Geochemistry of carboxylic acids in the sediments from Lake Cadagno (Switzerland)

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Abstract

The free and bound fatty acids, including saturated and unsaturated monocarboxylic acids, dicarboxylic acids, hydroxyacids (α, β, ω and ω-1) and phenolic acids, were analyzed in a 248 cm long sediment core from Lake Cadagno (Switzerland) to determine the variations of the sources of the organic matter and depositional conditions with the depth. The results show that the sedimentary deposit in the top 0 to 51 cm of the core was disturbed by frequent episodic events such as avalanches, landslides or torrential flood. In contrast, sedimentation between 51 and 245 cm depth was calmer, slower and characterized by a higher contribution of organic matter produced from higher plants. The microscopic study of the organic matter also confirms these results. The iso- and anteiso- branched fatty acids in the C_{21}-C_{25} range, which have not been previously reported in geochemical literature, were detected in bound fractions. They most probably originate from bacteria specific to the lake. Finally, the source of the sedimentary α- and β-hydroxyacids in the $<C_{10}$ range has been shown to be the same as for their higher homologues, i.e. Gram-negative bacteria.

Keywords: *Lake Cadagno, fatty acids, sediment, herbaceous plants, algae chara, organic matter, bacteria, Switzerland.*

Résumé

Géochimie des acides carboxyliques dans les sédiments du lac Cadagno (Suisse)

Les acides gras libres et liés, comprenant les acides monocarboxyliques saturés et insaturés, les acides dicarboxyliques, les (α, β, ω et ω-1) hydroxyacides et les acides phénoliques, ont été analysés le long d'une carotte sédimentaire de Cadagno (Suisse) dans le but de déterminer les variations des sources et des conditions de déposition de la matière organique en fonction de la profondeur. Les résultats montrent que des événements épisodiques tels que les avalanches, glissements de terrains, crues torrentielles, sont plus fréquents entre 0 et 51 cm. Par contre, entre 51 et 245 cm, la sédimentation était plus calme, faible et caractérisée par une contribution plus élevée de la matière organique des plantes supérieures. L'étude microscopique de la matière organique confirme aussi ces résultats. Des acides gras branchés iso- et anteiso- ayant un nombre d'atomes de carbone entre C_{21} et C_{25}, non mentionnés dans la littérature géochimique jusqu'à présent, ont été détectés dans les fractions liées. Ils proviennent probablement des bactéries spécifiques à ce lac. Finalement, il a été démontré que la source des α- et β-hydroxyacides sédimentaires ayant un nombre d'atomes de carbone $<C_{10}$ est la même que celles de leurs homologues supérieurs, c.à.d., les bactéries Gram-négatives.

Mots-clefs: *Lac de Cadagno, acides gras, sédiment, plantes herbacées, algues chara, matière organique, bactéries, Suisse.*

Introduction

The sedimentary fatty acids, biological markers (Eglinton and Calvin 1967) commonly occurring in nature, are widely studied (Eglinton and al. 1968; Cranwell 1974; Farrington and Quinn 1973; Kawamura and Ishiwatari 1984; Zegouagh and al. 2000) as they allow establishing different sources contributing to the sedimentary lipids and of estimating changes. They can survive the transformations that occur during early diagenesis (Stefanova and Disnar 2000) and persist for a long time since they have been found in hundred millions years old sediments (Douglas and al. 1966). They are present either as free fatty acids or bound fatty acids (bonded to polymeric matrix through ester, amide or sulfur linkages). The geochemical studies of fatty acids (nature, distribution and depth profiles) provide information about the sources and the diagenetic degradation of

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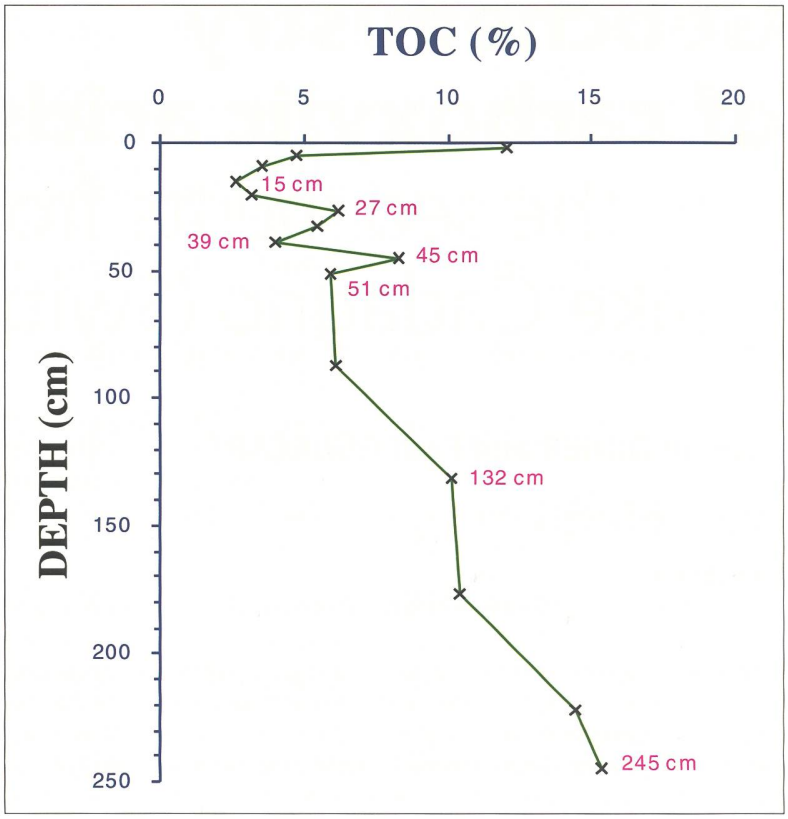


Fig. 1. Depth profile of total organic carbon (TOC) contents in a 248 cm long sediment core taken from lake Cadagno.

organic matter (Cooper 1962; Meyers and al. 1980; Leo and Parker 1966; Boon and al. 1978; Perry and al. 1979; Fulco 1967; Cranwell 1981).

Lake Cadagno is a small meromictic lake located at an altitude of 1923 m in the Valley of Piora in the Southern Swiss Alps (46°33´ N, 8°43´ E). The surface of the lake is $26x10^5$ m^2 and the maximum depth is 21 m. At present it is characterized by a permanent and natural stratification of water (Wagener and al. 1990; Peduzzi and al 1993). The lake basin has been formed during the last glacial period, about 8000 years ago (Stapfer 1991; Del Don and al. 1998, 2001). The depth profile of oxygen allows dividing this lake into three layers: mixolimnion, chemocline and monilimnion. The composition of mixolimnion (oxic layer), poor in salt content, is determined by the water from the north which is in contact with silicate rocks; the oxygenic algae proliferate in this layer (Schanz and Stalder 1998). The chemocline, situated at a depth of 9 to 14 m, is dominated by the presence of blooms of phototrophic purple sulfur bacteria (Tonolla and al. 1999). The monilimnion (anoxic layer) at depth down to 15 m is characterized by a high salt content due to the high input of sulfate from gypsum (infiltration of water through the dolomite) (Wagener and al. 1990; Peduzzi and al. 1993, 1998; Del Don and al. 2001). Presently there is no forest in the catchment area of the lake and the organic matter contribution of higher plants might be not very important (Daher 2004).

In this paper, we report the detailed analysis of the free and bound organic fatty acids in sediment cores from Lake Cadagno in order to establish the evolution of deposition conditions and, possibly, to produce new information on the sources of organic matter specific to the meromictic lakes of high altitude.

Materials and methods

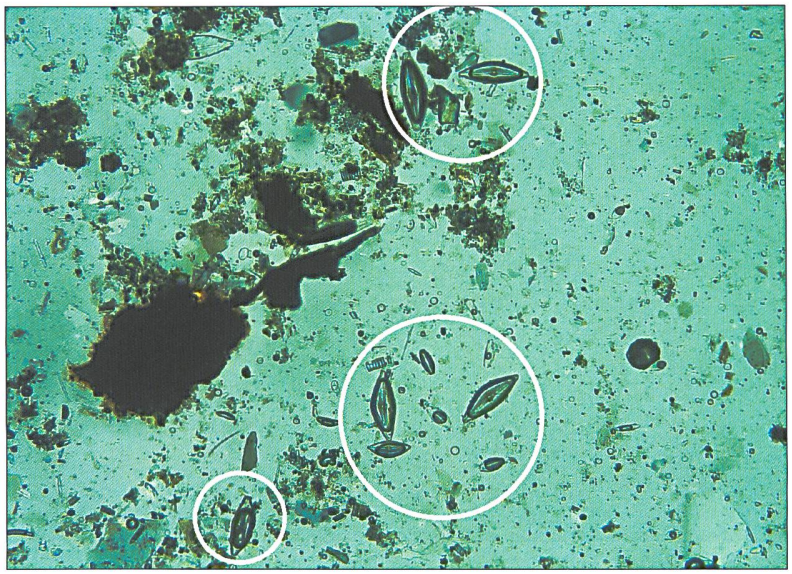
Sediment sampling, under 21 m water column, was carried out during two visits to Cadagno in July 2000 and July 2002. A sediment core of 54 cm length was taken during the first visit, using a gravity corer. A second sediment core of 248 cm length was collected during the second visit, using a pneumatic corer. The sediment cores, frozen at –20°C, were split into 2, 4 or 6 cm thickness. Total organic carbon (TOC) contents of dry and ground samples was determined by catalytic oxidation at 900-980 °C using a Shimadzu TOC-5000A (Total Organic Carbon Analyzer) coupled with a Shimadzu SSM-5000A (Solid Sample Module). Prior to TOC measure, the samples were wetted with HCl 6N and heated at 200-250°C under O_2 to remove inorganic carbon.

The macroscopic filamentous algae *Chara*, very prolific in the oxic zone of the lake and probably a significant autochthonous source of the sedimentary organic matter, were collected under a water column of 6 to 10 m.

