13}C$ values of the C_{27} to C_{33} *n*-alkanes lie in the range -33 to -29‰. Assuming that lipids are depleted by around 5‰ relative to bulk plant matter, this gives a range of roughly -28 to -24‰ for the precursor organisms. C_3 plants are known to have $\delta^{13}C$ values in the range -35 to -20‰, with a mean of around -29 to -26‰ (Bender, 1971; Smith and Epstein, 1971; Nakai, 1972; Pearson and Coplen, 1978; Schidlowski, 1988; Descolas-Gros and Fontugne, 1990; Martinelli *et al.*, 1991; Proctor *et al.*, 1992; Killops and Killops, 1993; Meyers and Eadie, 1993; Schleser, 1995; Tyson, 1995; Waichman, 1996; Meyers and Takemura, 1997; Meyers and Lallier-Vergès, 1999). CAM plants have a wider $\delta^{13}C$ range which includes that covered by C_3 plants, but they are not thought to be present in significant quantities in the Lochan Uaine catchment. The isotopic data thus support the view that the C_{27} to C_{33} *n*-alkanes originate in C_3 terrestrial higher plants.

C_{21} to C_{25} mid chain-length *n*-alkanes have $\delta^{13}C$ values of -30 to -24‰, which would give a range of around -25 to -19‰ for the precursor organisms. This lies towards the less-depleted end of the C_3 plant range, and almost enters the range associated with C_4 plants (Bender, 1971; Smith and Epstein, 1971; Pearson and Coplen, 1978; Schidlowski, 1988; Martinelli *et al.*, 1991; Schleser, 1995; Waichman, 1996; Meyers and Takemura, 1997; Meyers and Lallier-Vergès, 1999). Naraoka and Ishiwatari

(2000) argue that a $\delta^{13}C$ value of -26.1‰ for lipids indicated either a mixed C_3/C_4 input or a C_3/marine organism input, as the bulk isotopic signature of the source would be significantly less depleted than that of the lipids. However, C_4 plants are not currently found in the catchment of Lochan Uaine, and are not likely to have been present there during the Holocene. A C_4 input of mid chain-length *n*-alkanes to the sediment can be discounted. The isotopic data thus suggest that the mid chain-length *n*-alkanes originate in C_3 plants, with a possible input from aquatic organisms. Evidence presented previously in Chapter 5 and by Nott *et al.* (2000) indicates that mid chain-length *n*-alkanes are potential indicators of *Sphagnum*. However, the data presented in Figure 6.6 show mid chain-length *n*-alkanes extracted from *Sphagnum* from the Lochan Uaine catchment to have $\delta^{13}C$ values in the range -33 to -31.5‰. These are more depleted than the corresponding values for mid chain-length *n*-alkanes extracted from the sediment, and suggest that *Sphagnum* does not provide the only input of these compounds into the sedimentary record.

6.8.1.5 $\delta^{13}C$ of the C_{17} *n*-alkane as an indicator of organic source

The C_{17} *n*-alkane has a $\delta^{13}C$ range of -23.5 to -15‰, giving a probable range of -18.5 to -10‰ for the precursor organisms. Although in the range of C_4 plants, these are not present at Lochan Uaine. The C_{17} *n*-alkane is attributed to an algal or bacterial source. A very wide range of $\delta^{13}C$ values are given for these organisms in the literature, from -41 to -3‰ (Degens, 1969; Smith and Epstein, 1971; Nakai, 1972; Fry, 1986; Schidlowski, 1988; Meyers and Benson, 1988; Michel *et al.*, 1989; Descolas-Gras and Fontugne, 1990; Meyers and Eadie, 1993; Tyson, 1995; Meyers and Lallier-Vergès, 1999; Burkhardt *et al.*, 1999; Sachs *et al.*, 1999). Some authors note that $\delta^{13}C$ of plankton should be the same as for C_3 plants when only dissolved CO_2 in isotopic equilibrium with the atmosphere is used in photosynthesis (Stuiver, 1975; Krishnamurthy *et al.*, 1986; Meyers and Eadie, 1993; Meyers and Ishiwatari, 1993; Meyers and Takemura, 1997). Less isotopic depletion is expected if bicarbonate is used as well as dissolved CO_2, but this is unlikely to be the case at Lochan Uaine. On this basis, algal and bacterial biomarkers from UACT6 sediment are expected to have similar $\delta^{13}C$ values to terrestrial biomarkers. However, this relationship is not seen by all authors (*e.g.* Schidlowski, 1988; Michel *et al.*, 1989; Rieley *et al.*, 1991b),

and the heavy n-C_{17} $\delta^{13}C$ values are thus not inconsistent with an algal/bacterial origin. This has important implications for the interpretation of the bulk organic $\delta^{13}C$ record, as shifts to less negative values may indicate an increasing importance of autochthonous algal and bacterial input, and a decreasing importance of allochthonous higher plant input. It is possible that the n-C_{17} $\delta^{13}C$ values may also be due in part to any decreased fractionation associated with shorter chain-length n-alkyl lipids, as discussed above.

6.8.1.6 Correlations between n-alkane $\delta^{13}C$ trends

The downcore differences in isotopic trend of the n-alkanes are best depicted as the deviation from the most abundant homologue, n-C_{31} (Figure 6.7). The deviations seen in the long chain-length n-C_{27} to n-C_{33} n-alkanes are relatively constant downcore. Variation of only 1-2‰ is seen, which is within the calculated error range of ±1‰. The C_{21} to C_{25} mid chain-length n-alkanes show a consistent increasing positive deviation in $\delta^{13}C$ towards the top of the core of around 2‰ in total. The n-C_{17} alkane shows a total variation in deviation from n-C_{31} of 8‰. The significances of the correlations in downcore $\delta^{13}C$ trend between pairs of n-alkanes are given in Table 6.1, and select pairs are shown diagrammatically in Figure 6.8. Correlations between C_{27} to C_{33} long chain-length n-alkanes are all significant at above the 99% level, whereas the C_{17} homologue is only correlated significantly with n-C_{23}. Ficken *et al.* (1998) used the method of comparing isotopic deviations to distinguish components which were likely to have originated from different sources. The data at Lochan Uaine suggest that C_{27} to C_{33} n-alkanes originate from an identical source, C_{21} to C_{25} n-alkanes originate from a slightly different source, and the C_{17} n-alkane is from a very different source. This conclusion agrees with those based on carbon chain-lengths (Chapter 5) and isotopic values (above) of the n-alkanes.

6.8.1.7 Other hydrocarbons

In addition to n-alkanes, several other hydrocarbon components are present in the sediment in sufficient concentrations to obtain compound-specific $\delta^{13}C$ measurements. These are the C_{23} and C_{25} n-alkenes, and diploptene. Their downcore $\delta^{13}C$ profiles are given in Figure 6.9. All three components show a total variation of *c.* 5‰. The C_{23} n-

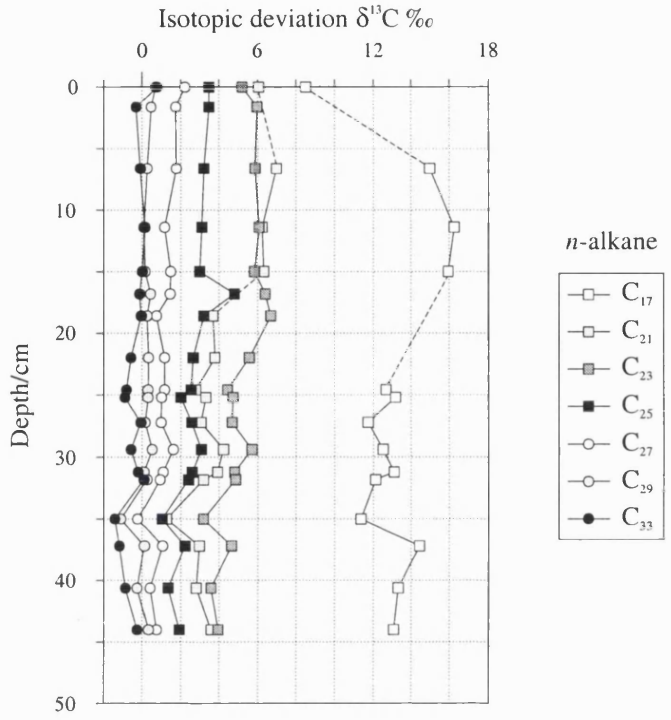


Figure 6.7 Deviation in carbon isotope fractionation of major *n*-alkanes from that of the most abundant homologue, *n*-C_{31}, core UACT6.

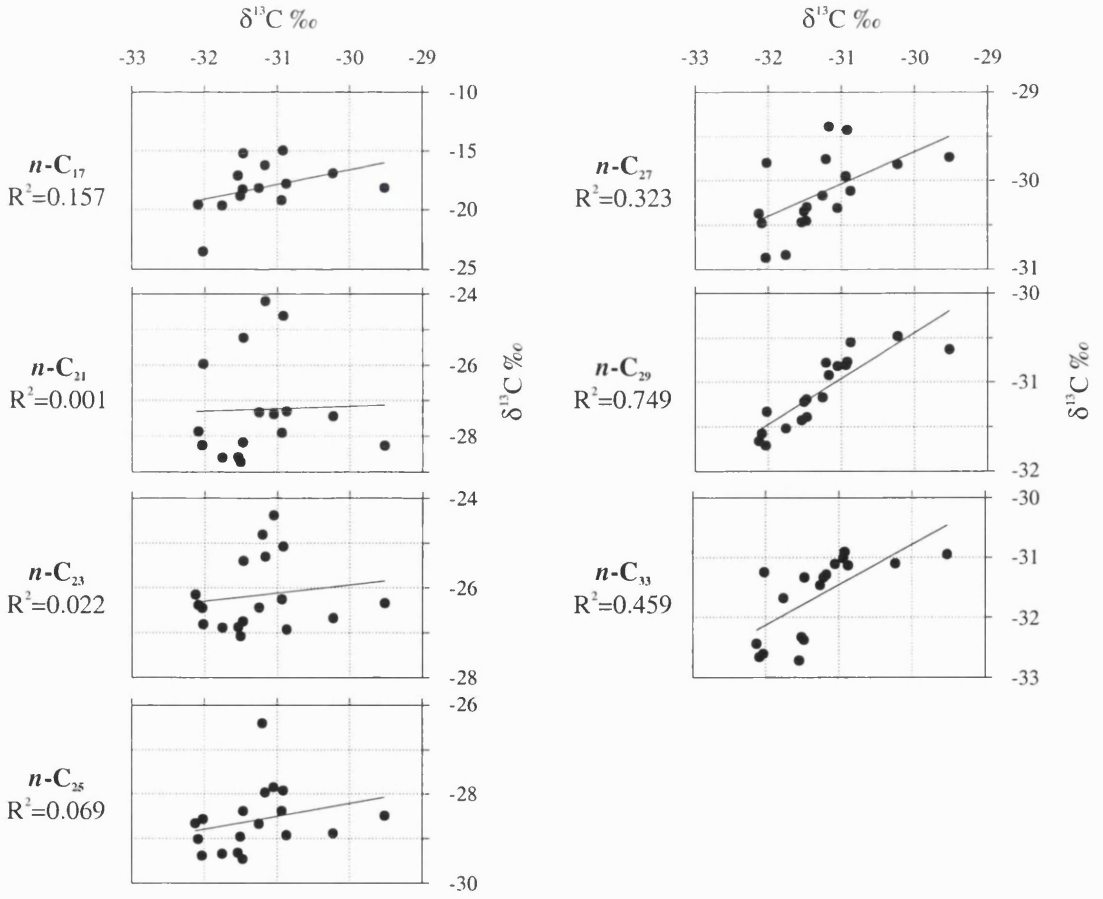


Figure 6.8 Regression of $\delta^{13}C$ of major *n*-alkanes (vertical axis) with the most abundant homologue, *n*-C_{31} (horizontal axis). The C_{27}, C_{29} and C_{31} *n*-alkanes are all correlated with *n*-C_{31} at the 99% significance level; the other *n*-alkanes are not. See also Table 6.1.

Table 6.1 Correlations between downcore *n*-alkane $\delta^{13}C$ trends in UACT6. R^2 values are given at lower left, significance limits are given at upper right. Correlations significant at the 95% level are given in bold.

alkane	*n*-C_{17}	*n*-C_{21}	*n*-C_{23}	*n*-C_{25}	*n*-C_{27}	*n*-C_{29}	*n*-C_{31}	*n*-C_{33}
n-C_{17}		90-95	**> 99**	80-90	80-90	80-90	90-95	70-75
n-C_{21}	0.146		75-80	**> 99**	**> 99**	75-80	< 55	**97.5-99**
n-C_{23}	0.397	0.386		**> 99**	**95-97.5**	80-90	70-75	**95-97.5**
n-C_{25}	0.111	0.512	0.663		**> 99**	**97.5-99**	80-90	**> 99**
n-C_{27}	0.062	0.477	0.167	0.416		**> 99**	**> 99**	**> 99**
n-C_{29}	0.112	0.049	0.077	0.220	0.507		**> 99**	**> 99**
n-C_{31}	0.157	0.001	0.022	0.069	0.323	0.749		**> 99**
n-C_{33}	0.025	0.270	0.180	0.315	0.511	0.616	0.459	

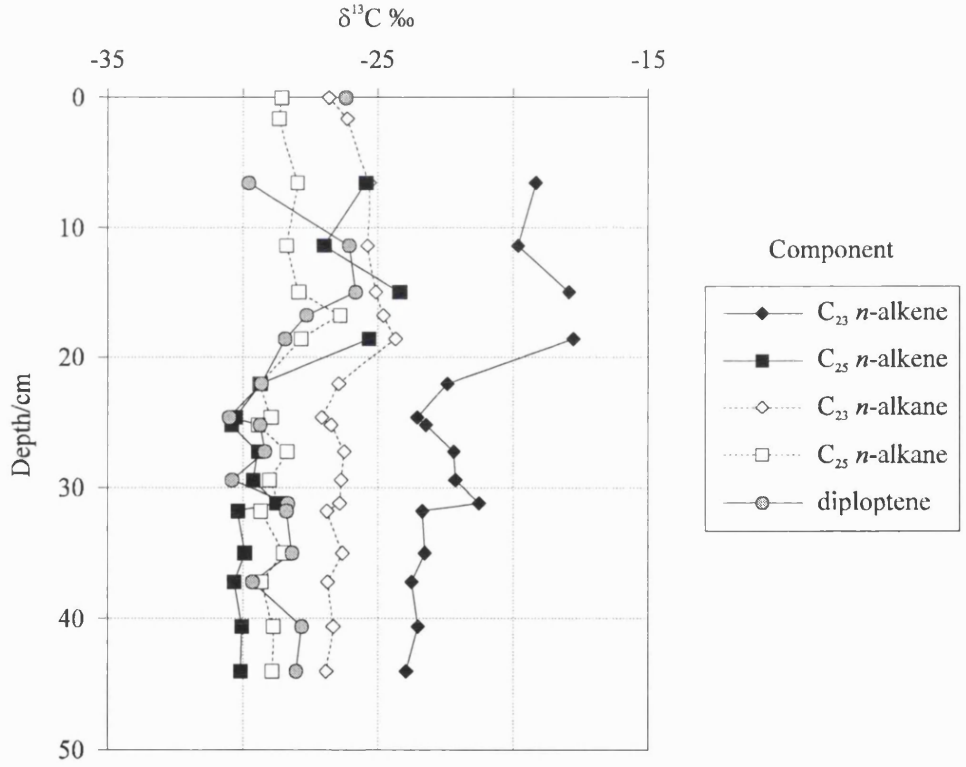


Figure 6.9 Compound-specific $\delta^{13}C$ of C_{23} and C_{25} *n*-alkenes and diploptene. C_{23} and C_{25} *n*-alkanes are included for comparison with the alkenes. Missing lines indicate a concentration too low to allow reliable isotopic measurement.

alkene shows the least ^{13}C depletion, with values of -24 to -18‰. The C_{25} *n*-alkene measures from -31 to -24‰. Also shown are the C_{23} and C_{25} *n*-alkanes, as these may be biosynthetically related to the corresponding *n*-alkenes. The C_{23} *n*-alkene is consistently less depleted than the C_{23} alkane, by about 5‰ in the top 20 cm of UACT6 and 3‰ below this level. A different pattern is seen with the C_{25} components, with the alkene exhibiting *c.* 3‰ less depletion in the top 20 cm as for the C_{23} components, but 1‰ greater depletion than the alkane below 20 cm depth. If the alkenes and alkanes are biosynthetically related similar $\delta^{13}C$ values may be expected, or at least a similar difference in fractionation. The differences in $\delta^{13}C$ between the C_{23} components, and the non-constant difference in $\delta^{13}C$ between the two sets of components raises the possibility that they are not biosynthetically related, and may in fact be from different precursor organisms altogether. The same is true regarding the differences in $\delta^{13}C$ between diploptene, which lies in the range -31 to -26‰, and the algal/bacterial C_{17} *n*-alkane discussed previously. However, given the number and variety of possible autochthonous precursor organisms for these two compounds the difference in fractionation is perhaps not unexpected. All five of the hydrocarbons in Figure 6.9 show a trend of becoming less depleted towards the top of the core, with the main change occurring at around the 20 cm level.

6.8.2 *n*-Alkanols

Downcore $\delta^{13}C$ profiles of the five major *n*-alkanols are given in Figure 6.10. Only even numbered carbon chain-lengths are shown. The intermediate odd numbered homologues are present in lower concentrations, resulting in correspondingly greater errors in the determination of $\delta^{13}C$. The values obtained for these odd chain-lengths are nonetheless in the same range as the even chain-length *n*-alkanols, with the exception of the C_{25} and C_{29} *n*-alkanols which show greater ^{13}C depletion. This may be indicative of co-elution with other components, especially in the latter case as the majority of sterols elute at around the same time as the C_{29} *n*-alkanol.

6.8.2.1 *n*-Alkanol chain-length and $\delta^{13}C$

The total spread of $\delta^{13}C$ values remains relatively constant in each of the five main *n*-alkanols at *c.* 3‰, although the actual values vary (Figure 6.11). The least depleted

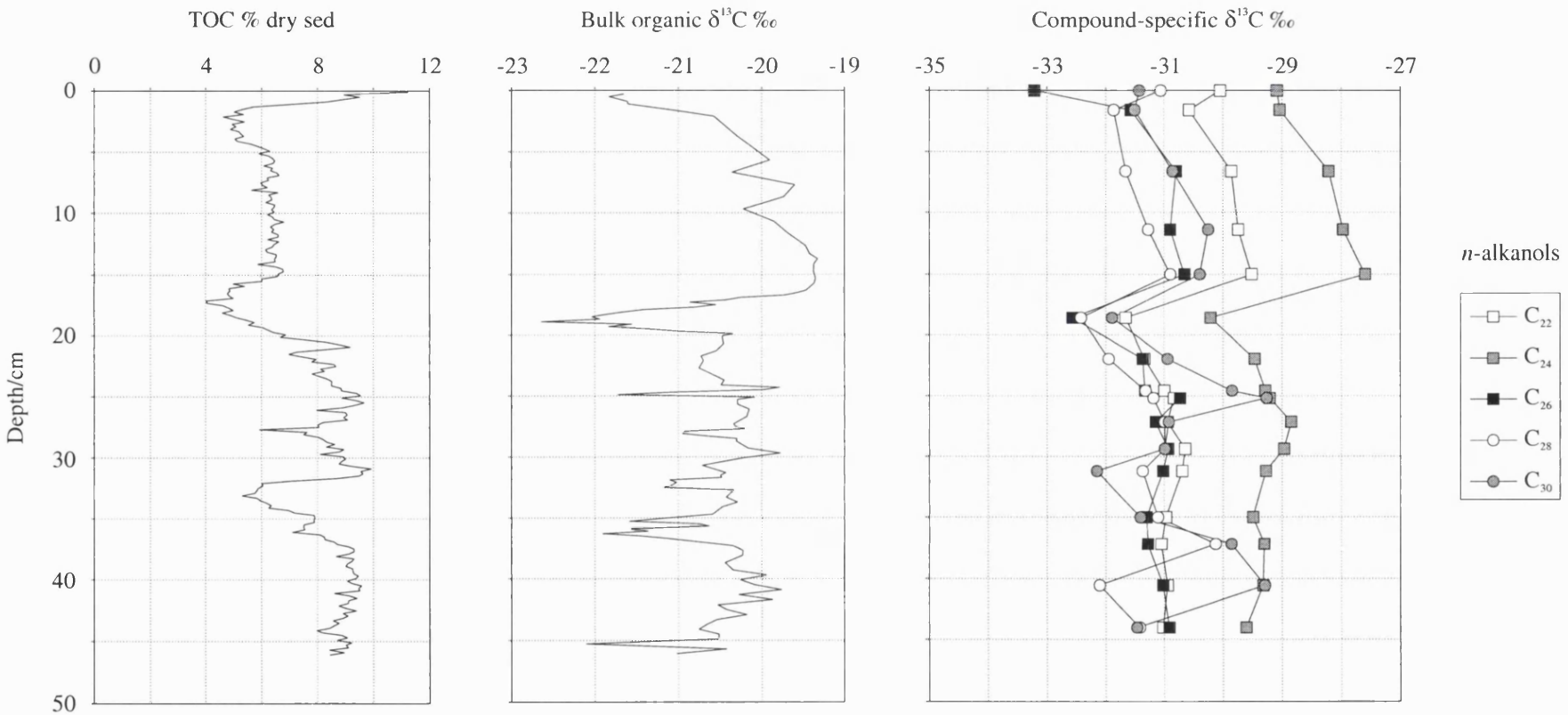


Figure 6.10 Downcore variation of TOC, bulk organic $\delta^{13}C$, and $\delta^{13}C$ of selected *n*-alkanols, core UACT6.

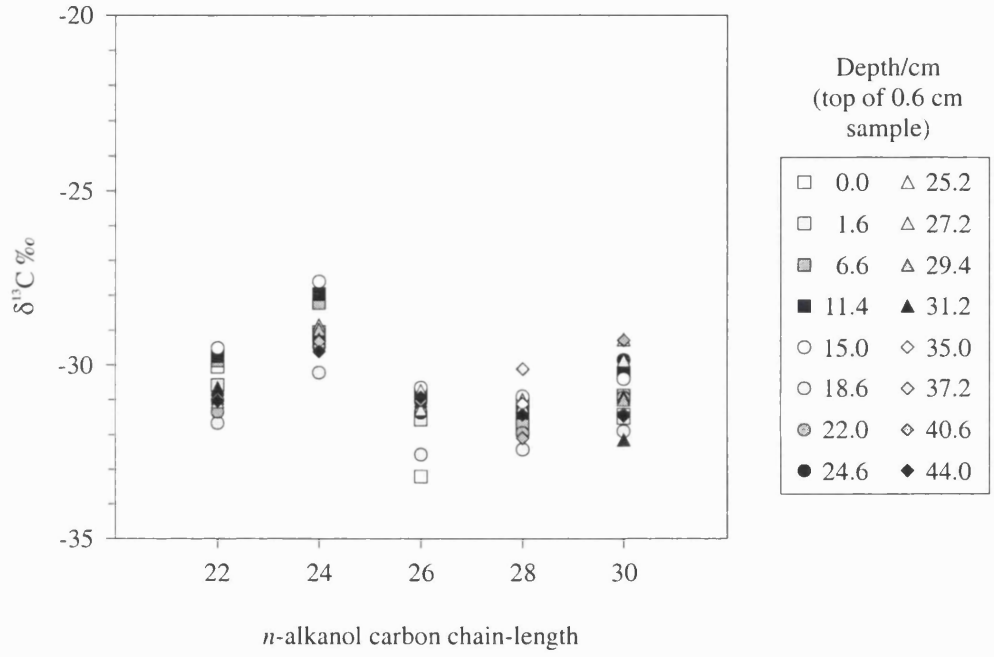


Figure 6.11 Range of $\delta^{13}C$ values exhibited by the major *n*-alkanols in the sixteen depths analysed, core UACT6.

value is -27.5‰ in the C_{24} *n*-alkanol at 15.0-15.6 cm depth, and the most depleted is -33‰ in the C_{26} *n*-alkanol at 0.0-0.6 cm depth. The increase in fractionation with carbon chain-length seen in the *n*-alkanes is not repeated in the *n*-alkanols. In all samples the C_{24} *n*-alkanol is least depleted, whilst the greatest depletion at any one level varies between the C_{26}, C_{28} and C_{30} *n*-alkanols. The reasons for the lack of correlation between $\delta^{13}C$ and chain-length in *n*-alkanols are not known. *n*-Alkanols and *n*-alkanes are biosynthetically related, both being formed from fatty acids, so it might be expected that both groups would display similar isotopic trends. The differences may be explained by the co-elution of *n*-alkanols with other components. Whereas the hydrocarbon fraction contains very few components other than *n*-alkanes, the alcohol fraction contains numerous components other than *n*-alkanols. This raises the possibility that two or more components will co-elute. The $\delta^{13}C$ value recorded for the resulting peak is thus an amalgam of the values of the individual components of that peak. If the co-eluting components have different $\delta^{13}C$ values, the measured $\delta^{13}C$ of the peak will differ from those of the components. In the Lochan Uaine *n*-alkanol record, the problem may be most acute at longer chain-lengths as it is in this region that the majority of sterols elute. Co-elution of components with *n*-alkanols may be sufficient to disguise any chain-length/$\delta^{13}C$ relationship, although the overall similarity in the $\delta^{13}C$ ranges of longer chain-length *n*-alkanols and *n*-alkanes suggests that the magnitude of these errors is no more than a few permil. The ±1‰ error in measurement must also be taken into account.

