

High spatial resolution analysis of lake sediment cores by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS)

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Abstract

A procedure is presented for the high-resolution analysis of lake sediment cores. Sections of a sediment core collected by freeze coring in a dimictic lake were prepared by slow drying. Clear visual laminations in the prepared sections indicated that the layering of accumulated sediments was preserved during sampling and sample preparation. Concentration profiles for Al, Si, Fe, S, As, Cu, and Zn at a 0.25-mm resolution were obtained for 2 core sections corresponding to pre-industrial and industrial periods. Detection limits of 0.09% for Al, 0.006% for Fe, 0.07% for S, 0.75% for Si, $0.7 \mu\text{g g}^{-1}$ for As, $68 \mu\text{g g}^{-1}$ for Cu, and $32 \mu\text{g g}^{-1}$ for Zn enable the analysis of these elements in the sediment samples. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analysis enabled the resolution of subannual patterns in element concentrations. In the lake studied, a regular, alternating pattern of Al and S concentrations appears to provide markers of annual sediment accumulation in the relatively uncontaminated layers of the core. In the more highly contaminated layers, LA-ICP-MS provides a suitable tool for the detailed study of pollution events.

Introduction

The progressive accumulation of sediments in a lake and the simultaneous incorporation of particulate or particulate reactive pollutants have enabled the reconstruction of pollution history in contaminated watersheds (Spliethoff and Hemond 1996; Chillrud et al. 1999; Ruiz-Fernandez et al. 2004). Whereas analysis has typically been performed on 1- to 2-cm core sections, sediment accumulation rates less than 1 cm per year are typical, indicating that the temporal resolution corresponding to such analysis is inadequate to identify short pollution episodes or seasonal patterns in the sediment deposition process. Water chemistry in temperate lakes is often influenced by seasonal cycles resulting principally from variations in temperature, wind, and precipitation and in turn is expected to influence the deposition and composition of sediments (Wetzel 1975; Kalff 2002). Additional information may therefore be recoverable from a sediment core by means of a higher spatial resolution.

Efforts have been made to develop high-resolution sediment core analysis using microbeam X-ray fluorescence (Koshikawa et al. 2003). This technique enables submillimeter elemental analysis of relatively large samples and is, therefore, well-suited for high-resolution sediment core analysis. Commercial XRF core scanners have been developed for the analysis of sediments core at a maximum resolution of 0.1 to 1 mm (Jansen et al. 1998; Croudace et al. 2006) but are typically used at centimeter resolution (Röhl et al. 2000; Kuhlmann et al. 2004; Bahr et al. 2005). Lake sediment core analysis is limited by several difficulties, however, including the low concentrations of some elements and the relatively unconsolidated consistency of many sediments.

We propose a high-resolution analytical approach based on sediment core collection by freeze coring and analysis by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Freeze coring is well suited for the collection of relatively soft lake sediments and has been demonstrated to maintain integrity of sediment layering at a centimeter scale (Spliethoff and Hemond 1996; Gabler et al. 2003; Rauch and Hemond 2003). LA-ICP-MS, which uses a laser beam for direct solid sampling and sensitive analysis by ICP-MS, enables determination of the spatial distribution of a sample's elemental composition at micrometric resolution (Durrant 1999; Günther and Hattendorf 2005). This technique has been