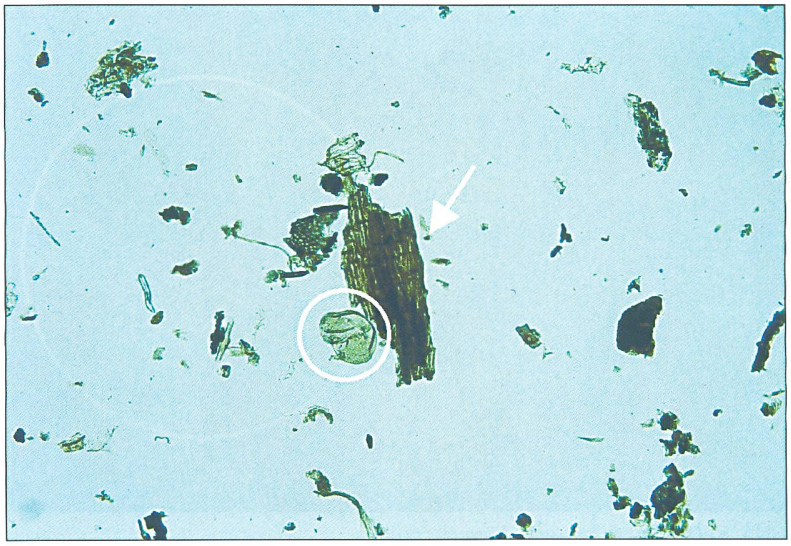
A mixture of herbaceous plants was also collected from the north slope of the lake. These plants are virtually the only allochthonous source of sedimentary organic matter in the neighborhood of the lake.

Lipids were extracted from the sediments, the algae and the herbaceous plants, fractionated and analyzed by gas chromatography-mass spectrometry (GC-MS) as described previously (Mendoza 1987a). After defrosting and freeze-drying, the sample was acidified to pH 3 with HCl 3N, transferred to a Soxhlet cartridge and extracted by ultrasonication with acetone (2 x 150 ml) and methylene chloride (3 x 150 ml). The acetone extracts were concentrated *in vacuo* and extracted with methylene chloride (2 x 150 ml).

Fig. 2. Microscopic photography of sections at 9 and 15 cm depth of sediment core from lake Cadagno: (depth in cm, a = untreated sediment and b = sediment after acidic treatment).

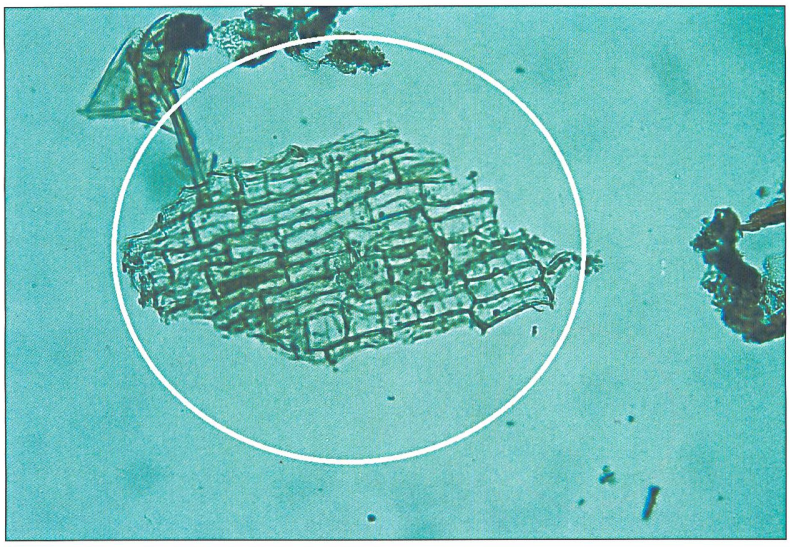


(9, a) Diatoms (circles) and black organic matter



(15, b) Pollen (circle) and detritus of preserved lignin (arrow)

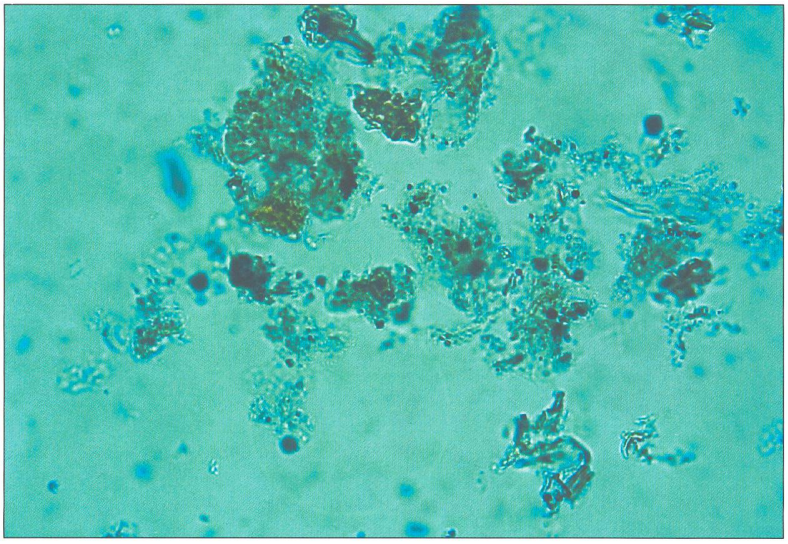
(15, b) Detritus of preserved cuticle (circle)



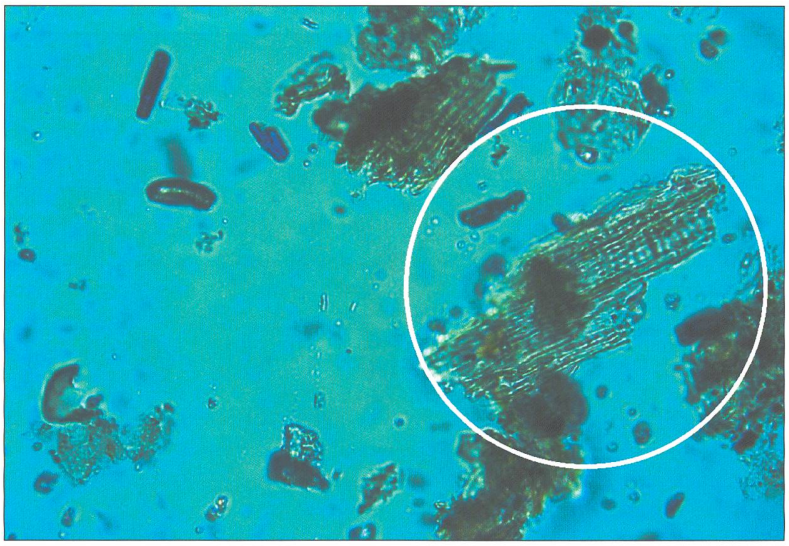
All the methylene chloride extracts were then combined and evaporated *in vacuo*. The resulting residue is the free organic matter.

The organic matter bonded to the polymeric matrix through ester or amide linkages was liberated by strong acid hydrolysis of the residue with HCl 6N at 120°C during 12 hours under nitrogen. The pH of the resulting solution was adjusted to 13-14 with KOH (conc.), and the mixture was refluxed during 4 hours under nitrogen to saponify the esters formed during the acid hydrolysis. After cooling, the solution was acidified to pH 3 with HCl 6N and extracted as described above to isolate the bound organic matter.

The organic residue was separated into neutral and acidic fractions by *SPE chromatography* (solid phase extraction) on a «Amino-2 g» (Separtis AG), anion exchanger cartridge. The neutral fraction and the acidic fractions were eluted with 32 ml ether/methanol (2:1), and 48 ml formic acid/ether (4% v/v), respectively. The acidic fraction was concentrated *in vacuo* and methylated with 14% BF_3/methanol (Fluka AG, Switzerland). The methyl esters were fractionated by flash chromatography over silica gel (Merck 60, 70-230 mesh; 20 cm x 0.6 cm i.d.). The esters of unsubstituted acids were eluted with 90 ml hexane/methylene chloride (3:1), the esters of hydroxyacids and dicarboxylic acids were eluted with 90 ml methylene chloride/ethyl acetate (8:2). The third fraction, eluted with 70 ml methanol/ethyl acetate (1:1), contained no GC-MS amenable compounds. The second fraction was trimethylsilylated with BSTFA (Fluka AG, Switzerland) before analysis.



(27, b) Amorphous and pyritized organic matter (dotted mass)



(245, b) Detritus of preserved lignin (circle)

(245, b) Amorphous and pyritized organic matter (black mass and dotted mass), dinoflagellates (white circle) and conifer pollen (red circle)

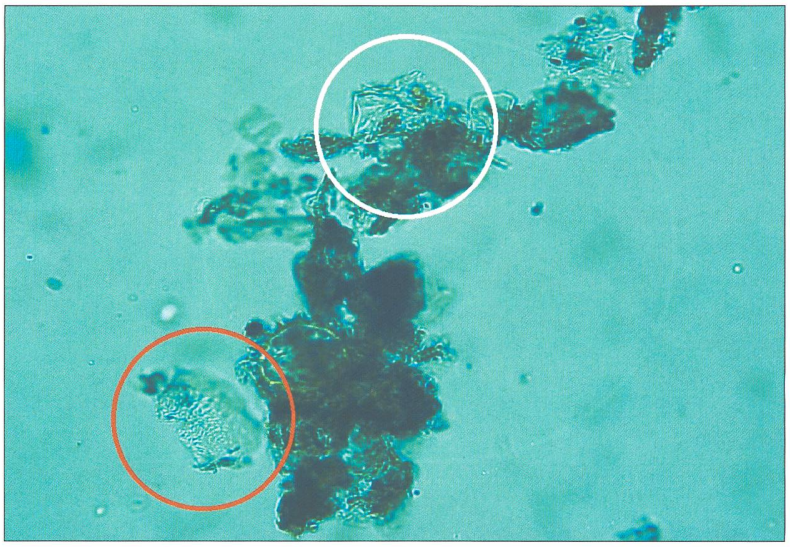


Fig. 2. Microscopic photography of sections at 27 and 245 cm depth of sediment core from lake Cadagno: (depth in cm, a = untreated sediment and b = sediment after acidic treatment).

