Lakes & Reservoirs: Research and Management 2004 **9**: 53–63

The impact of a sewage treatment plant's effluent on sediment quality in a small bay in Lake Geneva (Switzerland–France). Part 2: Temporal evolution of heavy metals

Jean-Luc Loizeau,[1,2]* Michel Pardos,[1] Fabrice Monna,[1,3] Christophe Peytremann,[1] Laurence Haller[1] and Janusz Dominik[1,2]
[1]F.-A. Forel Institute, University of Geneva, Versoix, Switzerland, and [2]Centre d'Etudes en Sciences Naturelles de l'Environnement, University of Geneva, Versoix, Switzerland

Abstract

The Bay of Vidy is the most contaminated area of Lake Geneva, Switzerland, as a result of the release of treated and untreated waste water from the municipal sewage treatment plant of the city of Lausanne and its surroundings. The reconstruction of the historical deposition of heavy metals in the sediment of the bay has been performed by the analysis of several dated (radiocaesium) sediment cores. The presence of sewage-derived contaminants in the Bay of Vidy since the beginning of the sewage treatment plant's operations in 1964 is clearly observed, when a sharp increase in heavy metal contents is recorded, with maximum concentrations of cadmium, copper, zinc and lead occurring between the late 1960s and early 1970s. Despite considerable improvement in recent times, the present concentrations of the investigated heavy metals in sediments of the Bay of Vidy are still higher than concentrations measured at the centre of the lake, the latter close to Lake Geneva's natural background values. It is concluded that the quantity of heavy metals deposited in the bay is considerable and, because of sediment instability, will constitute a potential hazard for biota.

Key words

heavy metals, Lake Geneva, pollution, sediment, sediment dating, sewage treatment plant.

INTRODUCTION

Many contaminants introduced into aquatic ecosystems via industrial and domestic sewage discharge, surface run-off and atmospheric fallout are adsorbed onto, and transported by, suspended sediments. After cycles of deposition, resuspension, transport, and biological and chemical interactions, contaminants associated with particles can be buried in bottom sediments, which become the ultimate pollutant sink (Burton 1992; Luoma & Ho 1993).

Studies assessing environmental contamination are complicated by a number of factors that contribute to pollutant carrier transport and distribution. Despite the possibility of remobilization, however, sediments can record states of environmental stress dating far back into the past. In that sense, lake sediment cores provide an invaluable record of the past variations occurring both in a lake and its watershed (e.g. Dominik *et al.* 1984, 1991; Wessels *et al.* 1995; Loizeau *et al.* 1997; Von Gunten *et al.* 1997; Mecray *et al.* 2001). It is difficult, however, to quantify the severity and extent of sediment contamination when, in many countries, criteria for distinguishing 'clean' from 'contaminated' sediments are either non-existent or are still being developed (Smith *et al.* 1996). Among different approaches, the degree of anthropogenic sediment contamination is evaluated by comparison of heavy metal concentrations in recent sediments to the natural background concentrations (Förstner & Wittmann 1979; Håkanson & Jansson 1983).

The companion study, which focused on the assessment of the quality of surface sediments collected in the Bay of

---

*Corresponding author.
E-mail: Jean-Luc.Loizeau@terre.unige.ch

Accepted for publication 15 March 2004.

[3]Present address: GéoSol, CST, UMR-INRA, University of Bourgogne, Dijon, France

Vidy shows that the sewage treatment plant's (STP) effluent is the main source of local sediment contamination (Pardos *et al.* 2004). The extent and spatial distribution of selected sediment contaminants was clearly established. Among the pollutants were heavy metals, such as copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb). These are ubiquitous in the environment. Heavy metals play an important role because they are hazardous at high concentrations. Within the framework of preparing a plan for proper remediation, heavy metal data obtained from sediment cores of Lake Geneva (Bay of Vidy and a reference site in the central part of the lake) are presented in this report. The historical sediment deposition in the bay is related to the STP's operation and to geochemical background concentrations.

SETTINGS

Lausanne is the biggest city discharging treated domestic and industrial waste water into Lake Geneva. The STP is located at Vidy, on the northern shore of the lake, and releases treated waters into the Bay of Vidy via an underwater pipe. The Flon River (Fig. 1) drained the untreated sewage of Lausanne and its surroundings until 1964 and presently receives storm overflows. The Vidy STP (≈ 412 000-equivalent inhabitants at the present time) was built in 1964–1965 (220 000-equivalent inhabitants) with biological treatment. It was equipped in 1971 with a chemical stage, consisting of adding ferric chloride which precipitates as iron hydroxide, thereby removing phosphate. In 1976, the STP was expanded and the efficiency of wastewater treatment improved. In 1986, drilling operations were undertaken in the lake to anchor the STP underwater pipe.

MATERIALS AND METHODS

Sampling

Twelve sediment cores (cores 1–8, 10–13) were taken in the Bay of Vidy (Fig. 1) in August 1995 and April 1996, using a gravity corer (polyvinyl chloride (PVC) liner, 200 cm in length; Benthos, North Falmouth, Massachusetts, USA), with the research vessel 'La Licorne.' The water depth ranged from 15–77 m and the core length from 69–105 cm (Table 1). Two additional sediment cores were sampled by the submersible F.-A. Forel in April 1997 (PVC tube corers, 50 cm in length), one in the Bay of Vidy at a depth of 51 m (core 9, core BV in Monna *et al.* 1999) ≈ 700 m from the STP's outlet, and the other at a depth of 307 m close to the deepest and central part of the lake, as far as possible from direct human influence (core 14, core PC in Monna *et al.* 1999). This sampling method allowed the selection of the position of coring regarding the appearance of the sediment–water interface in order to limit the disturbances and keep the corer as vertical as possible. At each site, five to eight cores were recovered, with the two best cores selected for further analysis.