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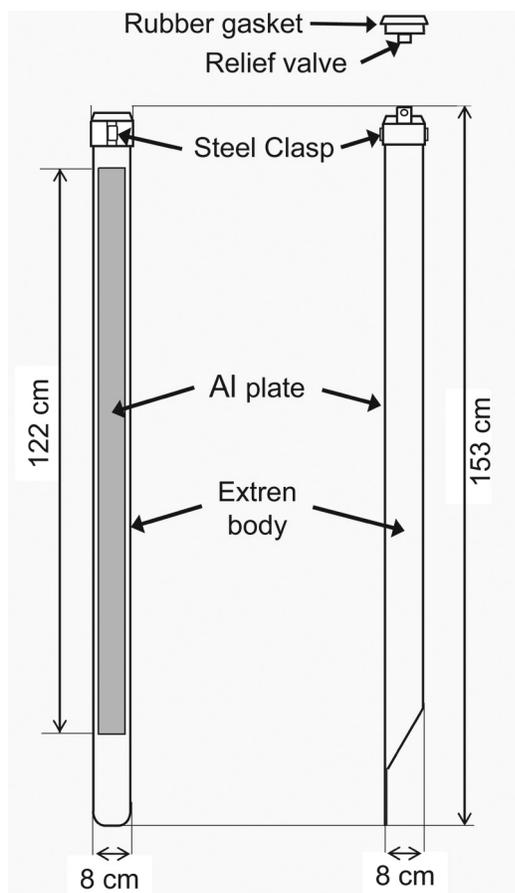


Fig. 1. Schematic description of the freeze corer, adapted from Spliethoff and Hemond (1996).

applied, for instance, to the spatially resolved analysis of individual sediment particles (Rauch and Morrison 2004) and the study of metal sulfides leaching from sediments (Motelica-Heino et al. 2003). Therefore, the combination of freeze coring and LA-ICP-MS analysis may enable sediment core analysis at a resolution sufficient for the study of seasonal variations, providing that the stratigraphy of analyzed core sections can be preserved during sampling and sample preparation. This approach was tested by applying LA-ICP-MS to the spatially resolved analysis of major and trace elements in sediment core sections from Upper Mystic Lake (UML), Massachusetts, USA.

Experiment procedure

Study site—Upper Mystic Lake (42°26'07" N, 71°09'35" W), located north of Boston, MA, USA, is strongly affected by seasonal climatic variations, with an ice cover in winter and stable stratification in summer (Senn and Hemond 2002). The main basin of UML has a volume of $5.4 \times 10^6 \text{ m}^3$, an area of 0.35 km^2 , and a maximum depth of 25 m. The lake receives the entire flow of the Aberjona River ($0.78 \text{ m}^3 \text{ s}^{-1}$), which drains a 67-km^2 area in a heavily developed suburban area of Boston. Indus-

trial activity has been important since the early 19th century and, until the mid-20th century, was dominated by leather tanning and chemical industries. Large amounts of chemical wastes were discharged to waterways, and metal-contaminated sediments occur throughout the watershed (Aurilio et al. 1995) and in Upper Mystic Lake (Spliethoff and Hemond 1996; Rauch and Hemond 2003).

Sediment core collection—A core was collected from UML by freeze coring in October 2003. The corer is a square tube composed of 3 sides of Extren and 1 side of aluminum with an internal lead weight at the bottom, filled with a coolant made of dry ice and ethanol (Figure 1). The corer is dropped vertically into the sediments and left for 10 to 15 min for the sediments to freeze and adhere on the aluminum face of the tubing. The corer is retrieved together with the frozen sediment. Sediment slabs are carefully separated from the corer, sealed in plastic wrap, and placed in a cooling box filled with dry ice. Sediments are kept frozen until sectioning.

Sediment cores collected by freeze coring and analyzed at 2-cm resolution have provided a first assessment of the coring technique (Spliethoff and Hemond 1996; Rauch and Hemond 2003; Rauch et al. 2004). Detailed, reproducible records of As, Cu, Cr, Os, Pb, Pt, Pd, Rh, and Zn and sharp, reproducible peaks observed for Cr and ^{137}Cs are a strong indication that little disturbance occurs during sampling (Spliethoff and Hemond 1996; Rauch and Hemond 2003; Rauch et al. 2004).

Sample preparation—Sample preparation was carried out as schematized in Figure 2. Frozen sediments were cut into 4.3-cm horizontal sections using a hacksaw. Sections were then cut vertically into 2.9-cm subsections to fit a 4.3 by 2.9 cm polyethylene box, the longer distance being the vertical axis of the core. Remaining sediments were used for XRF analysis. The external, potentially disturbed part of the core (approximately 5 mm) was removed using a stainless steel razor blade. Subsections were then dried at 40°C in an oven containing desiccant for approximately 24 h. The box avoids loss of structure as the interstitial water melts. A loss of volume was observed, however, due to the evaporation of interstitial water, and the size of the subsections was therefore measured before analysis to correct for shrinkage. The vertical length change ranged from 11% to 33%.