Analysis by gas chromatography-mass spectrometry (GC-MS) was performed using a Hewlett Packard 5890 gas chromatography coupled with a VG Masslab Trio-2 mass spectrometer (electron impact at 70 eV, m/z 45-700 full scan, cycle time 1 s). The gas chromatography was equipped with a J&W DB-5 column (30 m x 0.25 mm, 0.25 mm film thickness). Temperature program: 1 min at 80°C; 80 to 300°C at 3°C/min; 22 min at 300°C. Carrier gas: helium at a constant pressure of 75 kPa. Samples for analysis were injected splitless (320°C)

Results and Discussion

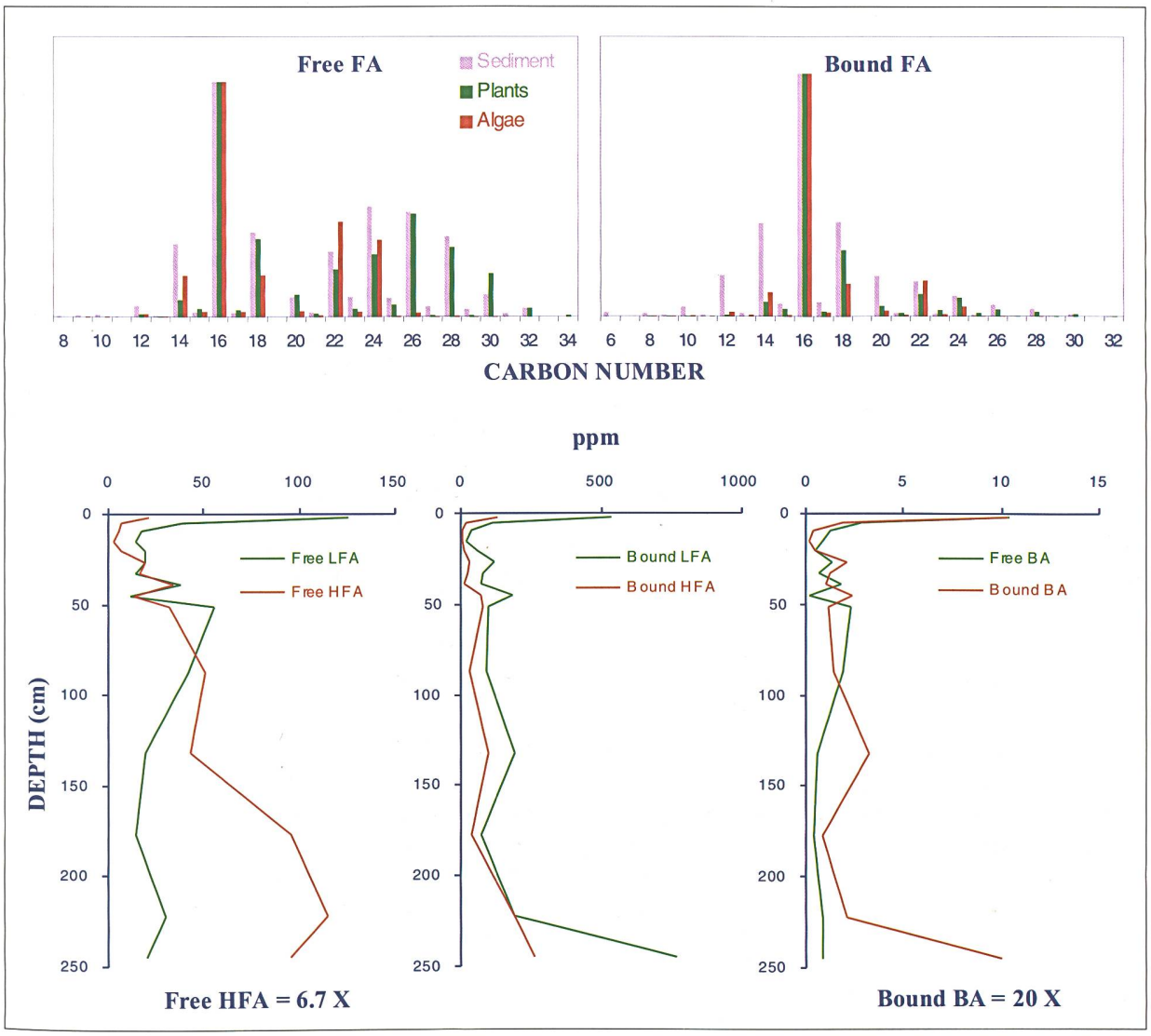
The total organic carbon (TOC) values (3-15 wt%) are characteristic of a sediment with high preservation of organic matter deposited in anoxic environment, all along the sediment core. However, the depth profile shows a sharp decrease from the top of the core down to 15 cm, strong fluctuations between 15-51 cm, then a smooth increase down to the deepest section, as shown in Fig. 1.

Radiological ^{137}Cs and ^{210}Pb dating of the cores was attempted by Dr. J.-L. Loizeau (Institut F.-A. Forel, section of Sciences de la Terre, University of Geneva), but the results have not been conclusive. Therefore, we will report the depth of sections rather than their age.

The optical microscopic analyses (Fig. 2) have been done on several sections of the core on untreated sediments as well as on concentrated organic matter (after treatment of the sediment with HCl (32%) and HF (70%)). Sections at 9 and 27 cm depths showed essentially diatoms and a black organic matter. The acid treatment of these sediments high-

lighted the presence of amorphous and pyritized organic matter indicating that the autochthonous inputs are dominant in these sections.
In the untreated sediments situated at 15 and 21 cm depth, diatoms and a mineral matter from external input (quartz and silicates, pyrite) were observed. Diatoms are present in these sections in smaller amounts than at 9 and 27 cm depth. Concentrated organic matter showed the presence of pollens and preserved cuticles and lignins. The composition of these sections shows the dominance of allochthonous inputs. If we admit a sedimentation rate of about 4mm/y for the first 50 cm depth (Züllig 1985; Birch 1996), the mineral matter in these sections is presumably from the input of clastic materials by a large avalanche which occurred in 1951 (Birch 1996). The increase of sedimentation rate on this event may also explain the better preservation of organisms remains. In fact, a quick burying allows the organic remains to escape the bacterial decomposition more rapidly. Highest contents of amorphous and pyritized organic matter were observed in the sediment section at 245 cm depth which contains detritus of lignins, conifer pollens, and dinoflagellates. Combined with the highest TOC content, this indicates a higher bacterial activity resulting either from a lower sedimentation rate or a higher bacterial population in the deepest section. The presence of conifer pollens in this section implicates that forests were closer to the lake during the corresponding period.

Fig. 3. Histograms of FA normalized to $C_{16:0}$ in the free and bound fractions of lake Cadagno surface sediments, plants and algae (top). Depth profiles of free and bound LFA, HFA and BA (Bottom). FA, total saturated and linear fatty acids; LFA, saturated, linear and low molecular weight fatty acids; HFA, saturated, linear and high molecular weight fatty acids; BA, saturated and branched fatty acids. Abundances in ppm should be multiplied by indicated factors for species given under the graphs.



			Sediments		Plants		Algae	
			Free	Bound	Free	Bound	Free	Bound
Branched	FA	Iso	C_{12-18}	C_{11-18}, C_{20-23}, C_{25}	C_{13-17}	C_{13-17}	C_{15-17}	C_{15-17}
		Anteiso	Odd C_{13-17}	Odd C_{11-17}, C_{21-25}	Odd C_{13-17}	Odd C_{13-17}	C_{15}, C_{17}	C_{15}, C_{17}
	α-OH	Iso	-	C_{11-17}, C_{21}	-	-	C_{15}	C_{15-17}
		Anteiso	-	Odd C_{13-17}, C_{21}	-	-	C_{15}	C_{15}
	β-OH	Iso	C_{13-17}	C_{10-21}	-	-	C_{15}, C_{17}	C_{13-17}
		Anteiso	Odd C_{13-17}	Odd C_{11-21}	-	-	C_{15}, C_{17}	Odd C_{13-17}
		Mid-chain	-	C_{15-18}, C_{21}	-	-	-	C_{17}
Unsaturated	FA		$C_{16:1-2}$, $C_{18:1-3}$, $C_{20:1}$, $C_{22-30:1}$, $C_{32:1}$	Even $C_{12-16:1}$, $C_{18:1-3}$, Even $C_{20-30:1}$	$C_{16:1-3}$, $C_{18:1-4}$, $C_{20:1-2}$, $C_{22-24:1}$, $C_{26:1}$	$C_{16:1}$, $C_{18:1-2}$, $C_{20:1-2}$, $C_{22:1}$, $C_{24:1}$	$C_{14:1}$, $C_{16:1-2}$, $C_{18:1-3}$, $C_{20:1-3}$, $C_{22:1}$, $C_{24:1}$	$C_{14:1}$, $C_{16:1}$, $C_{18:1-2}$, Even $C_{20-24:1}$
	α-OH		-	$C_{12:1}$, $C_{16:1}$	-	-	-	-
	β-OH		-	Even $C_{12-20:1}$, $C_{19:1}$	-	-	-	-

Table 1. Branched (iso-, anteiso and mid-chain) and unsaturated fatty acids (FA), α-hydroxyacids (α-OH) and β-hydroxyacids (β-OH) identified in the free and bound fractions of lake Cadagno sediments, plants and algae.

Unsubstituted acids

The saturated, linear and low molecular weight fatty acids (LFA < C_{20}) represent essentially a planktonic and bacterial input; they are present in plants in small amounts (Volkman and Johns 1977; Perry and al. 1979; Duan 2000). The saturated, linear and high molecular weight fatty acids (HFA > C_{20}) are generally considered as indicators of higher plant input (Meinschein and Kenny 1957; Cranwell 1974; Matsuda and Koyama 1977; Kawamura and Ishiwatari 1984; Franich and al. 1985; Hu and al. 1988) although they have also been found in yeasts (Fulco 1967; Welch and Burlingame 1973), cyanobacteria and algae (Rezanka and al. 1983). In our study, the linear and saturated fatty acids show a bimodal distribution (Fig. 3): the first is centered on C_{16} in the free and bound forms; the second on C_{24} (0-33 cm), C_{26} (39-45 cm) and C_{28} (51-245 cm) in the free form, and on C_{20} and C_{22} (0-45 cm), C_{28} (51 cm) and C_{26} (87-245 cm) in the bound form.

With depth, the LFA and HFA are subject to diagenetic degradation to give polymers (Haddad and al. 1992). As illustrated in Fig. 3, in lake Cadagno sediments, the abundance of free LFA presents a sharp decrease at the first 15 cm; then fluctuations are observed between 15 and 51 cm depth. The profile becomes almost stable under a depth of 51 cm. Free HFA shows the same evolution than free LFA between 0 and 51 cm depth followed by a steady increase until the deepest section of the core. We can explain this increase by a higher allochthonous contribution, and more precisely by an evolution of the surrounding vegetation. This is confirmed, as before mentioned, by the microscopic analysis showing the presence of conifer pollens only in the deepest sections of core.

Branched fatty acids

The branched fatty acids (BA) are present in small amounts in fungi, mollusks and phytoplankton, and in high concentrations in bacteria (Cranwell 1974; Volkman and al. 1980). In lake Cadagno sediments, *iso-* and *anteiso-* saturated acids were found, with odd and even carbon numbers, ranging from C_{10} to C_{20} (Table 1), with a maximum at C_{15}. However, *iso-* and *anteiso* acids > C_{20} (*i-* and *ai-* C_{21}, C_{23} and C_{25}) were also present in the bound fractions. This is unexpected because, to the best of our knowledge, they have never been reported in geochemical literature.

