High-resolution reconstruction of the 20th century history of trace metals, major elements, and organic matter in sediments in a contaminated area of Lake Geneva, Switzerland

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Abstract

Toxic trace metals in lacustrine sediments are of major concern since they can be hazardous to biota and human health. A high-resolution multiproxy study, including trace metals and major elements (measured by ICP-MS and XRF), total organic carbon, mineral carbon, Hydrogen Index, Oxygen Index, and C/N ratios, was performed on a sediment core from Vidy Bay in Lake Geneva. This bay has been affected by hazardous compounds released via the sewage effluent of a major wastewater treatment plant (WWTP). Anthropogenic trace metals, such as Pb, Cd, Cu, Zn, and Hg, increased following the industrial revolution in Europe. The highest amounts of these toxic metals, together with Ni, Cr, Co, Ag, Bi, and Fe, were recorded in sediments from 1964, the date of the WWTP implementation. During this period, all trace elements exceeded the sediment quality guideline “probable concentration effect” (PEC), with the following maximum concentrations (in mg kg⁻¹): Pb 4000, Cd 23, Cu 1200, Zn 8600, Hg 11, Ni 140, Cr 270, Ag 130, and Bi 310. The geochemistry of detrital elements (Al, Si, Ca, Ti, K, Zr, Rb, and Sr), as well as S, Fe,

P, and the nature and quality of organic matter were clearly also affected by the effluent. The sedimentary record revealed that, after some improvements in the wastewater treatment processes and the relocation of the outlet pipe, the sediments tended to return to concentrations similar to those prevailing before the WWTP implementation. However, despite the reduction in the contamination load from the WWTP, which could be reinforced with the construction of a new plant in the near future, the sediments deposited in the Vidy Bay represent a major contaminant legacy that constitutes a potential threat to the lake biota in the case of sediment remobilization.

Keywords: Heavy metals, trace metals, wastewater, sediment contamination, organic matter.

43 **1. Introduction**

44 Lake sediments are archives of climatic variations and pollution in the environment.
45 Trace, minor and major element signals recorded in sediments allow the
46 reconstruction of historical events, both natural and anthropogenic in origin. Detrital
47 trace metals are discharged through watershed runoff (directly or from fluvial inputs)
48 into lakes. Heavy metal emissions by anthropogenic activities have been shown to
49 increase local, regional, and global fluxes to the atmosphere since the beginning of
50 metallurgy (Nriagu, 1996; Vesely, 2000). Thus, trace metals are widely distributed in
51 the environment. Nevertheless, sewage waters and sludge directly discharged by
52 wastewater treatment plants (WWTP) also represent major sources of contamination
53 in lakes. Heavy metals accumulate in sediments via several mechanisms, such as
54 adsorptive attachment to fine-grained particles (Sholkovitz and Price, 1980),
55 precipitation of discrete metal compounds, coprecipitation of metals by Mn- and Fe-
56 oxyhydroxides and carbonates, and association with organic molecules (Forstner,
57 1982). The mobility and bioavailability of trace metals in lake sediments depend on
58 their speciation and stability (Calmano et al. 1993), which are controlled by chemical
59 conditions such as the sediment redox potential, pH, organic matter content, and Mn-
60 and Fe-oxyhydroxides. Sediment contamination can harm benthic infauna and
61 epifauna through superficial contact with polluted sediments and pore water, as well
62 through direct ingestion of sediments and detritus (Lawrence and Mason, 2001;
63 Reynoldson, 1987). Moreover, in case of sediment remobilization, trace metals are
64 likely released into the water column and may enter the aquatic life, which is
65 deleterious to organisms because they accumulate in food, leading to damage in
66 human organs and severe diseases (Alissa and Ferns, 2011; Hu, 2000; Ibrahim et al.
67 2006). In particular, mercury is a toxic trace metal that has gradually increased in

concentration in sediments due to anthropogenic activities. Since the industrial revolution (late 18th century), the burning of fossil fuels, nonferrous-metal industry, wood combustion, chlor-alkali industries, and waste incineration have been the principal sources of Hg to the atmosphere (AMAP/UNEP, 2013) and, consequently, to the aquatic environments and soils via deposition (Wang et al. 2004) all over the globe.