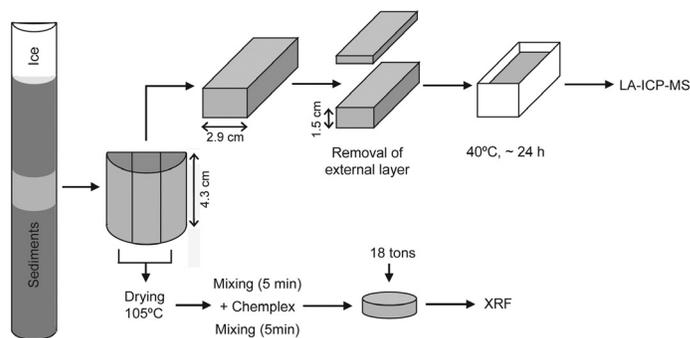


Fig. 2. Schematized sample preparation procedure for LA-ICP-MS analysis of sediment cores and XRF-based calibration.

Table 1. Instrumental parameters for LA-ICP-MS analysis.

LA parameter	Value
Carrier gas	Ar, 1 L min ⁻¹
Wavelength	UV 266 nm
Operating mode	Q-switch
Pulse width	< 6 ns
Repetition rate	20 Hz
Spot size	50 mm
Energy	0.5-0.7 mJ pulse ⁻¹
Scan speed	10 mm s ⁻¹
ICP-MS parameters	
RF Power	1000 W
Auxiliary gas	Ar, 0.9 L min ⁻¹
Plasma gas	Ar, 16 L min ⁻¹
Cones	Nickel
Analytes ^a	²⁴ Mg, ²⁷ Al, ²⁸ Si, ³¹ P, ³² S, ⁴⁴ Ca, ⁴⁸ Ti, ⁵² Cr, ⁵⁵ Mn, ⁵⁷ Fe, ⁶³ Cu, ⁶⁴ Zn, ⁷⁵ As
Data acquisition	Peak hopping
Dwell time	10 ms
Sweeps per reading	20

^aOnly results for Al, Si, S, Fe, Cu, Zn, and As are presented.

The procedure was applied to sediments deeper than 30 cm; some modification to the procedure may be necessary for shallower sediments because of their higher water content. Subsections or part of subsections were discarded if visual observation suggested the sediment had been disturbed or if cracks were visible on the surface.

The approximate age of each sediment core section was estimated by matching the profile of As in the core with the profile of As in a previously collected and dated core (Spliethoff and Hemond 1996). Subsections corresponding to layers deposited before the main period of industrial contamination were considered to be background for this study.

LA-ICP-MS analysis—LA-ICP-MS analysis was performed on a Cetac LSX-200 laser ablation system (Cetac, Omaha, NE, USA) coupled to an Elan 6000 quadrupole ICP-MS (Perkin Elmer Sciex, Toronto, ON, Canada). The subsection is placed in a sealed cell flushed with Ar, and the laser is focused onto its surface with a beam size of approximately 50 μm . The stage is moved (10 $\mu\text{m s}^{-1}$) while firing the laser, resulting in the ablation of scan lines. Scan lines were oriented perpendicular to visual laminations on the subsection surface to obtain vertical profiles of sediment composition. The ablated material is carried by the Ar stream to the plasma torch for ICP-MS analysis. Optimal working conditions are presented in Table 1. A target resolution of 0.25 mm was derived from visual observation of prepared subsections. Whereas the parameters in Table 1 provide a higher resolution, the signal was averaged to provide the target resolution and reduce dataset size and signal noise. Three parallel lines for each subsection were analyzed to check

for consistency. Blanks were acquired for 1 to 2 min before firing the laser for each analysis and were subtracted from the elemental signals. Signals were at least 10 times higher than blank signals for Al, Si, and Fe, at least 5 times higher for S, and at least 4 times higher for trace metals.