Fig. 3 shows that the depth profiles for free and bound branched acids are significantly different, suggesting that different microorganisms or different organs of these microorganisms produce each form of these acids. The contribution of these acids does not increase with depth, except for bound BA at 245 cm depth. It follows that the higher bacterial activity between 51 and 245 cm depth, as inferred from optical analysis of sediments, does not result from a higher bacterial population but rather from a lower sedimentation rate.

The depth profiles of BA and LFA are almost the same in the free and bound fractions, thus indicating that most of LFA also have a bacterial origin.

Unsaturated fatty acids

Unsaturated acids identified in lake Cadagno sediments, plants and algae are reported in Table 1. The short-chain unsaturated acids (LU) are common in plankton, higher plants and bacteria (Volkman and

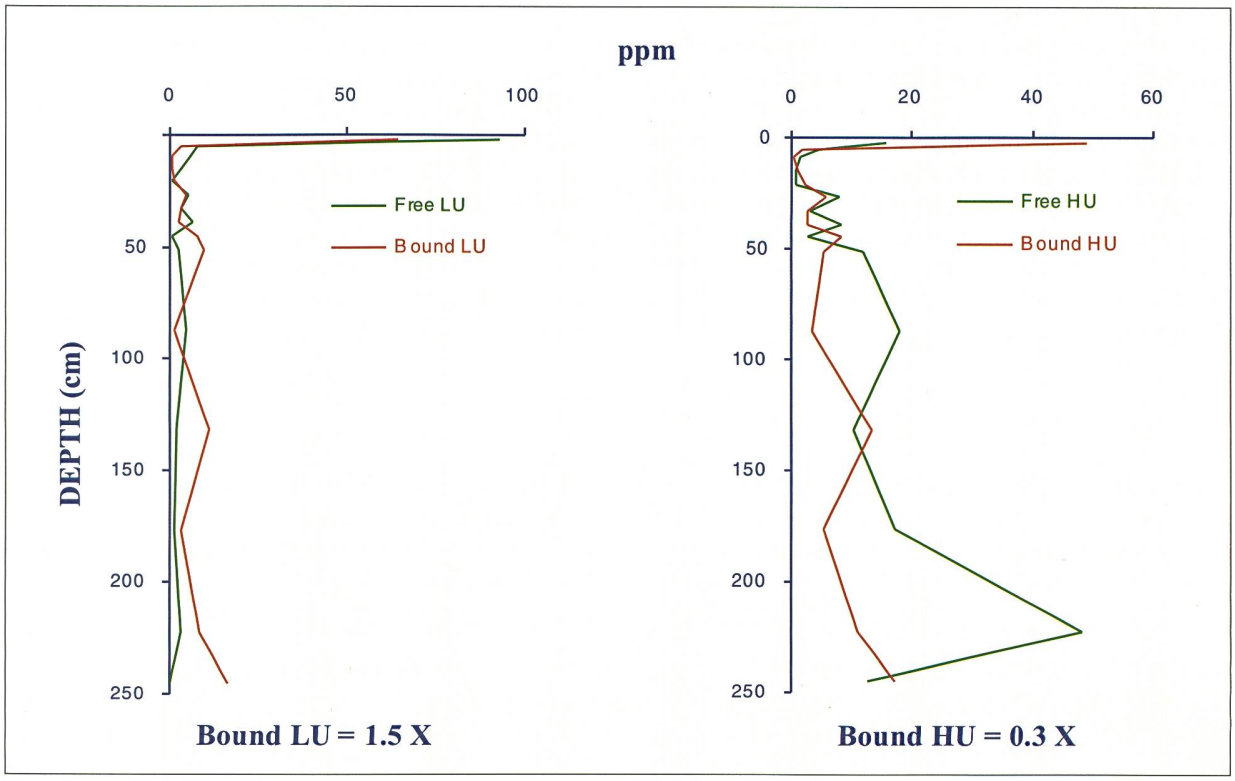


Fig. 4. Depth profiles of LU and HU in the free and bound fractions of lake Cadagno sediments, plants and algae. LU, insaturated, linear and short chain fatty acids; HFA, insaturated, linear and long chain fatty acids. Abundances in ppm should be multiplied by indicated factors for species given under the graphs.

Johns 1977; Boon and al. 1978; Perry and al. 1979). The depth profile of LU ($C_{16:1}$ and $C_{18:1}$), shown in Fig. 4, is fairly comparable to that of BA (Fig. 3) in the free fractions. We can conclude that the bacteria are the main source of free LU. In fact, LU and more particularly the polyunsaturated species, originated from plankton and higher plants, disappear very quickly in the first centimeters of sediments because they are too propitious to the diagenetic degradation. Those found in deeper sections of the core result therefore from bacterial reworking in the top 20 cm of the sediment. On the other hand, bound LU present in some sections of the core shows a different evolution compared to the bound BA. These sedimentary acids are therefore not only from bacteria but also probably from planktonic or/and terrestrial origin.

Yeasts (Fulco 1967; Welch and Burlingame 1973), mycobacteria (Matsuda and Koyama 1978), lichens (Dembitskii and al. 1991) and higher plants (Gaskell and al. 1975) produce long-chain unsaturated acids (HU: unsaturated acids between C_{20} and C_{32}). Although these compounds have also been reported in some algae and cyanobacteria (Rezanka and al. 1983), they can be used as indicators of terrestrial input, since yeast as well as mycobacteria are heterotrophic aerobes living mainly on soils or senescent plants (Brock and al. 1984; Mendoza 1987a). The depth profiles of HU (Fig. 4) and their saturated homologues HFA (Fig. 3) show a similar evolution in the free and bound fractions. This observation allows to assign to these unsaturated acids the same origins as to their homologues HFA, i.e. terrestrial sources.

β-hydroxyacids

The bound β-hydroxyacids < C_{20} are characteristic of cell walls of Gram-negative bacteria (Weckesser and al. 1979; Goossens and al. 1986; Mendoza and al. 1987b). These acids, in the C_8-C_{26} range, have also been found in cyanobacteria and in some micro algae (Eglinton and al. 1968; Cardoso and al. 1977; Kawamura and Ishiwatari 1982; Goossens and al. 1986; Mendoza and al. 1987b).

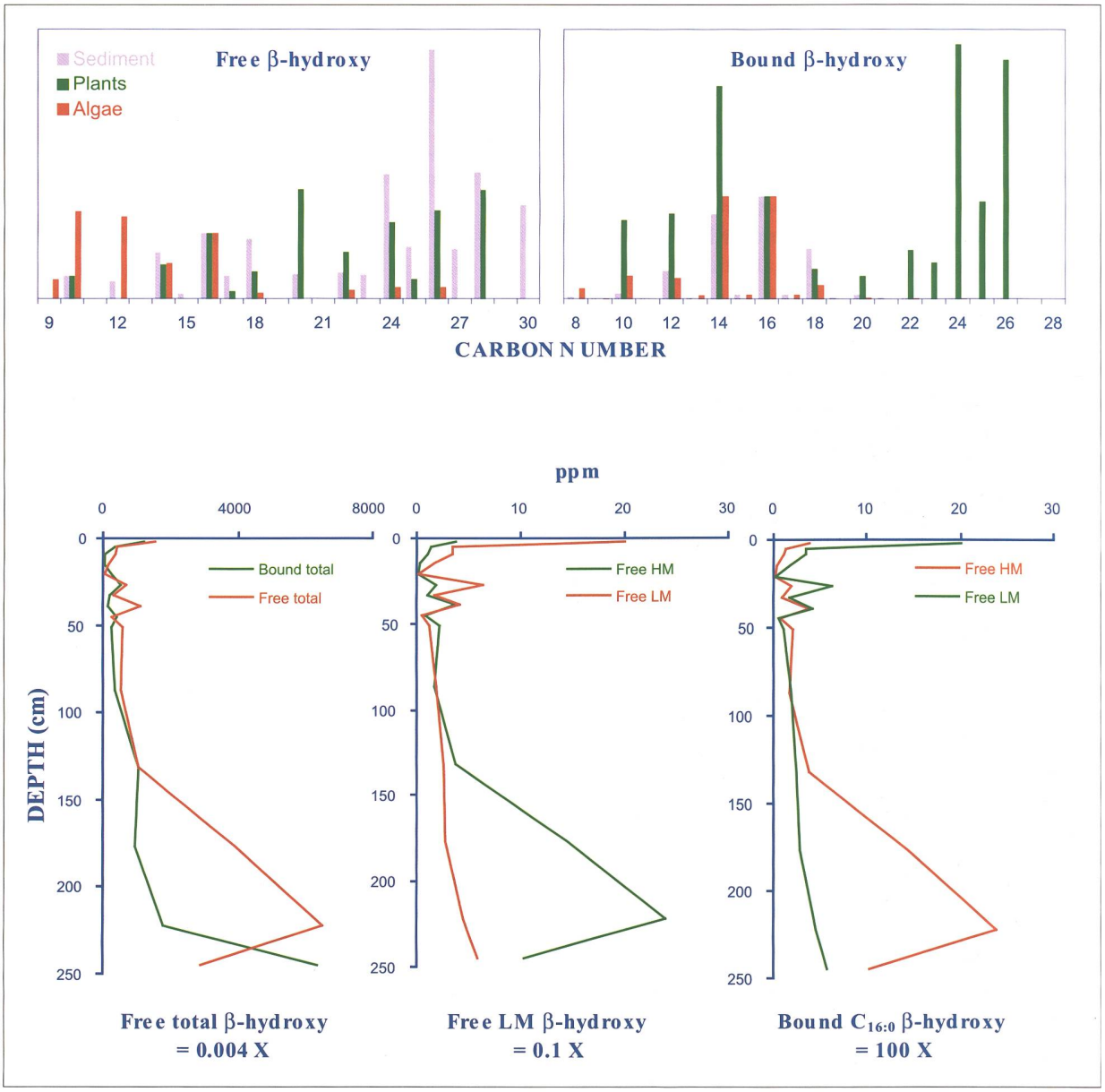
In lake Cadagno sediments, β-hydroxyacids are present in the C_8-C_{30} range; those > C_{20} are present in small amounts in the bound fractions only. Their total quantity in the free fractions is 7.6% of total acids. Iso-, anteiso and mid-chain methyl branched β-hydroxyacids as well as small amounts of unsaturated homologues were also detected besides saturated linear acids (Table 1). Typical distributions are shown in Fig. 5. It should be noted that during the

hydrolysis with HCl 6N, small proportions of β-hydroxyacids dehydrate to corresponding α,β-unsaturated acids characterized by a base peak at *m/z* 87 in their mass spectra (Mendoza and al. 1987b).