None of the other alcohols identified in the UACT6 sediment is present in sufficient concentration to allow reliable isotopic determination. In particular it would be interesting to obtain values for the sterols present, as these are the most abundant alcohols in the modern reference samples. The dominance of *n*-alkanols in the sediment and sterols in the modern samples prevents comparison between the two, and compound-specific $\delta^{13}C$ values of modern samples are not measured, with the exception of the hydrocarbon data presented previously (Figure 6.6). In future studies it may be profitable to separate sterols from other alcohols in sediment and reference samples and analyse the two groups separately. This would allow $\delta^{13}C$ values of the two groups to be compared between sediment and reference samples. It would also

help to alleviate any problems associated with the co-elution of sterols and long chain-length *n*-alkanols as mentioned previously.

6.8.2.2 Downcore variations in $\delta^{13}C$ of *n*-alkanols

In general, the downcore $\delta^{13}C$ profiles of the C_{22} to C_{30} *n*-alkanols are similar (Figure 6.10). $\delta^{13}C$ values become gradually less negative from the surface down to 15 cm depth. Between 15-18 cm depth there is a sharp increase in fractionation with a magnitude of 1.5 to 2.5‰. This is seen in all five main *n*-alkanols. Below 18 cm $\delta^{13}C$ becomes slightly heavier. Values then remain roughly constant from 22 cm to the base of the core, with the C_{22}, C_{24} and C_{26} *n*-alkanols varying by only *c.* 0.5‰. The greater variation seen in the C_{28} *n*-alkanol, and particularly in the C_{30} *n*-alkanol, may be related to the co-elution problem described above. The total variation displayed by the C_{30} *n*-alkanol below 22 cm is 3‰, which is only 1‰ greater than that found in long chain-length *n*-alkanes within the same section of core. The large excursion in *n*-alkanol $\delta^{13}C$ between 15-22 cm depth is synchronous with the main isotopic excursion in the bulk organic $\delta^{13}C$ curve. They are also of similar magnitude, with the total variation across the excursion measured at 2.5‰ in the C_{24} *n*-alkanol and *c.* 3‰ in the bulk material. Although the magnitude of change in the *n*-alkanols is not much greater than the estimated measurement errors, the fact that it is seen in all of the main *n*-alkanols in all three repeat analyses of the alcohol fraction of the 18.6-19.2 cm sample suggests that the event is real.

6.8.2.3 Correlations between *n*-alkanol $\delta^{13}C$ trends

Plots of the isotopic deviation from the most abundant *n*-alkanol, C_{26}, confirm that no homologues show a substantial difference in downcore isotopic trend (Figure 6.12). Correlations between downcore $\delta^{13}C$ variation of pairs of *n*-alkanols are given in Table 6.2, and pairings of all homologues with the C_{26} *n*-alkanol are shown graphically in Figure 6.13. Only three of the *n*-alkanol pairings are correlated at above the 95% significance level. This probably reflects the fluctuations seen in the lower half of the core, and the depleted surface sample in the case of the C_{26} *n*-alkanol.

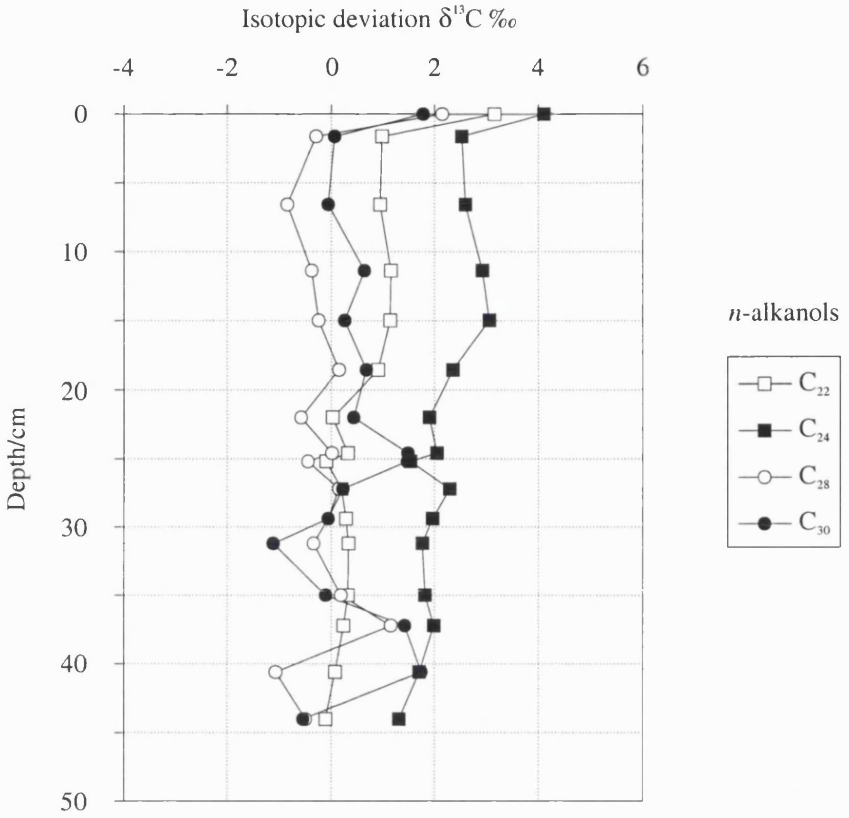


Figure 6.12 Deviation in carbon isotope fractionation of major *n*-alkanols from that of the most abundant homologue, the C_{26} *n*-alkanol, core UACT6.

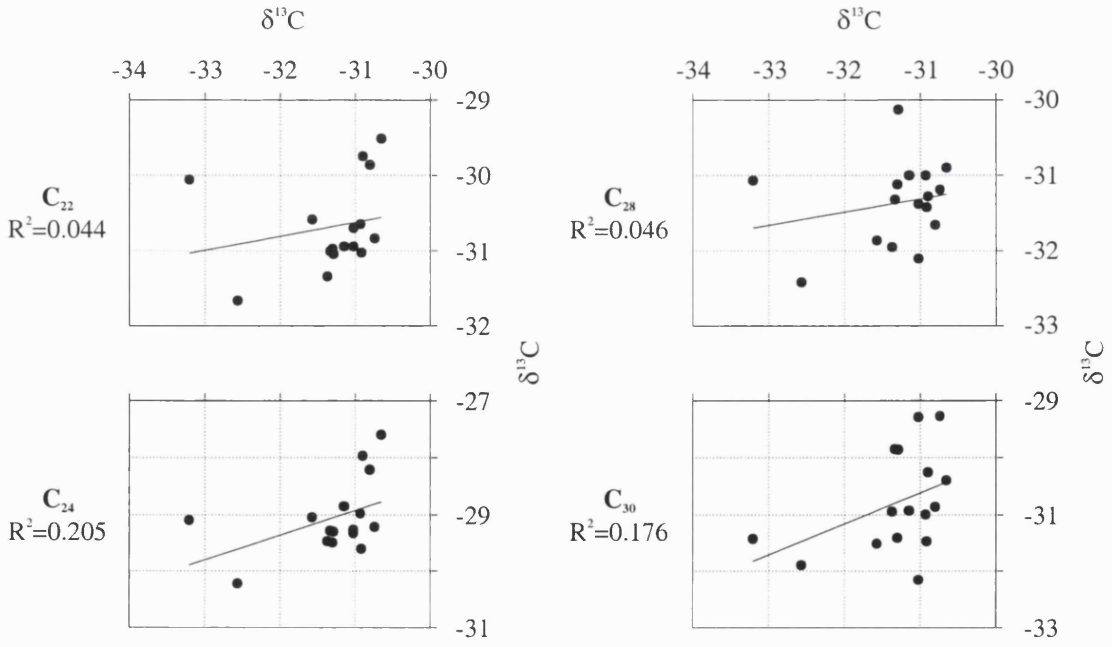


Figure 6.13 Regression of $\delta^{13}C$ of major *n*-alkanols (vertical axis) with the most abundant homologue, the C_{26} *n*-alkanol (horizontal axis). See also Table 6.2.

Table 6.2 Correlations between downcore *n*-alkanol $\delta^{13}C$ trends in UACT6. R^2 values are given at lower left, significance limits are given at upper right. Correlations significant at the 95% level are given in bold.

n-alkanol	C_{22}	C_{24}	C_{26}	C_{28}	C_{30}
C_{22}		**>99**	75-80	80-90	60-70
C_{24}	0.842		**97.5-99**	90-95	80-90
C_{26}	0.044	0.205		80-90	**97.5-99**
C_{28}	0.095	0.121	0.047		80-90
C_{30}	0.010	0.069	0.176	0.060	

6.8.2.4 $\delta^{13}C$ of *n*-alkanols as an indicator of organic source

By contrast with the hydrocarbon fraction which contains the short chain-length C_{17} *n*-alkane, all of the major *n*-alkanols detected are of mid and long chain-lengths. It is widely accepted in the literature that these compounds indicate a higher plant source, where they are found mostly as esterified components of waxes (Wünsche *et al.*, 1988; Farr *et al.*, 1990; Rieley *et al.*, 1991a; Volkman *et al.*, 1998). This is reflected in the modern reference samples from the Lochan Uaine catchment, where free *n*-alkanols are found above trace concentrations in only three of the eight samples. Free *n*-alkanols in the sediment originate mostly via the breakdown of waxes. The $\delta^{13}C$ values of *n*-alkanols in UACT6 are wholly consistent with a higher plant source. They lie in the range -33‰ to -27.5‰. As with *n*-alkanes, we can assume that *n*-alkanols are roughly 5‰ more depleted than bulk organic matter. This gives a $\delta^{13}C$ range for the precursor organisms of -28 to -21.5‰, which lies well within the accepted range for C_3 plants given previously. The mid chain-length C_{22} and C_{24} *n*-alkanols lie towards the heavier end of this range, and the long chain-length C_{26} to C_{30} *n*-alkanols lie towards the lighter end. This is also seen with *n*-alkanes: mid chain-length homologues suggest a range of -25 to -19‰ for their precursor organisms, and long chain-length homologues suggested a range of -28 to -24‰ for their precursor organisms. Mid chain-length *n*-alkanes appear to be a useful *Sphagnum* indicator in some instances (Nott *et al.*, 2000), although the corresponding mid chain-length *n*-alkanols are seen in all three of the modern reference samples which contained free *n*-alkanols, including *Sphagnum*. Also, the *n*-alkane $\delta^{13}C$ data presented previously suggest that *Sphagnum* may not be the sole source of mid chain-length *n*-alkanes found in the sediment. The $\delta^{13}C$ values of *n*-alkanols in UACT6 agree well with those

measured in sediment from Ellesmere by Rieley *et al.* (1991b), and are only a few permil heavier than the C_{24} *n*-alkanol measured in *Quercus robur* by Lockheart *et al.* (1997).

6.8.3 *n*-Alkanoic acids

Downcore variations in $\delta^{13}C$ of major *n*-alkanoic acids are shown in Figure 6.14. As with *n*-alkanols only even carbon number acids are shown, the odd carbon number homologues being present in a concentration too low to allow accurate determination of $\delta^{13}C$. The *n*-C_{20} alkanoic acid is excluded from the analysis for the same reason, as are any other acids present such as branched chain or cyclic acids. Odd numbered chain-length *n*-alkanoic acids all have $\delta^{13}C$ ranges similar to those of the even numbered *n*-alkanoic acids shown.

6.8.3.1 *n*-Alkanoic acid chain-length and $\delta^{13}C$

An overall increase in fractionation is seen with increasing carbon chain-length (Figure 6.15). This relationship was also seen in the *n*-alkanes but not in the *n*-alkanols. The relationship is not perfect in *n*-alkanoic acids. Specifically, $\delta^{13}C$ values of the C_{16} *n*-alkanoic acid are consistently lighter than those of the C_{18} *n*-alkanoic acid, and the C_{22} *n*-alkanoic acid is lighter than might be expected, having $\delta^{13}C$ values lighter than the C_{24} *n*-alkanoic acid and comparable to those of the C_{26} *n*-alkanoic acid. The example of the C_{22} *n*-alkanoic acid is analogous to that of the C_{21} *n*-alkane which appeared lighter than the general trend suggested should be the case (Figure 6.5). These lipids are biosynthetically related, as a $C_{(2n)}$ fatty acid is converted to a $C_{(2n-1)}$ alkane by enzymatic decarboxylation. Hence, the relative lightness of the C_{22} *n*-alkanoic acid and the C_{21} *n*-alkane compared to the respective trends of their *n*-alkyl homologues suggests a common process affecting the two compounds. This is most likely to be due to an origin in a different source compared to the other homologues present. A discussion of the possible causes of the $\delta^{13}C$/chain-length correlation was provided above with reference to *n*-alkanes.

The range covered by each alkanoic acid varies from a minimum of 2.5‰ for the C_{30} *n*-alkanoic acid to over 6‰ for the C_{18} *n*-alkanoic acid. In the latter case the large

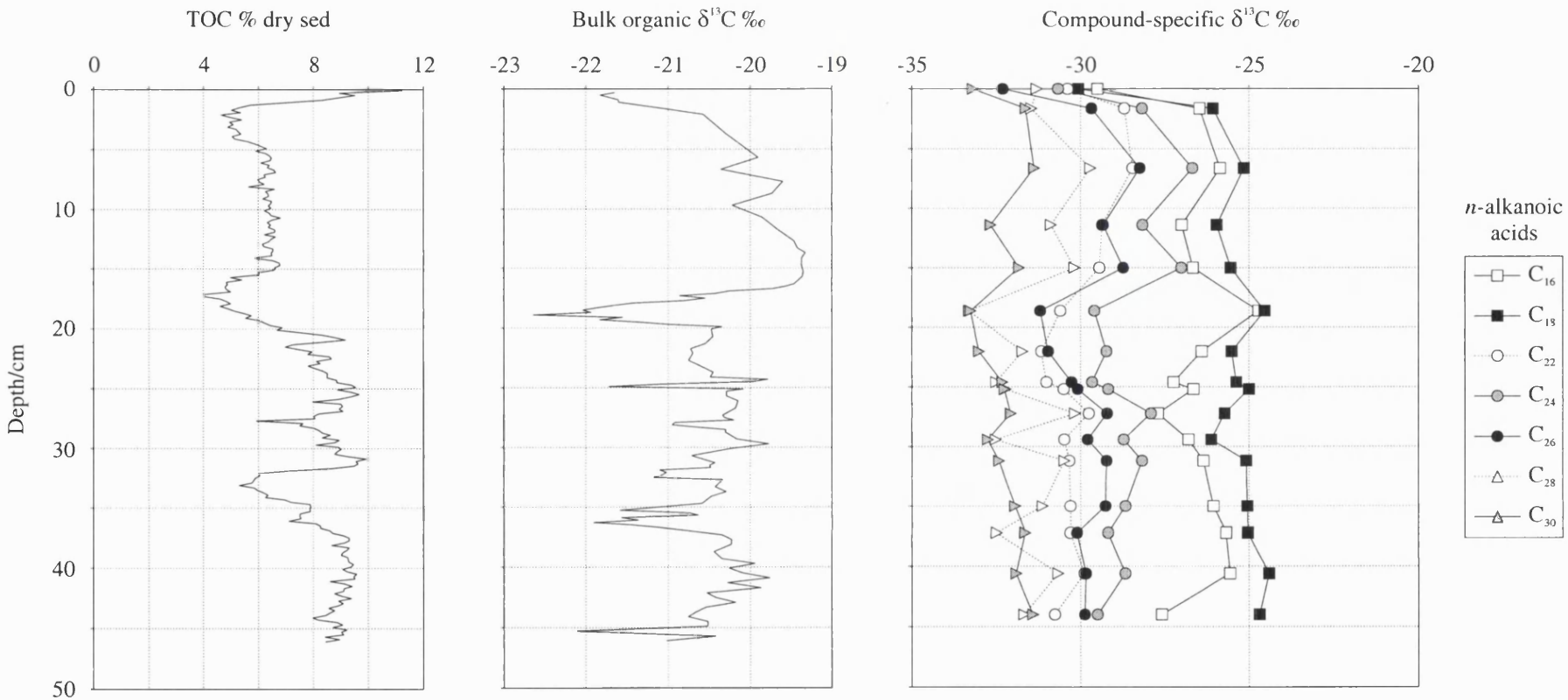


Figure 6.14 Downcore variation of TOC, bulk organic $\delta^{13}C$, and $\delta^{13}C$ of selected *n*-alkanoic acids, core UACT6.

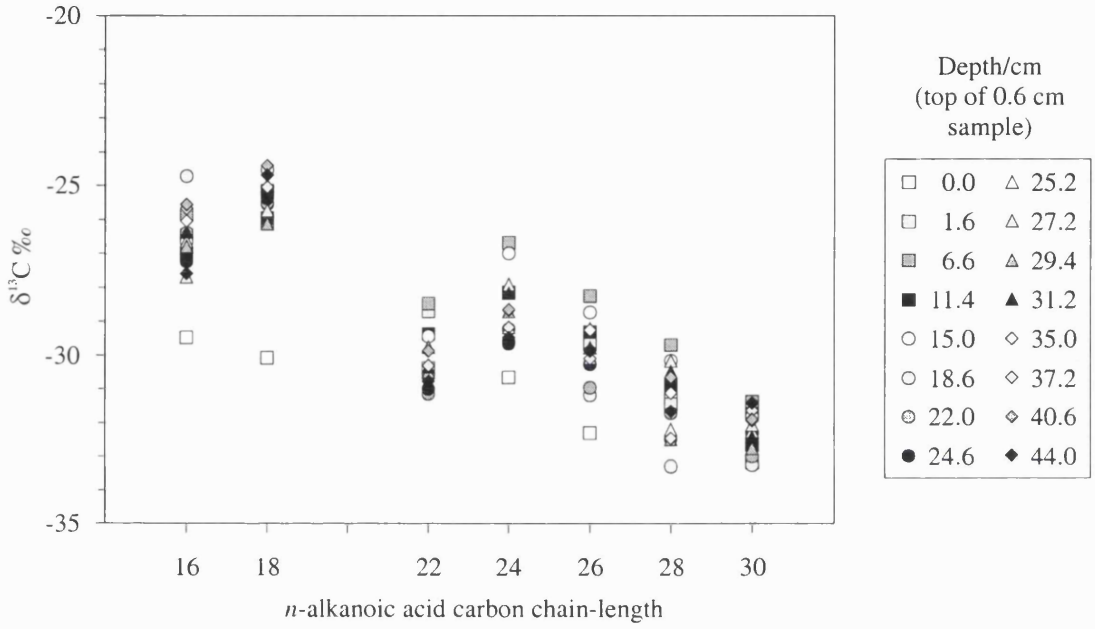


Figure 6.15 Range of $\delta^{13}C$ values exhibited by the major *n*-alkanoic acids in the sixteen depths analysed, core UACT6.

range is due to the isotopically light 0.0-0.6 cm sample - if this is excluded the range is reduced to only 2.5‰. This is not the only *n*-alkanoic acid to show this, and the surface sample is at least 1‰ more depleted than any of the other fifteen samples for the C_{16}, C_{24} and C_{26} *n*-alkanoic acids. Overall, the heaviest $\delta^{13}C$ values are found in the C_{18} *n*-alkanoic acid with a value of -24‰ recorded at 40.6 to 41.2 cm depth. The lightest value is -33‰ in the C_{28} *n*-alkanoic acid at 18.6-19.2 cm depth, although throughout the core the C_{30} *n*-alkanoic acid is more consistently depleted than any other *n*-alkanoic acid.

6.8.3.2 Downcore variations in $\delta^{13}C$ of long chain-length *n*-alkanoic acids

Of all three classes of aliphatic lipid studied, the *n*-alkanoic acids display the greatest range of $\delta^{13}C$ values at longer chain-lengths. Similarities are seen between the downcore profiles of the C_{24} to C_{30} *n*-alkanoic acids, and to a lesser extent the C_{22} *n*-alkanoic acid (Figure 6.14). There are also similarities between these and the *n*-alkanols. Most long chain-length *n*-alkanoic acids show a 2-3‰ rise in $\delta^{13}C$ between the surface sample and the 1.6-2.2 cm sample. $\delta^{13}C$ remains relatively stable down to 15 cm depth, followed by a large decrease of 2-3‰ between 15 and 18 cm. The $\delta^{13}C$ values then rise slightly and remain relatively stable from 18 cm to the core base, fluctuating by around 2‰. Although the depletion in the surface sample is not seen in the *n*-alkanols, the depletion event at 18 cm depth and the stable period below this are common to both the *n*-alkanol and the longer chain-length *n*-alkanoic acid profiles. Both depletion events are also seen in the bulk organic $\delta^{13}C$ record, as are the stable periods with low amplitude fluctuations from *c.* 2-17 cm and 20-46 cm depth.

6.8.3.3 Downcore variations in $\delta^{13}C$ of short chain-length *n*-alkanoic acids

The short chain-length C_{16} and C_{18} *n*-alkanoic acids show similar profiles to the longer chain-length homologues, with one main difference. A marked enrichment in $\delta^{13}C$ is seen from 15-18 cm depth, contrasting with the depletions in the longer chain-length *n*-alkanoic acid record, the *n*-alkanol record and the bulk record. This may be due to the short and long chain-length *n*-alkanoic acids originating from different sources, or different mixtures of sources.

6.8.3.4 Correlations between *n*-alkanoic acid $\delta^{13}C$ trends

The differences between the short and long chain-length *n*-alkanoic acid records are clearly visible when isotopic deviation from the C_{24} *n*-alkanoic acid is plotted (Figure 6.16). The deviations of the C_{22} to C_{30} *n*-alkanoic acids remain relatively constant downcore, varying by no more than *c.* 2‰. By contrast, the C_{16} and C_{18} *n*-alkanoic acids vary by 5‰, with a large positive deviation from 15-27 cm depth. This is seen in the regressions of one acid against another (Table 6.3, Figure 6.17). Correlations significant at the 95% level are seen between the C_{16} and C_{18} *n*-alkanoic acids, and between all combinations of the C_{22} to C_{30} *n*-alkanoic acids, but only two of the correlations between one short and one long chain-length acid are significant. This independent variation between short and long chain-length alkanoic acids supports the hypothesis that the two groups originate from different sources.

Table 6.3 Correlations between downcore *n*-alkanoic acid $\delta^{13}C$ trends in UACT6. R^2 values are given at lower left, significance limits are given at upper right. Correlations significant at the 95% level are given in bold.