Sample processing

Prior to sample processing, the volume magnetic susceptibility (VMS) profile at 1-cm intervals was obtained for every

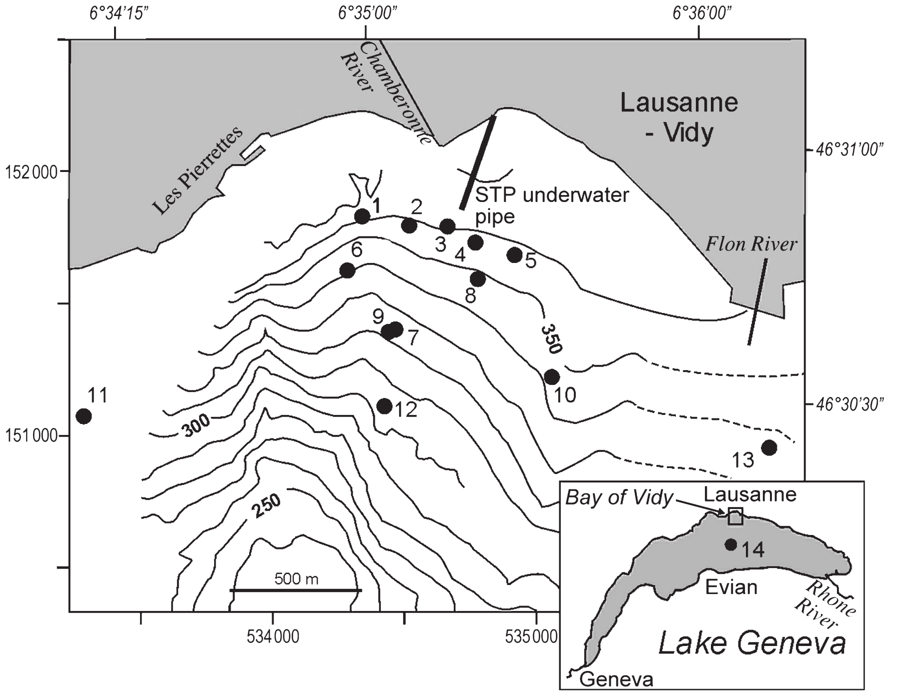

Fig. 1. Topographic map (Loizeau *et al.* 2003) and location of sampling sites. Note the sewage treatment plant (STP) underwater pipe and storm run-off (Flon River) in the Bay of Vidy (Lake Geneva). The mean lake level is 372 m a.s.l.. Inset: Map of Lake Geneva with location of core 14 in the central plain.

core, using a MS2C susceptibility meter (Bartington Instruments, Oxford, England). Cores 1–8 and 10–13 were opened longitudinally, whereas cores 9 and 14 were extruded with a piston and sliced. All the cores were immediately photographed and described. The subsampling of core 14 (44 cm long) was made with an interval of 0.5 cm for the upper 20 cm and 1 cm for the remainder of the core, whereas a constant interval of 1 cm was used for the full length of core 9 (41 cm long). Considering the previous studies undertaken in the same area (Luzzi 1989), this subsampling should provide yearly temporal resolution of one year or less. For the other cores, constant intervals of 1 or 2 cm were used in the uppermost, organic rich, contaminated core section, whereas larger intervals (5–10 cm) were used for the remainder of the core.

The samples were air-dried at 60°C for two days and the water content and porosity calculated following the procedure of Sugai *et al.* (1994). They were then carefully broken up in a acid-cleaned agate mortar. The depth scale is expressed in terms of mass-depth (g cm^{-2}), representing the cumulative mass of sediment, and is calculated from the porosity and density, corrected for organic matter content.

Analyses

Sediments were dated by using three time markers: radiocaesium-137 (^{137}Cs) atmospheric nuclear tests maximum activity (1963/1964), ^{137}Cs maximum activity from the Chernobyl reactor accident fallout (1986), and the appearance of a sharp increase in the VMS signal corresponding to the year 1971 in the Bay of Vidy (Loizeau *et al.* 2003). The VMS signal results from the presence of very fine-grained magnetite crystals (Gibbs-Eggar *et al.* 1999) in the sediment, most likely originating from the activity of dissimilatory iron-reducing bacteria (Snoeyenbos-West *et al.*, unpubl. data 2002). The activity of ^{137}Cs was directly measured on dry sediment by gamma spectroscopy, using a germanium well-detector (Dominik *et al.* 1987). For Lake Geneva, there was no evidence of diffusion or other displacement of this radionuclide within a complete sedimentary column, which could alter the dating (Dominik *et al.* 1991).

Chemical preparation for trace metals analysis, except mercury (Hg), consisted of the partial digestion of 0.5–1.0 g of sediment with 10 mL of super-pure nitric acid (HNO_3) in closed and pressurized Teflon bombs (TechniVerre, Villiers le Bel, France) heated to 150°C overnight (cores 1–12), or in a class 100–1000 clean room under Ethos microwave assistance (Milestone, Sorisole, Italy) and magnetic stirring (cores 9 and 14). The microwave settings were: 5 min at 400 W, 2 min at 100 W, 10 min at 600 W and 10 min at 700 W (stirring 100%). The residual solutions were evaporated to dryness and dissolved in HNO_3. For both procedures, no systematic differences were observed, with blanks always found to be negligible. The elemental concentrations were measured by quadrupole-based Poems 1 Inductivity Coupled Plasma Mass Spectrometry (ICP-MS)/Emission Spectrometry (Thermo Jarrell Ash, Offenbach, Germany) using internal calibration by a Rh/Re solution. Although the true analytical precision of concentration measurements by ICP-MS in precise mode is typically < 3% for all studied elements, numerous replicates have clearly demonstrated an overall

Table 1. List of sediment cores recovered in the Bay of Vidy (cores 1–13) and in the central part of Lake Geneva (core 14)

Core number	Date of recovery	Depth (m)	Core length (cm)	*n*	Position	
1	17/08/1995	15	103	8–15	46°30′52′N	6°34′59′E
2	15/08/1995	18	77	16–34	46°30′51′N	6°35′07′E
3	15/08/1995	19	69	12–34	46°30′51′N	6°35′14′E
4	15/08/1995	17	80	12–35	46°30′49′N	6°35′20′E
5	16/08/1995	15	95	13–33	46°30′48′N	6°35′27′E
6	23/08/1995	37	102	5–7	46°30′46′N	6°34′56′E
7	24/08/1995	47	94	11–27	46°30′39′N	6°35′04′E
8	17/08/1995	30	102	5–14	46°30′44′N	6°35′20′E
9	30/04/1997	51	41	12–41	46°30′38′N	6°35′04′E
10	23/08/1995	31	101	3–7	46°30′32′N	6°35′34′E
11	30/04/1996	27	80	5–12	46°30′27′N	6°34′08′E
12	24/08/1995	77	101	7–35	46°30′29′N	6°35′03′E
13	24/08/1995	58	105	6–12	46°30′24′N	6°36′14′E
14	24/04/1997	307	44	28–56	46°28′38′N	6°38′35′E

n, number of samples (depending on analysis).

precision of ≈ 10%, probably because of the variability of the partial digestion step. Such precision is comparable to what was preliminarily observed for a large set of international standards. The Hg levels were determined by cold vapour Atomic Absorption Spectroscopy (Hach & Ott 1968), after digestion of the sediment at 95°C with concentrated nitric acid and hydrochloric acid, with a reproducibility of 15%.