The depth profiles of total free and bound β-hydroxyacids [ΣC_8-C_{30}], shown in Fig. 5a, are different, suggesting different sources for each form. In the bound fraction, these acids show an increase with depth, indicating that the contribution of Gram-negative bacteria was more important during the corresponding periods.

The long-chain β-hydroxyacids profile (HM) (Fig. 5b) resembles to the HFA profile in the free fraction. Considering the resemblance of the chain length distribution, one can infer a relation between free unsubstituted acids and β-hydroxyacids. Eglinton and al. (1968) suggested a possible oxidative transformation of unsubstituted acids to β-hydroxyacids presumably in the oxic zone of the water column. Analysis of particulate organic matter might provide supplementary information about this transformation.

Fig. 5. Histograms of β-hydroxyacids normalized to $C_{16:0}$ in the free and bound fractions of lake Cadagno surface sediments, plants and algae (top). Depth profiles of (a) free and bound total β-hydroxyacids [ΣC_8-C_{30}], (b) free LM and HM β-hydroxyacids, (c) bound $C_{8:0}$, $C_{10:0}$ and $C_{16:0}$ β-hydroxyacids (Bottom). LM, short chain β-hydroxyacids (< C_{20}); HM, long chain β-hydroxyacids (≥ C_{20}). Abundances in ppm should be multiplied by indicated factors for species given under the graphs.



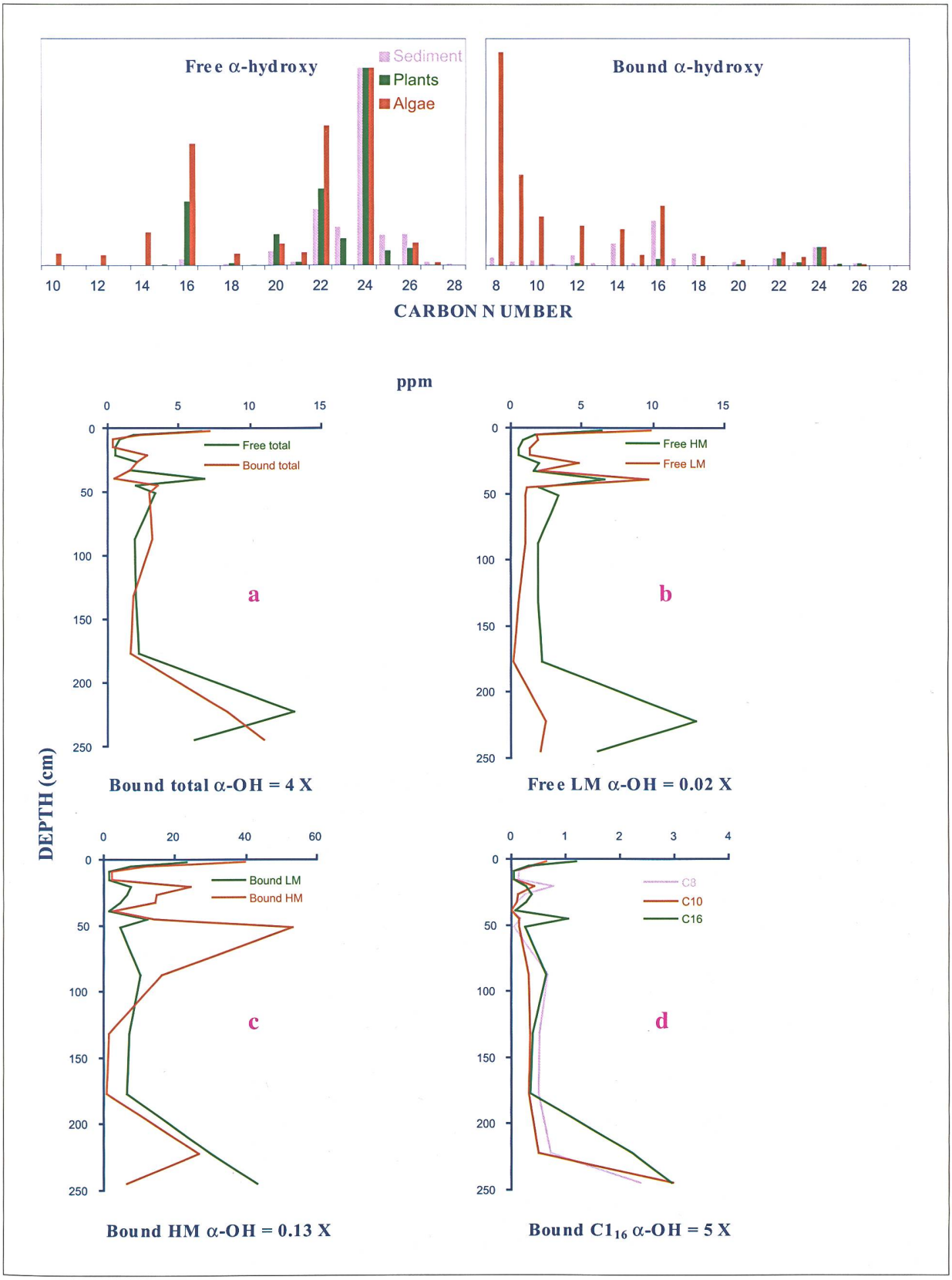


Fig. 6. Histograms of α-hydroxyacids normalized to $C_{24:0}$ in the free and bound fractions of lake Cadagno surface sediments, plants and algae (top). Depth profiles of (a) free and bound total α-hydroxyacids, (b) free LM and HM α-hydroxyacids, (c) Bound LM and HM α-hydroxyacids, (d) bound $C_{8:0}$, $C_{10:0}$ and $C_{16:0}$ α-hydroxyacids. LM, short chain α-hydroxyacids ($\leq C_{18}$); HM, long chain α-hydroxyacids ($\geq C_{20}$). Abundances in ppm should be multiplied by indicated factors for species given under the graphs.

Mendoza and al. (1987b) have mentioned the presence of bound β-hydroxyacids ≤ C_{10} (C_8, C_9 and C_{10}) in an anoxic lacustrine sediment, but because of the complexity of the mass fragmentograms no quantification could be made. More recently, Keinänen and al. (2003) identified β-hydroxyacid methyl esters between C_8 and C_{20} in soil and sediment by GC-MS, using SIM mode (*m/z* 103) without purification or derivatization of the hydroxyl groups. However, they made no mention of possible sources for the acids ≤ C_{10}. Fig. 5c illustrates the depth profiles of bound β-OH(TMS)-$C_{8:0}$, -$C_{10:0}$ and -$C_{16:0}$ in our samples. All three acids follow the same evolution; thus suggesting that b-hydroxyacids C_8-C_{10} are also produced by Gram-negative bacteria.

The distributions of β-hydroxyacids found in algae and sediments, are different in the free fractions, while they are similar in the bound fractions (Fig. 5). The presence of these acids in the algae bound fraction results probably from the parasitic Gram-negative bacteria living on these algae. On the other hand, it is difficult to interpret the free β-hydroxyacids of the algae, which are quantitatively much less important.

The distributions of β-hydroxyacids are rather peculiar in herbaceous plants (Fig. 5) The high proportions of > C_{18} homologues may be indicative for a production by the metabolism of plant monocarboxylic acids by parasitic microorganisms.

α-hydroxyacids

The short-chain α-hydroxyacids (≤ C_{18}) occur in Gram-negative bacteria (Jantzen 1984) Generally, they are present in lesser amounts than corresponding β-hydroxyacids. The long-chain (≥ C_{20}) members are rather terrestrial; they are synthesized by yeasts (Fulco 1967; Nurminen and Suomalainen 1971) and in small amounts by higher plants or by microorganisms living in symbiosis on the plants (Hu and al. 1988).

In sediments from lake Cadagno, they are present in the C_8 to C_{30} range with a bimodal distribution (Fig. 6). The short mode (< C_{18}) is more important in the bound fraction, except for the section at 51 cm. Its origin is the bacterial cell walls, since odd-carbon numbered iso- and anteiso- branched acids are predominant (Table 1) (Yano and al. 1976; Cranwell 1981). The long mode, centered on C_{24}, is more important in the free fraction. Fig. 6a shows the depth profiles of total free [ΣC_9-C_{30}] and bound [ΣC_8-C_{30}] a-hydroxyacids. The difference of these profiles implicates that these acids in free and bound forms originate from different sources. The depth profiles of long mode (HM) α-hydroxyacids (Fig. 6b) and of HFA (Fig. 3) are more or less the same in the free fractions suggesting that the former may be produced from the microbial metabolism of the latter. The differences can be explained if we consider that the HFA are directly derived from higher plants, while the HM α-hydroxyacids are indirectly derived. The short mode (LM) α-hydroxyacids profile (Fig. 6c) resembles to the α-hydroxyacids profile in the bound fraction in accord to their common bacterial origin.

To determine the origin of α-hydroxyacids ≤ C_{10} not mentioned in the geochemical literature, we illustrated in Fig. 6d the depth profiles of bound α-OH(TMS)-$C_{8:0}$, -$C_{10:0}$ and -$C_{16:0}$ acids. The similarity of these profiles is in accord with the same bacterial origin for all of these acids. Keinänen and al. (2003) have also identified α-hydroxyacids in the C_7 to C_{27} range in soil and sediment by SIM (*m/z* 90 and M-59). α-hydroxyacids in the C_{16}-C_{26} range have been found in a few algae species (Matsumoto and al. 1984). They are also present in *chara* with a bimodal distribution. Since the branched acids iso- and anteiso- are exclusively bacterial, the short mode is certainly derived from organisms living in symbiosis on these algae (Table 1).

The distributions of α-hydroxyacids ≥ C_{20} found in the free and bound fractions of plants are similar to those of sediments (Fig. 6). This suggests that the sedimentary acids are mainly originated from terrestrial input. As previously pointed out, they are probably derived from the metabolism of parasitic microorganisms present on the plants.