Calibration of LA-ICP-MS signal intensities was performed using concentrations measured by XRF in remaining sediments for each horizontal core section (Figure 2). For calibration, the average net LA-ICP-MS signal was considered to correspond to the concentration obtained by XRF, assuming horizontal homogeneity at centimeter scale. For XRF analysis, each sample was dried at 103 °C for 6 h and milled for 5 min in polyethylene containers using a polyethylene bead. A binding resin (X-Ray Mix Powder; Chemplex Industries, Palm City, FL, USA) was added, and the mix was further milled for 5 min. The resulting powder was pressed into a 3.1-cm-diameter pellet under an 18-ton load and analyzed by XRF (X-Lab 2000; Spectro Analytical Instruments, Kleve, Germany). Al, Cu, Fe, S, Si, As, Cu, and Zn were determined using a calibration database obtained from a number of well-characterized materials (reference materials and alloys). The calibration of the XRF instrument was tested against a soil reference material (Montana soil, CRM 2710; NIST, Gaithersburg, MD, USA) and 3 mixtures of homogenized UML sediments spiked with soil reference material (2.9 \pm 0.1 g; 2.7 \pm 0.3 g; 2 \pm 1 g of sediment plus reference material). Deviation from expected concentrations was within 10% for all elements. Similar concentrations for As, Cu, and Zn have been reported at corresponding depths in Upper Mystic Lake sediments (Spliethoff and Hemond 1996), providing further confidence in the results.

Results are presented for 2 sediment core subsections: subsection 1 (76.0 to 80.3 cm, approximately 1850) represents pre-industrial conditions; subsection 2 (57.8 to 62.1 cm, approximately 1900) corresponds to the main period of industrial contamination by sulfuric acid production, leather tanning, and pesticide production in the Aberjona Watershed from 1880 to 1930 (Spliethoff and Hemond 1996). A third subsection was used to illustrate repeatability for the analysis of parallel lines. Only parts of the sediment core subsections without visible cracks were analyzed. Interference on ICP-MS signals was considered to be relatively insignificant because of the high concentration of elements of interest and reduced interference in dry plasma conditions resulting from sample introduction by LA.

Assessment

Preservation of sediment stratigraphy—The preservation of sediment stratigraphy is crucial to the determination of concentration trends in sediment cores. It has been demonstrated that layering of sediments is preserved at a centimeter resolution during freeze coring (Spliethoff and Hemond 1996), but preservation at a finer resolution has not been demonstrated.

Potential disturbance resulting from sampling and sample handling includes shearing resulting from corer penetration

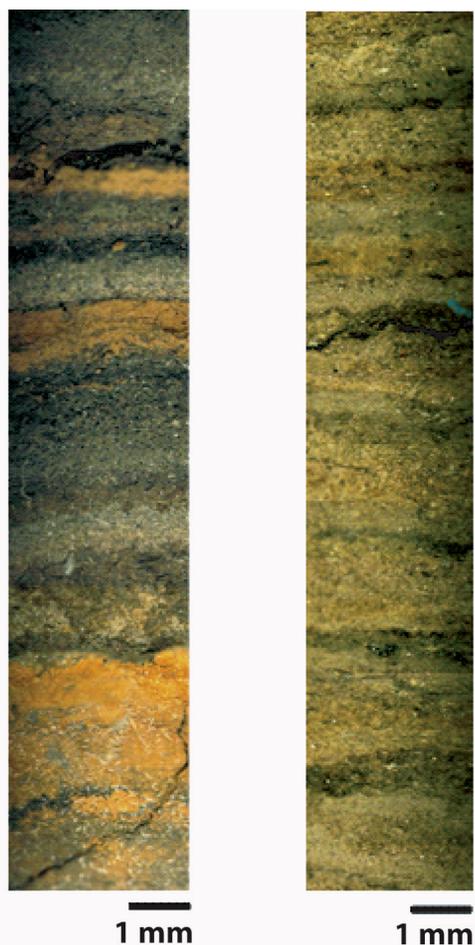


Fig. 3. Composite images of sections of UML sediment core subsections taken using the optics of the Cetac LSX-200 laser system (parfocal video-microscope used at $\times 80$ magnification with top illumination). Right, subsection 1: 78.6–80.3 cm; left, subsection 2: 59.2–60.9 cm.