The present study aims to reconstruct the trace element history during the last century in the sediments of Vidy Bay, a fresh water bay in Lake Geneva (Switzerland). Recent sediments contain approximately fifty times more Hg and Pb than pre-industrial sediment measured in the deepest part of the lake (Thevenon et al. 2011). This area has been the object of several studies that found that it is the most contaminated site in the lake due to the discharge of local WWTP effluent. Trace metal contamination (Hg, Pb, Cd, Cu, Zn and Mn), fecal indicator bacteria activity, and antibiotic-resistant bacteria genes in Vidy Bay sediments increased since the implementation of the WWTP in 1964 (Loizeau et al. 2004; Monna et al. 1999; Thevenon and Pote, 2012; Czekalski et al. 2014). Nevertheless, no detailed chronology of contamination events before and after the WWTP outlet pipe emplacement in the bay has been conducted. Moreover, very few published studies exist on lake sediment contaminated by urban wastewater. To start to fill this gap, we studied anthropogenic trace element contents of Pb, Cd, Cu, Zn, Ni, Cr, Co, Ag, Bi, Hg, S, P and Fe, the detrital trace elements Al, Si, Ca, Ti, K, Zr, Rb, and Sr, and organic matter in the contaminated Vidy Bay sediments.

1.1. Setting

Lake Geneva is a warm monomictic peri-alpine lake in central Europe, located at the border between Switzerland and France (Fig. 1). It is the largest freshwater reservoir in Western Europe, with a surface area of 580.1 km², a volume of 89 km³ and an average depth of 152.7 m (maximum depth: 309 m). The Lake Geneva catchment area (including the lake) is 7999 km², and the Rhône River is the major tributary (75% of the total water input), with a mean inflow of 185 m³ s⁻¹ and a mean outflow of 250 m³ s⁻¹. Complete vertical mixing does not occur every year at the end of the winter (Loizeau and Dominik, 2005). A main drinking water pumping station is located in Saint-Sulpice, approximately 4 km west of Vidy Bay. Since 1964, the bay has received domestic and industrial sewage water from (1) the outlet pipe of a wastewater treatment plant (WWTP), which initially discharged into the lake 300 m distance from shore and at 12 m depth; (2) the Flon River, which collects surface water and wastewater from the west side of the city during floods (when discharge is greater than 4–5 m³ s⁻¹) and discharges through a pipe at 12 m depth; and (3) the Chamberonne River, which drains the watershed and also carries some urban runoff (Thevenon et al. 2011). The sewer system is only partially separated and collects a significant amount of urban runoff during rain events. The WWTP was conceived for 220,000 equivalent inhabitants and treats 1–3 m³ s⁻¹ of wastewater. The wastewater treatment consists of pre-treatments (grit removal and screening at 1 cm), primary clarifiers, biologically activated sludge treatment without nitrification, or, for 5% of the flow, a moving bed bioreactor (MBBR) with partial to complete nitrification (<1 mg N-NH₄ L⁻¹) (Margot et al. 2013).

1.2. Important dates for the WWTP

Since the late 1960s, the lake has featured meso-eutrophic conditions (Lang, 1985; Monod, 1983). For that reason, in 1971, ferric chloride (FeCl₃) was used to

precipitate and eliminate the phosphorous present in wastewater as a measure to reduce the P load in the lake. The WWTP was extended in 1976, introducing a physico-chemical treatment that increased the water treatment capacity by $1 \text{ m}^3 \text{ s}^{-1}$. A second chain of sludge incineration was put into operation in 1979. In 2001, the outlet pipe was extended to the present location, 700 m from shore and at 35 m depth (Fig. 1). A specific treatment of greasy residues was introduced in 2002 and new chemical deodorization washing facilities were installed to complement the existing equipment in 2003. In 2005, road bag treatments began using filtering dumpsters. Finally, in September 2008, the new boiler furnace #2 started functioning, increasing the daily tonnage of incinerated sludge in Vidy. The Vidy WWTP facilities do not meet current standards in terms of the quality of the releases (Préavis N° 2010/65, 2010). Vidy Bay remains the most contaminated area in Lake Geneva because the WWTP effluent still contains pollutants that settle to surface sediments, such as Hg and other trace metals, fecal indicator bacteria and organic matter (Gascon Diez et al. 2014; Czekalski et al. 2014; Masson and Tercier-Waeber, 2014; Sauvain et al. 2014).

2. Materials and Methods

2.1. Sampling and subsampling

A 103-cm-long sediment core (EGD3) was retrieved at 21 m depth on October 2010 between the current WWTP outlet and the old outlet ($6^{\circ}35'17.97''$ E, $46^{\circ}30'48.30''$ N; Fig. 1) using a polyvinyl chloride liner in a UWITEC gravity corer and weight hammering while aboard the “La Licorne” scientific vessel.