ω-hydroxyacids

The short-chain ω-hydroxyacids (≤ C_{18}) are markers for cutins of vascular plants (Holloway 1972; Kolattukudy 1980). The long-chain (≥ C_{20}) members are components of suberins of some plants (Holloway 1972). Marine plants also produce this type of acids, but only in the free fractions (Volkman and al. 1980; Nichols and al. 1982; Shaw and Johns 1985). Some studies suggest that they might result from aerobic oxidation of unsubstituted acids within the water column (Johns and Onder 1975; Boon and al. 1977; Kawamura and Ishiwatari 1984). The ω-oxidation of monocarboxylic acids by aerobic microorganisms has been proved by laboratory experiments (Tulloch and al. 1962; Kester and Foster 1963; Stodola and al. 1967)

In lake Cadagno samples, these acids are observed in the free and bound fractions, and they are dominated by even carbon numbered compounds (Fig. 7). The bound fraction constitutes 68% of the total quantity of these acids.

The depth profile of free long-chain ω-hydroxyacids (HM, Fig. 7b) shows only a slight resemblance with that of free HFA. If they originate from aerobic oxidation of HFA, the difference may be explained by the

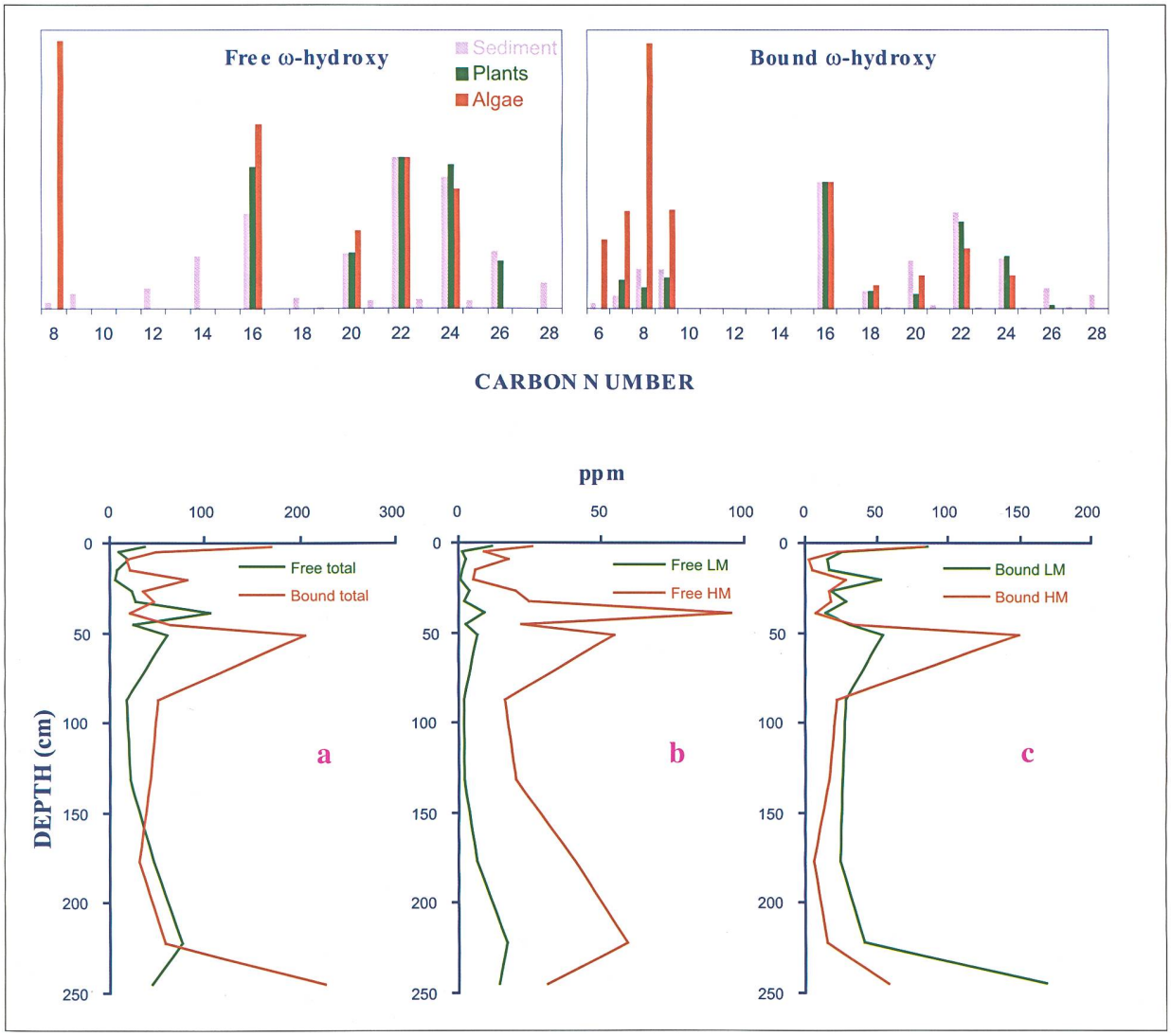


Fig. 7. Histograms of ω-hydroxyacids normalized to $C_{22:0}$ in the free fraction and to $C_{16:0}$ in the bound fraction of lake Cadagno surface sediments, plants and algae (top). Depth profiles of (a) free and bound total ω-hydroxyacids, (b) free LM and HM ω-hydroxyacids, (c) Bound LM and HM ω-hydroxyacids. LM, short chain ω-hydroxyacids (≤ C_{18}); HM, long chain ω-hydroxyacids (≥ C_{20}).

fact that the HFA are directly biosynthesized by higher plants, while the HM ω-hydroxyacids are indirectly derived and their profile is certainly dependent on the nature of microorganisms in the oxic water column.

The evolution of the long mode (HM) ω-hydroxyacids (Fig. 7b) is more or less the same as that of the long mode (HM) α-hydroxyacids (Fig. 6b) in the free fractions. The slight differences may be due to the fact that different microorganisms with different specificities synthesize these acids from unsubstituted acids.

The distributions of ω-hydroxyacids in the free and bound fractions of sediments, plants and algae are similar for the even carbon numbered acids > C_{16} (Fig. 7). This suggests that plants and algae are contributors to the sedimentary acids. The ω-hydroxyacids in the C_6-C_{10} range in sediments might result from biogenic and/or abiogenic degradation of unsubstituted acids. The odd carbon numbered acids, present in small proportions in sediments but absent in plants and algae, may be derived from aerobic oxidation of unsubstituted acids within the water column.

(ω-1)-hydroxyacids

An example of distribution of (ω-1)-hydroxyacids is shown in Fig. 8 for the surface sediment. In the free fraction, centered on C_{28}, the even carbon numbered acids (C_{20} to C_{30}) and the branched homologue C_{31} (methyl group branching at position (ω-2)) (Mendoza and al. 1987c) have been detected. Small amounts of short chain homologues (C_{10}, C_{14}, C_{16} and

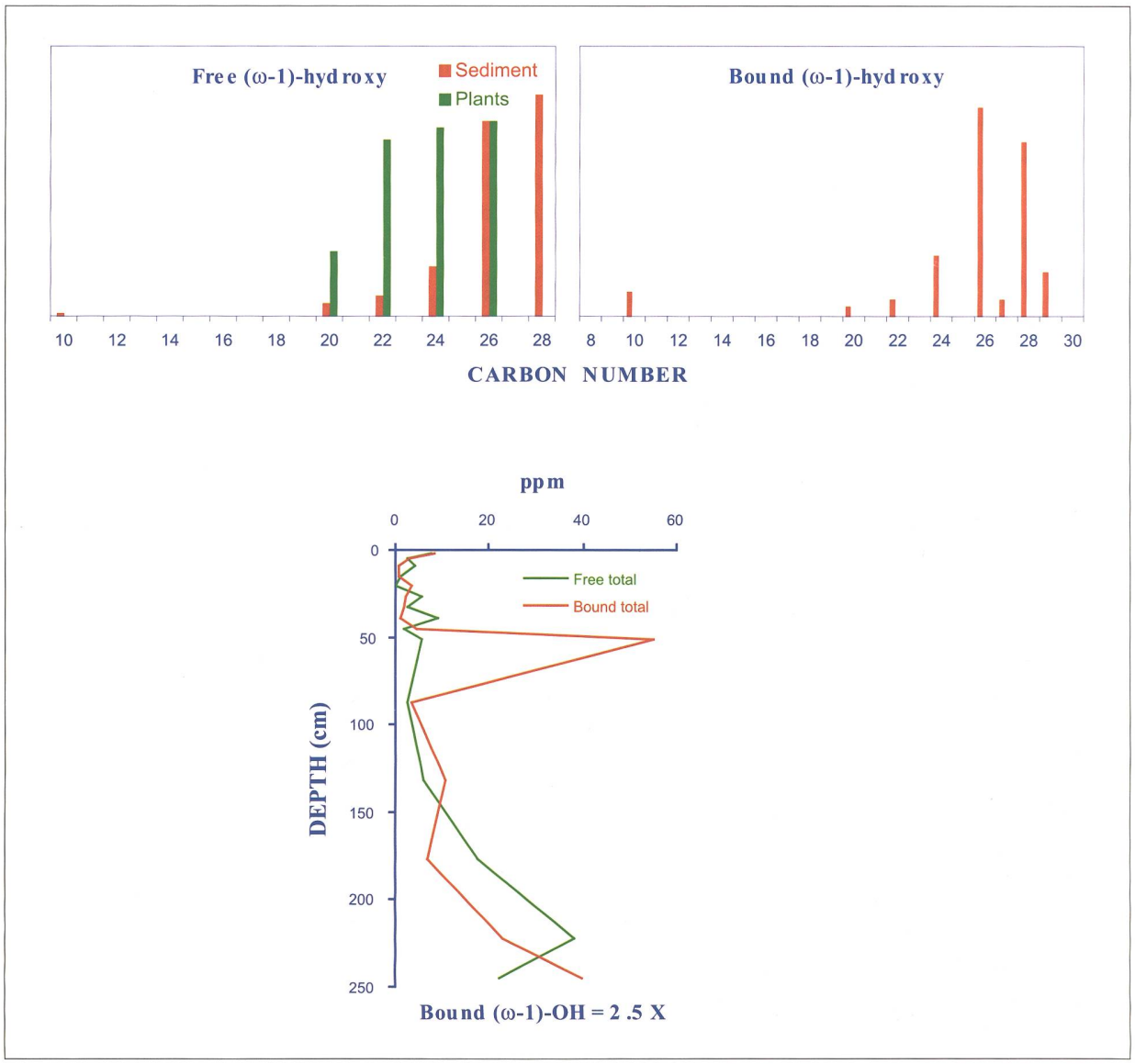


Fig. 8. Histograms of (ω-1)-hydroxyacids normalized to $C_{26:0}$ in the free and bound fractions of lake Cadagno surface sediments and plants (top). Depth profiles of free and bound total (ω-1)-hydroxyacids (bottom). Abundances in ppm should be multiplied by indicated factors for species given under the graphs.