into the sediments, contamination by particles sticking to the core when it is removed, and melting/frosting of the outer core layer at ambient temperatures. The extent of shearing could be judged from sediment laminations visible at the core surface directly after retrieval. These lines tended to disappear soon after sampling due to frosting or melting of the outer part of the core. However, the lines persisted a few millimeters below the surface of the sediment slabs. Observation of the side of frozen cores revealed that the lines were curved in the direction of corer penetration for a distance of approximately 5 mm from the aluminum face of the corer. An approximately 1-mm-thick layer of ice was also observed on the side of the core closer to the corer, probably resulting from water freezing onto the aluminum plate when the corer was dropped through the water column into the sediments. To prepare a surface for analysis that is free of artifacts, the outer layer of the core was removed using a stainless steel razor blade, and laser ablation was performed on material at a thickness of

approximately 1.5 cm from the corer side of the sediment cores, where visual observations of laminations consistently revealed minimal disturbance.

Sediment laminations were visually pronounced on the surfaces of dry subsections, providing clear evidence that sediment sequence is preserved during sampling and sample preparation (Figure 3). Although the thickness of laminations varies greatly, thin lines observed in subsections 3 and sharp transitions between different layers in both subsections 2 and 3 (Figure 3) indicate that stratigraphy is preserved down to at least 0.1 mm.

Sediment core analysis—Average trace and major element concentrations in each sediment core subsection were obtained by XRF and used for the calibration of LA-ICP-MS signals, assuming horizontal homogeneity of sediments over a distance of 7 cm (the sediment core width). The assumption of horizontal homogeneity is supported by the presence of horizontal laminations and reported between-core reproducibility (Spliethoff and Hemond 1996). Concentration profiles of Al, As, Cu, Fe, S, Si, and Zn obtained by LA-ICP-MS for 2 core sections are presented in Figure 4.

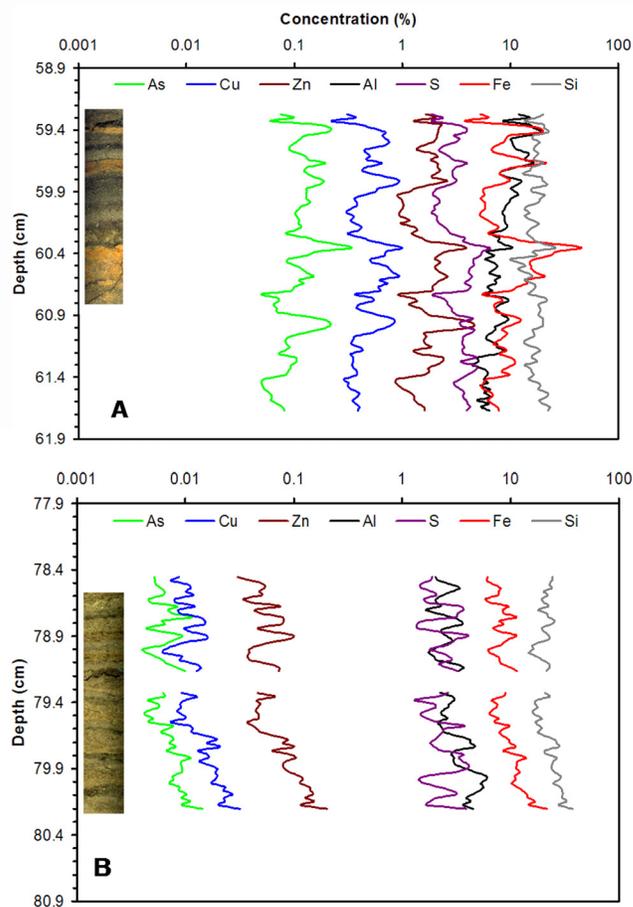
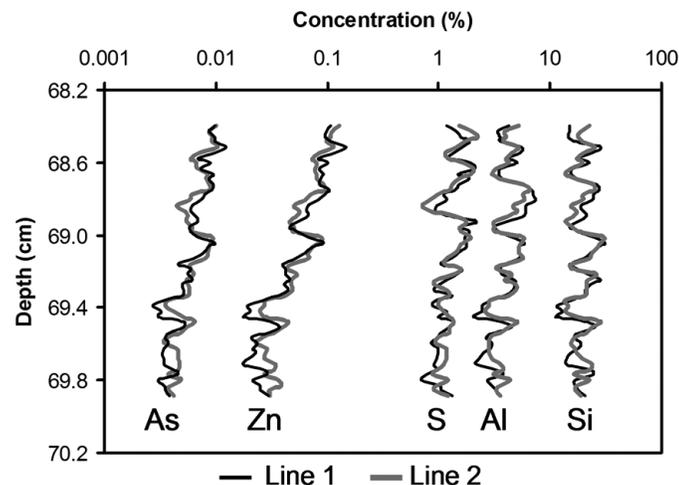