Grain size distribution was determined by laser diffraction, using a LS-100 particle size analyser (Beckman Coulter, Fullerton, CA, USA), following ultrasonic dispersal in deionized water (Loizeau *et al.* 1994). The loss on ignition (LOI), a surrogate for organic matter content, was measured by calcination after 4 h at 550°C (Dean 1974), and carbonate by titrimetry, following acidification of the sample with hydrochloric acid.

RESULTS

Dating and sediment accumulation rate determination

Sediment accumulation rates (SARs) were calculated between the sediment layers having the maximum ^{137}Cs activities corresponding to the years 1964, 1986 and the surface (date of recovery 1995–1997), as well as between the horizon corresponding to the appearance of a sharp increase of VMS (1971) and the surface, when ^{137}Cs dating was not available (Table 2). A total of four out of 11 dated cores exhibited two distinct, sharp peaks of ^{137}Cs activity, allowing an absolute dating of both 1963–1964 and 1986 horizons. For these cores, two SARs were estimated. Three cores were characterized by only one distinct peak of ^{137}Cs activity. Based on these results, it was possible to calculate average SARs for 11 cores that varied between 0.95 g cm^{-2} year^{-1} close to the effluent mouth, and ≈ 0.07 g cm^{-2} year^{-1}. Moreover, SARs appeared to be generally higher after 1986 than between 1964 and 1986 (Table 2, cores 7 and 9). As lateral variations are important in the proximity of an effluent discharge, individual SARs are valid only for the coring location. Thus, extrapolation to larger areas or undated cores was not attempted. Moreover, as sedimentation pattern and amplitude probably have been modified by sediment loads from the STP, it was not possible to obtain data to estimate SARs for the period before the STP's construction in 1964.

Grain size, loss on ignition and heavy metals

Median values of selected heavy metals, LOI and mean grain size in dated cores are summarized in Fig. 2 for post-1964 and pre-1964 periods. Sediments in all cores consisted of a majority of silts, with lower grain size mean values in the pre-1964 period. Mean grain size in both periods tended to decrease with the distance from the outlet, which is

Table 2. Mass depth (g cm^{-2}) of the three time markers used in this study to calculate sediment accumulation rates (SARs)

Core number	^{137}Cs-1986 (g cm^{-2})	^{137}Cs-1964 (g cm^{-2})	VMS-1971 (g cm^{-2})	SAR 1 (g cm^{-2} year^{-1})	SAR 2 (g cm^{-2} year^{-1})	SAR 3 (g cm^{-2} year^{-1})
1	AP	AP	8.72	–	–	0.35
2	7.04	28.16	23.08	0.76	0.95	–
3	AP	24.14	19.99	–	0.76	–
4	AP	25.5	20.72	–	0.77	–
5	1.69	AP	2.75	0.12	–	–
6	AP	AP	2.67	–	–	0.11
7	6.13	15.92	12.85	0.66	0.44	–
8	AP	AP	1.61	–	–	0.07
9	3.73	8.11	4.94	0.61	0.16	–
10	AP	AP	2.46	–	–	0.10
14	1.48	3.53	AP	0.13	0.09	–

Sediment accumulation rates are estimated using volume magnetic susceptibility (VMS) signal only, in cores where ^{137}Cs is not available. Cores 11, 12 and 13 have not been dated because of the absence of VMS peak and interpretable ^{137}Cs.

SAR 1 is calculated between Cs-1986 and the sediment surface; SAR 2 is calculated between Cs-1964 and Cs-1986, except for cores 3 and 4, calculated between Cs-1964 and the sediment surface; SAR 3 is calculated between the VMS-1971 horizon and the sediment surface, for cores without ^{137}Cs dating.

AP, absence of peak.

likely to be related to a selective transport of fine particles to a greater distance from the shore (with the exception of core 7 in the post-1964 period). Similarly, the organic matter content was systematically lower in the pre-1964 period, with high values in the post-1964 period (maximum value to 37.2% in core 7). The metal concentrations in the sediments from cores taken in close proximity to, and in the axis of, the STP's outlet pipe (cores 3 and 7) are the highest (period post-1964; Fig. 2, with median concentrations for Cd and Zn in core 7, for example, being 14.1 and 3447 mg kg^{-1}, respectively). As expected from the results of the companion work (Pardos *et al.* 2004), the trace metal content in post-1964 sediments depended mainly on the distance from the STP's outlet, with the core sampled in the central plain of the lake (14) having the lowest metal concentrations. Two dated cores (7 and 14) were selected for a detailed presentation. Profiles of porosity, LOI, VMS and ^{137}Cs activity values are presented in Fig. 3 and heavy metals concentrations in Fig. 4.

Detailed sedimentary record

Core 7: Bay of Vidy

Three distinct units are distinguished in core 7 by variations in colour and texture. The first upper 23 cm (0–7.9 g cm^{-2}) have a dark aspect resulting from reduced conditions. It consists of silty (mean ≈ 22 µm), organic rich sediment (10–20%). From 23–45 cm (7.9–17.7 g cm^{-2}), the silty (≈ 24 µm) and organic rich (≈ 27%) sediment turns to a brown colour with the presence of laminae. Deeper sediments (> 45 cm or 17.7 g cm^{-2}) are grey, less organic (≈ 5%), finer-grained (≈ 10 µm) and exhibit numerous laminae. The porosity profile indicates a downward compaction below the 40-cm depth, with few ample oscillations in the first 40 cm (Fig. 3). The VMS profile was characterized from bottom to core top by: (i) constant values around 5×10^{-5} (52–13.5 g cm^{-2}); (ii) an increase at a mass depth of 13.5 g cm^{-2}; and (iii) two distinct peaks reaching $\approx 70 \times 10^{-5}$ at a mass depth of 9.5 and 3.2 g cm^{-2}, separated by a trough (14×10^{-5}) at 6.5 g cm^{-2}.