	16	18	22	24	26	28	30
16		**>99**	60-70	90-95	90-95	75-80	75-80
18	0.6217		60-70	90-95	**>99**	60-70	**97.5-99**
22	0.0153	0.011		**>99**	**>99**	**>99**	**>99**
24	0.1081	0.128	0.5849		**>99**	**>99**	**>99**
26	0.1017	0.275	0.3769	0.8268		**>99**	**>99**
28	0.0321	0.0055	0.4103	0.5097	0.3828		**>99**
30	0.0306	0.1896	0.2486	0.2869	0.4889	0.1794	

6.8.3.5 $\delta^{13}C$ of *n*-alkanoic acids as an indicator of organic source

Further evidence that short and long chain-length acids originate from different sources is given by the $\delta^{13}C$ values of the acids. Shorter chain-lengths are consistently less depleted at all depths than the longer homologues. Acids of length C_{22} and longer have $\delta^{13}C$ values in the approximate range of -33 to -27‰. Assuming a 5‰ depletion in lipids relative to bulk material, the range of $\delta^{13}C$ of the precursor organisms is -28 to -22‰. As with long chain-length *n*-alkanes and *n*-alkanols, this $\delta^{13}C$ range is strongly indicative of a C_3 higher plant origin. This is consistent with the literature in which there is general agreement that long chain-length *n*-alkanoic acids originate

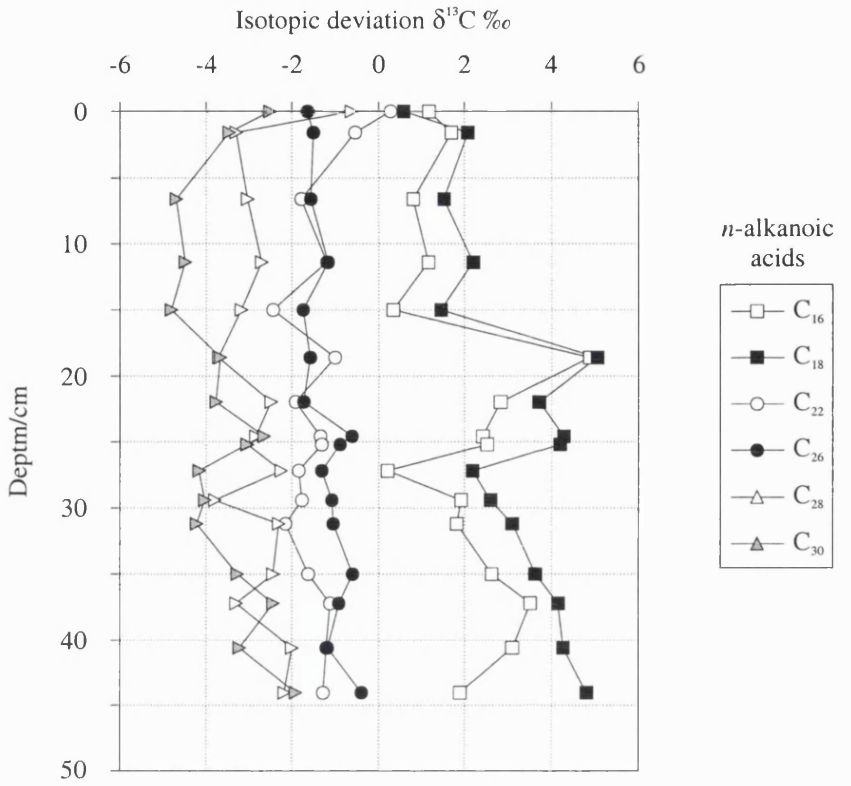


Figure 6.16 Deviation in carbon isotope fractionation of major *n*-alkanoic acids from that of the most abundant homologue, the C_{24} *n*-alkanoic acid (in some samples the C_{26} *n*-alkanoic acid is most abundant, whilst the C_{16} *n*-alkanoic acid predominates from 0.0-0.6 cm depth).

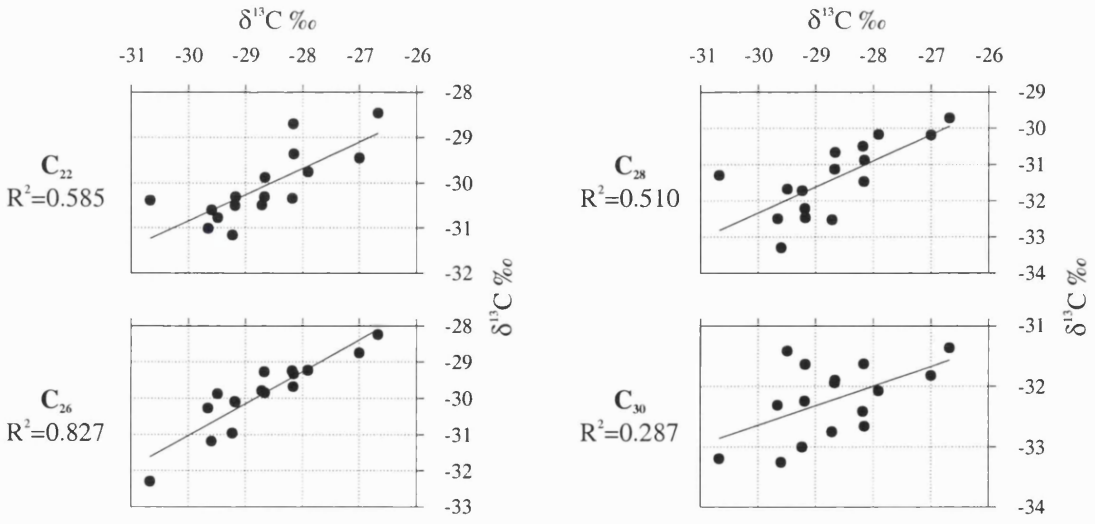


Figure 6.17 Regression of $\delta^{13}C$ of major *n*-alkanoic acids (vertical axis) with the most abundant homologue, the C_{24} *n*-alkanoic acid (horizontal axis). See also Table 6.3.

from higher plants where they are components of leaf surface waxes (Eglinton and Hamilton, 1967; Cranwell, 1978, 1982).

The situation is less clear with the short chain-length acids, for two reasons. Firstly, short chain-lengths in alkanoic acids do not necessarily indicate an algal or bacterial origin as they do with *n*-alkanes. Short chain-length acids are common in higher plants, where they are important constituents of glycerides and waxes. Secondly, algae and bacteria are known to exhibit a very wide range of isotopic fractionations, hence it is not possible to unambiguously assign a compound to an algal or bacterial origin on the basis of $\delta^{13}C$ alone. However, in UACT6 a much lighter $\delta^{13}C$ value is recorded in the C_{17} *n*-alkane than in longer chain-length *n*-alkanes. As this compound is an algal/bacterial biomarker, it is reasonable to infer that compounds originating in algae and bacteria in Lochan Uaine have less depleted $\delta^{13}C$ values than compounds from higher plants. Furthermore, alkanes are synthesised from alkanoic acids. It seems likely that short chain-length alkanes and acids originating from the same source will have similar $\delta^{13}C$ values. Similarity in $\delta^{13}C$ between the C_{17} *n*-alkane and the C_{16} and C_{18} *n*-alkanoic acids should indicate an algal/bacterial origin for the acids. The total $\delta^{13}C$ range seen in the C_{17} *n*-alkane is from -23.5 to -15‰, although only one sample lies outside the range -20 to -15‰. The corresponding range for the C_{16} and C_{18} *n*-alkanoic acids is -30 to -24‰, with all but the surface sample lying in the range -28 to -24‰. This is towards the heavier end of the range expected for lipids from a C_3 plant. There is thus a large discrepancy between the $\delta^{13}C$ values. The C_{16} and C_{18} *n*-alkanoic acids are consistently 8-9‰ more depleted than the algal/bacterial C_{17} *n*-alkane, and are also consistently less depleted than the longer chain-length homologues from a higher plant origin. Given that the C_{16} and C_{18} *n*-alkanoic acids are ubiquitous in algae/bacteria and higher plants, it is reasonable to assume that their presence in UACT6 reflects a mixed input from both autochthonous and allochthonous sources. This has the effect of shifting the algal/bacterial and higher plant $\delta^{13}C$ signatures to an intermediate value. The fact that the C_{16} and C_{18} *n*-alkanoic acid $\delta^{13}C$ values lie at the heavier end of the C_3 plant range, and are significantly more depleted than the C_{17} *n*-alkane algal/bacterial signature, suggests

that the input of these acids to the sediment is predominantly from a C_3 higher plant source.

6.9 Summary

Of the twenty-eight sediment samples analysed for lipid content (Chapter 5), sixteen samples were chosen for GC-IRMS analysis of the alcohol and acids fractions, whilst hydrocarbons were analysed in these sixteen plus a further two samples. In all cases only the most abundant components were analysed, as determination of $\delta^{13}C$ is unreliable for smaller peaks. These components included the odd number carbon chain-length *n*-alkanes, and the even number carbon chain-length *n*-alkanols and *n*-alkanoic acids. Although present in low concentrations only, the C_{17} *n*-alkane was analysed due to its importance as an algal/bacterial biomarker. Larger errors in $\delta^{13}C$ determination are probable for this compound, as discussed previously.

6.9.1 *n*-Alkanes

A strong relationship is seen between increasing *n*-alkane chain-length and increasing isotopic discrimination. In all but one sample the $\delta^{13}C$ of the C_{17} *n*-alkane lies in the range -20 to -15‰, whereas the C_{21} to C_{27} *n*-alkanes lie in the range -31 to -24‰, and the C_{29} to C_{33} *n*-alkanes lie in the range -33 to -30‰. This trend is commonly seen in plants, and may be related to the larger number of steps in the biosynthesis of longer chain-length compounds by comparison with shorter chain-lengths. It may also reflect the differing origins of the compounds. The C_{17} *n*-alkane is an algal/bacterial biomarker, and long chain-length *n*-alkanes are characteristic of higher plants. This difference in organic source is also suggested by the large downcore variation in $\delta^{13}C$ of the C_{17} *n*-alkane. A similar variation in long chain-length *n*-alkanes may be expected if they originate from the same source, but no such variation is seen. It is possible that the higher variation observed for the C_{17} *n*-alkane is partly attributable to the low concentrations of this compound throughout the core, and the correspondingly higher measurement errors. However, the total magnitude of variation, 8.5‰, is considered too large to be solely attributable to measurement errors.

The $\delta^{13}C$ profile of the C_{17} *n*-alkane shows similarities with the bulk organic $\delta^{13}C$ curve, despite the absence of $\delta^{13}C$ values for four samples where concentrations were too low to allow measurement. Smaller changes are seen in the C_{21} to C_{25} mid chain-length *n*-alkanes, but no significant variations are seen in the long chain-length C_{27} to C_{33} *n*-alkanes. Given the number of factors which could potentially determine $\delta^{13}C$, and given the inadequate knowledge of the influence of such factors at Lochan Uaine, it is difficult to interpret the *n*-alkane $\delta^{13}C$ profiles. The C_{17} *n*-alkane variation is considered unlikely to reflect any limitation of dissolved CO_2 over the last 2000 yr due to the ultra-oligotrophic nature of the lake. It is possible that temperature changes have affected $\delta^{13}C$ during this period. However, the magnitude of such changes is unlikely to have been great enough to cause the magnitude of variation observed in the $\delta^{13}C$ of the C_{17} *n*-alkane. Understanding of downcore variations in compound-specific $\delta^{13}C$ values awaits further investigation.

Although the downcore variations in *n*-alkane $\delta^{13}C$ are hard to interpret, the overall range of values exhibited by each compound is indicative of the organic source. Assuming a ^{13}C depletion of *c.* 5‰ in lipids by comparison with bulk tissue, long chain-length *n*-alkanes are identified as originating in C_3 higher plants. The heavier values of the C_{17} *n*-alkane are indicative of an algal/bacterial source, as the possibility of a C_4 source plant can confidently be discounted at Lochan Uaine. The identification of comparatively light isotope values in higher plant biomarkers, and comparatively heavy isotope values in algal/bacterial biomarkers, provides strong support for the interpretation of the bulk organic $\delta^{13}C$ profile as reflecting variations in relative input from allochthonous and autochthonous sources (Chapter 4).

Downcore variations in other hydrocarbons present are equally difficult to interpret. However, the differences between the C_{23} and C_{25} *n*-alkane profiles and those of the C_{23} and C_{25} *n*-alkenes suggest that the compounds are not biosynthetically related. The origin of *n*-alkenes in the sediment is not known.

6.9.2 *n*-Alkanols

The increase in fractionation with carbon chain-length seen in the *n*-alkanes is not repeated in the *n*-alkanols. Such a relationship might be expected as *n*-alkanes and *n*-alkanols have an common biosynthetic precursor in *n*-alkanoic acids. The alcohol fraction contains a greater number of components other than *n*-alkanols than does the hydrocarbon fraction with respect to *n*-alkanes. This increases the possibility that co-elution of compounds is occurring.

Downcore $\delta^{13}C$ profiles of the five most abundant *n*-alkanols all show similarities with the bulk organic $\delta^{13}C$ profile, most notably in the presence of a depletion event between 15-22 cm depth. The magnitude of this event in the *n*-alkanols varies from 1.5 to 2.5‰. This is smaller than the 3.3‰ variation in bulk organic $\delta^{13}C$. It is also similar in magnitude to the estimated measurement error of around ±1‰, although the fact that the event is seen in all major *n*-alkanols in duplicate samples suggests that it may be real. When isotopic deviations from the most abundant *n*-alkanol, C_{26}, are plotted, no *n*-alkanols show a variation with a magnitude greater than *c.* 3‰. This supports the hypothesis that C_{22} to C_{30} *n*-alkanols originate from similar organic sources. The compound-specific values of -33‰ to -27.5‰ almost certainly indicate a C_3 higher plant origin for these *n*-alkanols.

6.9.3 *n*-Alkanoic acids

In common with the *n*-alkanes, the *n*-alkanoic acids exhibit an overall increase in ^{13}C discrimination with increasing chain-length. The only exceptions are the C_{16} and C_{22} *n*-alkanoic acids, which show slightly greater depletion than the C_{18} and C_{24} *n*-alkanoic acids respectively.

Long chain-length *n*-alkanoic acids show considerable variability in downcore $\delta^{13}C$ profiles. Nonetheless, similarities with the bulk organic $\delta^{13}C$ profile are visible, including the depletion event at 18 cm depth which is seen in all long chain-length *n*-alkanoic acids, and the depletion at the surface seen in all of these acids except for C_{28}. The magnitudes of these depletion events are in the range *c.* 2-3‰. These are

similar to the magnitudes of the depletion events seen in the bulk $\delta^{13}C$ curve, but are not much greater than the estimated measurement error of ±1‰.

The principal difference between the $\delta^{13}C$ profiles of the long and short chain-length *n*-alkanoic acids is that in short chain-length acids a period of relative ^{13}C enrichment is recorded from *c.* 15-25 cm depth. Relative to the depletions seen in long chain-length *n*-alkanoic acids, this enrichment has a magnitude of around 3-5‰. With *n*-alkanes, the different $\delta^{13}C$ profiles shown by the long and short chain-lengths suggested different organic sources, as described previously. This may also be the case regarding the different $\delta^{13}C$ profiles shown by long and short chain-length *n*-alkanoic acids. However, the $\delta^{13}C$ values of the C_{16} and C_{18} *n*-alkanoic acids appear to lie between the ranges expected of a wholly C_3 higher plant source and a wholly algal/bacterial source. This may suggest an input of the C_{16} and C_{18} *n*-alkanoic acids from a variety of sources, both allochthonous and autochthonous, as these acids are known to be ubiquitous. By contrast, long chain-length *n*-alkanes exhibit $\delta^{13}C$ values which suggest a sole source in C_3 plants.

Chapter 7

Discussion and Conclusions

7.1 Introduction

The preceding three chapters have presented the results of the main analyses carried out on the UACT6 sediment. Chapter 4 discussed bulk sediment analysis, including CHN, chlorin and bulk organic $\delta^{13}C$ analysis. Chapter 5 discussed the results of the lipid analysis, and Chapter 6 discussed compound-specific $\delta^{13}C$ analysis. Downcore changes were seen in a number of variables which may potentially be indicative of changes in productivity and changes in organic matter source. The following section summarises the main changes seen, and discusses the potential responses of these variables to climate change. Subsequent sections will examine the data with respect to known climatic variations in Scotland and northwest Europe over the last *c.* 2000 cal yr, as reconstructed from instrumental and palaeoclimate proxy records. A summary and conclusions of the study are presented, and recommendations for future research possibilities are made.

7.2 Summary of potential productivity indicators in the sediment record of Lochan Uaine

7.2.1 Bulk analyses (CHN, TOC, chlorins, bulk organic $\delta^{13}C$)

Synchronous downcore variations are seen between LOI and concentrations of carbon, nitrogen and hydrogen (Figures 4.1 and 4.4). This is to be expected as organic matter provides the major input of these elements to the sediment. In the case of total carbon, virtually no carbonate is present, and almost all of the carbon is thus organic in origin. A very strong correlation is seen between LOI and TOC (Figure 4.3).

It is hypothesised that the cycles in LOI seen in cores from Lochan Uaine, and hence also the cycles in TOC in core UACT6, reflect changes in lake primary productivity during the Holocene. A large fraction of the sediment consists of diatom remains, indicating the potential importance of algae, and presumably other aquatic organisms, in providing inputs to the lake sediment. It is further hypothesised that the changes in lake primary productivity are a response to Holocene climate variability. This may be through the influence of air temperature on lake ice-cover, as the two are closely

related (Doran *et al.*, 1996). The duration of winter ice-cover affects the timing and duration of the growing season in the lake, which in turn dictates the amount of lake primary production and hence the amount of organic material entering the lake sediment from the water column. Likewise the growing season in the catchment will be affected by temperature, either directly via plant physiological responses to cold temperatures, or indirectly via the effects of extended periods of snow cover. In other words, the variations in LOI and TOC seen in Lochan Uaine cores are caused by changes in the input of organic matter rather than changes in the input of inorganic matter. The system is complicated by the fact that inorganic matter could enter the sediment either through the inwash of clastic material from the catchment, or through the deposition of biogenic inorganic matter such as diatom silica. This latter point is important given the high proportion of diatom remains in the sediment of Lochan Uaine.

Willemse and Törnqvist (1999) identify a climate signal in LOI records from six lakes in West Greenland. Synchronous changes in LOI seen in cores from these six lakes are thought to reflect variations in productivity. The LOI is driven by changes in either the diatom silica or organic matter content of the sediment. In addition to the effect of lake ice-cover duration on growing season, Willemse and Törnqvist also note that a shorter period of ice-cover is associated with improvements in the exchange of gases and nutrients, wind-driven circulation, and light conditions. Close correlations are seen between lake sediment LOI or ROI (residue-on-ignition) and the $\delta^{18}O$ records of the GISP and GRIP2 ice cores, indicating the strong response to climate forcing of the sediment organic/mineral ratio in suitably sensitive sites.

C/N and C/H ratios

Given the hypothesis outlined above, the identification of an indicator of primary productivity in the Lochan Uaine sediment record is of potential great importance. Several such indicators are investigated through the bulk sediment analysis. These are the C/N and C/H ratios, the chlorin concentration, and bulk organic $\delta^{13}C$ (Figure 4.16). The C/N and C/H ratios provide inconclusive results. The former is used to indicate whether the organic matter originates from an algal/bacterial source, which at

Lochan Uaine would be primarily autochthonous, or a higher plant source, which at Lochan Uaine would be primarily allochthonous as aquatic macrophytes are largely absent from the lake. Apart from the suggestion of a larger autochthonous component in the top 5 cm of sediment, which may be related to a delay in organic matter mineralisation near the mud-water interface, little or no variation in C/N ratio is seen throughout UACT6. The values of around 10-13 suggest a range of values from both autochthonous and allochthonous organic inputs, which tend to have ratios of <10 and >20 respectively (Tyson, 1995; Meyers and Lallier-Vergès, 1999; Bianchi *et al.*, 1999). Likewise, little significant variation is seen in the downcore profile of C/H ratio. This may also be used to indicate organic matter sources, although the boundary values between different inputs are less well known than for the C/N ratio. The C/H ratios of around 4-7 seen in UACT6 probably reflect a mixed input of algae, bacteria and higher plants (Talbot and Livingstone, 1989). The sensitivity of C/N and C/H ratios to changes in organic matter source is not known.

Bulk organic $\delta^{13}C$

Total variation of almost 4‰ is seen in the bulk organic $\delta^{13}C$ of UACT6, with values ranging from -22.7 to -19.3‰ (Figure 4.16). The most noticeable event is the peak in discrimination occurring between 15-20 cm depth. C_3 land plants, which are the only type found in the Lochan Uaine catchment, are known to exhibit $\delta^{13}C$ values peaking at around -29 to -26‰. The lighter values from 15-20 cm depth suggest an increased importance in organic input from the catchment during this period. Although a wide variety of $\delta^{13}C$ values for algae and bacteria have been quoted in the literature, it is thought that the autochthonous input at Lochan Uaine contributes heavier $\delta^{13}C$ values than those from catchment vegetation. Specifically, the C_{17} *n*-alkane, an algal and bacterial biomarker, is consistently less depleted in ^{13}C throughout UACT6 by comparison with terrestrial plant biomarkers. Thus the variation in bulk $\delta^{13}C$ from heavy to light values is thought to represent a change in importance from autochthonous to allochthonous inputs to the sediment, although there are many potential additional influences as discussed in Chapter 4. The major depletion event in the bulk organic $\delta^{13}C$ record from 15-20 cm is also seen in the TOC profile, but no depletion is seen during the other two periods of low TOC content. Overall, no

significant relationship is found between $\delta^{13}C$ and TOC in UACT6 (Figure 4.15), in contrast to the section of core UACT4 analysed by Battarbee *et al.* (in press) in which a strong correlation between LOI and $\delta^{13}C$ is observed.

Chlorins

Perhaps the most promising bulk indicator of lake primary productivity examined is the chlorin concentration (Figure 4.16). Chlorins are thought to be the diagenetic products of algal chlorophyll, hence should provide a direct proxy for lake primary productivity. The downcore chlorin concentration expressed as percentage of sediment dry weight shows a very similar trend to the LOI and TOC profiles. More significantly, the downcore chlorin concentration expressed *as a proportion of TOC* shows the same trend. This indicates that the chlorin concentration is varying independently of the sediment mineral content - rather, it is varying as a proportion of the sediment organic content. The implication is that not only has the amount of organic matter input to Lochan Uaine changed during the course of deposition of UACT6, but the composition of that organic matter has changed too. This provides support for the hypothesis that the LOI cycles in Lochan Uaine are driven by changes in organic matter input, and that these changes are related to lake primary productivity.

7.2.2 Lipid analysis

The use of lipid analysis in the study of changes in productivity lies in the ability to ascribe components to certain precursor organisms, which gives the potential to reconstruct past vegetation changes. There is also a potential to reconstruct past inputs of organic matter to the lake. In particular, lipid biomarkers of algal/bacterial or higher plant material are important as it is thought that any climatic influence on Lochan Uaine may manifest itself as a change in lake primary productivity. Of the various lipid fractions analysed, the hydrocarbon fraction proves most useful for the reconstruction of relative autochthonous and allochthonous inputs.

The hydrocarbon fraction is dominated by *n*-alkanes, and of these the greatest concentrations recorded are of the C_{27} to C_{31} odd carbon-numbered *n*-alkanes. These

are biomarkers of higher plants. When expressed as a proportion of TOC, minimal downcore variations in concentration are seen, with the exception of slightly increased concentrations from 15-20 cm depth. This suggests that higher plant input as a proportion of total organic input has varied little over the past *c.* 2000 yr, apart from a slightly higher input during the period mentioned. By contrast, two components exhibited significant downcore variation. These were the C_{17} *n*-alkane and a C_{25} highly branched isoprenoid (HBI) monoene. The former is indicative of an algal or bacterial source, and the latter is thought to be found specifically in diatoms. Both components show strong correlations with TOC when expressed as a proportion of TOC. These results compare favourably with those from the bulk chlorin analysis described above. All three variables are indicative of lake productivity, and all three exhibit the lowest values during periods of low sediment organic content. Variations in the C_{21} and C_{23} *n*-alkanes also appear to follow the TOC profile, although the relationship is not as strong as with the C_{17} *n*-alkane and the C_{25} HBI monoene. The C_{21} and C_{23} *n*-alkanes are potential biomarkers for *Sphagnum* moss. Their downcore variation may thus provide a potential proxy for past moisture variations, although further work would be needed to clarify this hypothesis.

Analysis of other lipid fractions adds little to the hydrocarbon record. The acid and alcohol/sterol fractions are dominated by even carbon-number *n*-alkanoic acids and *n*-alkanols respectively. Long chain-lengths indicative of higher plant input predominate. None of the major compounds, the C_{24}, C_{26} and C_{28} *n*-alkanols and *n*-alkanoic acids, shows downcore variations which are synchronous with the changes seen in the TOC, chlorin, C_{17} *n*-alkane and C_{25} HBI monoene records. In all cases the records are quite noisy. A lack of change in the long chain-length *n*-alkanols and *n*-alkanoic acids corresponds with the similar lack of changes seen in the long chain-length *n*-alkanes, as all are higher plant biomarkers. Although most sterols appear to be degraded rapidly in Lochan Uaine, several are identified in the sediment. The concentration of one of these, brassicasterol, is found to correlate with the TOC profile at a significance level of 99%. This sterol is known to be an important component of many diatoms, although it has also been identified in numerous other organisms, including higher plants collected from the Lochan Uaine catchment.

7.2.3 Compound-specific stable carbon isotope analysis

Compound-specific isotope values of the major *n*-alkanes, *n*-alkanols and *n*-alkanoic acids are compared to the bulk organic $\delta^{13}C$ profile for UACT6. There is some evidence that downcore profiles of certain components show similar changes to those seen in the bulk $\delta^{13}C$ curve. These components include the C_{17} *n*-alkane and the even carbon number long chain-length *n*-alkanols. With the exception of the C_{17} *n*-alkane, the magnitude of these downcore changes is generally only *c.* 2‰, which is probably within the error limits of the measurement technique. These are estimated at *c.* ±1‰. Other major components such as the long chain-length *n*-alkanes and *n*-alkanoic acids show very little downcore variation.