Fig. 4. Concentration profiles of Al, Fe, S, Si, As, Cu, and Zn. (A) Subsection 2: 59.2–61.8 cm (approximately 1900). (B) Subsection 1: 78.5–80.2 cm (approximately 1850). Partial composite images are provided for each subsection.

Table 2. Mean concentrations, SDs, minimum concentrations, and maximum concentrations in subsections 1 and 2.

Element	Subsection 1 concentrations, %				Subsection 2 concentrations, %			
	Mean	SD	Min.	Max.	Mean	SD	Min.	Max.
Al	3.13	1.08	1.65	5.95	8.70	3.03	4.43	19.52
Si	22.6	4.7	14.8	37.3	17.4	3.0	10.1	26.3
Fe	9.5	2.9	5.9	21.7	10.3	6.4	3.8	45.9
S	2.40	0.80	1.29	4.14	3.39	0.98	1.85	6.48
Cu	0.014	0.005	0.006	0.032	0.50	0.18	0.22	1.00
Zn	0.073	0.036	0.031	0.203	1.79	0.71	0.87	4.61
As	0.007	0.002	0.004	0.014	0.11	0.05	0.05	0.34

Detection limits for LA-ICP-MS analysis estimated using the 3-s blank values measured for Ar gas were 0.09% for Al, 0.006% for Fe, 0.07% for S, 0.75% for Si, $0.7 \mu\text{g g}^{-1}$ (0.00007%) for As, $68 \mu\text{g g}^{-1}$ (0.0068%) for Cu, and $32 \mu\text{g g}^{-1}$ (0.0032%) for Zn. Concentrations for the 2 samples analyzed are presented in Table 2. Detection limits enable the determination of all analyzed elements, although 1 point in the Cu profile was below detection limits. Reproducibility of the LA-ICP-MS analysis was evaluated by the ablation of parallel scan lines in subsections (Figure 5). Reproducibility was assessed by averaging the standard deviation of individual data points for 3 parallel lines in a sample. The average relative standard deviation was 10% for Al, 12% for As, 16% for Cu, 11% for Fe, 12% for S, 11% for Si, and 13% for Zn. Additional data on the reproducibility of the ablation of parallel lines are presented in Table 3. Although the results typically are in good agreement, local variations in sediment composition are reflected in the maximum variation between 2 horizontal points and may affect the determination of the reproducibility of the method. However, comparison of

**Fig. 5.** Concentration profiles for 2 parallel lines on a sediment core subsection showing reproducibility of LA-ICP-MS analysis. Distance between lines: 1 mm.**Table 3.** Mean concentrations, mean SDs for horizontal points, and maximum concentration variation between 2 horizontal points for 3 vertical parallel lines in a sediment core section.