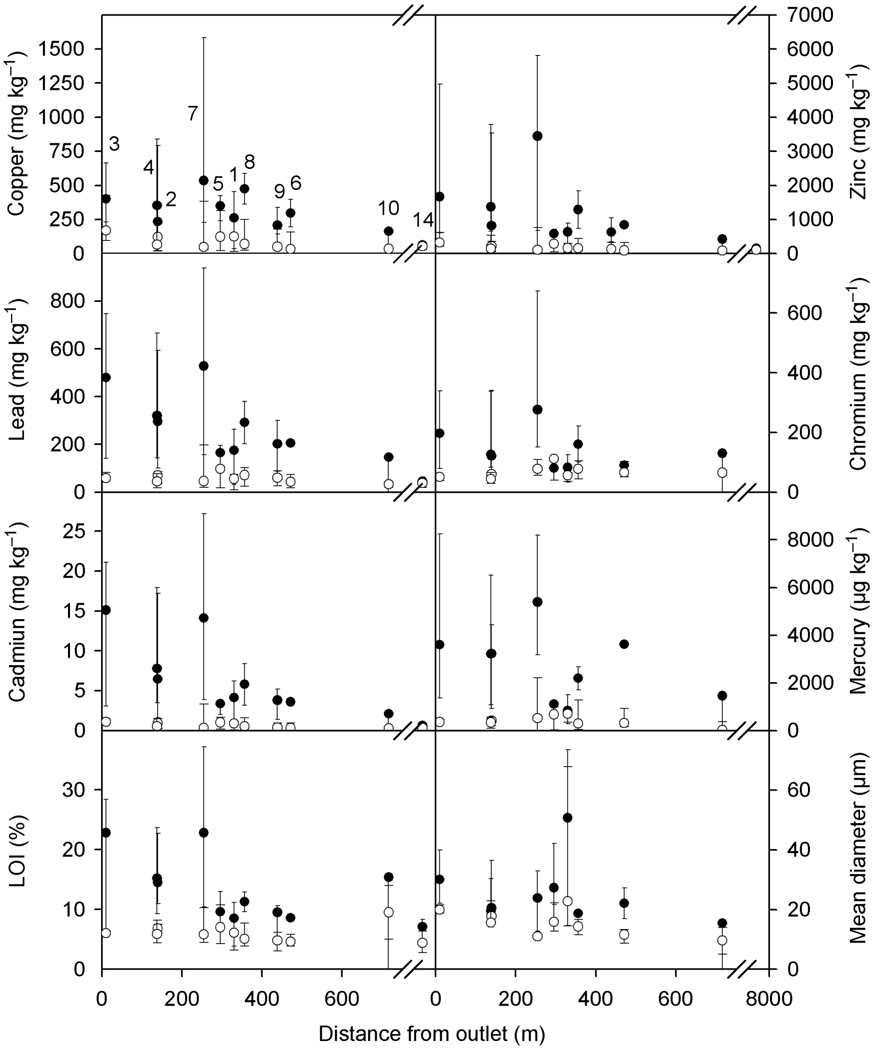

Fig. 2. Median values of selected heavy metals, loss on ignition (LOI) tests and grain size for the post-1964 (●) and pre-1964 (○) periods in the 11 dated cores, ordered with increasing distance from the sewage treatment plant outlet. Whiskers indicate the minimum and maximum values. Numbers in the upper left of the diagram indicate the core label. Except for core 14, all cores exhibit significantly higher heavy metal concentration in the post-1964 period, compared to the pre-1964 period.

The ^{137}Cs activity exhibited two distinct peaks reaching 155 Bq kg^{-1} and 404 Bq kg^{-1} at mass depths of 15.9 and 6.1 g cm^{-2}, attributed to the fallout of 1964 and 1986, respectively. Based on the ^{137}Cs 1964 horizon, the mean sedimentation rate for core 7 was 0.50 g cm^{-2} year^{-1} during the last 31 years.

The profiles representing the quantity of metals in core 7 are depicted in Fig. 4. Low contents are observed at the core bottom (Cd = 0.2 mg kg^{-1}, Cu = 28 mg kg^{-1}, Zn = 74 mg kg^{-1}, Pb = 19 mg kg^{-1}). They correspond to reference values usually mentioned for uncontaminated sediments in Lake Geneva (Vernet & Viel 1984). The general contamination of the environment since the beginning of the 20th century was not observed in this core. The contamination increases in the early 1960s, however, rising strongly when the STP started operation in 1964, to a point where it reaches very high maximum values (Cd = 27.2 mg kg^{-1}, Cu = 1583 mg kg^{-1}, Zn = 5817 mg kg^{-1}, Pb = 939 mg kg^{-1}). The transition between background values and high, STP-related values is very sharp. High values are observed between 16 and 7.5 g cm^{-2}, followed by a minimum for all metal concentrations, as well as for VMS and LOI (Fig. 3), between 7.5 and 5.4 g cm^{-2}. Finally, from 5.4 g cm^{-2} to the sediment surface, metal concentrations show a marked decrease, by a factor of 3.1 for Cd, 4.6 for Cu, 3.4 for Zn and 2.4 for Pb between the sediment layers presenting the maximum concentration and the present sediment surface. Despite their comparable trends, a few notable punctual discrepancies are observed between metals, such as the position of the maximum contamination (deeper for Cu compared to Zn).

Core 14: Central part of Lake Geneva

The profile of porosity (Fig. 3) indicates a downward progressive compaction. A few sudden low porosity layers, however, are noticed at mass depth around ≈ 1 g cm^{-2} and at 4.3 g cm^{-2}. From the core bottom, ^{137}Cs activity (Fig. 3) is present at a depth of 5.5 g cm^{-2}, with two peaks clearly observed at 3.5 and 1.5 g cm^{-2}. Based on ^{137}Cs dating, the