These results suggest that the changes seen in the bulk $\delta^{13}C$ profile are driven by changes in organic source rather than changes in the isotope ratios of the organisms contributing organic carbon to the sediment. It is possible that the large downcore variations in the C_{17} *n*-alkane of *c.* 8‰ are due to changes in the isotopic composition of the source organisms. As this compound originates from algae and bacteria within the lake, the isotopic variation may be driven by carbon availability. This in turn may be climatically related through the influence of temperature on lake ice-cover, and hence on growing season, lake primary productivity, and within-lake carbon utilisation. However, there are several difficulties with this explanation. Lochan Uaine is an ultra-oligotrophic lake and it seems unlikely that productivity would ever be high enough during the Holocene to cause carbon limitation and affect isotopic fractionation. Although the C_{17} *n*-alkane is known to originate from algal and bacterial sources, these are a large and diverse group of organisms. The observed variations in $\delta^{13}C$ of the C_{17} *n*-alkane could merely reflect changes in the algal/bacterial composition between species with differing carbon isotopic fractionation values. Finally, the C_{17} *n*-alkane is present in much lower concentrations than the longer chain-length *n*-alkanes, and the determination of $\delta^{13}C$ of this compound is thus subject to larger measurement errors. The large observed downcore variation in $\delta^{13}C$ of the C_{17} *n*-alkane may thus not be significant. It should be remembered that lipids only form a few percent of the total sedimentary organic matter, and analysis of lipid $\delta^{13}C$ is thus only a proxy for the changes influencing bulk organic $\delta^{13}C$.

Perhaps the most important finding from the compound-specific stable isotope analysis is that the C_{17} *n*-alkane algal/bacterial biomarker displays far greater isotopic discrimination than the longer chain-length higher plant biomarkers, even allowing for large measurement errors. If we assume that all organic matter derived from algae and bacteria is isotopically heavier than organic matter from higher plants, we can place more confidence in the interpretation of the bulk $\delta^{13}C$ profile as representing changes in the relative importance of autochthonous and allochthonous inputs, as discussed previously. Hence the low chlorin concentrations from 15-20 cm depth, which suggest low lake productivity, are mirrored by the greater depletion in bulk ^{13}C which suggests a decreased contribution from autochthonous inputs.

7.3 Sediment responses to climate change

Before making comparisons between the potential climate record of Lochan Uaine and climate records from other instrumental or proxy studies, it is worth discussing what the expected responses would be. Certain non-lacustrine climate proxies respond in a comparatively direct manner to climate variability - peat humification reflects the combined effects of precipitation and temperature on water table height, tree-ring widths reflect temperatures during the growing season, ice core melt layers reflect summer warmth, and so on. By contrast, the response of montane lakes such as Lochan Uaine to climate variability is likely to be indirect. If, as is thought, the chlorin record is a proxy indicator of lake productivity, we must then ask what climatic factors could influence this productivity. The following section explores some of the potential responses of montane lakes to climate change, and demonstrates some of the gaps in our understanding of these responses. It should be noted that although Willemse and Törnqvist (1999) associate high LOI with either increased or decreased productivity, depending respectively on whether an increase in autochthonous organic input or diatom silica input occurs, only the former situation is thought to apply at Lochan Uaine. The evidence for this comes from the chlorin and biomarker records, which are indicators of lake productivity. These demonstrate that low LOI, and hence low TOC content, is associated with low productivity. Importantly, the chlorin and biomarker records are expressed as a proportion of TOC, and as such are independent

of changes in sedimentary mineral content. By contrast, diatom concentrations in UACT4 show no covariance with LOI (Battarbee *et al.*, in press). We can conclude that low LOI and TOC in Lochan Uaine sediment is indicative of low lake productivity.

One hypothesis to explain the quasi-cyclic episodes observed in LOI and other records from Lochan Uaine has been discussed previously. It is thought that effect of variations in air temperature may influence the duration of winter ice-cover. This in turn may alter the timing and duration of the growing season, and the subsequent variations in lake primary productivity are expressed as variations in LOI, TOC, chlorin content, and lipid biomarker concentrations (Willemse and Törnqvist, 1999). Recent studies using long instrumental records to reconstruct ice-cover have shown that over the past 200 years the duration of the ice free period in Cairngorm lakes has varied by more than 50 days (Barber *et al.*, 1999; Agusti-Panareda *et al.*, in press). This high interannual variability is a consequence of the strong oceanic influence at this altitude. It seems reasonable to assume that such changes would have a significant impact on the lake system in terms of water temperature, nutrient availability, and total lake biomass productivity (Battarbee *et al.*, in press).

It is possible that the air temperature variations are a response to changes in solar radiation, in the same way that 'Milankovitch' forcing drives global climate at millennial timescales. There are, however, certain inadequacies with this hypothesis. Whilst air temperature is undoubtedly the main factor controlling ice break-up dates (Doran *et al.*, 1996; Livingstone, 1997), relating such temperature changes to variations in solar radiation is much more difficult. This problem is not unique to this particular study. Indeed, a common theme of palaeoclimate studies globally over the last few decades has been the search for a link between solar variability and climate variability at sub-Milankovitch timescales (*e.g.* Stuiver, 1980; Schove, 1987; Willett, 1987; Kelly and Wigley, 1990, 1992; Anderson, 1992; Schlesinger and Ramankutty, 1992, 1994; Stuiver *et al.*, 1995; Waple, 1999; Beer *et al.*, 2000; Hong *et al.*, 2000). Even with those proxies which are thought to indicate solar variability directly, such as ^{14}C in tree-rings and ^{10}Be in ice cores, it is not always possible to identify even the

best known solar variations such as the *c.* 11 yr sunspot cycle. Given these difficulties, it seems unreasonable to assume that the signal in the Lochan Uaine sediment record should be directly comparable with reconstructed solar variability. It is more likely that the Lochan Uaine signal represents a response to just one facet of the climate system. The influence of the oceanic climate on duration of ice-cover in the high Cairngorms (Agusti-Panareda *et al.*, in press) suggests that the North Atlantic Oscillation (NAO) may play a significant role at Lochan Uaine.

The principle effects of the NAO are felt during the Northern Hemisphere winter. 'Positive' years - those with a large pressure gradient between Icelandic low and the Azores high - are characterised by stronger Westerlies across the North Atlantic and more intense storm tracks, giving warmer, wetter winters in northwest Europe (Perry, 2000; Sarachik and Alverson, 2000). Negative years are characterised by weaker Westerlies and colder, drier winters. If productivity variations in Lochan Uaine are related to the large changes in duration of winter ice-cover, it seems likely that the NAO is the main feature of the climate system which determines this ice-cover duration. The hypothesis linking climate to the sediment record must be amended accordingly. Thus, long duration of winter ice-cover is caused by a negative NAO, rather than a temperature decrease in response to reduced intensity of solar radiation. The distinction is important. Tree-ring based reconstructions of the NAO for the period 1701-1980 suggest periodicities of around 24, 8 and 2.1 yr (Cook *et al.*, 1998). These periodicities are in poor agreement with those measured in instrumental, historical or proxy records of solar activity (Schove, 1967, 1987; Stuiver and Braziunas, 1992, 1993). This suggests that the NAO does not respond measurably to solar forcing over annual to decadal timescales, and therefore a lake sediment record driven primarily by the strength of the NAO could not be expected also to contain a solar signal. This hypothesis may be better tested as and when a longer NAO record becomes available (*e.g.* Proctor *et al.*, in press), which will also allow comparisons of lower frequency, decadal to centennial cyclicity. It is also significant that there appears to be a strong seasonal influence, with autumn, winter and spring climate having a greater effect on the lake system than summer climate. Analysis of the long instrumental record from Edinburgh shows that winter climate varies more than

summer climate (R. Thompson, pers. comm.). This potential seasonal influence at Lochan Uaine also has implications for the comparison of the lake record with other palaeoclimate proxies, especially those such as tree-ring width and density which tend to respond mainly to summer temperatures.

For the purposes of the above discussion, it was assumed that cold winters with long periods of ice-cover result in shorter growing seasons and decreased primary productivity. Such periods would be expressed in the lake sediment record as minima in LOI and chlorin content. Likewise, warm winters would be expressed as maxima in LOI and chlorin content. In reality, the relationship between temperature and organic matter production is not well understood, to the extent that it is not known whether increased productivity is characteristic of warmer or colder periods (Battarbee *et al.*, in press). Willemse and Törnqvist (1999) present evidence to suggest that productivity in West Greenland lakes is increased during warm periods. However, there is evidence from an ongoing study of Scottish lakes that cold winters are often followed by an increase in nutrient content and a corresponding increase in primary productivity (D. Monteith unpublished). This may be a result of lower retention of nutrients in the catchment and greater mixing of the water column in the year following a cold year (Battarbee *et al.*, in press). In this case, the interpretation of the LOI, chlorin and biomarker profiles in Lochan Uaine would be reversed, with high concentrations corresponding to cold periods and low concentrations corresponding to warm periods. Battarbee *et al.* (in press) suggest that the current evidence favours this interpretation. Nonetheless, it is clear that much work needs to be done to establish the true responses of montane lake sediments to climate change.

7.4 Interpretation of UACT6 with respect to late Holocene climate variability

7.4.1 Dating of events in the UACT6 organic matter record

Chapter 3 (Section 3.5) discussed the construction of a chronology for UACT6. This chronology is based upon the transfer of a calibrated radiocarbon chronology from UACT4 to UACT6 by correlation of the LOI profiles of the two cores. Numerous

errors and uncertainties are associated with this process. Potential errors may exist in the original ^{14}C dating, in the assumption of a *c.* 500 year correction for contamination by old carbon, in the calibration of the corrected ^{14}C dates, in the correlation between the two cores, and in the construction of a linear depth-age model for UACT4. Nonetheless, the chronology given in Figure 3.16 is thought to be the most likely for UACT6 for reasons discussed in Chapter 3. The accumulation rate is consistent with those calculated for UACT4 and by Rapson (1985), and using this chronology the base of UACT6 is estimated to represent a date of around 50 BC. It is thus possible to use this chronology to date events seen in the various records of UACT6, allowing comparison with other dated palaeoclimate sequences. All dates for UACT6 are quoted to the nearest 10 cal yr according to the linear depth-age model. The potential for larger dating inaccuracies must be assumed throughout, even where not explicitly stated.

The LOI and TOC profiles from UACT6 are very closely correlated, and the following discussion applies to both curves. The profiles are characterised by a series of oscillations between high and low values (Figure 7.1 - LOI not shown). The three most prominent minima in LOI/TOC are dated to 500-590, 1170-1310 and 1850-1940 AD. Of these, the event occurring at 1170-1310 AD has the lowest LOI/TOC values, representing the lowest sedimentary organic content. The periods of higher organic content that occur in the intervals around these three minima are not identical. Near the core top, the organic content increases rapidly from 1940 AD onwards to reach a maximum for the whole core at the surface, which is assumed to represent the present day. By contrast the period from 1310-1850 AD is characterised by low values. These are higher than the surrounding minima at 1170-1310 and 1850-1940 AD, but similar in magnitude to the earliest minimum at 500-590 AD. This period is also remarkably stable, showing very little variation in LOI/TOC which could not be attributed to random noise. This stability is not seen in the period from 600-1110 AD which contains higher frequency fluctuations than seen elsewhere in the core. Hence, peaks in LOI/TOC at 600-720, 860-920 and 1090-1110 AD are interspersed by comparatively low values at 720-800 and 1030-1070 AD. Finally, the lowermost

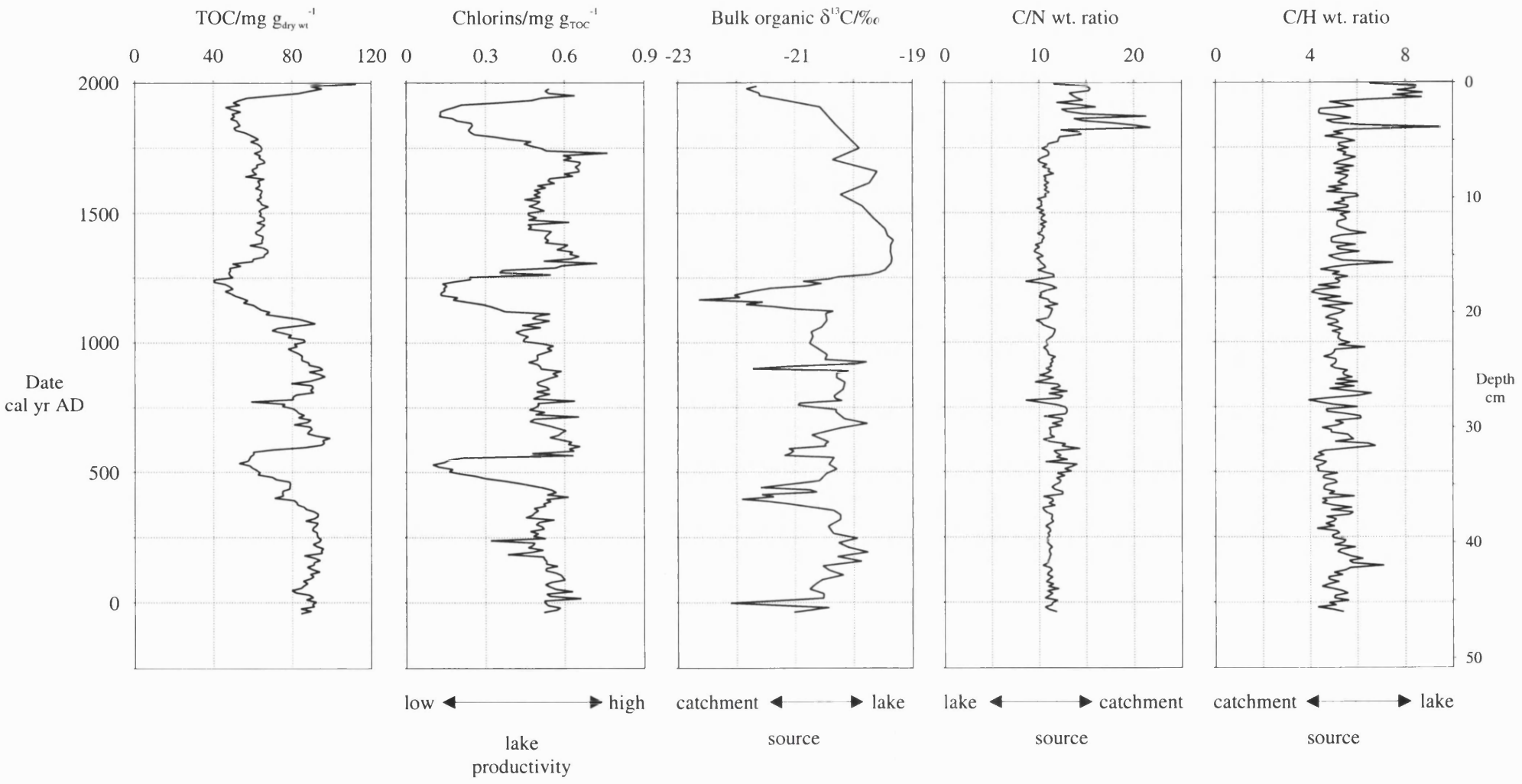


Figure 7.1 Potential bulk indicators of palaeoproductivity, core UACT6, against the preferred dating model. Depth is given at far right.

maximum from 50 BC-370 AD is different again in that it combines high LOI/TOC values with generally high stability.

It is important to consider the chlorin concentration profile separately from the LOI/TOC curves, not solely because of the slightly different forms of the curves, but because the chlorin record represents a signal which, unlike LOI and TOC, is independent of any potential changes in sedimentary mineral content. The three minima identified in the LOI/TOC records are present in the chlorin record, but are much more pronounced (Figure 7.1). They are dated to approximately 460-560, 1120-1280 and 1740-1940 AD, and are thus in good agreement with the dates of the three minima in LOI/TOC at 500-590, 1170-1310 and 1850-1940 AD. Other than the more pronounced minima in the chlorin concentration profile, the other main difference between the chlorin and LOI/TOC profiles is in the periods around the minima. In the LOI/TOC profiles these exhibit significant variability, yet in the chlorin profile they are all of a similar magnitude. They are dated to 50 BC-460 AD and 560-1120, 1280-1740 and 1940-2000 AD. The period from 1280-1740 AD consists of two peaks in chlorin concentration towards the start and end of this period, with slightly lower values during the central period from 1440-1560 AD.

In addition to the principal maxima and minima seen, another feature common to the LOI, TOC and chlorin curves is the rapidity of change from one state to another at certain points. For instance, in all three profiles a very large increase is seen between 31.9 and 31.7 cm depth. This increase is dated to between 590-600 AD. Even allowing for dating inaccuracies and the fact that the sediment accumulation rate is unlikely to be perfectly linear as assumed by the depth-age model, it nonetheless seems likely that the change occurred over a timescale of at most a few decades. Although major climate shifts on similarly rapid timescales are thought to have occurred during the transitions between glacial and interglacial periods (*e.g.* Alley *et al.*, 1993), events of this scale have yet to be identified in the Holocene. The shifts seen in UACT6 are unlikely to be due solely to climatic factors. A climatically-mediated switch across a threshold state of primary productivity is a possibility, although without further study such a process must remain conjecture.

The bulk organic $\delta^{13}C$ curve shows some features in common with the LOI, TOC and chlorin curves. Specifically, a major lightening of isotopic values is seen at about 17-20 cm depth. This event is dated to approximately 1120-1250 AD with the most depleted value occurring at 1160 AD, a few decades before the corresponding minima in LOI, TOC and chlorins. No major periods of ^{13}C depletion are seen coinciding with the other two minima in LOI, TOC and chlorins. Other features of the bulk $\delta^{13}C$ curve include a period of comparatively heavy values from 1250-1750 AD, and lighter values from 350-470 and 1910-2000 AD. Smaller fluctuations of less than *c.* 1‰ are probably not significant given the measurement errors involved.

The minimum seen at 1120-1280 AD in the LOI, TOC and chlorin records from UACT6 is interesting in that it coincides with the major depletion event in the bulk organic $\delta^{13}C$ record. These data are consistent if it is assumed that autochthonous organic matter is less depleted than allochthonous organic matter, as is suggested by compound-specific $\delta^{13}C$ analysis of autochthonous and allochthonous biomarkers. It is also assumed that the signal recorded in the sediment has not been modified significantly by diagenetic processes. Hence, the depletion in bulk $\delta^{13}C$ represents a decreased importance in autochthonous inputs to the sediment, and a corresponding increased importance of higher plant matter from the Lochan Uaine catchment.

Dating of events in the lipid record of UACT6 is hindered by the low sample resolution, with only twenty-eight samples analysed for the whole core (Figure 7.2). Also, the need to combine three contiguous 2 mm intervals for each sample means that the time-span represented by each sample is almost 30 cal yr, compared to *c.* 10 cal yr for all other analyses. The downcore changes in concentration seen in many of the more important biomarkers are similar to those in the main bulk measurements. For example, the C_{17} *n*-alkane, the C_{25} HBI alkene, brassicasterol, the C_{21} and C_{23} *n*-alkanes and the C_{23} and C_{25} *n*-alkenes all show concentration minima at around 1100-1250 AD, whilst the C_{29} and C_{31} *n*-alkanes show slight maxima across the same interval. Likewise, some changes across this interval are seen in compound-specific $\delta^{13}C$ values, such as for the C_{17} *n*-alkane and the long chain-length *n*-alkanols,

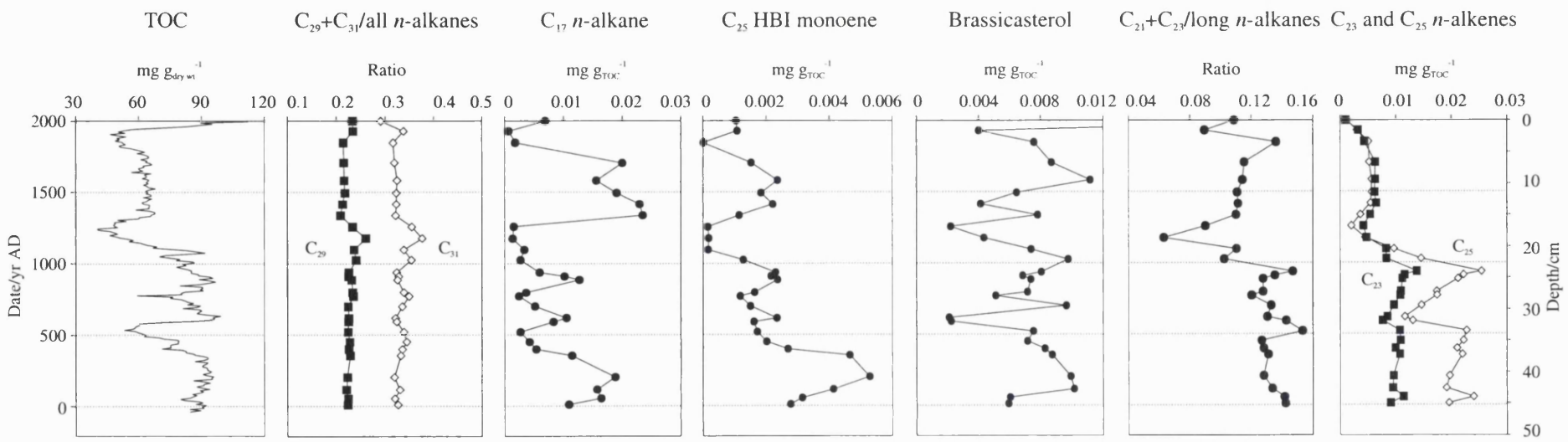


Figure 7.2 Lipid indicators of organic matter source and autochthonous primary productivity, core UACT6, against the preferred dating model. Depth is given at far right.

although given the potential measurement errors associated with the technique the significance of the smaller variations must be questioned.

7.4.2 Comparison of UACT6 with other Holocene climate records

Having constructed 'best estimate' depth-age models for core UACT6 and dated the principal events identified in the sediment record, it is possible to compare the potential climate record of Lochan Uaine with other climate records from the same period. No complete Holocene sequences have been recovered from Lochan Uaine to date. The depth-age models suggest that the master core used in the TIGGER IIa project, UACT4, represents the last *c.* 4000 cal yr. Core UACT6, the main core analysed for this study, represents the last *c.* 2000 cal yr. The comparison between the Lochan Uaine record and other Holocene climate sequences will thus focus on the last 2000 cal yr. This period encompasses both the 'Little Ice Age' and 'Mediaeval Warm Period' climatic events at approximately 1100-1300 and 1500-1850 AD respectively, and both will be discussed in relation to the Lochan Uaine record.

Chapter 1 discussed the present knowledge of Holocene climate. This is based on a wide variety of instrumental, historical and proxy sources, covering a range of different climatic parameters, spatial and temporal scales, and response times (Table 1.1). It is not always possible to compare different proxy climate records. For instance, it may not be suitable to compare the Holocene record from Lochan Uaine, a high altitude Northern Hemisphere lake, with a low altitude Southern Hemisphere lake. Lakes tend to be highly sensitive to local and regional environmental conditions, and are thus less likely to reflect hemispherical or global climate signals. For this reason comparisons will not be made between the Lochan Uaine climate record and hemispheric or global climate signals. Recent reconstructions of such large scale climate signals have focused on the integration of many different proxy methods (*e.g.* Jones *et al.*, 1998; Mann *et al.*, 1998). While this may produce a 'global average' climate signal, the smoothing of climate proxy records from different regions tends to obscure any differences in climate regime between these regions. Briffa and Jones (1993) have shown that spatial coherence between recent instrumental climate records

is low over continental and larger scales. Thus, discussion of the Lochan Uaine climate record will be restricted to a northwest European context.

The comparison of the Lochan Uaine record with other climate records will focus on two different spatial scales. Firstly, the record will be compared with other climate records from Scotland, including those from instrumental data, peat bogs, pollen, and speleothems. These records produced under a similar regional climatic regime should exhibit greater coherence than more distal records produced under slightly differing climatic regimes. However, Thompson (1995) has shown that there is significant spatial coherence between instrumental records of air temperature, and hence presumably between longer proxy records, over regional scales. This coherence is even seen between areas with maritime and with more continental climate regimes. Thus, the second section will focus on comparisons between the Lochan Uaine record and other late Holocene climate reconstructions from across northwest Europe.