Element	Mean concentration, %	Mean SD for horizontal points, %	Maximum variation between horizontal points, %
Al	4.1	0.4	1.6
Si	19.7	2.2	9.8
Fe	7.8	0.7	3.1
S	1.30	0.14	0.79
Cu	0.012	0.002	0.010
Zn	0.057	0.007	0.057
As	0.0061	0.0007	0.0039

parallel lines indicates that the method provides relatively reproducible profiles (Figure 5).

The thickness of laminations observed on the surface of core subsections ranged from 0.1 to 5 mm and was typically ≥ 0.5 mm (Figure 3). After data reduction, 4 data points were obtained per millimeter, allowing the resolution of most visual patterns. Qualitative comparison of laminations and major element profiles in analyzed subsections indicates a good agreement between visual patterns and concentration profiles. For quantitative comparison, composite images obtained using the optic of the LA system (Figure 3) were treated using ArcView GIS 3.3 (ESRI, Redlands, CA, USA) to convert the 3-layer RGB color coding into a monolayer coding with values from 0 to 255. Ten vertical lines 1 pixel wide were then obtained using Matlab 7 (Mathworks, Natick, MA, USA) and averaged. A significant correlation with color codes was found for S (linear regression, $r = 0.69$, $P < 0.01$) and Fe (linear regression, $r = 0.59$, $P < 0.01$) concentrations, with the most distinctive visual Fe- and S-containing features being the bright orange laminations in subsection 2. In contrast, Al and Si presented lower correlations with color.

Discussion

Potential for biogeochemical studies and accumulation rate determination—The LA-ICP-MS procedure enables the submillimeter analysis of sediment cores. At this resolution, it is possible to observe variations in concentration (Table 2) and relatively regularly spaced and coincident Fe and S peaks, separated by Al peaks in pre-industrial samples (Figure 4B), with a positive correlation between Fe and S (linear regression, $r = 0.62$, $P = 0.01$) and a weak negative correlation between Al and S (linear regression, $r = -0.20$, $P = 0.01$). Aluminum peaks are attributed to increased runoff from fall to spring and particle settling conditions when the lake is frozen in winter (Wetzel 1975; Kalff 2002). Fe and S peaks are attributed to the formation of insoluble metal sulfides, including Fe(II)S in

summer when the lake is stratified and bottom waters are anoxic (Wetzel 1975; Kalff 2002). The results are therefore evidence that summer (stratification period) and winter (mixed period) episodes are being resolved in these sediment cores. Trace element profiles also demonstrate subannual variations in the deposition of As, Cu, and Zn. Major and trace element profiles obtained by LA-ICP-MS demonstrate that the procedure enables the study of seasonal changes in the composition of deposited sediments and may provide a further understanding of biogeochemical processes occurring in lakes.

To the extent that relatively elevated S and relatively low Al represent deposition conditions occurring during summer stratification, these elements represent annual markers that can be used for the determination of sediment accumulation rates in dimictic lakes. The spatial periodicity of S and Al was estimated by Fourier spectral analysis of the Al/S ratio. The ratio has a period of 0.29 cm in background subsections (in the depth range of 65 to 85 cm) and, therefore, an overall accumulation rate of 0.29 cm y^{-1} was inferred. An average accumulation rate of 0.57 cm y^{-1} has been reported at corresponding depths based on Pb concentration trends and historical records of Pb emission in the Aberjona Watershed (Spliethoff and Hemond 1996). LA-ICP-MS provides accumulation rates for a few years, whereas reported accumulation covers a period of 38 years. The difference may be the result of temporal variations in sedimentation rates or estimation errors using Pb concentrations.