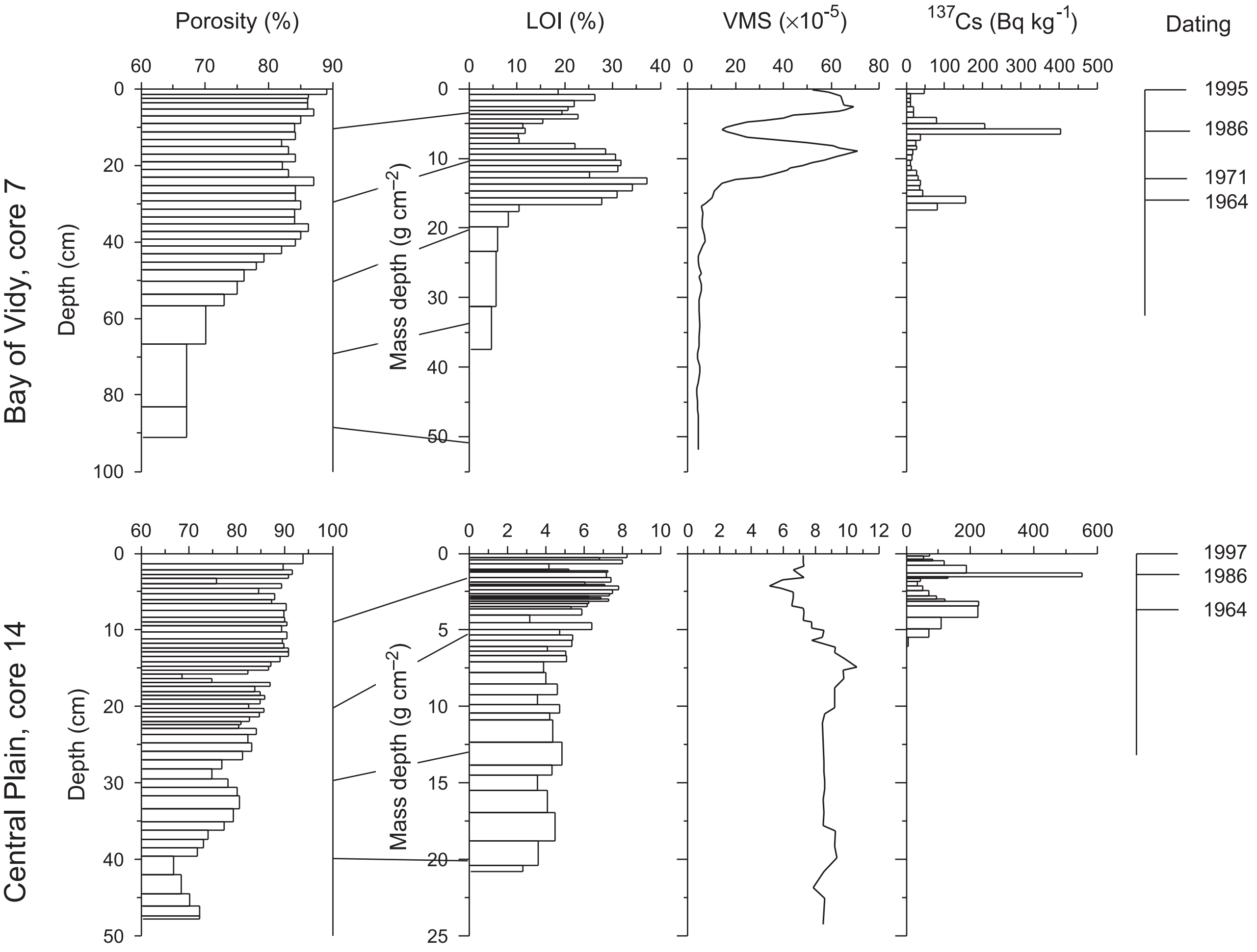

Fig. 3. Profiles of porosity, loss on ignition (LOI), volume magnetic susceptibility (VMS) and radiocaesium (^{137}Cs) activity in cores 7 and 14.

mean SAR is 0.09 g cm^{-2} year^{-1} between 1964 and 1986, and 0.013 g cm^{-2} year^{-1} between 1986 and 1997, with the date of the core recovery being 1997. The VMS profile (Fig. 3) is relatively constant with values around 8×10^{-5} and characterized by the absence of a sharp increase of the signal. Volume magnetic susceptibility values in core 14 are approximately one order of magnitude lower than maximum values in core 7. The LOI profile (Fig. 3) shows values generally decrease from the core top to 7 g cm^{-2} despite some shifts in the layers, corresponding to the decrease in the porosity, and then stabilizes around 4%.

In regard to trace metals (Fig. 4), the Cd and Zn profiles and the Pb profile to a lesser extent, follow approximately the same trends, with a maximum located at a mass depth of 2.7 g cm^{-2}. In contrast, Cu reaches its maximum deeper in the core (at 7 g cm^{-2}), remaining nearly at this level up to 2.7 g cm^{-2}. However, in contrast to core 7, the concentrations always remain low (median values of 0.53 mg kg^{-1} for Cd, 58 mg kg^{-1} for Cu, 134 mg kg^{-1} for Zn and 41 mg kg^{-1} for Pb), with the highest degree of contamination (1.1 mg kg^{-1} for Cd, 79 mg kg^{-1} for Cu, 63 mg kg^{-1} for Pb and 201 mg kg^{-1} for Zn) being ≈ 15–30 times lower than in the Bay of Vidy's core 7. However, the slow increase in metal contamination over time started some decades before 1964, probably at the beginning of the 20th century. Since ≈ 1980, metal concentrations decreased up to the present time; the concentrations recorded in the central part of the lake today are only marginally above their natural levels (Table 3). In addition, all the metals exhibited low concentrations in the low porosity layers. This is particularly clear in the horizon at the mass depth of 4.3 g cm^{-2}, which is characterized by metal (Fig. 4) and LOI (Fig. 3) contents lower above and below.

Median heavy metal content: Comparison of pre- and post-1964 periods

Post-1964 to pre-1964, the ratios of trace metal median concentrations determined for the dated core 7 (Table 3) indicate that the heavy metal concentrations in the sediments of the Bay of Vidy have increased by factors ranging