7.4.3 Reconstructions of late Holocene climate variability in Scotland

7.4.3.1 Instrumental and historical climate records in Scotland

The longest continuous combined temperature and precipitation record in the world is the Edinburgh time series, with records beginning in 1764 (Thompson, 1995; Conway, 1998). The proximity of Edinburgh to the Cairngorms means that the instrumental record should provide an accurate guide to direction of temperature variations at Lochan Uaine during this period. The actual temperature at Lochan Uaine could be calculated from the Edinburgh data using the method of Agusti-Panareda *et al.* (in press), allowing for the fact that mountain regions tend to amplify the climate signal (Beniston *et al.*, 1997). Precipitation is thought to be less spatially coherent than air temperature, but given the importance of the NAO on climate across northern Britain it is reasonable to assume that the broad precipitation changes seen in the Edinburgh time series will reflect those seen at Lochan Uaine. The main climate changes recorded in the Edinburgh time series include a general increase in temperature over the last two centuries, along with a decrease in the annual temperature range by about 1°C. Stable or slightly increasing temperatures during the nineteenth century are seen across western Europe, although temperatures generally

decreased in eastern Europe (R. Thompson, pers. comm.). The warming during the twentieth century appears to be a global phenomenon (Jones *et al.*, 1998; Mann *et al.*, 1998), and is reflected in the overall decrease in the period of ice-cover at Lochan Uaine as estimated from the Edinburgh time series by Barber *et al.* (1999). No long term trends are seen in the precipitation in Britain, although other long term records show that northern Europe has become wetter over the last few centuries.

Historical records of climate in Scotland date from well before the period of instrumental observation. Lamb (1995) describes a wide variety of such sources. He cites an extension of tillage to higher altitudes in Northumberland and Dartmoor, and a wide distribution of vineyards, as evidence for the Mediaeval Warm Period. Lamb suggests that summer temperatures during this period were 0.7-1.0°C higher than during the twentieth century. Historical evidence is also presented in support of a Little Ice Age cooling in Scotland, including reports of an Inuit [sic] canoe landing on the Scottish mainland, permanent snow on summits in the Cairngorms, failure of harvests, abandonment of settlements, and so on. However, it should be noted that the historical record is fragmentary, with a bias towards recording extreme or unusual events. In particular, the evidence for a pronounced and prolonged Mediaeval Warm Period is not supported by many proxy climate records (Hughes and Diaz, 1994).

7.4.3.2 Pollen palaeoclimate records in Scotland

Much of our knowledge of climatic change in Scotland during the Holocene has come from two sources - studies of pollen and studies of peat bogs. Numerous authors have used the advance and retreat of *Pinus sylvestris*, as indicated by changes in relative pollen concentrations and the presence of *Pinus* macrofossils, as a proxy for Holocene climatic variation (Bennett, 1984, 1989; Dubois and Ferguson, 1985, 1988; Lowe, 1991; Gear and Huntley, 1991; McConnell and Legg, 1995). The major changes in *Pinus* distribution during the Holocene are well documented, including the northward expansion through Britain from *c.* 7500 ^{14}C yr BP onwards, and the subsequent decline at around 4000 ^{14}C yr BP. These changes are typically related to the amelioration of the climate during the early to mid-Holocene climatic 'optimum' and the subsequent climatic deterioration, although there is some disagreement as to

whether this deterioration resulted in a shift to wetter (*e.g.* Anderson *et al.*, 1998) or drier (*e.g.* Gear and Huntley, 1991) conditions. Comparatively few studies have examined the pollen evidence for climate change during the last 2000 cal yr. This is partly due to the low sensitivity of the pollen record to climate change, the wide tolerances displayed by many plants towards climate, the significant lags associated with vegetational migration in response to climatic shifts, and the increasing human influence on the vegetation landscape during the latter part of the Holocene (Lowe, 1991).

One attempt to reconstruct late Holocene climates from pollen data is the study of Huntley (1994), who used pollen assemblage data to reconstruct the mean temperature of the coldest month (MTCO) at the Morrone Birkwoods, a site just southeast of the main Cairngorm massif. This study found that the MTCO varied little from 6000-1500 ^{14}C yr BP, but in the last 1500 ^{14}C yr there were noticeable fluctuations (Figure 7.3). At *c.* 1300 ^{14}C yr BP a warming in MTCO of around 2°C was apparent, to a temperature roughly 1.5°C higher than in the surface sample. This was followed by a cooling to -1.7°C which was only reversed in the topmost sample. Huntley speculated that these fluctuations may correspond to the 'Mediaeval Warm Period' and 'Little Ice Age' events, and notes that the magnitude of temperature change is similar to that quoted by other authors (*e.g.* Lamb, 1995). However, the study suffers from a low sample resolution, with only five samples to cover the last 1500 ^{14}C yr at a resolution of only 300 ^{14}C yr per sample. Also, the temperature reconstruction is based on pollen analysis and is thus susceptible to the problems of delayed species migration and human impact. Nonetheless, the study provides a potentially useful local climate signal with which to compare the Lochan Uaine record (below).

7.4.3.3 Peat palaeoclimate records in Scotland and northern England

The climate record contained in peat bogs tends to relate to species assemblage changes in response to variations in bog surface wetness (Aaby, 1976; Blackford and Chambers, 1991; Barber, 1994; Barber *et al.*, 1994a,b; Battarbee *et al.*, 1996; Chambers *et al.*, 1997; Mauquoy and Barber, 1999a,b; Barber *et al.*, 1999; Charman

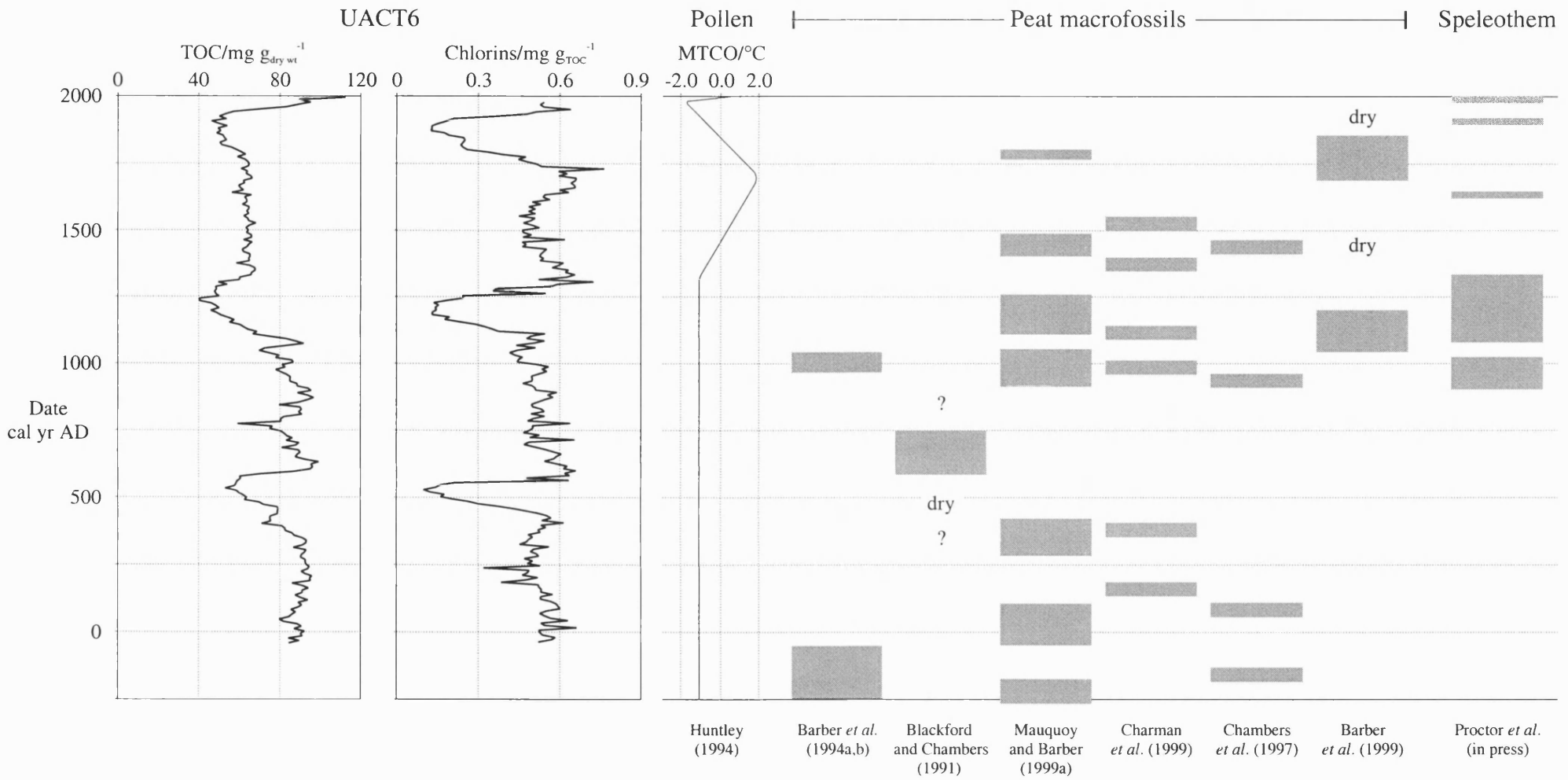


Figure 7.3 Summary of proxy climate reconstructions from Scotland for the last 2000 cal yr. Shaded areas indicate periods of time where a wetter climate has been identified.

et al., 1999). Several studies from Scotland and the northwest of England detect shifts in surface wetness over the last two millennia (Figure 7.3). Barber *et al.* (1994a,b) noted periods of increased surface wetness in bogs across NW Europe occurred at 4000, 3500-3000, 2800-2500, 2000-1800 and *c.* 1000 cal yr BP. These wet periods were caused by higher rainfall and/or lower temperatures, and reoccurred with a periodicity of roughly *c.* 800 cal yr. Blackford and Chambers (1991) detected evidence for a shift to wetter conditions at 1400 BP in five upland blanket mires in Britain. Ten wetter periods in the last 3000 cal yr were seen in two bogs in northern England by Mauquoy and Barber (1999a), occurring at 1770-1880 AD, 1400-1470 AD, 1110-1260 AD, 920-1060 AD, 550-670 AD, 210-360 AD, 30 BC-80 AD, 180-130 BC, 590-520 BC and 760-710 BC. Similarly, Charman *et al.* (1999) recorded a dry shift at 1900 BC, followed by wet shifts at 1550, 950-750, and 200 BC, and 400, 600, 950, 1100, 1350 and 1500 AD. The local extinction of *Sphagnum imbricatum* was dated to 1160-1400 AD in two bogs, 1395-1485 AD in two more bogs, and 1030-1400 AD in a further two bogs by Mauquoy and Barber (1999b), who suggest that the decline may be explained by competition between *Sphagnum* species during the early Mediaeval Warm Period and the Little Ice Age. Chambers *et al.* (1997) detected a number of wet shifts over the last 5500 yr, including one at 1700 BP, and suggest a possible cyclicity of *c.* 210 yr, although this is highly dependent upon the accuracy of the radiocarbon dating. Finally, Barber *et al.* (1999) analysed a peat record from Moine Mhor, a montane blanket bog 6 km west of Lochan Uaine in the Cairngorms. Macrofossil analysed revealed a wet period from *c.* 1050-1200 AD, a dry period from *c.* 1290-1680 AD, a further wet period from 1680-1850 AD, and a final switch to a dry period from 1850 AD onwards. The proximity of this site to Lochan Uaine, both spatially and altitudinally, makes it an important record to compare with UACT6.

7.4.3.4 Speleothem palaeoclimate records in Scotland

Recent analysis of a 1100 cal yr speleothem record form Uamh an Tartair in the Cnoc nan Uamh cave system, Assynt, northwest Scotland, is described by Proctor *et al.* (in press). Comparison of annual stalagmite band width with instrumental records of temperature and precipitation for the last *c.* 120 cal yr reveals a strong correlation

between band width and NAO. This relationship is then extended back in time to infer a 1100 cal yr NAO record. Such a record is of particular importance for the study of the Lochan Uaine proxy climate record, as the North Atlantic climate is thought to be the dominant influence controlling the annual duration of lake ice-cover. The speleothem reconstruction indicates that the NAO has fluctuated between periods characterised by positive or negative states over the last 1100 cal yr. Positive states, associated with warmer, wetter winters, are recorded during the Mediaeval period from 1080-1330 AD, with briefer events occurring from *c.* 910-1020, 1630-1650, 1900-1920 AD, and from 1980 AD to the present (Figure 7.3). Negative states, associated with cooler, drier winters, are recorded from *c.* 1020-1080, 1440-1460, 1600-1620 and 1930-1980 AD. In addition, the entire period from *c.* 1330-1850 AD is characterised by a generally negative NAO, with the exception of the positive event from *c.* 1630-1650 AD as mentioned previously. Proctor *et al.* suggest that this negative NAO is a factor in influencing the cool conditions of the Little Ice Age. Work is underway to extend the speleothem NAO record to cover the last 3000 cal yr (A. Baker, pers. comm.) which will allow comparison with the whole of core UACT6.

7.4.4 Comparison of Lochan Uaine record with proxy climate records from Scotland

It is clear from the above discussion of proxy climate records from Britain that a number of different interpretations of late Holocene climate exist, some of which are contradictory. This is partly, but not entirely, due to the problems mentioned by Jones *et al.* (1998) of comparing proxies which respond to different climatic parameters (temperature, precipitation *etc.*) with varying seasonal importance (*e.g.* winter *vs.* summer temperatures), and with different response times. The lack of comparable climatic reconstructions from montane lakes in northern Britain means that the Lochan Uaine data must always be compared with 'non-equivalent' proxies, such as reconstructions from pollen profiles, peat macrofossils, tree-rings, and so on. The exception is for the last few centuries where instrumental records are available.

7.4.4.1 Comparison with instrumental and historical climate records

The downcore profiles of those variables in UACT6 with a potential climate connection were given in Figures 7.1 and 7.2. Although sampled at the comparatively high resolution of 2 mm, the slow rate of sediment accumulation means that the last 200 cal yr are covered by the top *c.* 4.5 cm. This has implications for the comparison of the sediment record with the Edinburgh time series. The main bulk measurements show significant changes over the last 200 cal yr. Increases are seen in LOI, TOC and chlorin profiles, mainly due to the switch from a period of minimum values to higher values at around 1940 AD. If these increases in lake primary productivity are related to twentieth century warming, the data would support the theory that productivity is enhanced during warmer periods. However, it is possible that variations in the top few centimetres of sediment are a result not of climate change but of processes occurring at or near the mud-water interface such as organic matter mineralisation. Lipid analysis shows that certain components decrease in concentration rapidly below the top few centimetres of sediment, presumably due to diagenetic processes. These include the C_{16} and C_{18} *n*-alkanoic and *n*-alkenoic acids and numerous sterols. Such diagenetic processes may also affect the LOI, TOC and chlorin profiles. Furthermore, the increased bulk organic ^{13}C depletion at the top of UACT6 suggests a decreased importance of autochthonous inputs relative to allochthonous inputs. This is in contrast to the increase in lake productivity suggested by the LOI, TOC and chlorin profiles, although the interpretation of the $\delta^{13}C$ curve relies on the assumption that autochthonous matter is less depleted in ^{13}C than allochthonous matter. Given the short length of the Edinburgh instrumental record and the problems of low sample resolution and organic matter diagenesis, it is thought unwise to over-interpret the comparison between instrumental and proxy records in the top few centimetres of UACT6.

The problem of comparison with the instrumental record is more acute for the lipid analyses. Due to the lower resolution only three non-contiguous samples from the last 200 cal yr were analysed. Large decreases in concentration of some components are seen, such as the sterols and short chain-length *n*-alkanoic and *n*-alkenoic acids mentioned above. It is thought that these decreases are due to diagenetic processes

near the mud-water interface and do not represent a response to climate change. It is perhaps significant that components thought to be less susceptible to diagenesis in the sediment, such as the *n*-alkanes, show very little variation over the last few hundred years.

Over the full *c.* 2000 cal yr record of UACT6 the LOI and TOC profiles both exhibit a comparable series of maxima and minima, thought to date from *c.* 460-560, 1120-1280 and 1740-1940 AD. The minima are more pronounced in the chlorin profile which is thought to give a reliable measure of lake productivity. Similar profiles are seen in C_{17} *n*-alkane and C_{25} HBI monoene concentrations. These are also considered reliable autochthonous indicators, although these records suffer slightly from the low sampling resolution. Neither the C/N nor C/H ratio are thought to be sensitive enough to display the variations in productivity detected by other analyses, and neither will be discussed further here with respect to climate change.

7.4.4.2 Comparison with pollen palaeoclimate records

Comparison of UACT6 with Scottish pollen records is hampered by the lack of high resolution records from the last two millennia, and the minimal amount of vegetation change during this period that can be attributed solely to climatic forcing. The pollen-based reconstruction of mean temperature of the coldest month during the Holocene by Huntley (1994) fails to mention the strong possibility that vegetation assemblage composition and distribution, and hence pollen composition and distribution, may have been influenced by human activity over the last few millennia. Although Huntley presents evidence for Mediaeval Warm Period and Little Ice Age temperature variations, the low (300 ^{14}C yr) sample resolution limits the comparisons that can be made with a high resolution decadal record such as that in UACT6.

7.4.4.3 Comparison with peat palaeoclimate records

The three minima seen in the LOI, TOC, chlorin, and algal/bacterial biomarker profiles, representing periods of low lake primary productivity, date to around 460-560, 1120-1280 and 1740-1940 AD. Allowing for dating errors, these last two periods coincide closely with the wet periods seen by Barber *et al.* (1999) in the

Moine Mhor peat record 6 km west of Lochan Uaine. These wet periods occurred at *c.* 1050-1200 and 1680-1850 AD, with dry periods from *c.* 1290-1680 AD and from 1850 onwards. There is, however, a danger in assuming that these two records show concurrent climate variability in the Cairngorm mountains. The flexibility in the dating model makes it comparatively easy to assume that the dates from UACT6 are in error and to 'fix' the dates to match those from Moine Mhor. A similar problem can frequently be seen in the assignation of climatic events to the so-called 'Mediaeval Warm Period' or 'Little Ice Age' climatic anomalies, generally assumed to have occurred at around 1100-1300 and 1500-1850 AD respectively (Bradley and Jones, 1993; Hughes and Diaz, 1994; Lauritzen and Lundberg, 1999; Verschuren *et al.*, 2000).

It is also not certain that montane lakes and bogs respond to the same climate variations. The changes seen in peat bog sequences are usually a consequence of changes in surface wetness. This will be influenced by precipitation mainly, but also by temperature through its effect on evapotranspiration (Barber, 1994). If, as hypothesised, the productivity in Lochan Uaine is controlled mainly by the duration of winter ice-cover then temperature is likely to be the most important climatic parameter. With such a process the effect of precipitation would be relatively minor. However, the main differences between peat bog and lake sediment proxy climate records are likely to lie not in the climatic parameters to which the systems are responding, but in the seasonality of that response. The duration of ice-cover at Lochan Uaine depends mainly on temperatures during the colder seasons, not just winter but particularly spring when ice break-up occurs (Barber *et al.*, 1999). By contrast, peat bog surface wetness is most likely to affected by high evapotranspiration during the summer months, rather than during winter when evapotranspiration is low and the peat is permanently saturated. It is possible that differences between peat bog and lake sediment proxy climate reconstructions could reflect seasonal variations in the climate regime.

For the reasons given above, the correlation between the low chlorin events in UACT6 and climatic events in peat records must be treated with caution.

Nonetheless, if we assume that the dating of UACT6 is broadly correct then the coincidence of wet periods in the Moine Mhor peat record with LOI, TOC and chlorin minima in UACT6 is significant. If the climate of Scotland is mainly controlled by the NAO, wet bog surfaces are most likely to result from periods of strongly positive NAO which are characterised by increased precipitation and warmer winter temperatures (Perry, 2000; Sarachik and Alverson, 2000). The low LOI, TOC and chlorin values associated with these events suggests that productivity is decreased during periods of warmer temperature. This contradicts the hypothesis advanced previously that warm years are associated with greater productivity, as early ice break-up results in a longer growing season (Willemse and Törnqvist, 1999). By contrast, these data support the hypothesis based on recent observations that warm winters are followed by nutrient minima, resulting in reduced lake primary productivity (D. Monteith unpublished). Periods of peat bog wetness which may coincide with some or all of the chlorin troughs in UACT6 are also recorded by Blackford and Chambers (1991), Mauquoy and Barber (1999a) and Charman *et al.* (1999). In the case of Mauquoy and Barber, three of the ten wet shifts they observe in the last 3000 cal yr are dated to 550-670, 1110-1260 and 1770-1880 AD, comparable to the ages of the chlorin minima (460-560, 1120-1280 and 1740-1940 AD). As before, though, it must be born in mind that there are likely to be significant errors associated with the dating, not just of UACT6 but of the peat bogs which also rely principally on radiocarbon chronologies.

7.4.4.4 Comparison with speleothem palaeoclimate records

The Uamh an Tartair speleothem record indicates periods of positive NAO from *c.* 910-1020, 1080-1330, 1630-1650, 1900-1920 AD, and from 1980 AD to the present, and negative states from *c.* 1020-1080, 1440-1460, 1600-1620, 1930-1980 AD, and most of the period from *c.* 1330-1850 AD (Proctor *et al.*, in press). Of the two LOI/TOC/chlorin minima occurring during the last 1100 cal yr, the 1120-1280 AD event falls within the Mediaeval period of positive NAO. This appears to be at odds with the earlier hypothesis that lake productivity is decreased during cold periods, as the NAO record suggests a warm, wet climate. By contrast, the 1740-1940 AD event in the LOI/TOC/chlorin record is broadly synchronous with a switch from strong

negative NAO to strong positive NAO. There is no obvious explanation for these results. Even when smoothed, the major fluctuations in the speleothem NAO reconstruction occur at a far greater frequency than do the major fluctuations in the UACT6 productivity record. It is clear that further work is required to attempt to link these records.

7.4.5 Evidence for the Mediaeval Warm Period and Little Ice Age in UACT6

The lack of a reliable chronology for UACT6 means that the dating model as given in Figure 3.16 is potentially flexible. There is a danger in assuming synchroneity between events seen in UACT6 and those in other proxy records, as noted earlier. However, given that two such events are thought to occur within the timescale of the UACT6 core it is worth examining whether any evidence for these can be seen. These two events are the Mediaeval Warm Period and the Little Ice Age, described in greater detail in Chapter 1. The Mediaeval Warm Period is thought to have lasted from around 1100-1300 AD and the Little Ice Age from around 1500-1850 AD (Bradley and Jones, 1993; Hughes and Diaz, 1994; Lamb, 1995; Lauritzen and Lundberg, 1999; Verschuren *et al.*, 2000). There has been much debate on the nature and extent of these climate events, although the evidence for the existence of a Little Ice Age seems more compelling than that for a Mediaeval Warm Period.

In Lochan Uaine the three minima in lake primary productivity are dated to 460-560, 1120-1280 and 1740-1940 AD. The middle event appears to overlap closely with the approximate timing of the Mediaeval Warm Period. This suggests that productivity is decreased during warm periods, an interpretation that is at odds with the hypothesis linking warm years to longer growing seasons and increased productivity (Willemse and Törnqvist, 1999). However, these results appear to support the hypothesis that warm years are followed by decreased productivity in response to the greater retention of nutrients in the catchment (D. Monteith unpublished). The interpretation of these results should be treated with caution for two reasons. Firstly, multi-proxy climate reconstructions have failed to find convincing evidence for the existence of a multi-century Mediaeval Warm Period across Europe (Hughes and Diaz, 1994; Briffa *et al.*, 1995). Secondly, the documentary evidence cited by Lamb (1995) suggests an

increase in summer temperatures during the Mediaeval period. Even if genuine, such a temperature rise may not have much impact at Lochan Uaine where the ice-cover duration, and hence lake primary productivity, is determined by temperatures during the colder seasons.

By contrast, the early part of the most recent (1740-1940 AD) low productivity event in UACT6 appears to overlap with the end of the Little Ice Age. This is analagous to the relationship seen between UACT6 productivity and the Uamh an Tartair speleothem NAO reconstruction (Proctor *et al.*, in press), where the two UACT6 productivity minima coincide with periods of different NAO state, and the most recent minimum spans a change in NAO state from one extreme to the other. Evidence for the Little Ice Age in the Lochan Uaine sediment organic matter record is thus unconvincing, even allowing for the potentially large dating inaccuracies. It is interesting that a potential Little Ice Age signal observed in the diatom-based pH reconstruction of UACT4 bears no relation to the LOI fluctuations in the core (Battarbee *et al.*, 1996). As with the Mediaeval Warm Period discussed above, the evidence for the Little Ice Age as a multi-century period of consistently lower temperatures is questioned by numerous recent studies (*e.g.* Bradley and Jones, 1993) which suggest rather that the Little Ice Age was a period of both warm and cold anomalies which varied spatially. Although the UACT6 LOI, TOC and chlorin profiles are dominated by the three concentration minima, they also exhibit smaller magnitude fluctuations throughout. Some of this variability is likely to be random noise, but some is likely to reflect genuine productivity variations. This fine-scale variability is similar to that seen in other high resolution proxy records such as tree-rings, ice cores and speleothems, an may reflect a response to climate variability at annual to decadal rather than centennial timescales.