C_{18}) have also been detected in some sections of the core. The bound fraction (68% of total (ω-1)-hydroxyacids in the surface sediment) also contained the branched odd carbon numbered homologues in the C_{27} to C_{33} range and the C_8 homologue.

The sources of these acids are not well known. In fact, Boon and al. (1977) assume that they originate from aerobic organisms (yeasts and fungi), while Shaw and Johns (1985) suppose that they may derive from marine plants. A diagenetic oxidation of unsubstituted acids has also been envisaged (Boon and al. 1975; Kawamura and Ishiwatari 1984). It is interesting to note that the long-chain acids have never been detected in organisms, but the C_{16} acid have been found in cutins of vascular plants (Caldicott and Eglinton 1976).

In the free fraction of lake Cadagno sediments, the depth profile of (ω-1)-hydroxyacids (Fig. 8) resembles to that of HFA. Therefore, these components are probably produced by aerobic oxidation of unsubstituted acids like the free long-chain β-hydroxyacids. If we compare the profile of (ω-1)-hydroxyacids in the bound fraction (Fig. 8) with that of ω-hydroxyacids (Fig. 7a), we observe a similar evolution. This suggests a common origin for both of them. The presence of (ω-1)-hydroxyacids in the C_{20} to C_{26} range only in the free fraction of plants allows to conclude that these acids are not constituents of cutins and suberins, but they are probably produced from the metabolism of parasitic microorganisms. The differences in their distributions in the free fractions of sediments and plants may result from contribution of

such microorganisms, living in the water column for example. The (ω-1)-hydroxyacids are completely absent in the algae *chara*. Since the bound ω- and (ω-1)-hydroxyacids seem to derive from the same sources, it can be deduced that the herbaceous plants are the main contributors to ω-hydroxyacids, while the algae *chara* are the secondary contributors.

α,ω-dicarboxylic acids

The α,ω-dicarboxyacids (or diacids) ≥ C_{13} are constituents of epicuticular waxes and cutins/suberins of higher plants (Eglinton and al. 1968; Holloway 1972; Kollattukudy 1980) but may also be produced by abiotic or microbial oxidation of corresponding fatty acids or ω-hydroxyacids (Eglinton and al. 1968; Ishiwatari and Hanya 1975; Johns and Onder 1975). Those ≤ C_{12} derive from complete oxidation of the double bounds of unsaturated monocarboxylic acids, and they can also be observed in atmospheric particles (Kawamura and Gagosian 1987; Kawamura and al. 1996).

These acids are detected in lake Cadagno sediments in the C_8 to C_{30} range. An example of their distributions, in the free and bound fractions of the upper section (2 cm) is shown in Fig. 9. The bound fractions contain 69% of the total dicarboxyacids.

In the free and bound fractions of the sedimentary samples, the diacids ≥ C_{13} (Fig. 9b) show a similar depth profile with the ω-hydroxyacids. This indicates that, like the ω-hydroxyacids, they occur mainly from higher plants. However, considering the difference of carbon number distribution of these two classes of acids in the free fractions of plants, we can conclude that the sedimentary free diacids derive from microbial ω-oxidation of fatty acids rather than from ω-hydroxyacids. On the other hand, they show a similarity in their distribution in the bound fraction of

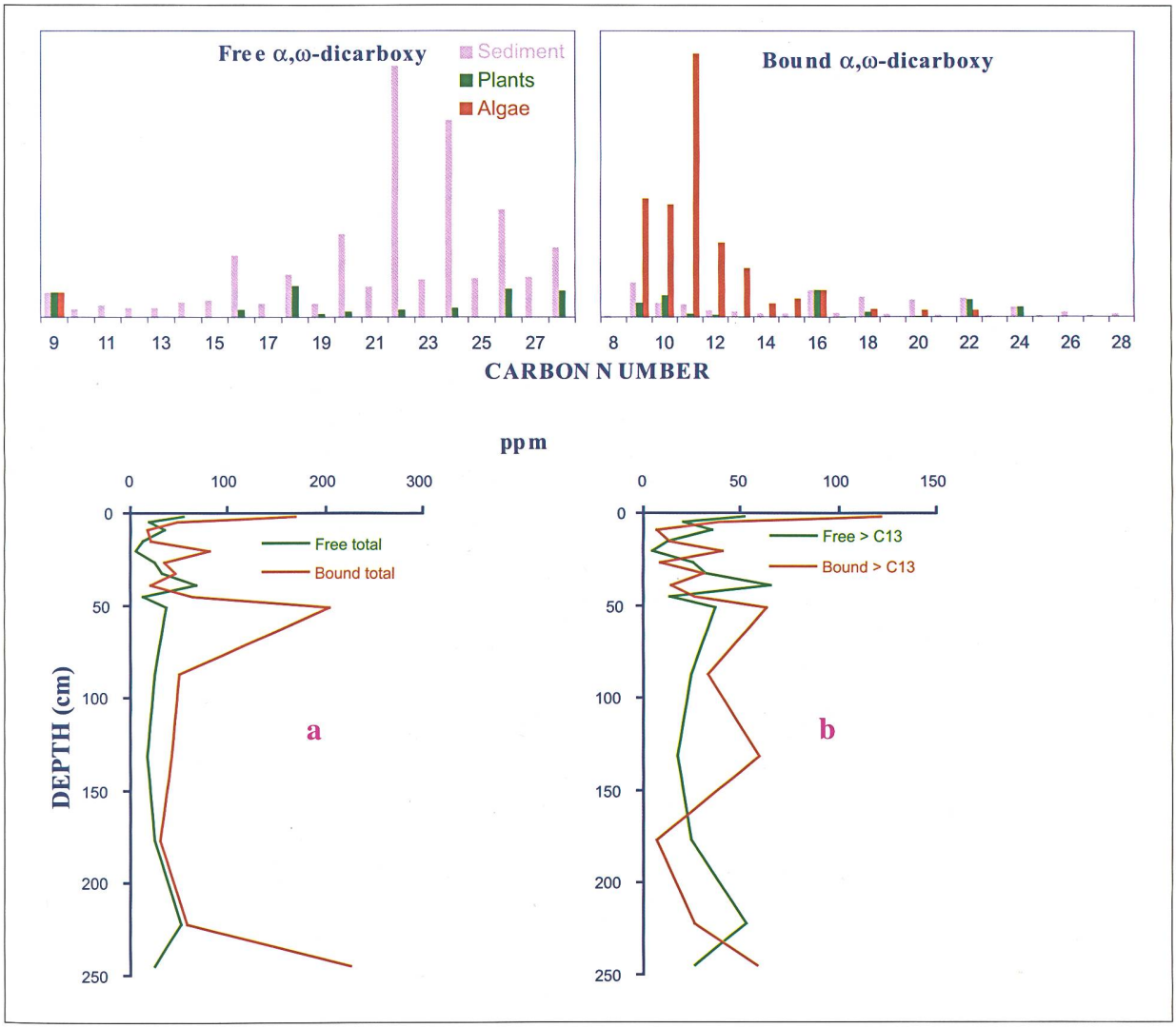


Fig. 9. Histograms of α,ω-dicarboxyacids normalized to $C_{9:0}$ in the free fraction and to $C_{16:0}$ in the bound fraction of lake Cadagno sediments, plants and algae (top). Depth profiles of free and bound (a) total α,ω-dicarboxyacids, (b) ≥ C_{13} α,ω-dicarboxyacids (bottom).

No	Ester	MM	Fraction	Formule
1	Benzoic acid trimethylsilyl ester	194	a,b,c,d,e,f	$C_{10}H_{14}O_2Si$
2	Benzoic acid, 4-(trimethylsilyloxy)-, methyl ester	224	a,b,d,f	$C_{11}H_{16}O_3Si$
5	Benzoic acid, x,y,z-trimethyl-, trimethylsilyl ester	236	a	$C_{13}H_{20}O_2Si$
12	Cinnamic acid, 4-(trimethylsiloxy)-, methyl ester	250	b,c,d	$C_{13}H_{18}O_3Si$
7	Cinnamic acid, 2-(trimethylsiloxy)-, methyl ester	250	c	$C_{13}H_{18}O_3Si$
8	Benzeneacetic acid, 3-methoxy-4-(trimethylsilyloxy)-, methyl ester	268	b,d	$C_{13}H_{20}O_4Si$
16	Cinnamic acid, 3-methoxy-4-(trimethylsiloxy)-, methyl ester	280	a,b,c,d	$C_{14}H_{20}O_4Si$
3	Benzoic acid, 2-(trimethylsilyloxy)-, trimethylsilyl ester	282	d,f	$C_{13}H_{22}O_3Si_2$
4	Benzoic acid, 3-(trimethylsilyloxy)-, trimethylsilyl ester	282	a,b,d,f	$C_{13}H_{22}O_3Si_2$
6	Benzoic acid, 4-(trimethylsilyloxy)-, trimethylsilyl ester	282	a,b,d	$C_{13}H_{22}O_3Si_2$
15	Cinnamic acid, 4-(trimethylsiloxy)-, trimethylsilyl ester	308	b,c,d	$C_{15}H_{24}O_3Si_2$
9	Benzoic acid, 2,4-bis(trimethylsiloxy)-, methyl ester	312	d	$C_{14}H_{24}O_4Si_2$
11	Benzoic acid, 3-methoxy-4-(trimethylsilyloxy)-, trimethylsilyl ester	312	a,b,c,d,f	$C_{14}H_{24}O_4Si_2$
10	Benzoic acid, 3,4-bis(trimethylsiloxy)-, methyl ester	312	b,d	$C_{14}H_{24}O_4Si_2$
14	Cinnamic acid, 4-methoxy-3-(trimethylsilyloxy)-, trimethylsilyl ester	338	d	$C_{16}H_{26}O_4Si_2$
17	Ferulic acid, trimethylsiloxy, trimethylsilyl ester	338	b,c,d,f	$C_{16}H_{26}O_4Si_2$
13	Benzoic acid, 3,5-dimethoxy-4-(trimethylsilyloxy), trimethylsilyl ester	342	a,b,d	$C_{15}H_{26}O_5Si_2$
18	m-OH(TMS)-α,ω-dicarboxy$C_{14:0}$ où m = 6 et 7	374	b,d,f	$C_{19}H_{38}O_5Si$
19	10-OH(TMS)-n$C_{18:0}$ FAME	386	a,b,c,d,f	$C_{22}H_{46}O_3Si$
20	m-OH(TMS)-α,ω-dicarboxy $C_{15:0}$ (m = 6 and 7)	388	b,d,f	$C_{20}H_{40}O_5Si$
22	m-OH(TMS)-α,ω-dicarboxy $C_{16:0}$ (m = 7 and 8)	402	b,d,f	$C_{21}H_{42}O_5Si$
24	m-OH(TMS)-α,ω-dicarboxy $C_{17:0}$ (m = 7, 8 and 9)	416	b,d	$C_{22}H_{44}O_5Si$
26	m-OH(TMS)-α,ω-dicarboxy $C_{18:1}$ (m = 7, 8 and 9)	428	b,d	$C_{23}H_{44}O_5Si$
27	m-OH(TMS)-α,ω-dicarboxy $C_{18:0}$ (m = 7, 8 and 9)	430	b,d	$C_{23}H_{46}O_5Si$
21	m,16-diOH(diTMS) $C_{15:0}$ (m = 8, 9 and 10)	432	b,d	$C_{22}H_{48}O_4Si_2$
29	m-OH(TMS)-α,ω-dicarboxy $C_{19:}0$ (m = 8 and 9)	444	d	$C_{24}H_{48}O_5Si$
23	m,16-diOH(diTMS) $C_{16:0}$ (m = 8, 9 and 10)	446	b,d,f	$C_{23}H_{50}O_4Si_2$
25	m,17-diOH(diTMS) $C_{17:0}$ (m = 8, 9 and 10)	460	d	$C_{24}H_{52}O_4Si_2$
28	m,18-diOH(diTMS) $C_{18:0}$ (m = 8, 9, 10 and 11)	474	b,d,f	$C_{25}H_{54}O_4Si_2$
30	m,19-diOH(diTMS) $C_{19:0}$ (m = 8, 9 and 10)	488	b,d	$C_{26}H_{56}O_4Si_2$