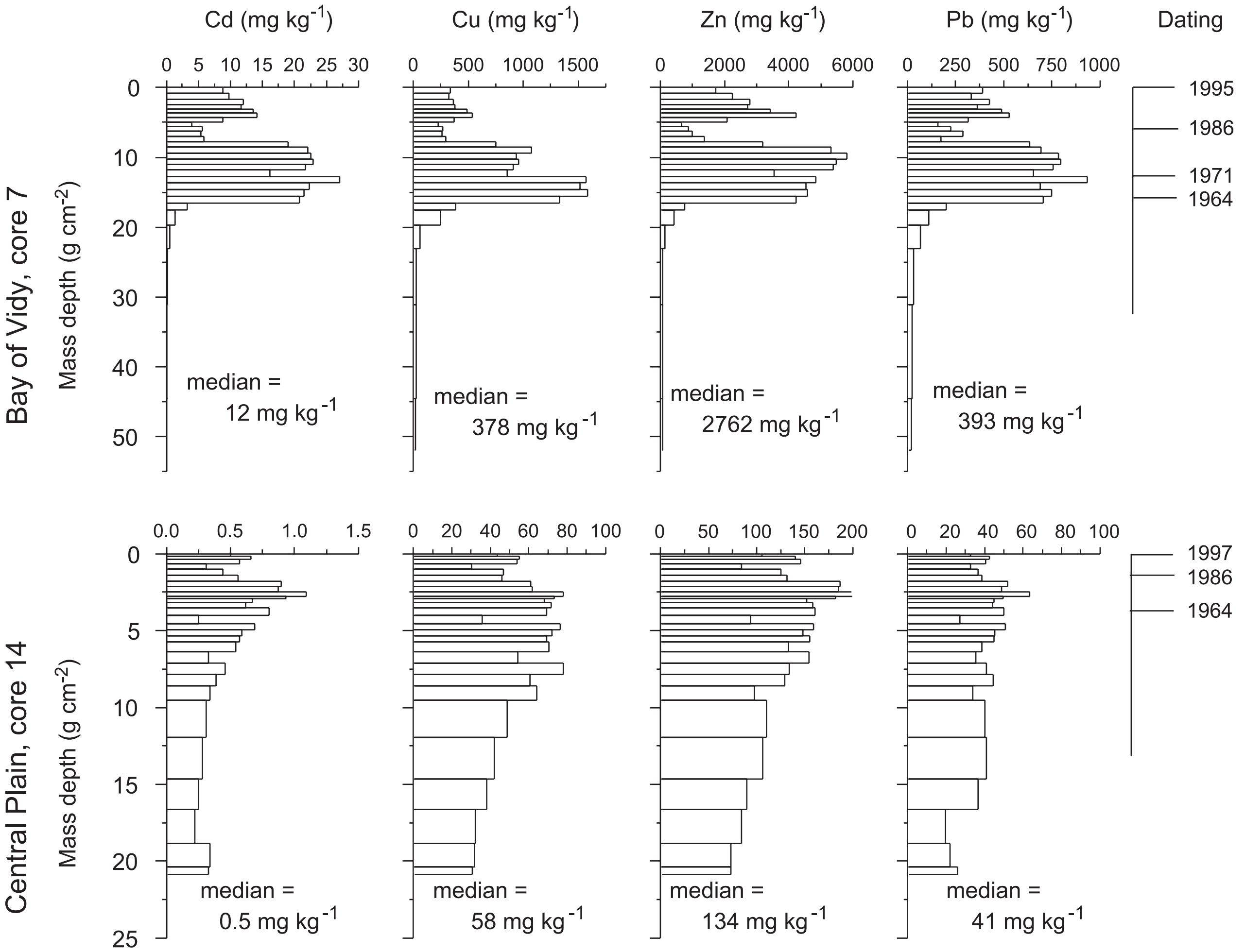

Fig. 4. Profiles of selected heavy metals (cadmium, copper, zinc, lead) in cores 7 and 14.

from 10.4 (Hg) to 39.8 (Cd) since the beginning of the STP's activity. Similarly, ratios of post-1964 trace metal median values in core 7 over post-1964 values in core 14 vary between 8.7 (Cu) and 22.7 (Zn), confirming the strong contamination of the sediments in the proximity of the STP. Comparison of the heavy metal median concentrations during the period post-1964 with the background concentrations ('reference values') observed prior to industrialization (Vernet & Viel 1984) again clearly indicates the presence of contaminated sediment (e.g. ratios ranging from 17.6 (Pb) to 180 (Hg) in core 7). In contrast to core 7, heavy metal contents at the surface of core 14 remain low, very close to Lake Geneva reference values.

DISCUSSION

The study of the depositional history of heavy metals in Lake Geneva within the Bay of Vidy (which receives a STP discharge), and in the central part of the lake, is based on their profiles measured in dated cores. Surveys of metal contamination in aquatic sediments must account for possible postdepositional mobility of metals in sediment records (e.g. the redox speciation of iron, that might affect its own mobility and the mobility of other metals within a given core) before conclusions can be drawn regarding the temporal variability of inputs of metals discharged into lake waters (Santschi *et al.* 1990). In the present case, concordance of concentration of heavy metals and physicochemical properties (^{137}Cs, VMS, colour, odour) in 14 sediment cores gave no evidence of mobility. In general, the trend of heavy metal concentrations over time clearly indicates that, since 1964, sediments with elevated median metal concentrations in the cores are present where the STP's effluent enters the Bay of Vidy (Fig. 2). This suggests that, since the beginning of the STP's operation in 1964, the input of particulate matter from the STP's effluent added large amounts of metals to the lake floor.

Core dating

In the Bay of Vidy, complex sedimentation processes occur, resulting in incomplete sequences or redeposited layers. The following evidence supports this conclusion:

1. Only five cores exhibit the two ^{137}Cs peaks that allowed an absolute dating of both 1964 and 1986 horizons, which correspond to world-wide maximum deposition of Cs derived from the atmospheric nuclear weapon tests and to the Chernobyl accident fallout, respectively. For the other nine cores, the perturbations of the ^{137}Cs activity profiles indicate that the sedimentary record has been affected.

2. Cores that display the two ^{137}Cs peaks showed atypical low porosity, VMS, LOI and heavy metal values in few horizons.

3. Monna *et al.* (1999) found in core 9 that ^{210}Pb$_{xs}$ and ^{137}Cs inventories in the upper horizons appeared high, compared to data from core 14 and other sites in Lake Geneva.

4. The heavy metals, as well as ^{137}Cs activity profiles, in core 7 present a very sharp transition between uncontaminated sediment to contaminated sediment. It appears that sediments deposited between the start of the industrialization era and 1964 are missing. This assumption is supported by a ^{210}Pb$_{xs}$ profile (Rozé 2001) in a core close to core 7, which shows an extremely low sediment accumulation rate of 0.04 g cm^{-2} year^{-1} before 1964.

These observations can be explained by phenomena such as erosion and rapid deposition of sediments initially deposited elsewhere around the coring area. They are probably related to sporadic events such as turbidity currents, floods, man-made impact (drilling operations to anchor the STP's underwater pipe in 1986, resuspending older, uncontaminated sediment horizons), and the focusing of the storm overflow from Lausanne's agglomeration into the lake via the Flon River. These phenomena

Table 3. Post-1964 to pre-1964 ratios of trace metal median concentrations for core 7 (Bay of Vidy) and core 14 (Central Plain), and comparison with reference values

Ratio	Cadmium	Copper	Lead	Zinc	Mercury
(7) post-1964/(7) pre-1964	39.8	11.1	11.5	30.4	10.4
(7) post-1964/(14) post-1964	21.8	8.7	12.0	22.7	NC
(7) post-1964/REF value	70.7	17.8	17.6	57.5	180
(7) surface/REF value	43.8	11.4	13.1	28.9	255
(7) surface/(14) surface	17.2	7.8	12.1	16.4	NC
(14) surface/REF value	2.6	1.5	1.1	1.8	NC

REF values (Vernet & Viel 1984): cadmium = 0.2 mg kg^{-1}; copper = 30 mg kg^{-1}; lead = 30 mg kg^{-1}; zinc = 60 mg kg^{-1}; mercury = 0.03 mg kg^{-1}.

