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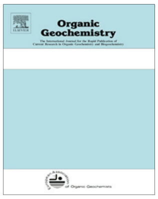

Recent vegetation history from a swampy environment to a pond based on macromolecular organic matter (lignin and fatty acids) and pollen sedimentary records

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ABSTRACT

Evidence of environmental and vegetation changes in the catchment area of a small pond created artificially during the Middle Ages from a swampy area was provided by coupling palynology data and a detailed study of macromolecular organic matter (OM). Tetramethylammonium hydroxide (TMAH) thermochemolysis after solvent extraction was used to characterize macromolecular OM and particularly lignin and fatty acids (FAs). Molecular ratios such as $TAR_{(FA)}$, $C_{16:1}/C_{16:0}$ and $C_{18:1}/C_{18:0}$ were calculated to characterize the FAs incorporated into the macromolecular OM. Moreover, syringyl vs. vanillyl phenols (S/V) and cinnamyl vs. vanillyl phenols (C/V) molecular ratios were investigated to fingerprint the lignin sources. These different markers suggested that the swampy area was dominated by a non-woody angiosperm input and gave rise to pond status over a period of several centuries. Indeed, $TAR_{(FA)}$ correlated with the aquatic contribution, which became predominant after creation of the pond. The use of ratios of total acid phenols to the total aldehyde phenols of syringyl or vanillyl units ($Ad/Al_{(s)}$, $Ad/Al_{(v)}$), which are related to the degree of oxidation of lignin, revealed the irregular operation of oxidative conditions.

1. Introduction

A key goal in the reconstruction of lake and catchment history is to distinguish the sources of allochtonous and autochtonous organic matter (OM) and therefore to access any input modification that might be associated with environmental changes in the surrounding catchment. Reconstruction of lacustrine paleoenvironments and paleovegetation is based mainly on molecular biomarkers in the solvent-extractable OM, which represents only a minor fraction of the total OM. Few investigations have been devoted to the study of the complex macromolecular OM in lacustrine sediments (Orem et al., 1997; Tareq et al., 2004, 2006; Yamamoto et al., 2005; Ishiwatari et al., 2006; Hyodo et al., 2008), although investigation of macromolecular OM provides important insights into the origin and fate of the insoluble OM.

Lignin is a stable phenolic macromolecular material, which is abundant in the woody tissue of vascular land plants, but is essentially absent from all other organisms (Hedges and Mann, 1979b). Lignin-containing plant debris delivered to lacustrine sediments via rivers and streams includes vascular plants which grew in the catchment area as well as emergent and submerged/floating lake vegetation. In most cases, degradation of lignin is slow in comparison with other biopolymers. This is due in part to its predominantly aromatic structure and to the fact that only few organisms utilize it as sole carbon source in their metabolic pathways (Hatcher et al., 1995). Hence, the refractory character of lignin in the environment makes it an ideal marker for vascular plant material (Hedges and Mann, 1979b).

Several techniques have been developed for the analysis of lignin in sediments. Alkaline CuO oxidation yields four groups of lignin phenols: *p*-hydroxyl, vanillyl, syringyl and cinnamyl (Hedges and Ertel, 1982). Woody and non-woody vascular plants synthesize each of these groups in different but specific proportions. Such characteristic distributions of lignin phenols have been used as a proxy for vegetation analysis in paleoenvironmental studies.

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Challinor (1989) developed a thermochemolysis technique using a derivatizing reagent, tetramethylammonium hydroxide (TMAH), at elevated temperature. Thermochemolysis is effective in cleaving hydrolysable bonds in the macromolecular structure and the resulting CO_2H and OH groups are transformed in situ to the corresponding methyl esters and methyl ethers (Morrison III and Mulder, 1994; Clifford et al., 1995; Hatcher and Minard, 1996). Hence, thermochemolyis yields lignin phenols equivalent to those produced by conventional alkaline CuO oxidation (Clifford et al., 1995; Hatcher et al., 1995) and allows calculation of specific ratios used as robust markers for land use change (Yamamoto et al., 2005; Ishiwatari et al., 2006). More recently, Filley et al. (1999, 2000) and Nierop and Filley (2007) have used ^{13}C-labeled TMAH thermochemolysis to differentiate lignin-phenols from other non-lignin polyphenols.

Apart from characterization of lignin, thermochemolysis has also been applied to the characterization of a number of synthetic and natural materials and has provided compositional information and molecular signatures of specific contributions (Del Rio et al., 1994, 1998; Hatcher and Clifford, 1994; Martin et al., 1994, 1995; Saiz-Jimenez, 1994; Challinor, 1996, 2001; Del Rio and Hatcher, 1996; McKinney et al., 1996; McKinney and Hatcher, 1996; Fabbri and Helleur, 1999; Mansuy et al., 2001; Faure et al., 2004).