2.2. Volume magnetic susceptibility, freeze-drying and sediment grain size distribution

A Volume Magnetic Susceptibility (VMS) profile was determined using a MS2 susceptibility meter (Bartington Instruments, England) at 1-cm resolution. Afterwards, the core was split lengthwise, photographed, sedimentologically described and subsampled down-core with 1-cm resolution. Particle grain size distributions were determined on wet sediments using a laser diffraction Coulter LS-100 analyzer following the procedure described by Loizeau et al. (1994). Sediments were freeze-dried in a CHRIST BETA 1-8 K freeze-drying unit (-54 °C, 6 Pa) for a minimum of 48 h. Dry samples were ground and homogenized with an agate mortar.

2.3. Dating

The age-depth model was obtained by radiometric dating (^{137}Cs and ^7Be) using a HPGe well gamma spectrometer (Ortec EG&G). Five time markers were used: the first occurrence of ^{137}Cs in 1954; two ^{137}Cs fallout peaks, one in 1964 (atmospheric nuclear weapon testing) and one in 1986 (the Chernobyl accident); the VMS maximum gradient in 1971 (Loizeau et al. 2003); and the surface sediment in 2010, confirmed by the presence of ^7Be , a naturally occurring radioisotope of short half-life (53.3 days). It is produced in the stratosphere by the interaction of cosmic rays with atmospheric molecules, and transported to the Earth surface mainly through wet deposition (Kaste et al. 2002). Water content measurements and porosity calculations (Hankanson and Jansson, 1983) were necessary to estimate the *in situ* density of dry particles to obtain the mass of accumulated sediment per centimeter. The depth scale was converted to a mass scale to calculate sediment accumulation rates (SAR) [$\text{g cm}^{-2} \text{y}^{-1}$].

2.4. Total organic carbon, mineral carbon, Hydrogen Index and Oxygen Index

Characterization and quantification of the organic matter were performed on

powdered bulk sediment at the Institute of Earth Sciences at the University of Lausanne using Rock-Eval 6 following the method described by (Behar et al. 2001; Espitalie et al. 1985a; Espitalie et al. 1985b). The samples were placed in an oven and first heated to 300 °C under an inert atmosphere then gradually pyrolyzed to 650 °C. After complete pyrolysis, samples were transferred into another oven and gradually heated to 850 °C in the presence of air. The determined parameters were total organic carbon (TOC), the Hydrogen Index (HI as mg HC g⁻¹ TOC) and the Oxygen Index (OI as mg CO₂ g⁻¹ TOC), which permit an overall characterization of the sedimentary organic matter. The HI and OI values are proportional to the H/C and O/C ratios of the organic matter, respectively, and can be used for OM classification in Van Krevelen-like diagrams (Espitalie et al. 1985a). The standard used was IFP 160000 Rock-Eval, and the analyses were carried out on 50–100 mg of powdered dry sediment under standard conditions. Analytical precision was higher than 0.05 wt % (1σ) for TOC, 10 mg HC g⁻¹ TOC (1σ) for HI, and 10 mg CO₂ g⁻¹ TOC (1σ) for OI.

2.5. Total nitrogen analysis

Total nitrogen concentration (% N) was analyzed in a CHN Elemental Analyzer (Carlo Erba Flash EA 1112 CHNS/MAS200) using approximately 10 mg of dry powdered sediment. The carbon/nitrogen (C/N) ratio was calculated as the weight ratio of the total organic carbon measured by the Rock-Eval pyrolysis (see above) and the N content analyzed by the CHN Elemental Analyzer. The precision was better than 1% based on an internal standard, and replicate samples.

2.6. Mercury analyses

Total mercury was analyzed by Cold Vapor Atomic Absorption Spectrophotometry (CV-AAS) using an Advance Mercury Analyzer (Model AMA 254, Altec, Czech Republic) through dry mineralization and pre-concentration of Hg and amalgamation on a gold trap (Szakova et al. 2004). All analyses were run in triplicate. The detection limit and working range were 0.01 ng and 0.05–600 ng, respectively. The relative error was usually $\pm 5\%$ and always less than 10% (Roos-Barracough et al. 2002). The concentrations obtained for repeated analyses of the certified reference material never exceeded the specified range of concentrations given for the MESS-3 reference material (National Research Council Canada).