NC, not calculable.

might complicate considerably the establishment of a reliable chronology and, as a consequence, the historical trend of contamination cannot be precisely established in all collected cores. For the purpose of this study, however, changes and trends in temporal concentration are more important than absolute values and are consistent between the cores taken in the Bay of Vidy.

Heavy metals trends

In Figs 3 and 4, profiles of cores 7 and 14 are shown in detail, as these sites presumably contain the best sedimentary record of heavy metals over time among the sampled cores. An important feature of the core profiles shown in Fig. 4 concerns the differences in metal concentrations between the two geographical locations. For core 14, collected as far as possible from direct human influence, there is a clear indication that anthropogenic inputs have increased significantly during the last century, with a maximum in the mid-1970s, as was observed for European lakes (Vernet & Thomas 1972; Förstner & Wittmann 1979; Dominik *et al.* 1984; Verta *et al.* 1989). For core 7, the median concentrations of heavy metals before 1964 (Fig. 2) are similar to those of core 14 for the same period. However, an increase of heavy metal concentrations can be observed since the late 1950s, confirming the Monod (1956) study. It resulted from population growth and human activities in the catchment area (e.g. from the discharge of untreated sewage via the Flon River and contamination of the Chamberonne River (Fig. 1). From 1964 (i.e. from the beginning of the STP's operation), the concentration of heavy metals in core 7 dramatically increased, reaching maximum values in the late 1960s or the beginning of the 1970s. In general, the highest metal concentrations in surface sediments of the bay occurred where high sediment accumulation rates coincided with the proximity of the source. Moreover, in depositional areas, a layer of sewage-derived material displaying high VMS values, to ≈ 70 cm thick, has metal concentrations nearly one order of magnitude above pre-1971 horizon values.

An important feature of the profiles of cores 7 and 14 is the decline of their concentrations since the 1980s, indicating that the input of these metals to the bay and lake, and their subsequent accumulation in the sediments, have decreased in recent years. Although concentrations of all metals have decreased at the surface of core 7, none of the investigated heavy metals has yet reached the concentrations measured at the surface of core 14, which are close to reference values for Lake Geneva (Table 3). This decrease probably results from several effects, such as the improvement of the STP's operation (e.g. improvement of wastewater treatment efficiency in 1976), improved environmental quality of the Chamberonne River (Burkard 1972; Siwertz 1973), changes in industrial products and methods, more stringent legal regulations for releases of pollutants to the environment and growing public awareness of environmental problems. In core 7, the sediment layers between 5.4 and 7.5 g cm^{-2} present a minimum in heavy metal concentration, as well as low values in LOI and VMS. This is characteristic of an alteration of the sediment sequence succession by an event which rapidly deposits older, less contaminated particles. Dating shows that these less-contaminated sediments were deposited in ≈ 1986. This date corresponds to the time of engineering works performed in the bay to anchor the effluent pipe. Such works might have resuspended old sediment, which spread over the bay floor.

As described above, the concentrations of heavy metals are elevated above background levels in sediments that have been affected by human activity and a potential enrichment of trace metals in modern surface samples might be determined by comparison with samples from deeper and older horizons (Table 3). However, considerable uncertainty exists about metal concentrations that pose significant ecological risks because the bioavailable fraction of metal in sediments cannot be determined in a straightforward manner. Extensive research has shown that metal concentrations that elicit toxicity can vary by one or more orders of magnitude among different sediments (Adams *et al.* 1992). Hence, even when concentrations in sediments substantially exceed background levels, metal bioavailability can be minimal and adverse impacts might not occur.

Bioassays performed on aqueous extracts to mimic the open-water disposal of dredged material and organic extracts of different sediment horizons in cores taken in the Bay of Vidy identify ammonia (NH_3)and elemental sulphur (S) as important sediment-associated toxicants (Peytremann & Haller 1997). As NH_3 is not a persistent compound and elemental S probably is not harmful to aquatic and benthic organisms, future work should focus on techniques for coping with samples containing NH_3 and elemental S. Based on these results, the potential hazard of heavy metals and organic contaminants for biota in the bay is unknown, particularly in the case of dredging activity to remove contaminated sediments. Thus, efforts should be undertaken to rectify this situation.

CONCLUSIONS

The dramatic increase of heavy metals concentrations in sediment cores since the beginning of STP operations in 1964 clearly demonstrates that the STP is an important source of contaminants for the Bay of Vidy. Maximum contamination factors vary from 18 (Pb) to 180 (Hg), relative to the natural background levels. Highly contaminated sediment from the late 1960s and beginning of the 1970s are now covered by less contaminated layers, although heavy metal concentrations are still elevated and well above background levels. Furthermore, the transport of sediment (slumps), with associated pollutants, is occurring in the Bay of Vidy with an unknown impact on Lake Geneva.

This study established heavy metal trends over time, providing a framework for future scientific research, and can serve as a basis for investigations of the efficiency of environmental remediation efforts in the Bay of Vidy. Future work should focus on: (i) identifying the relative importance of various transport and remobilization processes for contaminants' fate; and (ii) determining their bioavailability to provide a basis for chemical and biological guidelines for sediment pollution.

As chemical contamination of sediments might be the result of either past and/or present disposal practices, and because eliminating the source or improving water quality does not always solve the problem, dealing with sediment contamination is not an easy task. In order to prepare a plan for proper remedial action, extensive survey, monitoring and research activities are required to assess the contaminant levels and sediment volumes in the areas to be dredged or remedied.

ACKNOWLEDGEMENTS

We wish to express special thanks to J. Piccard and his crew for his precious help during sampling with the F.-A. Forel submersible. We thank the staff of the F.-A. Forel Institute, as well as J. Buffle and M. Martin for their assistance in various phases of the study.

REFERENCES

Adams W. J., Kimerle R. A. & Barnett J. W. Jr (1992) Sediment quality and aquatic life assessment. *Environ. Sci. Technol.* **26**, 1865–75.