In a previous study, we characterized the solvent-extractable OM in sediments in order to unravel the historical and environmental changes in the watershed of a pond (Bertrand et al., 2012, 2013). Characterization of macromolecular OM, together with palynological data can also be used as a proxy for vegetation analysis to complement previous paleoenvironmental and paleoecological investigations of the pond. The major aims of the present study were therefore to (i) identify the different products generated by way of thermochemolysis combined with gas chromatography–mass spectrometry (GC–MS), (ii) evaluate the fatty acids (FAs) and lignin phenols as proxies for paleovegetation and paleoenvironment in comparison with pollen analysis, and thereby to assess the changes in landscape in the surrounding catchment of the pond, and (iii) evaluate the preservation degree of lignin phenols with respect to changes in depositional conditions.

2. Material and methods

2.1. Sampling site and core collection

The Lansquenet pond is in the northeastern part of France, in Lorraine and was created artificially in the Middle Ages for fish farming. It covers an area of 342×10^3 m^2, with a maximum depth of 3 m (Fig. 1). Its small watershed (585×10^4 m^2) developed on a Keuper marl substratum. In October 2009, three cores, LAN0901 (A and B), LAN0902 and LAN0903 were sampled using a UWITEC gravity coring system (EDYTEM, University of Chambery) at a maximal sediment depth of 235 cm (48°49′40″N, 6°49′50″E). Back in the lab, the cores were opened and divided into 1 cm slices, weighed and stored frozen in glass bottles.

2.2. Total organic carbon (TOC) and total N

Concentration of total C was determined via high temperature combustion. TOC and total N were determined on the carbonate-free samples (1 M HCl, 1 h; shaken 0.5 h). Total C, TOC and total N were measured using a Carlo Erba 1108 CHNS Elemental Analyser.

2.3. Pollen analysis

Subsamples from cores LAN0903 and LAN0901B were taken at 5 cm intervals. Extraction of pollen grains was carried out using the classical method of concentration in a heavy liquid ($ZnCl_2$ or Thoulet specific gravity 2) after treatment with HCl to dissolve carbonate and the destruction of silica with HF (Faegri and Iversen, 1989; Argant, 1990; Etienne et al., 2011). At least 500 pollen grains from terrestrial plants were identified and counted for each subsample. Pollen identification was based on identification keys (Beug, 2004) and photography books (Moore et al., 1991; Reille, 1992–1998). Pollen and other palynomorph counting was performed using a constant volume sample extract and the proportions (%) were calculated on the basis of the pollen sum.

2.4. Lignin and FA analysis using on-line TMAH thermochemolysis

Samples from cores LAN0901 (A and B) and LAN0902 were freeze-dried for 24 h and then ground (500 μm). Dried samples were extracted using dichloromethane (DCM) with an automatic extractor (Dionex ASE 350; 100 °C, 10^6 Pa). After removal of the solvent extractable OM from each sample, the insoluble organic fraction was analyzed using on-line thermochemolysis.

Solvent-extracted sediments were mixed with TMAH (1:5 wt.) according to the procedure of Hatcher and Clifford (1994). An aliquot (10–15) mg of the mixture was placed into a quartz tube and thermochemolysis-GC–MS analysis carried out with a Hewlett Packard 6890 Series, using a split/splitless injector, coupled to a Hewlett Packard 5972 mass spectrometer. On-line flash pyrolysis at 620 °C was performed with a CDS 2000 Pyroprobe for 15 s. Pyrolysis products were separated on a DB 5-MS 60 m × 0.25 mm column. Samples were injected in splitless mode at 300 °C. The oven temperature was cooled to 0 °C (held 0.5 min) by injecting liquid CO_2 and was programmed to 40 °C (held 10 min) at 45 °C/min, then to 315 °C (held 10.5 min) at 5 °C/min.

Flash pyrolysis products were assigned from GC retention times and from mass spectra with reference to the WILEY Library. Assignment was also based on comparison with the spectra of pyrolysis products (Hatcher et al., 1988; Challinor, 1995). Integration of mass chromatograms with relevant m/z values was performed and the peak areas obtained were multiplied by a correction factor calculated from the mass spectrum of each compound (lignin compounds and FAs), by taking the inverse of the proportion (%) of the relevant m/z value in the total spectrum and multiplying by 100 (Hartgers et al., 1992).

3. Results

3.1. Sedimentological description and history of Lansquenet pond

The sedimentological descriptions for LAN0901 (A and B), LAN0902 and LAN0903 are presented in Fig. 2. The three cores comprised mainly gray and blue–gray clay with a varying amount of organic debris. However, two particular levels were noticed: the first appeared at 54 cm for LAN0901A and 48 cm for LAN0903, separating a black mud from the clayey part, and the second, between 90 and 120 cm, made up of an accumulation of woody material.

Evidence of a changing environment in the catchment area of the pond was provided (Bertrand et al., 2012) by coupling palynology data and organic ratios, such as terrestrial vs. aquatic ratio [$TAR_{(HC)}$], C_{29} vs. C_{27} sterols [$C_{29}/C_{27(ST)}$], n-alkane average chain length (ACL_{27-33}) and aquatic vs. macrophytes ratio (P_{aq}). Depositional and alteration conditions for the OM were provided by the $5\alpha(H)$-stanols/Δ^5-sterols ratio. This allowed us to clearly identify