Potential for anthropogenic contamination studies—Contaminated UML sediments (subsection 2) corresponding to industrial contamination in the early 1900s (Spliethoff and Hemond 1996) were analyzed to determine the potential of the procedure for the study of contaminated sediments. Whereas previous analysis of UML sediments at 2-cm resolution has demonstrated the occurrence of elevated trace contaminant concentrations at depths corresponding to subsection 2 (Spliethoff and Hemond 1996; Rauch and Hemond 2003), profiles of As, Al, Cu, Fe, S, Si, and Zn at submillimeter resolution (Figure 4A) reveal sharp variations in the concentrations of these elements. In this subsection, no clear annual pattern of Al and S could be found, suggesting that natural deposition patterns were altered by anthropogenic activities and that sedimentation rate determination by the LA-ICP-MS procedure is limited to sediments with no or limited anthropogenic disturbance. Thick orange laminations observed in subsection 2 (Figure 3) correspond to elevated Fe and S concentrations, possibly resulting from sporadic emissions from the use of pyrite (FeS_2) for sulfuric acid manufacture in the Aberjona Watershed. In contrast, elevated Al, As, Cu, and Zn concentrations compared with pre-industrial levels (Figure 4B) were found throughout the subsection, indicating a more constant source for these elements. Peaks for As, Cu, and Zn, which generally correspond to the observed Fe and S peaks, indicate that the sulfuric acid manufacture is an additional source of these elements in the Aberjona Watershed. Results for UML sediments demon-

strate that the LA-ICP-MS procedure enables the characterization of contamination events recorded in lake sediments. The procedure could be used for source characterization, with simultaneous peaks indicating a common source, and could provide a further understanding of past contamination events.

Comments and recommendations

Freeze coring was found to maintain sequence integrity at submillimeter resolution in a core collected from a dimictic lake. Analysis of dry sediment core sections by LA-ICP-MS provides detailed profiles of both major (Al, Fe, S, Si) and trace (As, Cu, Zn) elements with spatial resolution of approximately 0.25 mm. Data at this degree of resolution contain information at the subannual scale, and the resolution of summer and winter depositional periods appears possible in sediments relatively undisturbed by anthropogenic activities. The technique also enables the detailed study of pollution events and could provide a further understanding of the impact of pollution on biogeochemical cycles.

Comparison with other analytical techniques enabling submillimeter spatially resolved analysis, such as microbeam-XRF and electron microprobe analysis, should be performed to validate the procedure and further assess the quality of the results. Each of these techniques presents its own advantages and weaknesses, and therefore, suitable techniques should be used complementarily; the advantage of LA-ICP-MS lies in its high sensitivity and the possibility to determine both major elements and trace contaminants.

Samples obtained by the proposed preparation procedure are fragile and have to be handled carefully. Embedding the samples in a resin would consolidate the samples and enable easier sample handling and preservation. Embedding may also enable the analysis of sediment core sections with high water content, such as unconsolidated sediments at the top of sediment cores. It is important, however, that the resin used contains only trace amounts of the elements of interest and that the embedding procedure does not affect sediment distribution and composition. Two water soluble resins (Nanoplast Embedding Kit FB101 and JB-4 Embedding Kit 00226; Polysciences, Warrington, PA, USA) were tested. After 6 h in the oven at 40 °C, partially dried samples were transferred to glass Petri dishes containing resin solutions prepared according to manufacturer specifications and left for 1 h for the resin to penetrate into the samples. Samples prepared with Nanoplast were then further dried in the oven for 24 h. Samples prepared with JB-4 were left at room temperature (approximately 20 °C) to polymerize. Embedding with JB-4 resulted in crumbly samples. Better results were achieved with Nanoplast, for which well-defined visual laminations were obtained. Nanoplast is a melamine resin prepared by mixing a catalyst (*p*-toluene sulfonic acid) and an aqueous melamine resin solution (hexamethylol-melamine-methyl ether). After fixing, the resin was estimated to represent approximately 30% of the sample dry weight. Although the resin contains relatively low levels of Al,

Si, Fe, As, Cu, and Zn, the S content resulting from the catalyst (corresponding to an estimated S concentration of approximately 0.1% for an average sediment concentration of 4% to 5% and a minimum measured concentration of 0.7% in analyzed samples) may affect the S signal in layers with low S concentration.

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