7.4.6 Reconstructions of late Holocene climate variability in NW Europe

Any proxy climate records from Lochan Uaine may be expected to show similar trends to other palaeoclimate records from Scotland, as climatic change appears to be reasonably homogenous over small spatial scales. However, the discovery that climate variability is also coherent over larger scales suggests that palaeoclimate records from

Scotland should show similarities to those from other parts of northwest Europe (Thompson, 1995). This section examines these correlations, beginning with a discussion on the current knowledge of late Holocene climate variability in northwest Europe. As was the case with Scotland, palaeoclimate records from northwest Europe originate from a variety of different proxies. Some of these are not available in the UK during the late Holocene period, such as reconstructions based on lake varves or glacier advances.

7.4.6.1 Instrumental and historical climate records from NW Europe

In addition to the Edinburgh time series in Scotland, numerous instrumental climate records of the last 200-300 cal yr exist from other parts of Europe. Some of these are listed by Thompson (1995). They include the Central England temperature record, which is the longest record of mean monthly temperatures in the world, beginning in 1659 AD (Manley, 1974; Parker *et al.*, 1992), although unlike the Edinburgh time series this record does not include precipitation data. Other long temperature records are from Utrecht (1706 AD), Berlin (1755 AD), Stockholm (1756 AD), and Uppsala (1774 AD). Complex demodulation of these records by Thompson shows that changes in mean annual temperature range were coherent across much of Europe. In particular, the period from *c.* 1910-1930 was very 'maritime' in character, as shown by the low yearly temperature ranges in each of the long records. By contrast, the periods displaying the greatest 'continentality' were during the 1770s and 1800s when yearly temperature ranges were high. Similar changes have been recorded elsewhere in Europe including the Alps, where decreasing temperatures during the nineteenth century were followed by increasing temperatures during the twentieth century (Psenner and Schmidt, 1992; Sommaruga-Wögrath *et al.*, 1997; Koinig *et al.*, 1998).

In some areas it has been possible to add to instrumental temperature records using historical sources. Pfister (1992) used documentary evidence to extend the temperature curve for Switzerland back to 1535 AD. The resolution and accuracy of such reconstructions are obviously not as high as for instrumental records. For instance, the reconstruction of winter temperature from 750-1300 AD by Pfister *et al.* (1998) is based upon historical observations of anomalous winters, and as such is not

a continuous record but is dictated by the presence or absence of extreme climatic events. The decrease in number of historical sources with increasing age is marked, so that prior to 1000 AD gaps of several decades can exist between sources. Nonetheless, Pfister *et al.* were able to make inferences about the climate of the last millennium. They concluded that severe winters were less frequent from 900-1300 AD than during the ninth century and from 1300-1900 AD. They suggested that this was due to the influence of the Mediaeval Warm Period, while also pointing out that although winter temperatures from 1180-1299 AD were similar to those during the twentieth century, the corresponding temperatures from 1090-1179 AD were similar to those during the Little Ice Age. The Little Ice Age itself was thought to have begun with a 1°C cooling from 1300-1329 (Pfister *et al.*, 1998).

7.4.6.2 Tree-ring climate reconstructions from NW Europe

Studies of tree-ring widths, densities and isotope ratios during the Holocene are important in that they provide accurately datable, annual records over periods longer than those provided by instrumental records. Long tree-ring sequences have been constructed from various parts of Europe including Ireland, Fennoscandia and Germany. Briffa *et al.* (1990) describe a 1400 cal yr temperature reconstruction from Fennoscandia based on tree-ring widths. They show that there is great variability throughout this period at annual, decadal and centennial timescales. Regarding the Mediaeval Warm Period and the Little Ice Age, Briffa *et al.* show that there is no convincing evidence in the tree-ring data that these were major climatic events lasting several centuries or more. During the period normally associated with the Mediaeval Warm Period, reconstructed summer temperatures in Fennoscandia were very warm during the late twelfth century but very cold during the early twelfth century, and were similar to the 1951-1970 AD average during the eleventh and thirteenth centuries. Likewise, although the Little Ice Age is variously quoted as lasting for several centuries, Briffa *et al.* identify anomalously cold temperatures from 1570-1650 AD only. Similar cold periods were recorded in the late eighth to early ninth centuries, the early twelfth century, and the late fourteenth century. Briffa *et al.* conclude that either the northern Fennoscandian climate was remarkably different from that in the

rest of Europe, or that the significance of the Mediaeval Warm Period and the Little Ice Age has been overstated.

Other studies fail to identify long term climate anomalies in tree-rings on centennial timescales. Lipp and Trimborn (1991) reconstructed summer temperature from 1004-1982 AD in the Black Forest, Germany, from $\delta^{13}C$ values of cellulose. A general warming from 1000-1400 AD and a decrease from 1400 AD to present were overlain by many smaller fluctuations on an annual and decadal timescale. It should be noted that $\delta^{13}C$ is unlikely to respond solely to climate, but also to such factors as atmospheric CO_2 content and local growing conditions (see Chapter 4). A 1000 cal yr temperature reconstruction based on ring widths shows that the eleventh and twelfth centuries in the northern Urals were characterised by cool conditions at the supposed height of the Mediaeval Warm Period (Briffa *et al.*, 1995). Likewise, the period associated with the Little Ice Age (*c.* 1500-1850 AD) was characterised by a series of fluctuations between cool and warm conditions. Many of the most extreme events seen in tree-ring records are not long term decadal and centennial climate anomalies, but short term fluctuations lasting no more than a few years. These are often linked to global climate cooling following major volcanic eruptions (Baillie and Munro, 1988; Kelly *et al.*, 1989; Baillie, 1994; Briffa *et al.*, 1998).

7.4.6.3 Other proxy records of NW European climate variability

A wide variety of other proxy methods have been used to reconstruct late Holocene climate in northwest Europe. Although these are too numerous to discuss in detail here, it is worth mentioning some of the techniques and their findings.

In common with Scotland, peat and pollen records have been widely used across Europe. For example, the classic study of Aaby (1976) on peat sequences in Denmark revealed cyclic climate variations over the last 5500 cal yr with a periodicity of *c.* 260 cal yr, although given potential inaccuracies in the radiocarbon dating it is not possible to say whether these events are truly cyclic or merely episodic. The problems with using pollen data to infer climate change over the last 2000 cal yr are the same in northwest Europe as for Scotland - namely, that pollen abundances are likely to be

determined not just by climate change, but also by factors such as species migration and human influence (Lowe, 1991). The slow rate of migration of many species is particularly noticeable during the Holocene as vegetation has responded to the deglaciation. Attempts to reconstruct regional Holocene climate from large numbers of pollen records have also been hampered by dating inaccuracies and the insensitivity of many species to small amplitude climate variations. It is perhaps understandable that such attempts have generally been restricted to reconstructing climate variations at a temporal resolution of several centuries or millennia (*e.g.* Berglund, 1991; Huntley and Prentice, 1993; Huntley, 1999). These reconstructions are obviously unsuitable for comparison with the high resolution record from Lochan Uaine.

Climate reconstructions at much higher resolutions than are possible from pollen data have come from varve, glacier and speleothem studies. Under certain conditions varve thickness is shown to be climatically sensitive (Leemann and Niessen, 1994b). Zolitschka (1996) suggests that in proglacial lakes with clastic varves under continental climate regimes the summer temperature is the main climatic control on varve thickness, while in oceanic climate regimes the main control is mean summer precipitation. In lakes with organic varves the relationship is more complex. At one such lake, Lake Holzmaar in Germany, Zolitschka determines that varve thickness is controlled by winter and spring temperatures. His analysis of a 1000 cal yr varve sequence identifies periods of colder winter and spring temperatures from 1250-1310, 1470-1510 and 1650-1890 AD. These are attributed either to the effects of solar forcing or to the influence of volcanic activity on climate.

Glacier advances and retreats are determined by both temperature and precipitation, although Meier (1984) and Oerlemans (1988) both assumed temperature to be the more important variable. Nesje and Johannessen (1992) compiled data on global glacier activity during the Holocene. Although they observed a strong link between glacier advances and the combined effects of high volcanic aerosol levels and decreasing northern hemisphere summer insolation, by grouping the data into 250 yr blocks any glacier movements on shorter timescales are obscured. Documentary evidence suggests that there may have been increased glacial activity during the

sixteenth to seventeenth centuries, usually taken as an indication of Little Ice Age cooling (Lamb, 1995). Other studies of north European glaciers present evidence for pulses of glacial advance over the last two millennia, although the reliance of these studies on radiocarbon or lichenometric dating makes comparisons with other proxy records less reliable (Nesje and Dahl, 1991; Werner, 1993; Dahl and Nesje, 1994; Leemann and Niessen, 1994a).

Lauritzen and Lundberg (1999) used a speleothem $\delta^{18}O$ record from northern Norway to reconstruct absolute temperatures throughout the Holocene. These temperatures compare favourably with those reconstructed from the GISP2 Greenland ice core. The authors also claim that the temperature record of the last 2000 cal yr corresponds well with established records as given in Crowley and North (1991). The main features are 1) temperatures 1°C warmer than the modern mean during the Roman period from 0-400 AD, 2) the 'Dark Age (Mediaeval) Cold Epoch' from 500-1000 AD, 3) the 'Mediaeval Optimum' from 1100-1300 AD with temperatures 1°C above present, 4) Little Ice Age deterioration from 1450 AD with cold periods during the seventeenth and nineteenth centuries. However, given that the nature of both the Mediaeval Warm Period and the Little Ice Age are currently under debate (Briffa *et al.*, 1990, 1995; Bradley and Jones, 1993; Hughes and Diaz, 1994) it is possible that the interpretation of the speleothem data may need revision.

7.4.7 Comparison of Lochan Uaine record with other proxy climate records from NW Europe

Comparisons between the sedimentary record of Lochan Uaine and climate records from northwest Europe suffer from many of the same problems as were discussed previously in relation to Scotland. The records are of variable length and resolution, respond to different climatic elements (temperature, precipitation) and are sensitive to different seasons. The main features in core UACT6, which are seen in the LOI, TOC, chlorin and lipid biomarker records, are dated to 460-560, 1120-1280 and 1740-1940 AD. It is difficult to find climatic reconstructions from anywhere in northwest Europe which show concurrent fluctuations in climate.

The difficulties of using northwest European instrumental records in evaluating climatic impacts at Lochan Uaine are the same as for the Edinburgh time series discussed above, namely that the length of instrumental records is too short and the accumulation rate of Lochan Uaine too slow to allow adequate comparison. Furthermore, given the coherence between the Edinburgh time series and other northwest European instrumental records (Thompson, 1995), the interpretation of the comparisons are the same. Increases are seen in LOI, TOC and chlorins over the last 200 cal yr, but the resolution of UACT6 is too low to determine whether this is a response to climate change as shown by the instrumental records. The large magnitude of the UACT6 productivity minimum from 1740-1940 AD suggests a large magnitude climate change, but the instrumental data do not support such an interpretation. Likewise the main features of the instrumental records, such as the decrease in yearly temperature range over the last 200 cal yr and the highly oceanic climate regime from 1910-1930 AD, do not have any obvious analogue in the sediment data. The timing of the 1740-1940 AD event in UACT6 appears too late to be associated with a Little Ice Age cooling event. Lipid concentrations from UACT6 cannot be compared with the instrumental data as only three samples are analysed from the section of core corresponding to the instrumental period.

Climate reconstructions for the last 2000 cal yr based on pollen data generally have a resolution too low to allow comparison with the Lochan Uaine data. They are insensitive to small amplitude climate variations and too easily affected by non-climatic influences. By contrast, peat bogs provide a potential high resolution climate signal. However, the *c.* 260 cal yr cyclicity recorded by Aaby (1976) is considerably greater than the main features in UACT6 which appear to have a recurrence interval of around 700 cal yr. Other cores analysed from Lochan Uaine appear to contain higher frequency variations, most notably UACT3 and UACT4 in which the LOI maxima and minima vary with a periodicity of around 200 cal yr in the older parts of the core. However, the radiocarbon dating of both the peat and lake sequences does not provide sufficient accuracy to determine whether the variations observed are cyclic or merely episodic.

Although tree-rings provide a high resolution climate record of the whole 2000 cal yr period represented in UACT6, the variability evident in tree-ring records tends to occur over annual to decadal timescales (Baillie and Munro, 1988; Kelly *et al.*, 1989; Briffa *et al.*, 1990, 1995, 1998; Lipp and Trimborn, 1991; Baillie, 1994). The bulk measurements from UACT6 suggest that the three main depletion events in LOI, TOC and chlorins last for 1-200 cal yr each. The duration of these events shows greater similarity to the duration of the cold events identified in the Lake Holzmaar varve record (Zolitschka, 1996). These cold periods were dated to 1250-1310, 1470-1510 and 1650-1890 AD, and two of these are thus of comparable age to the 1120-1280 and 1740-1940 AD chlorin minima in UACT6. Zolitschka attributed these periods mainly to sunspot minima, but also to other factors such as increased volcanic activity for the period 1715-1890 AD. The varve thickness appears to be driven mainly by winter and spring temperature. If the productivity in Lochan Uaine is primarily determined by the duration of ice-cover, the winter and spring temperatures are of greater importance than summer temperatures. It is possible that the Holzmaar varve sequence is recording the same signal that drives productivity in Lochan Uaine, but is not seen in records such as tree-rings which are more sensitive to summer temperatures.

As with pollen records, records of glacial advances and retreats in Europe during the last 2000 cal yr tend to lack the resolution and chronological control to allow useful comparison with the Lochan Uaine sediment record, at least until the last few centuries where, as with instrumental records, the problem is superseded by that of the low sediment accumulation rate in Lochan Uaine. Glacial advances and retreats have almost certainly occurred throughout the last 2000 cal yr, but there is no general consensus on when these have occurred. Evidence for glacial advances attributed to Little Ice Age cooling is strong, as is that for their subsequent retreat (Lamb, 1995). It is possible that the 1740-1940 AD LOI/TOC/chlorin minima in UACT6 is a response to Little Ice Age cooling, but without better dating control this remains speculation. Similarly, some of the temperature changes recorded in a Norwegian speleothem by Lauritzen and Lundberg (1999) may coincide with the minima in UACT6. The 'Dark Age (Mediaeval) Cold Epoch' from 500-1000 AD, the 'Mediaeval Optimum' from

1100-1300 AD and the Little Ice Age cold period during the nineteenth century could conceivably correspond the the UACT6 minima at 460-560, 1120-1280 and 1740-1940 AD. However, this would suggest that the minima in UACT6 are caused by both cold and warm climate anomalies rather than the same climatic forcing. The data are also at odds with recent tree-ring and instrumental records which question the duration, regional coherence and significance of the Mediaeval Warm Period and the Little Ice Age (Briffa *et al.*, 1990, 1995; Bradley and Jones, 1993).

7.4.8 Potential cyclicity in the Lochan Uaine sediment record

The above sections have compared the Lochan Uaine sediment record to other palaeoclimate records from Scotland and northwest Europe in an attempt to determine whether they show synchronous changes, and hence whether the variations seen in organic components in Lochan Uaine are a response to climate change. Given the recurrent nature of maxima and minima recorded in LOI and other bulk measurements from Lochan Uaine cores, it is worth considering whether these variations could represent a cyclicity, and if so what the forcing mechanism could be.

Variations in the amount of solar radiation reaching the earth are widely cited as an influence on climate change. The Milankovitch cycles caused by changing orbital parameters at millennial timescales are well documented (Lowe and Walker, 1997). Over a much shorter timescale, the annual solar cycle is obviously of great importance. However, evidence in proxy records for cyclicity at periodicities greater than 1 yr, but shorter than Milankovitch cycles, is poor.

The best studied cycle is the 11 yr sunspot cycle which has been reconstructed for the past few centuries from instrumental and historical records (Schove, 1967; Eddy, 1976). In fact, even this is not perfectly cyclic but varies in length between *c.* 10-12 yr (Friis-Christensen and Lassen, 1991). Some studies find evidence for the 11 yr cycle in proxy records, such as tree-ring ^{14}C and ice core ^{10}Be (Attolini *et al.*, 1991; Stuiver and Braziunas, 1993), whereas others find no such evidence (Stuiver, 1980). Longer periodicities are frequently identified in proxy records (Gleissberg, 1965; Schove, 1967; Cole, 1973; Feynman and Fougere, 1984; Schove, 1987; Stuiver and Braziunas,

1989, 1992, 1993; Anderson, 1992; Schlesinger and Ramankutty, 1994; Waple, 1999; Hong *et al.*, 2000). Like the 11 yr cycle these are not perfectly cyclic, and the calculated periodicity can change depending on the method of spectral analysis used (Stuiver and Braziunas, 1992).

The lack of strong evidence for decadal to centennial solar cyclicity in proxy records is probably a function of the small magnitude of variation involved. During the 11 yr cycle total solar irradiance varies by only 0.1-0.3%, which is insufficient to alter climate significantly (Eddy *et al.*, 1982; Vita-Finzi, 1995; Beer *et al.*, 2000). Over longer timescales variability in irradiance may be greater, although the influence on climate is still likely to be minimal (Kelly and Wigley, 1990, 1992; Schlesinger and Ramankutty, 1992). Hence, it is difficult to conceive how solar variability alone would be sufficient to alter climate at decadal and centennial timescales to the extent suggested by the Lochan Uaine sediment record and other Holocene climate records.

Analysis of potential cyclicity in LOI and other organic components in cores from Lochan Uaine is hampered by the lack of adequate dating control. This makes it impossible to determine whether the observed variations are cyclic or episodic. Comparison of the number of distinct LOI fluctuations in core UACT4 with the radiocarbon dates suggests a periodicity of *c.* 200 cal yr for these fluctuations (Battarbee *et al.*, 1996). By contrast, the three principal fluctuations in chlorin concentration in core UACT6 appear to have a periodicity of *c.* 700 cal yr, although additional fluctuations of smaller magnitude are apparent in the LOI and TOC profiles which allow the correlation with UACT4 to be made (Figure 3.7). Periodicities of around 700 cal yr are not seen in many Holocene palaeoclimate records from northwest Europe. One exception is the *c.* 800 cal yr periodicity recorded in reconstructed bog surface wetness at Bolton Fell Moss, northern England (Barber *et al.*, 1994a,b). This was thought to be ocean-driven. If the variations in UACT6 and at Bolton Fell Moss are comparable, this appears to support the hypothesis that the productivity variations observed at Lochan Uaine are a response to forcing by the North Atlantic climate.

It is also interesting to compare the UACT6 productivity record with reconstructed solar variations. The minima in chlorin concentration in UACT6 are dated to 460-560, 1120-1280 and 1740-1940 AD. Periods of low sunspot activity, associated with decreased total solar irradiance, are thought to have occurred from 1010-1050 AD (the 'Oort' minimum), 1280-1340 AD (the 'Wolf' minimum), 1420-1530 AD (the 'Spörer' minimum), 1645-1715 AD (the 'Maunder' minimum), 1795-1830 AD (the 'Dalton' minimum) and 1880-1915 AD (the 'modern' minimum) (Vita-Finzi, 1995). There is thus little evidence to suggest a correlation between productivity and sunspot minima. The 1120-1280 AD chlorin minimum falls between two sunspot minimum, while two sunspot minima lie within the 1740-1940 AD chlorin minima. The lack of correlation is perhaps not surprising given the limited evidence for climate change related to solar variability seen in other proxy records.

7.5 Summary

This chapter has discussed the possibility that the sedimentary organic matter record of Lochan Uaine contains a response to late Holocene climate variability. Analysis of core UACT6, representing the last *c.* 2000 cal yr of sediment accumulation, reveals synchronous variations in a number of measured parameters, including LOI, bulk organic $\delta^{13}C$, and concentrations of TOC, chlorins, and biomarkers of aquatic organisms. The three main periods of low LOI, TOC, chlorins and aquatic biomarkers are dated to 460-560, 1120-1280 and 1740-1940 AD, although numerous variations of smaller magnitude are observed throughout the core. These variations are thought to indicate changes in lake primary productivity. A selection of the main productivity indicators is presented in Figure 7.4. However, it is not yet possible to apply an unambiguous climatic interpretation to these productivity changes, as it is not known whether increased productivity is associated with warmer or colder climatic conditions. Willemse and Törnqvist (1999) suggest that higher temperatures result in higher productivity, whereas the data of D. Monteith (unpublished) suggest that the opposite is true, and higher productivity occurs as a result of lower temperatures.

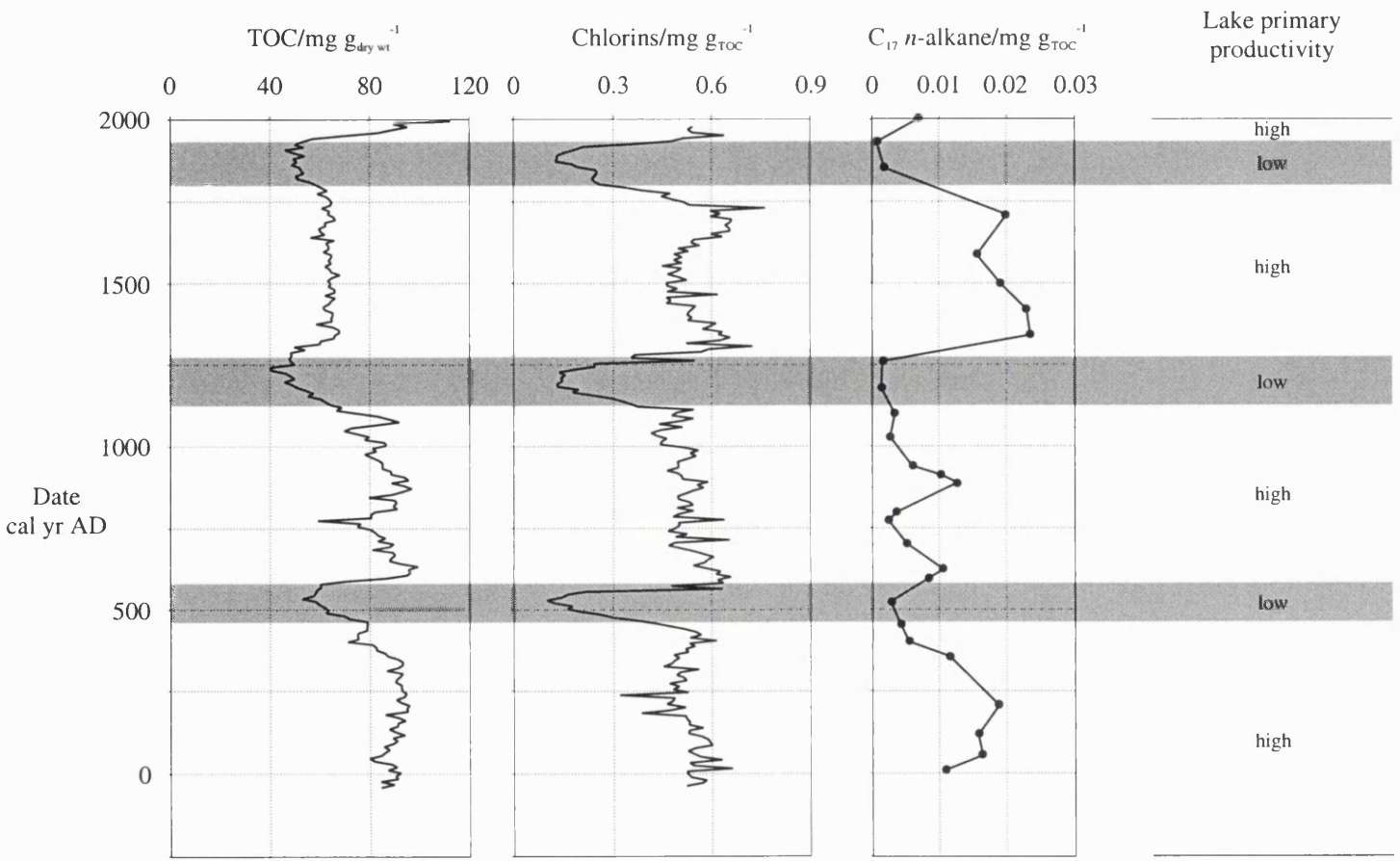


Figure 7.4 Summary of selected productivity indicators in Lochan Uaine core UACT6.