Table 2. Benzoic acids, dihydroxylated acids and m-OH(TMS)-α,ω-dicarboxyacids identified by GC-MS in the lake Cadagno sediments (a free, b bound), plants herbaceous (c free, d bound) and algae (e free, f bound). The compounds derived from lignins can be regrouped in: p-hydroxyl 2; vanillyl 11; cinnamyl 7, 12, 14, 15, 16, 17; syringyl 13. In the couples (2 et 6), (12 et 15) and (16 et 17) the ester fonctions COO-Me are transesterified into COO-TMS. NO, elution order in the chromatogram.

plants (Figs. 7 and 9), involving that the bound diacids result from plants by biosynthetic oxidation of corresponding ω-hydroxyacids.

The presence of diacids < C_{22}, in the bound fraction of algae suggests a possible contribution of algae to the sedimentary diacids. Since the diacids > C_{22} have not been found in the algae, it follows that *chara* contribute only partially to the bound sedimentary diacids. This is also the case for the free diacids, since we found only the diacid C_9 in the algae.

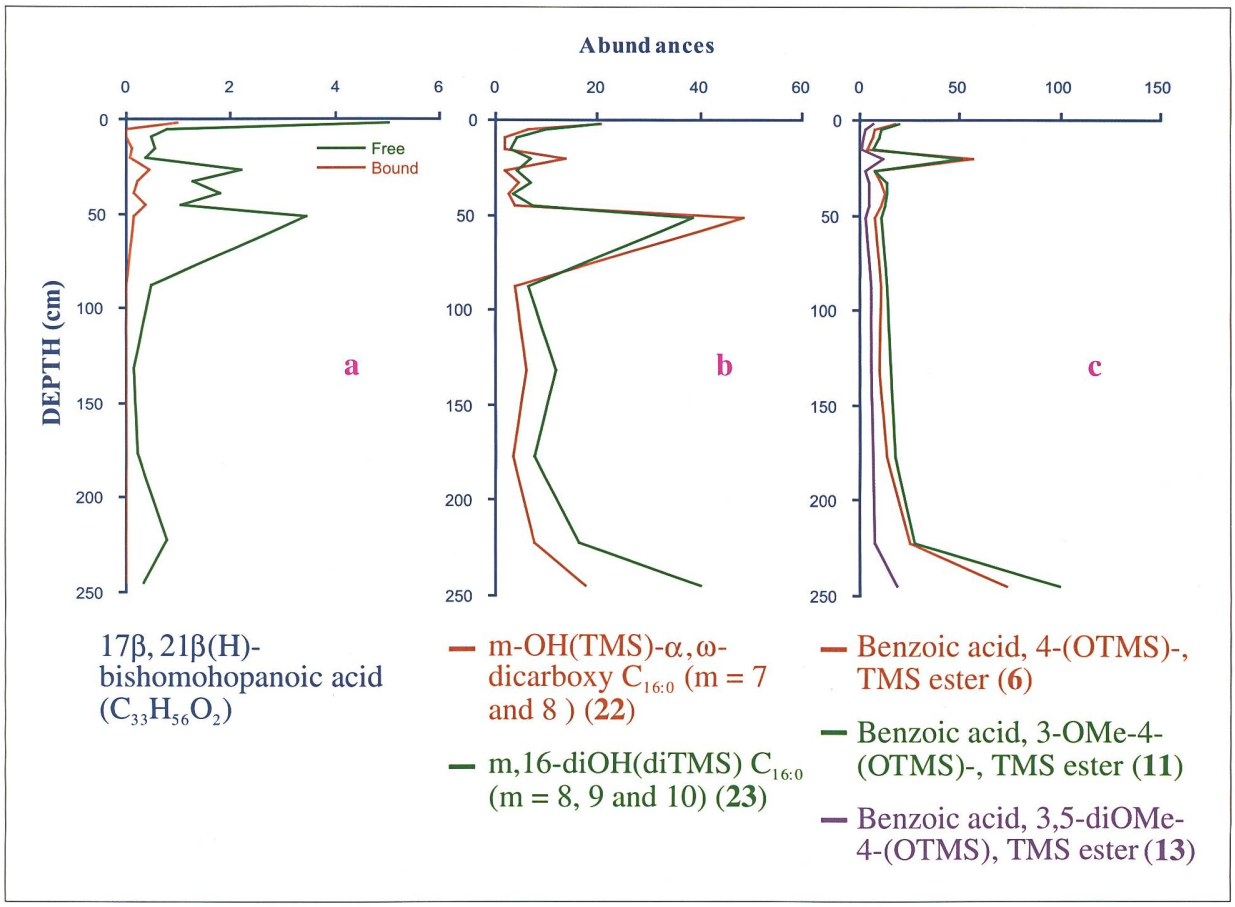


Fig. 10. Depth profiles of (a) free and bound 17β,21β(H)-bishomohopanoic acid ($C_{33}H_{56}O_2$), (b) bound m-OH(TMS)-α,ω-dicarboxyacid (22) and dihydroxyacid (23), (c) bound benzoic acids (6, 11 and 13) found in the lake Cadagno sediments. The abundances are in arbitrary units for each of these acids.

Hopanoic acids

Hopanoids (acids, ketones, alcohols or alkenes) are a family of pentacyclic triterpenoids biosynthesized almost exclusively by bacteria. During early diagenesis, the bacteriohopanetetrols (polyhydroxy-bacteriohopanes), which control the fluidity of bacterial cell membranes (Ourisson and al. 1987), are the major precursors of ketones and hopanoic acids. The latter, in the C_{31} to C_{33} range, are ubiquitous components in the recent sediments, where the 17β,21β(H)-bishomohopanoic acid ($C_{33}H_{56}O_2$) is often the most abundant one (Hartgers and al. 2000; Naraoka and al. 2000; Stefanova and Disnar 2000; Winkler and al. 2001).

In our samples, the 17β,21β(H)-bishomohopanoic acid is more abundant in the free fraction than in the bound fraction. In Fig. 10a, the depth profile of the free acid shows that the bacterial input has been subjected to fluctuations between 9 and 87 cm depth, while it was more stable in the deepest sections of core. It also shows that the bacterial contribution was not more important in deep sections, as was also inferred from the BA profiles.

Other constituent acids of Cutins, suberins and lignins

Cutins and suberins are polymers composed mainly by: ω-hydroxyacids (C_{12}-C_{16}, $C_{18:1}$, and traces of ≥ C_{20}), α,ω-dicarboxylic acid $C_{16:0}$, 9,10-epoxy-18-hydroxyacid $C_{18:0}$, m,16-dihyroxyacid $C_{16:0}$ (m=8, 9 or 10) and m-OH-α,ω-dicarboxy $C_{15:0}$ and $C_{16:0}$ (m=7 or 8); some phenolic acids (coumaric and ferulic acids) are also present (Holloway 1972 and 1982; Kolattukudy 1980).

Lignins are polymers containing four different phenolic monomers with p-hydroxyl, vanillyl, cinnamyl and syringyl groups (Hedges and Mann 1979; Maman and al. 1996). The products derived from lignins are considered as useful indicators of vascular plants in sediments (Hedges and Parker 1976; Hedges and al. 1988; Pulchan and al. 2003).

Table 2 reports the typical acids of cutins, suberins and lignins we identified in the herbaceous plants, in the algae *chara* and in Cadagno sediments.

The depth profiles of a dihydroxyalkanoic acid, a mid-chain hydroxy-α,ω-dicarboxylic acid and three benzoic acids, all of them derived from cutin or lignin

(Maman and al. 1996; Stefanova and Disnar 2000), are shown in Fig. 10b and 10c. All profiles are indicative of a highest contribution from vascular plants in the deepest sections of the core, in accord with the HFA profile and with the microscopic study.

Conclusions

- Geochemical study of acidic lipids in a sediment core from Cadagno allowed to establish past variations of the depositional environment. Although in the absence of a liable datation we cannot relate sediment depth with age, our results show that the sedimentation rate of the deepest sections of the core was lower and more stable than for the top 0-50 cm section of the core corresponding approximately to 100 yrs of deposition.

- Allochthonous organic matter input was highest during the deposition of deepest sediments and decreased steadily with time. Biomarker analyses and microscopic examinations show that coniferous forests were closer to the lake in the past explaining the above observation. This is not necessarily related to a climatic change but may also result from anthropogenic activity.

- The top 0-50 cm sections of the sediment core show abrupt fluctuations in all parameters studied in this work, indicative of frequent disturbances in the sedimentation. These disturbances are explained by the occurrence of sporadic events such as flood waters, avalanches and landslides, much more frequent in the last century.

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