Burkard P. (1972) Etude des affluents du lac Léman et du Rhône entre Genève et Chancy. Annual report. Commission Internationale pour la Protection des Eaux du Léman contre la Pollution, Lausanne.

Burton G. A. Jr (1992) Assessing contaminated aquatic sediments. *Environ. Sci. Technol.* **26**, 1862–3.

Dean W. E. (1974) Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *J. Sediment. Petrol.* **44**, 242–8.

Dominik J., Burrus D. & Vernet J.-P. (1987) Transport of the environmental radionuclides in an alpine watershed. *Earth Planet. Sci. Let.* **84**, 165–80.

Dominik J., Loizeau J.-L., Favarger P.-Y., Vernet J.-P. & Thomas R. L. (1991) History of mercury contamination reconstructed from high-resolution radioisotopic dating of sediment cores in Lake Geneva. In: *Heavy Metals in the Environment* (ed. J.-P. Vernet) pp. 273–96. Elsevier, Amsterdam.

Dominik J., Mangini A. & Prosi F. (1984) Sedimentation rate variations and anthropogenic metal fluxes into Lake Constance sediments. *Environ. Geol.* **5**, 151–7.

Förstner U. & Wittmann G. T. W. (1979) *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.

Gibbs-Eggar Z., Jude B., Dominik J., Loizeau J.-L. & Oldfield F. (1999) Possible evidence for dissimilatory bacterial magnetite dominating the magnetic properties of recent lake sediments. *Earth Planet. Sci. Let.* **168**, 1–6.

Hach W. R. & Ott W. L. (1968) Determination of submicrogram quantities of mercury by atomic absorption spectroscopy. *Anal. Chem.* **40**, 2085–7.

Håkanson L. & Jansson M. (1983) *Principles of Lake Sedimentology*. Springer-Verlag, Berlin.

Loizeau J.-L., Arbouille D., Santiago S. & Vernet J.-P. (1994) Evaluation of a wide range laser diffraction grain size analyser for use with sediments. *Sedimentology* **41**, 353–61.

Loizeau J.-L., Dominik J., Luzzi T. & Vernet J.-P. (1997) Sediment core correlation and mapping of sediment accumulation rates in Lake Geneva (Switzerland, France) using volume magnetic susceptibility. *J. Great Lakes Res.* **23**, 391–402.

Loizeau J.-L., Rozé S., Peytremann C., Monna F. & Dominik J. (2003) Mapping sediment accumulation rate by using volume magnetic susceptibility core correlation in a contaminated bay (Lake Geneva, Switzerland). *Eclo. Geol. Helv.* **96**, S73–9.

Luoma S. N. & Ho K. T. (1993) Appropriate uses of marine and estuarine sediment bioassays. In: *Handbook of Ecotoxicology.* (ed. P. Calow) pp. 193–226. Blackwell Scientific Publications, Oxford.

Luzzi T. (1989) Origine et applications de la susceptibilité magnétique dans les sédiments du delta du Rhône, Léman (Suisse–France). Unpublished thesis. University of Geneva, Switzerland.

Mecray E. L., King J. W., Appleby P. G. & Hunt A. S. (2001) Historical trace metal accumulation in the sediments of an urbanized region of the Lake Champlain watershed, Burlington, Vermont. *Water, Air, Soil Poll.* **125**, 201–30.

Monna F., Dominik J., Loizeau J.-L., Pardos M. & Arpagaus P. (1999) Origin and evolution of Pb in sediments of Lake Geneva (Switzerland – France). Establishing a stable Pb record. *Environ. Sci. Technol.* **33**, 2850–7.

Monod R. (1956) Contribution à l'étude des variations de la composition chimique des eaux du lac Léman, phénomènes de pollution et d'autoépuration à l'embouchure du Flon à Vidy. *Ann. Stat. Cent. Hydrobiol. App.* **6**, 233–345.

Pardos M., Benninghoff C., de Alencastro L. F. & Wildi W. (2004) The impact of a sewage treatment plant's effluent on sediment quality in a small bay in Lake Geneva (Switzerland–France). Part 1: Spatial distribution of contaminants and the potential for biological impacts. *Lakes Reserv.: Res. Manage.* **9**, 41–52.

Peytremann C. & Haller L. (1997) Etude sédimentologique, géochimique et écotoxicologique des sédiments de la baie de Vidy. Unpublished thesis. University of Geneva and Lausanne, Switzerland.

Rozé S. (2001) Evaluation des processus sédimentaires et du transport des sédiments contaminés dans la baie de Vidy. Unpublished thesis. University of Geneva and Lausanne, Switzerland.

Santschi P. H., Höhener P., Benoit G. & Bucholtzten Brink M. (1990) Chemical processes at the sediment–water interface. *Mar. Chem.* **30**, 269–315.

Siwertz E. (1973) Etude des affluents au lac Léman et du Rhône entre Genève et Chancy. Annual report. Commission Internationale pour la Protection des Eaux du Léman contre la Pollution, Lausanne. No. 1973.

Smith S. L., MacDonald D. D., Keenleyside K. A., Ingersoll C. G. & Field L. J. (1996) A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *J. Great Lakes Res.* **22**, 624–38.

Sugai S. F., Alperin M. J. & Reeburgh W. S. (1994) Episodic deposition and ^{137}Cs immobility in Skan Bay sediments: a ten-year ^{210}Pb and ^{137}Cs time series. *Mar. Chem.* **116**, 351–72.

Vernet J.-P. & Thomas R. L. (1972) Levels of mercury in the sediments of some Swiss lakes including Lake Geneva and the Rhone River. *Eclo. Geol. Helv.* **65**, 293–306.

Vernet J.-P. & Viel M. (1984) Métaux lourds dans les sédiments lacustres. Annual report. Synthesis 1957–82. Commission Internationale pour la Protection des Eaux du Léman contre la Pollution, Lausanne.

Verta M., Tolonen K. & Simola H. (1989) History of heavy metal pollution in Finland as recorded by lake sediments. *Sci. Total Environ.* **87/88**, 1–18.

Von Gunten H. R., Sturm M. & Moser R. N. (1997) 200-year record of metals in lake sediments and natural background concentrations. *Environ. Sci. Technol.* **31**, 2193–7.

Wessels M., Lenhard A., Giovanoli F. & Bollhofer A. (1995) High resolution time series of lead and zinc in sediments of Lake Constance. *Aquat. Sci.* **57**, 291–304.