The organic matter record of UACT6 is compared with late Holocene climate records from Scotland and northwest Europe. These records originate from a variety of sources, including instrumental measurements, historical documents, peat bog sequences, tree-rings, speleothems, and varved lake sediments. There is no convincing evidence that any other proxy records show events of comparable age, duration, and periodicity to those seen in Lochan Uaine. The closest comparisons appear to be with peat bog records from northern Britain. In particular, the bog surface wetness record from Moine Mhor, 6 km west of Lochan Uaine, indicates periods of wetness from *c.* 1050-1200 and 1680-1850 AD. These broadly coincide with the periods of low productivity recorded in UACT6 from 1120-1280 and 1740-1940 AD. As the Scottish climate is dominated by the influence of the NAO, it is possible to say that increased wetness is related to higher winter temperatures. Hence, the UACT6-Moine Mhor correlation suggests that low productivity in Lochan Uaine is associated primarily with higher winter temperatures. This contradicts the hypothesis that increased productivity is a result of warmer summer temperatures and a correspondingly longer growing season, but supports the alternative hypothesis that warm temperatures reduce productivity as nutrients are retained in the catchment. Indeed, the effect of seasonal and annual temperature variability on productivity in mountain lakes is one of the major gaps in our understanding of lake sediment climate records.

Other climate reconstructions show even less relationship with UACT6 than do peat bog sequences. Records with an annual resolution, such as those from tree-rings, speleothems and varves, tend to be dominated by short term variability at annual to decadal timescales. This often has the effect of obscuring evidence of longer climatic trends at centennial and millennial timescales. Instrumental climate records are much more accurate and can be used to reconstruct long term trends. However, instrumental records are only available for the last 2-3 centuries. This is not long enough to allow comparison with records such as UACT6 which have a decadal sampling resolution. Pollen records suffer from the problem that they respond slowly to climate changes and rarely indicate climate change at less than centennial timescales. They are comparatively insensitive to low magnitude climatic variability.

In Scotland, any pollen-climate relationship for the last few thousand years has probably been distorted or obscured by anthropogenic influences.

The comparison of the Lochan Uaine record and other climate records highlights a number of difficulties regarding the use of lake sediments to investigate climate change, and in the use of proxy climate records in general. The seasonality of response varies between different proxy indicators, so that a record which responds primarily to summer temperature may not show the same trends as one which responds to winter temperature. This may be significant at Lochan Uaine, as the influence of the NAO on ice-cover duration suggests that temperatures during the colder seasons may be more important than those during summer. There is a lack of high resolution records covering 2000 cal yr or more of Holocene climate history. This was mentioned previously with respect to instrumental records, but is also true of many tree-ring and speleothem records.

One of the major obstacles to the interpretation of the Lochan Uaine lake sediment record is the lack of a reliable chronology. Any sequences which rely on radiocarbon dating, including most lake sediments and peat bogs, are subject to the errors inherent in the radiocarbon calibration. Error margins associated with calibrated radiocarbon dates are often several hundred years in magnitude. This is sufficient to prevent the accurate correlation between sequences of events occurring at decadal timescales. An attempt to validate the UACT6 chronology by analysis of microtephra layers was unsuccessful. However, the development of better dating methods is considered essential to the further use of lake sediment records to study Holocene climate variability at decadal and centennial timescales.

7.6 Conclusions

This thesis has described the geochemical analysis of the sedimentary organic matter fraction of Lochan Uaine, a remote mountain lake in the Cairngorms, Scotland, with respect to late Holocene climate variability. The main conclusions of the work can be summarised as follows:

- Cores recovered from Lochan Uaine exhibit significant fluctuations in the ratio of organic to mineral matter (LOI).
- The LOI variations can be used for core correlation. This correlation may be used to derive a chronology for an undated core from a radiocarbon dated core.
- Radiocarbon dating of core UACT4 indicates a substantial input of inactive ('old') carbon to the sediment, giving an error of *c.* 500 ^{14}C yr (Battarbee *et al.*, 1996). It is necessary to correct radiocarbon ages for this old carbon error prior to calibration of the ages and transfer of the chronology to core UACT6.
- The chronology constructed for core UACT6 suggests that the core represents the last *c.* 2000 cal yr of sediment accumulation.
- Validation of radiocarbon-based chronologies by the identification of microtephra layers is problematic. Such layers are not stratigraphically well-constrained. This is thought to be due to long term inwash of tephra shards from the lake catchment.
- Carbon, hydrogen and nitrogen concentrations from core UACT6 exhibit similar downcore variations to LOI, indicating a derivation principally from organic sources.
- Practically no carbonate is present in the sediment. LOI and total organic carbon (TOC) are very strongly correlated.
- Chlorin concentrations exhibit synchronous, though more pronounced, downcore variations to LOI and TOC. Chlorin concentration is considered a direct proxy for lake primary productivity. By expressing chlorin concentration as a proportion of TOC, a signal is derived which is independent of changes in mineral input to the sediment. The chlorin analysis from Lochan Uaine represents the first study of its kind.
- Downcore shifts in bulk organic δ^{13}C show some similarities with the LOI, TOC and chlorin profiles, although the correlation is not significant. Lighter values are interpreted as originating in C_3 higher plants, and heavier values are interpreted as originating in aquatic organisms, principally algae and bacteria.
- Lipid analysis can be used to indicate inputs from different organic sources. Long chain-length *n*-alkanes, *n*-alkanols and *n*-alkanoic acids are higher plant biomarkers, and show no major downcore variations. This suggests the input of organic material to Lochan Uaine from the catchment has varied little over the last *c.* 2000 cal yr. These long chain-length components are used as indicators of catchment productivity.

- The C_{17} *n*-alkane is an algal/bacterial biomarker, and a C_{25} highly branched isoprenoid (HBI) monoene is a diatom biomarker. Both show variations in concentration which are synchronous with the main fluctuations in LOI, TOC and chlorin concentration. This suggests the input of organic material to Lochan Uaine from autochthonous sources has varied significantly over the last *c.* 2000 cal yr. The C_{17} *n*-alkane and C_{25} HBI monoene profiles are interpreted as reflecting changes in lake primary productivity.
- Compound-specific $\delta^{13}C$ analysis shows the C_{17} *n*-alkane to be significantly less depleted in ^{13}C than longer chain-length components. This supports the interpretation of the bulk $\delta^{13}C$ profile as reflecting changes in relative inputs from autochthonous and allochthonous sources.
- The chlorin and lipid analyses indicate that LOI variations in Lochan Uaine are a response principally to variations in lake primary productivity.
- It is hypothesised that lake primary productivity is determined by air temperature, through the influence of ice-cover duration on the length of the growing season in the lake.
- The main periods of low productivity suggested by the chlorin and lipid analyses are thought to occur at *c.* 460-560, 1120-1280 and 1740-1940 AD.
- Few proxy climate records of the last *c.* 2000 cal yr show responses of similar magnitude, age and duration to those identified in UACT6.
- Comparison of proxy climate records is hindered by inadequate dating, differing seasonal responses, varying resolution and length of records, and poor understanding of system responses to climate variability. Further work is needed to resolve these problems.

7.7 Recommendations for future work

The analyses undertaken during the course of this thesis have revealed numerous areas which should be considered for further research. Precise and accurate dating of lake sediment cores is obviously a problem. Errors inherent in the measurement and calibration of radiocarbon dates, and potential improvements to radiometric dating methods, have been discussed at length elsewhere and need not be discussed further

here (*e.g.* Pilcher, 1991a,b; Jones *et al.*, 1993a; Taylor *et al.*, 1996; Oldfield *et al.*, 1997a,b; Björck *et al.*, 1998; Stuiver *et al.*, 1998a). However, the nature of the calibration curve means that the precision of calibrated radiocarbon dates will always be in the range of decades, rather than single years. This may prevent reliable correlation between lake sediments and other proxy records, such as tree-rings and speleothems, which are dominated by annual to decadal variability. The use of microtephra layers to date lake sediments was discussed in Chapter 3. Although unsuccessful at Lochan Uaine, it is nonetheless considered that tephra analysis has the potential to improve radiocarbon-based chronologies, especially in lakes with an old carbon input. The main problem to be addressed appears to be the diffuse stratigraphic spread of tephra layers, thought to be caused by inwash of tephra shards from the catchment. Future work should concentrate on determining the extent of this problem, and whether it is possible to correct for it. One possibility may be to study the occurrence of a recent tephra of known age, such as the 1947 Hekla eruption, in an annually-laminated lake sediment. The use of annually-laminated sediments appears to be the only way by which a chronology with an annual precision and accuracy may be obtained. Identification of the lamina corresponding to 1947 AD, and analysis of the spread of tephra shard concentrations in the surrounding years, would indicate the extent of tephra reworking from the catchment. It would also indicate whether the date of eruption is represented by the first increase in tephra shard concentration, the peak in concentration, or another part of the tephra concentration profile.

Analysis of an annually-laminated lake sediment using the same techniques as at Lochan Uaine would allow a direct comparison to be made between the organic matter record, and other proxy climate records with an annual resolution. In particular, comparison with the instrumental record is considered vital to the understanding of how lake productivity responds to climate change. Such a study would allow testing of the two conflicting hypotheses, namely the hypothesis linking a warm climate with increased productivity (Willemse and Törnqvist, 1999), and that linking a cold climate with increased productivity (D. Monteith unpublished). Although few annually-laminated sediments are found in Britain, and none are known from remote mountain lakes such as Lochan Uaine, they are relatively common in

Scandinavia. Annually-laminated sediments from this region could be compared with the long instrumental climate records from Stockholm and Uppsala.

Apart from the need to improve the dating of lake sediments, the work undertaken for this thesis has revealed numerous potentially important avenues of research in the analysis of sedimentary organic matter. One example is in the novel use of chlorin concentrations as a proxy for lake primary productivity in lake sediments. Identification of chlorins would help to confirm their assumed derivation from chlorophyll in lake biota, as would compound-specific stable carbon isotope analysis. Likewise, there is a need to investigate the methods of chlorin formation, possibly using grazing experiments similar to those of Talbot *et al.* (1999a,b) but with lacustrine rather than marine organisms, and with an emphasis on benthic rather than planktonic taxa. This hints at a more general problem affecting the analysis of sediments from Lochan Uaine. Many of the physical, chemical and biological processes occurring in the lake and its catchment are not known. A detailed study of the present-day system would aid the interpretation of the sediment record. This could include study of such processes as water column stratification and oxic conditions at the mud-water interface, timing of the growing season, the nutrient cycle in the lake and catchment and its relation to meteorological conditions, catchment erosion, quantification of inputs to the sediment from different sources, degradation of organic matter between organism death and deposition in the sediment record, and so on.

Analysis of sedimentary lipid distributions in this study was confined mainly to the major aliphatic compound classes, including the *n*-alkanes, *n*-alkanols and *n*-alkanoic acids. Future research could examine other potential biomarkers in greater detail. Separation of sterols from the alcohol fraction would allow a more detailed analysis than was possible here. Likewise, further study of the ketone and wax ester fraction would be profitable. Wax esters from higher plants are thought to be an important source of aliphatic acids and alcohols in the sediment, while long chain-length alkenones potentially contain a palaeotemperature record, as seen in marine sediments (Cranwell, 1985; Brassell *et al.*, 1986; Prahl and Wakeham, 1987; Prahl *et al.*, 1989; Rosell-Melé *et al.*, 1994). The interpretation of sedimentary lipid distributions is aided

by concurrent analysis of present day organisms from the lake and catchment. It is recommended that future studies include such analyses, if necessary using laboratory cultures of algae and bacteria to avoid the contamination with higher plant detritus experienced in this study.

Compound-specific stable isotope analyses of present day vegetation would allow comparison with the corresponding values in the sediment record. An effort should be made to determine the range of isotope values displayed by aquatic organisms, as this will aid interpretation of any downcore shifts observed in bulk organic $\delta^{13}C$. Furthermore, compound-specific isotope analysis need not be limited to carbon isotopes. The techniques exist to measure oxygen and hydrogen isotope values in organic matter. Such analyses could add to our understanding of lake sediment responses to climate change.

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Appendix A

Bulk organic stable carbon isotopes, core UACT6. Average values of duplicate measurements are given.

Top cm	Bottom cm	$\delta^{13}C$ ‰	Top cm	Bottom cm	$\delta^{13}C$ ‰	Top cm	Bottom cm	$\delta^{13}C$ ‰
0.2	0.4	-21.66	19.6	19.8	-21.01	32.4	32.6	-21.18
0.4	0.6	-21.83	19.8	20.0	-20.35	32.6	32.8	-20.34
0.8	1.0	-21.61	20.0	20.2	-20.48	33.2	33.4	-20.43
1.0	1.2	-21.61	20.6	20.8	-20.46	33.6	33.8	-20.29
1.6	1.8	-20.97	21.2	21.4	-20.55	34.0	34.2	-20.47
2.0	2.2	-20.58	21.6	21.8	-20.73	34.6	34.8	-20.59
3.6	3.8	-20.30	22.0	22.2	-20.70	35.2	35.4	-21.59
5.6	5.8	-19.90	22.6	22.8	-20.75	35.4	35.6	-20.75
6.6	6.8	-20.36	23.2	23.4	-20.57	35.6	35.8	-20.63
7.6	7.8	-19.60	23.6	23.8	-20.45	35.8	36.0	-21.57
8.6	8.8	-19.73	24.0	24.2	-20.49	36.0	36.2	-21.36
9.6	9.8	-20.22	24.2	24.4	-19.78	36.2	36.4	-21.91
10.6	10.8	-19.85	24.4	24.6	-19.97	36.4	36.6	-21.47
11.6	11.8	-19.68	24.6	24.8	-21.10	36.6	36.8	-21.14
12.6	12.8	-19.47	24.8	25.0	-21.73	37.2	37.4	-20.35
13.2	13.4	-19.42	25.0	25.2	-20.08	37.6	37.8	-20.23
13.6	13.8	-19.33	25.2	25.4	-20.29	38.0	38.2	-20.23
14.0	14.2	-19.37	25.6	25.8	-20.29	38.6	38.8	-20.44
14.6	14.8	-19.38	26.0	26.2	-20.15	39.2	39.4	-20.35
15.2	15.4	-19.35	26.6	26.8	-20.18	39.6	39.8	-19.94
15.6	15.8	-19.37	27.2	27.4	-20.34	40.0	40.2	-20.26
16.2	16.4	-19.47	27.4	27.6	-20.32	40.4	40.6	-20.09
16.4	16.6	-19.57	27.6	27.8	-20.20	40.8	41.0	-19.76
16.6	16.8	-19.73	27.8	28.0	-20.92	41.2	41.4	-20.28
16.8	17.0	-20.26	28.0	28.2	-20.95	41.6	41.8	-19.87
17.0	17.2	-20.43	28.2	28.4	-20.66	42.0	42.2	-20.53
17.2	17.4	-20.86	28.4	28.6	-20.30	42.4	42.6	-20.42
17.4	17.6	-20.55	28.6	28.8	-20.31	42.8	43.0	-20.18
17.6	17.8	-20.81	29.2	29.4	-20.16	43.2	43.4	-20.54
17.8	18.0	-21.42	29.6	29.8	-19.77	43.6	43.8	-20.66
18.0	18.2	-21.67	30.0	30.2	-20.23	44.0	44.2	-20.76
18.2	18.4	-21.87	30.6	30.8	-20.72	44.4	44.6	-20.52
18.4	18.6	-22.04	31.2	31.4	-20.43	44.8	45.0	-20.52
18.6	18.8	-21.95	31.4	31.6	-20.50	45.2	45.4	-22.11
18.8	19.0	-22.65	31.6	31.8	-20.48	45.6	45.8	-20.42
19.0	19.2	-21.56	31.8	32.0	-21.11	46.0	46.2	-21.02
19.2	19.4	-21.84	32.0	32.2	-21.02			
19.4	19.6	-21.34	32.2	32.4	-21.07			

Appendix B

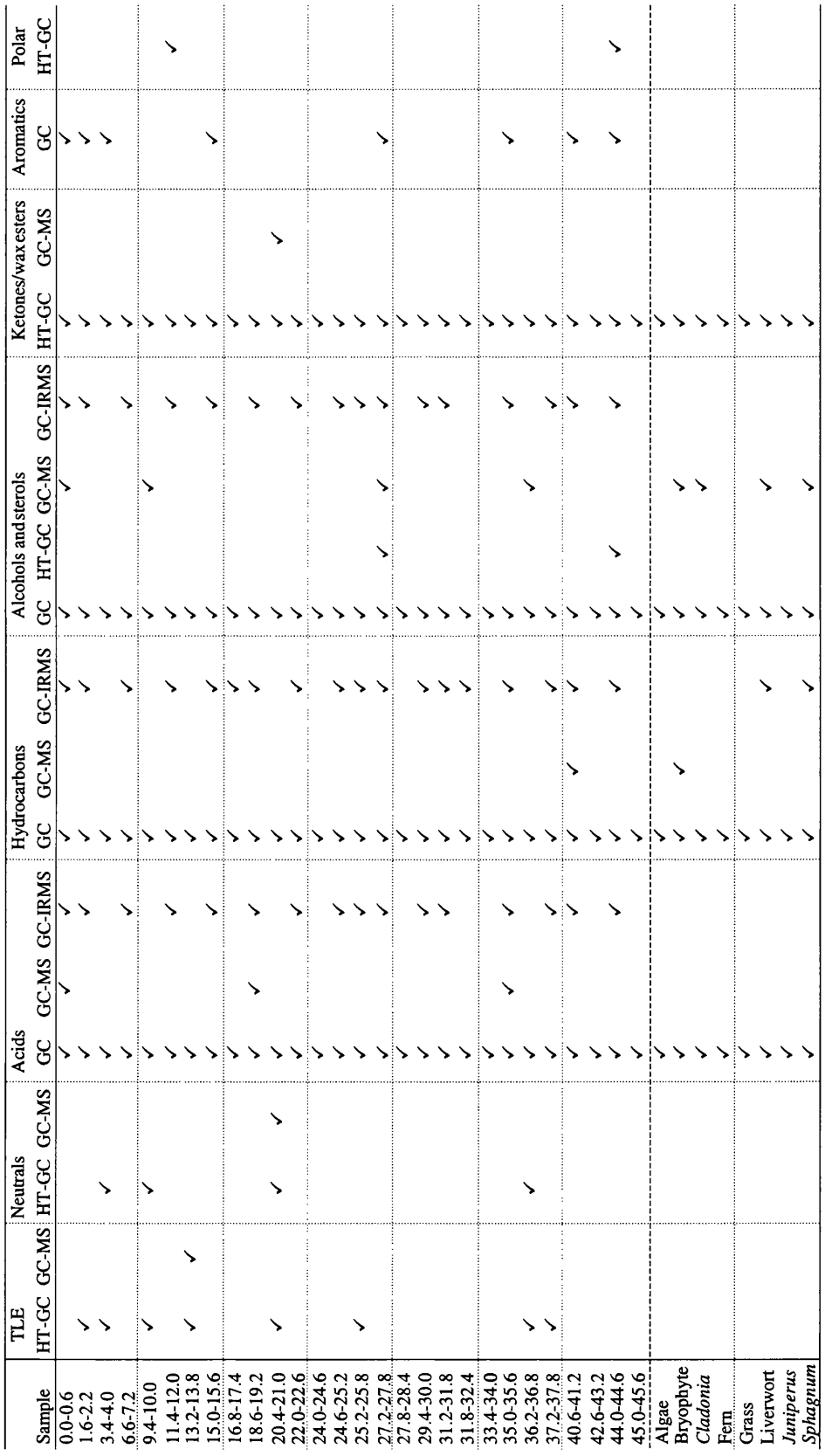
Dry masses of combined sediment samples and modern reference samples used for lipid extraction.

Sample/cm	Depths/cm	Mass/g	Sample/cm	Depths/cm	Mass/g
0.0-0.6	0.0-0.2	0.3993	25.2-25.8	25.2-25.4	0.4993
	0.2-0.4	0.4002		25.4-25.6	0.5000
	0.4-0.6	0.4065		25.6-25.8	0.5005
1.6-2.2	1.6-1.8	0.5001	27.2-27.8	27.2-27.4	0.5000
	1.8-2.0	0.4989		27.4-27.6	0.5008
	2.0-2.2	0.5047		27.6-27.8	0.5000
3.4-4.0	3.4-3.6	0.4977	27.8-28.4	27.8-28.0	0.5007
	3.6-3.8	0.4997		28.0-28.2	0.4986
	3.8-4.0	0.4676		28.2-28.4	0.5036
6.6-7.2	6.6-6.8	0.5049	29.4-30.0	29.4-29.6	0.5001
	6.8-7.0	0.4982		29.6-29.8	0.5028
	7.0-7.2	0.4994		29.8-30.0	0.4977
9.4-10.0	9.4-9.6	0.4953	31.2-31.8	31.2-31.4	0.5030
	9.6-9.8	0.5004		31.4-31.6	0.4988
	9.8-10.0	0.5029		31.6-31.8	0.5001
11.4-12.0	11.4-11.6	0.5021	31.8-32.4	31.8-32.0	0.5016
	11.6-11.8	0.4969		32.0-32.2	0.4983
	11.8-12.0	0.4984		32.2-32.4	0.5023
13.2-13.8	13.2-13.4	0.5010	33.4-34.0	33.4-33.6	0.4994
	13.4-13.6	0.4986		33.6-33.8	0.5013
	13.6-13.8	0.4997		33.8-34.0	0.5000
15.0-15.6	15.0-15.2	0.5006	35.0-35.6	35.0-35.2	0.5016
	15.2-15.4	0.4998		35.2-35.4	0.4986
	15.4-15.6	0.5023		35.4-35.6	0.5007
16.8-17.4	16.8-17.0	0.5000	36.2-36.6	36.2-36.4	0.5004
	17.0-17.2	0.5009		36.4-36.6	0.4995
	17.2-17.4	0.5006		36.6-36.8	0.5006
18.6-19.2	18.6-18.8	0.5014	37.2-37.8	37.2-37.4	0.5006
	18.8-19.0	0.5025		37.4-37.6	0.5012
	19.0-19.2	0.4987		37.6-37.8	0.4998
20.4-21.0	20.4-20.6	0.5005	40.6-41.2	40.6-40.8	0.5016
	20.6-20.8	0.4986		40.8-41.0	0.4985
	20.8-21.0	0.5005		41.0-41.2	0.4990
22.0-22.6	22.0-22.2	0.5028	42.6-43.2	42.6-42.8	0.5003
	22.2-22.4	0.4977		42.8-43.0	0.5012
	22.4-22.6	0.4986		43.0-43.2	0.4976
24.0-24.6	24.0-24.2	0.5000	44.0-44.6	44.0-44.2	0.4990
	24.2-24.4	0.4996		44.2-44.4	0.5019
	24.4-24.6	0.5025		44.4-44.6	0.4993
24.6-25.2	24.6-24.8	0.4996	45.0-45.6	45.0-45.2	0.4995
	24.8-25.0	0.5012		45.2-45.4	0.5007
	25.0-25.2	0.5007		45.4-45.6	0.5004

Reference samples/g	
Cladonia	0.4930
Liverwort	0.3873
Bryophyte	0.4055
Sphagnum	0.2098
Algae	1.5064
Fern	1.2143
Grass	1.0869
Juniperus	1.3404

Appendix C

GC, HT-GC, GC-MS and GC-IRMS analysis of samples from UACT6 and the Lochan Uaine catchment.



Sample	TLE		Neutrals		Acids			Hydrocarbons			Alcohols and sterols				Ketones/wax esters		Aromatics	Polar
	HT-GC	GC-MS	HT-GC	GC-MS	GC	GC-MS	GC-IRMS	GC	GC-MS	GC-IRMS	GC	HT-GC	GC-MS	GC-IRMS	HT-GC	GC-MS	GC	HT-GC
0.0-0.6					✓	✓	✓	✓		✓	✓		✓	✓	✓		✓	
1.6-2.2	✓				✓		✓	✓		✓	✓			✓	✓		✓	
3.4-4.0	✓		✓		✓			✓			✓				✓		✓	
6.6-7.2					✓		✓	✓		✓	✓			✓	✓			
9.4-10.0	✓		✓		✓			✓			✓		✓		✓			
11.4-12.0					✓		✓	✓		✓	✓			✓	✓			✓
13.2-13.8	✓	✓			✓			✓			✓				✓			
15.0-15.6					✓		✓	✓		✓	✓			✓	✓		✓	
16.8-17.4					✓			✓			✓				✓			
18.6-19.2					✓	✓	✓	✓		✓	✓			✓	✓			
20.4-21.0	✓		✓	✓	✓			✓			✓				✓	✓		
22.0-22.6					✓		✓	✓		✓	✓			✓	✓			
24.0-24.6					✓			✓			✓				✓			
24.6-25.2					✓		✓	✓		✓	✓			✓	✓			
25.2-25.8	✓				✓		✓	✓		✓	✓			✓	✓			
27.2-27.8					✓		✓	✓		✓	✓	✓	✓	✓	✓		✓	
27.8-28.4					✓			✓			✓				✓			
29.4-30.0					✓		✓	✓		✓	✓			✓	✓			
31.2-31.8					✓		✓	✓		✓	✓			✓	✓			
31.8-32.4					✓			✓			✓				✓			
33.4-34.0					✓			✓			✓				✓			
35.0-35.6					✓	✓	✓	✓		✓	✓			✓	✓		✓	
36.2-36.8	✓		✓		✓			✓			✓		✓		✓			
37.2-37.8	✓				✓		✓	✓		✓	✓			✓	✓			
40.6-41.2					✓		✓	✓	✓	✓	✓			✓	✓		✓	
42.6-43.2					✓			✓			✓				✓			
44.0-44.6					✓		✓	✓		✓	✓	✓		✓	✓		✓	✓
45.0-45.6					✓			✓			✓				✓			
Algae					✓			✓			✓		✓		✓			
Bryophyte					✓			✓	✓		✓				✓			
Cladonia					✓			✓			✓		✓		✓			
Fern					✓			✓			✓				✓			
Grass					✓			✓			✓				✓			
Liverwort					✓			✓		✓	✓		✓		✓			
Juniperus					✓			✓			✓				✓			
Sphagnum					✓			✓		✓	✓		✓		✓			

Appendix D

Extrusion notes for cores UACT6, UACT8, UACT10, UACT12.

UACT 6	Core length 46.2 cm
Extruded 19.9.97-22.9.97	[extrusion stopped over weekend at 20.0 cm]
0.0-0.6 cm	unidentified fibrous material present.
1.4-3.6 cm	medium brown sediment.
3.6 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
12.6-13.4 cm	unidentified fibrous material.
17.6-19.2 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown by 19.2 cm.
31.6-32.2	unidentified fibrous material.
32.2-34.8 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown by 34.8 cm.
42.6-46.2 cm	unidentified fibrous material.
46.2 cm	core base.

UACT 8	Core length 109.6 cm
Extruded 8.9.97-11.9.97	[extrusion stopped overnight at 13.8 cm, 48.6 cm, 93.8 cm]
Core top disurbed slightly	whilst setting up extrusion rig.
0-2 cm	dark brown/black sediment, unidentified fibrous material
2-13.8 cm	dark/medium brown sediment.
9.2-9.4 cm	unidentified fibrous material.
13.8 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
26.8 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
30.4 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
44.2 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
56.6 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
62.2 cm	unidentified fibrous material.
68.2-64.4 cm	large clast.
68.4-64.6 cm	very large clast.
70.0-70.2 cm	large clast.
70.2-70.4 cm	large clast.
70.6-70.8 cm	very large clast.
71.2-71.4 cm	very large clast.
*c.*74-75 cm	lighter sediment seen around edges of core (may be smeared material).
78.8-79.0 cm	large clast.
96.0-96.2 cm	large clast.
97.6-97.8 cm	large clast.
99.6-99.8 cm	large clast.
99.8-end	unidentified fibrous material.
102.8-103.0 cm	large clast.
107.6-107.8 cm	picked up unidentified fibrous material from up to 1.5 cm below actual level. Rest of core down to base was disturbed.
109.0-109.2 cm	clast.
109.6 cm	core base.

UACT 10	Core length 62.2 cm
Extruded 23.9.97-24.9.97	[stopped overnight at 35.0 cm]
0.0-0.4 cm	black, gritty sediment (possibly from lake sediment surface).
0.4-*c*.2.8 cm	rusty brown sediment.
c.2.8-7.8	colour change to medium/dark brown.
7.8 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
c.17 cm	unidentified fibrous material.
26.0 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
c.43.8-47.8	sediment changes colour to light brown/olive, gradually returns to dark/medium brown by 47.8 cm.
48.6 cm	core tube found to have lifted up by 6-7 mm during extrusion, hence previous few samples were from the wrong depths; the situation was corrected by merging the previous few samples and relabelling three sample bags, but some error is still probable.
52.6 cm	unidentified fibrous material.
53.4 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown over next few cm.
62.2 cm	core base.

UACT 12	Core length 31.8 cm
Extruded 29.9.97	
0.0-0.4 cm	light grey/brown clay (this material had resettled from the water column during the month in which the core was standing in storage).
c.18 cm	unidentified fibrous material.
19.2-25.6 cm	sediment changes colour to light brown/olive, gradually returns to dark/medium brown by 25.6 cm.
27.0-end	sediment changes colour to light grey/white.
c.30 cm	large orange/red balls of sediment; one extracted and placed in separate sample bag.
31.8 cm	core base.

Appendix E

Radiocarbon calibration date ranges for UACT4; no correction made for old carbon. The calibration was performed with program CALIB v4.1 (Stuiver and Reimer, 1986, 1993) using the atmospheric sample dataset INTCAL98.14C (Stuiver *et al.*, 1998).

Publication code	Depth cm	^{14}C age	95.4% (2σ) cal age ranges AD/BC	Relative area under distribution	Median date AD/BC
AA-14623	5.8-6.0	1695 ± 50*	not calculated	not calculated	not calculated
AA-14624	8.0-8.2	1415 ± 60*	not calculated	not calculated	not calculated
AA-14625	10.0-10.2	945 ± 45	1004-1007 AD	0.003	1098 AD
			1017-1192 AD	0.983	
			1200-1208 AD	0.014	
AA-14626	13.0-13.2	930 ± 60	1019-1213 AD	1.000	1105 AD
AA-14627	15.0-15.2	1160 ± 45	733-736 AD	0.003	877 AD
			774-985 AD	0.997	
AA-14628	16.8-17.0	1405 ± 45	543-551 AD	0.011	638 AD
			557-690 AD	0.989	
AA-14629	17.8-18.0	1225 ± 45	685-895 AD	0.983	803 AD
			924-938 AD	0.017	
AA-15218	19.0-19.2	1175 ± 65	691-703 AD	0.018	854 AD
			709-752 AD	0.085	
			759-990 AD	0.897	
AA-14631	20.2-20.4	1530 ± 45	428-620 AD	0.998	531 AD
			634-635 AD	0.002	
AA-14632	22.2-22.4	1480 ± 45	439-451 AD	0.020	582 AD
			464-503 AD	0.064	
			507-517 AD	0.016	
			529-657 AD	0.900	
AA-14633	25.4-25.6	1530 ± 50	426-623 AD	0.986	530 AD
			630-637 AD	0.014	
AA-14634	28.4-28.6	1455 ± 45	443-448 AD	0.004	603 AD
			469-481 AD	0.010	
			531-666 AD	0.987	
AA-14635	30.0-30.2	1745 ± 45	136-156 AD	0.025	298 AD
			173-194 AD	0.027	
			211-411 AD	0.948	
AA-14636	33.4-33.6	1585 ± 50	360-366 AD	0.006	481 AD
			383-601 AD	0.994	
AA-15219	36.6-36.8	2200 ± 85	401-43 BC	0.999	249 BC
			6-4 BC	0.001	
AA-14638	39.4-39.6	2380 ± 50	761-679 BC	0.193	486 BC
			669-627 BC	0.045	
			619-614 BC	0.002	
			593-575 BC	0.017	
			563-377 BC	0.743	
			266-264 BC	0.001	
AA-14639	41.2-41.4	2255 ± 55	400-198 BC	0.988	288 BC
			188-180 BC	0.012	
AA-14640	44.4-44.6	2230 ± 50	393-197 BC	0.967	283 BC
			191-175 BC	0.033	
AA-14641	47.8-48.0	2220 ± 55	397-162 BC	0.992	278 BC
			129-121 BC	0.008	
AA-14642	50.4-50.6	2485 ± 60	786-479 BC	0.872	610 BC
			470-446 BC	0.054	
			444-411 BC	0.075	
AA-14643	53.0-53.2	2615 ± 70	965-964 BC	0.001	782 BC
			921-535 BC	0.985	
			535-518 BC	0.012	
			457-454 BC	0.002	
			436-434 BC	0.001	
AA-14644	57.2-57.4	2495 ± 55	790-481 BC	0.901	617 BC
			468-447 BC	0.040	
			443-412 BC	0.059	
AA-14645	59.2-59.4	2745 ± 45	997-986 BC	0.021	885 BC
			976-976 BC	0.002	
			975-812 BC	0.978	

continued overleaf

Publication code	Depth cm	^{14}C age	95.4% (2σ) cal age ranges AD/BC	Relative area under distribution	Median date AD/BC
AA-15220	61.8-62.0	2640 ± 140	1125-1119 BC	0.003	784 BC
			1114-1096 BC	0.008	
			1092-1056 BC	0.017	
			1054-402 BC	0.972	
AA-14647	66.2-66.4	3105 ± 50	1498-1471 BC	0.038	1370 BC
			1462-1258 BC	0.943	
			1234-1217 BC	0.019	
AA-14648	68.6-68.8	3135 ± 50	1517-1365 BC	0.752	1407 BC
			1365-1295 BC	0.233	
			1274-1265 BC	0.014	
AA-14649	71.8-72.0	3350 ± 55	1856-1851 BC	0.002	1632 BC
			1768-1757 BC	0.008	
			1754-1513 BC	0.990	
AA-14650	75.4-75.6	3395 ± 55	1876-1841 BC	0.063	1688 BC
			1825-1823 BC	0.002	
			1813-1798 BC	0.022	
			1779-1596 BC	0.785	
			1594-1525 BC	0.127	
AA-14651	78.0-78.2	3495 ± 55	2005-2005 BC	0.001	1814 BC
			1952-1684 BC	0.999	
			1666-1664 BC	0.001	
AA-14652	81.0-81.2	3130 ± 65	1524-1256 BC	0.972	1397 BC
			1241-1213 BC	0.025	
			1197-1194 BC	0.002	
			1137-1134 BC	0.002	
AA-14653	83.2-83.4	3920 ± 55	2568-2518 BC	0.077	2400 BC
			2499-2276 BC	0.876	
			2253-2229 BC	0.031	
			2221-2206 BC	0.016	
AA-14654	85.0-85.2	3980 ± 55	2826-2824 BC	0.001	2493 BC
			2657-2653 BC	0.004	
			2622-2606 BC	0.024	
			2603-2302 BC	0.972	
AA-14655	86.6-86.8	4325 ± 55	3256-3249 BC	0.003	2957 BC
			3098-2871 BC	0.985	
			2802-2783 BC	0.010	
			2767-2764 BC	0.001	
			2715-2715 BC	0.000	
AA-14656	89.0-89.2	4170 ± 55	2884-2619 BC	0.963	2748 BC
			2610-2597 BC	0.025	
			2591-2583 BC	0.012	
AA-14657	92.0-92.2	4515 ± 65	3491-3470 BC	0.016	3207 BC
			3372-3016 BC	0.969	
			2978-2966 BC	0.007	
			2949-2933 BC	0.009	
AA-14658	93.2-93.4	4670 ± 70	3640-3334 BC	0.976	3459 BC
			3211-3190 BC	0.013	
			3154-3135 BC	0.012	

* Dates excluded from calibration

Appendix E (continued)

Radiocarbon calibration date ranges for UACT4, including correction made for 488 yr old carbon effect. The calibration was performed with program CALIB v4.1 (Stuiver and Reimer, 1986, 1993) using the atmospheric sample dataset INTCAL98.14C (Stuiver *et al.*, 1998).

Publication code	Depth cm	^{14}C age	Corrected ^{14}C age[†]	95.4% (2σ) cal age ranges AD/BC	Relative area under distribution	Median date AD/BC
AA-14623	5.8-6.0	1695 ± 50[*]	not calculated	not calculated	not calculated	not calculated
AA-14624	8.0-8.2	1415 ± 60[*]	not calculated	not calculated	not calculated	not calculated
AA-14625	10.0-10.2	945 ± 45	457 ± 45	1334-1337 AD	0.003	1445 AD
				1400-1517 AD	0.959	
				1597-1619 AD	0.038	
AA-14626	13.0-13.2	930 ± 60	442 ± 60	1403-1523 AD	0.861	1460 AD
				1565-1628 AD	0.139	
AA-14627	15.0-15.2	1160 ± 45	672 ± 45	1272-1332 AD	0.502	1329 AD
				1339-1399 AD	0.498	
AA-14628	16.8-17.0	1405 ± 45	917 ± 45	1024-1211 AD	1.000	1111 AD
AA-14629	17.8-18.0	1225 ± 45	737 ± 45	1195-1196 AD	0.001	1273 AD
				1211-1306 AD	0.925	
				1354-1387 AD	0.074	
AA-15218	19.0-19.2	1175 ± 65	687 ± 65	1223-1233 AD	0.020	1314 AD
				1236-1403 AD	0.980	
AA-14631	20.2-20.4	1530 ± 45	1042 ± 45	892-1041 AD	0.948	994 AD
				1095-1117 AD	0.031	
				1141-1153 AD	0.022	
AA-14632	22.2-22.4	1480 ± 45	992 ± 45	904-910 AD	0.005	1049 AD
				976-1162 AD	0.994	
				1175-1176 AD	0.001	
AA-14633	25.4-25.6	1530 ± 50	1042 ± 50	889-1045 AD	0.908	993 AD
				1047-1056 AD	0.007	
				1088-1122 AD	0.052	
				1138-1156 AD	0.033	
AA-14634	28.4-28.6	1455 ± 45	967 ± 45	993-1164 AD	0.975	1089 AD
				1170-1186 AD	0.025	
AA-14635	30.0-30.2	1745 ± 45	1257 ± 45	673-785 AD	0.665	758 AD
				786-883 AD	0.335	
AA-14636	33.4-33.6	1585 ± 50	1097 ± 50	782-790 AD	0.013	942 AD
				812-843 AD	0.043	
				857-1023 AD	0.943	
AA-15219	36.6-36.8	2200 ± 85	1712 ± 85	131-474 AD	0.935	327 AD
				476-532 AD	0.065	
AA-14638	39.4-39.6	2380 ± 50	1892 ± 50	4-9 AD	0.007	119 AD
				19-240 AD	0.993	
AA-14639	41.2-41.4	2255 ± 55	1767 ± 55	130-398 AD	1.000	271 AD
AA-14640	44.4-44.6	2230 ± 50	1742 ± 50	135-158 AD	0.032	299 AD
				171-195 AD	0.035	
				210-415 AD	0.933	
AA-14641	47.8-48.0	2220 ± 55	1732 ± 55	135-160 AD	0.029	308 AD
				170-196 AD	0.033	
				209-424 AD	0.938	
AA-14642	50.4-50.6	2485 ± 60	1997 ± 60	165-128 BC	0.049	1 AD
				121 BC-127 AD	0.951	
AA-14643	53.0-53.2	2615 ± 70	2127 ± 70	375-374 BC	0.001	161 BC
				364-268 BC	0.215	
				263 BC-2 AD	0.781	
				14-16 AD	0.003	
AA-14644	57.2-57.4	2495 ± 55	2007 ± 55	165-128 BC	0.056	10 BC
				122 BC-86 AD	0.914	
				102-122 AD	0.030	
AA-14645	59.2-59.4	2745 ± 45	2257 ± 45	398-334 BC	0.343	289 BC
				325-202 BC	0.657	

continued overleaf

Publication code	Depth cm	^{14}C age	Corrected ^{14}C age[†]	95.4% (2σ) cal age ranges AD/BC	Relative area under distribution	Median date AD/BC
AA-15220	61.8-62.0	2640 ± 140	2152 ± 140	756-702 BC	0.012	190 BC
				539-528 BC	0.003	
				523 BC-134 AD	0.983	
				163-167 AD	0.001	
				201-207 AD	0.001	
AA-14647	66.2-66.4	3105 ± 50	2617 ± 50	899-758 BC	0.836	799 BC
				684-662 BC	0.045	
				641-587 BC	0.075	
				582-545 BC	0.043	
AA-14648	68.6-68.8	3135 ± 50	2647 ± 50	918-762 BC	0.993	819 BC
				678-671 BC	0.007	
AA-14649	71.8-72.0	3350 ± 55	2862 ± 55	1256-1240 BC	0.013	1033 BC
				1213-1196 BC	0.022	
				1194-1137 BC	0.089	
				1134-898 BC	0.877	
AA-14650	75.4-75.6	3395 ± 55	2907 ± 55	1287-1283 BC	0.003	1097 BC
				1261-969 BC	0.951	
				961-925 BC	0.046	
AA-14651	78.0-78.2	3495 ± 55	3007 ± 55	1401-1109 BC	0.957	1246 BC
				1101-1073 BC	0.030	
				1062-1052 BC	0.012	
AA-14652	81.0-81.2	3130 ± 65	2642 ± 65	970-959 BC	0.009	915 BC
				936-757 BC	0.848	
				693-657 BC	0.038	
				650-542 BC	0.105	
AA-14653	83.2-83.4	3920 ± 55	3432 ± 55	1884-1604 BC	0.987	1738 BC
				1557-1540 BC	0.013	
AA-14654	85.0-85.2	3980 ± 55	3492 ± 55	1949-1683 BC	0.997	1811 BC
				1666-1664 BC	0.002	
				1645-1645 BC	0.001	
AA-14655	86.6-86.8	4325 ± 55	3837 ± 55	2462-2188 BC	0.924	2295 BC
				2182-2141 BC	0.076	
AA-14656	89.0-89.2	4170 ± 55	3682 ± 55	2266-2264 BC	0.002	2065 BC
				2202-1909 BC	0.992	
				1902-1894 BC	0.006	
AA-14657	92.0-92.2	4515 ± 65	4027 ± 65	2862-2808 BC	0.082	2557 BC
				2776-2773 BC	0.002	
				2758-2719 BC	0.034	
				2704-2399 BC	0.860	
				2380-2348 BC	0.023	
AA-14658	93.2-93.4	4670 ± 70	4182 ± 70	2905-2577 BC	1.000	2751 BC

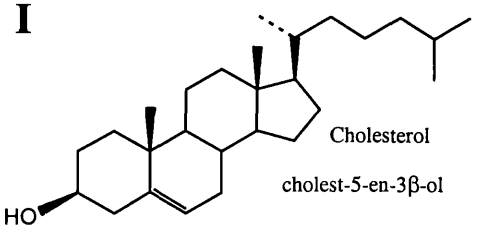
[*] Dates excluded from calibration

[†] Measured ^{14}C age minus 488 yr offset

Appendix F

Structures.

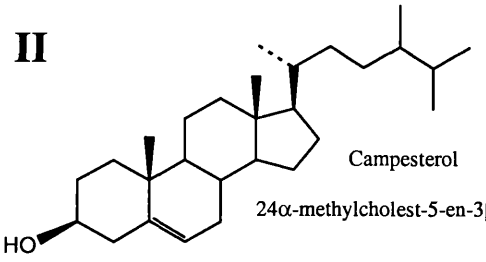
I



Cholesterol

cholest-5-en-3β-ol

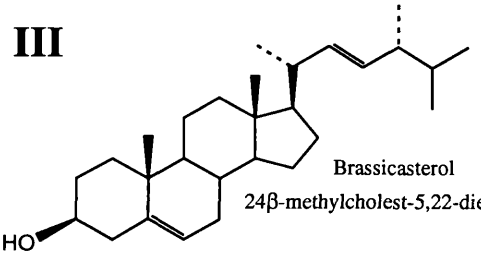
II



Campesterol

24α-methylcholest-5-en-3β-ol

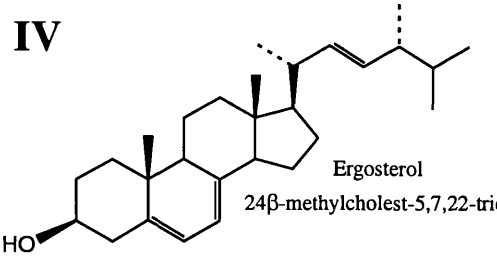
III



Brassicasterol

24β-methylcholest-5,22-dien-3β-ol

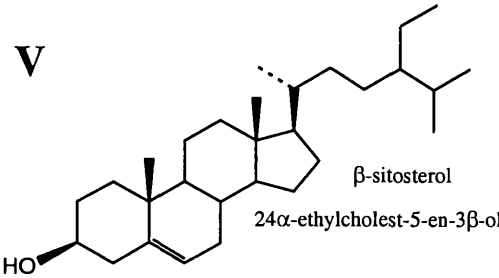
IV



Ergosterol

24β-methylcholest-5,7,22-trien-3β-ol

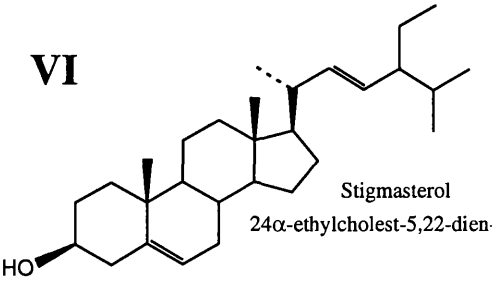
V



β-sitosterol

24α-ethylcholest-5-en-3β-ol

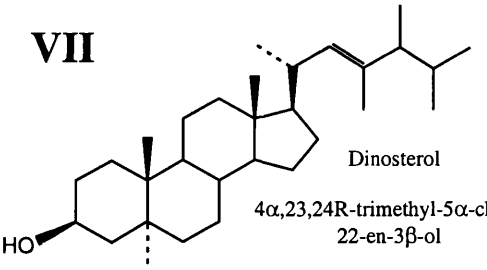
VI



Stigmasterol

24α-ethylcholest-5,22-dien-3β-ol

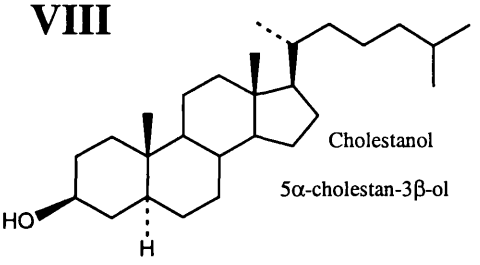
VII



Dinosterol

4α,23,24R-trimethyl-5α-cholest-22-en-3β-ol

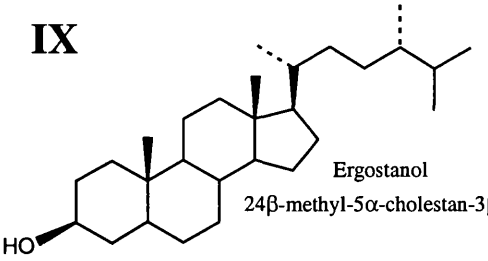
VIII



Cholestanol

5α-cholestan-3β-ol

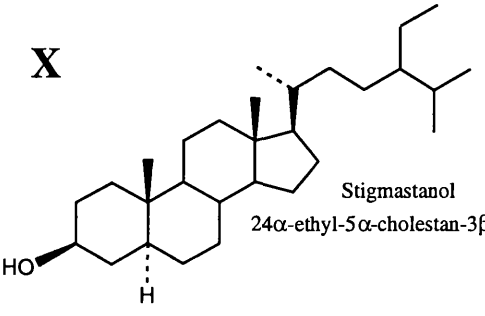
IX



Ergostanol

24β-methyl-5α-cholestan-3β-ol

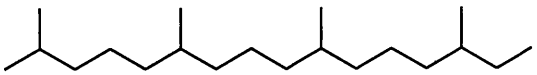
X



Stigmastanol

24α-ethyl-5α-cholestan-3β-ol

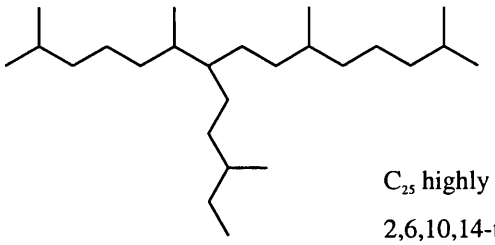
XI



Phytane

2,6,10,14-tetramethylhexadecane

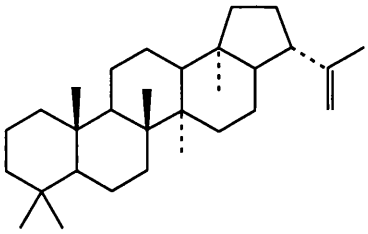
XII



C_{25} highly branched isoprenoid alkane*

2,6,10,14-tetramethyl-7-(3-methylpentyl)pentadecane

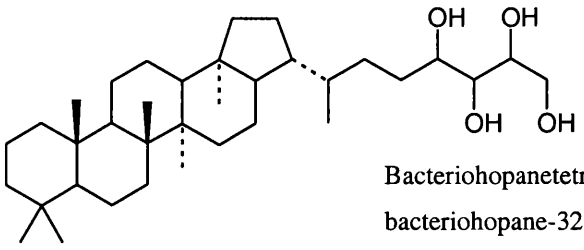
XIII



Diploptene

hopan-22-ene

XIV



Bacteriohopanetetrol

bacteriohopane-32,33,34,35-tetrol

* the position of the double bond in the C_{25} HBI monoene found in UACT6 was not determined