2.7. Trace and major element analyses

Two analytical techniques were used to measure element concentrations. The first one is a quantitative method. Quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, model 7700 series, Agilent) was performed following sediment digestion in Teflon bombs heated to 150 °C in analytical grade 2 M HNO₃ according to the Swiss Soil Protection Ordinance (OSol, OFEV, 1998). Multi-element standard solutions of different concentrations (0, 0.02, 1, 5, 20, 100 and 200 $\mu\text{g L}^{-1}$) were used for calibration. The total variation coefficients for triplicate sample measurements were less than 10%. The metal concentrations in the sediments are expressed in mg kg^{-1} of dry weight sediment. The ICP-MS measurements were carried out with 1-cm resolution. The second technique is based on X-ray fluorescence (XRF) element scanning using a model AVAATECH XRF core scanner (2000 A, 10-30 kV and 20-50 s measuring time) that measured every 2 mm. Core images were obtained using a high-resolution AVAATECH core scanner coupled camera. It is helpful to combine these two analytical techniques. On one hand, XRF is a higher-resolution, non-destructive technique but provides only semi-quantitative

geochemical information and measurements can be biased by humidity, porosity and particle grain size within the sediment (Hennekam and de Lange, 2012; Tjallingii et al. 2007). On the other hand, ICP-MS analyses of sediments extracted by the OSol method provides quantitative results, permitting more precise analysis of trace metals of which origin is mainly anthropogenic, and not locked in the mineral structure of sediment grains. For instance, previous studies in the region showed that the leachable Pb in the sediments of Vidy Bay was equivalent to total Pb in the bulk sediments (Thevenon et al., 2011). In addition, the maximum extraction efficiency with HNO₃ and subsequent ICP-MS analyses in domestic/industrial sewage sludge reaches Cr 88%, Cu 82%, Ni 71%, Pb 94%, Zn 89% (Gaber et al. 2011). Due to the partial digestion of the samples measured by ICP-MS and the semi-quantitative character of XRF data, the two methods are complementary. As the resolutions employed were different for each technique, the XRF data were averaged every five measurements to compare the results from both instruments.

2.8. Enrichment factor calculations

Enrichment factors (EFs) are commonly used to identify and quantify human interference in natural element cycles. It has been shown that normalizing data with the average crustal value can be erroneous (Reimann and De Caritat, 2000, 2005). A better approach is to use local non-contaminated sediments as a reference of pre-industrial conditions (Angelidis and Aloupi, 1995; Kersten and Smedes, 2002). In this study, EFs have been calculated and normalized using the average concentration of the bottommost 10 cm of the sediment core, which values are, in addition, very similar to those of the average crustal rock (Wedepohl, 1995). These sediments were clearly weakly affected by human contamination because concentrations were

comparable to the natural background reference values for Lake Geneva (Arbouille et al. 1988):

$$EF = \frac{M_{cm}/Al_{cm}}{M_{bottom}/Al_{bottom}} \quad (\text{eq. 1})$$

where M_{cm} is the metal concentration for each centimeter of the sediment core; Al_{cm} is the concentration of titanium at that cm; and M_{bottom} and Al_{bottom} are the average metal and aluminum concentrations, respectively, in the bottommost 10 cm of the core (94–103 cm).

All the anthropogenic trace elements were normalized to the conservative detrital element Al to confirm that the changes in concentrations of anthropogenic metals were not due to detrital input variations.

2.9. Statistics

The data were statistically described using SigmaPlot 11.0 software. The data were not normally distributed; therefore, correlation coefficients were calculated using the Spearman rank order method.

3. Results

3.1. Stratigraphic units

Stratigraphic units were defined according to visual variations in color, grain size, TOC, mineral carbon (MinC), HI and OI), water content, and C/N ratio (Fig. 2a). The sedimentary sequence was therefore divided into 5 main stratigraphic units, from the bottom to the top of the core:

256 Unit I (103–94 cm) was composed of homogeneous light-brown organic-rich silts
257 (TOC ~6% and of MinC ~3.20%). The OI values were the highest of the entire core
258 (~204 mg CO₂ g⁻¹ TOC), and the HI and C/N exhibited low values in this unit (~145
259 mg HC g⁻¹ TOC; C/N ~7–9).

260 Unit II (94–60 cm) was composed of plain dark brown silts (average TOC values
261 approximately 2.1% and MinC of ~3.23%). In this unit, the HI showed an increasing
262 trend at the top of the unit, while the OI decreased progressively. The C/N ratios were
263 overall similar to unit I, although with greater variability.

264 Unit III was the thickest unit (60–10 cm) and was composed predominantly of black
265 sandy silts punctuated by thin brown organic-rich layers. The TOC content reached
266 the highest values (~10%) in this unit, while the MinC values were the lowest (~2%)
267 for the entire core.

268 The OI values decreased dramatically on average from 177 in unit II to 99
269 OI mg CO₂ g⁻¹ TOC in unit III, with the lowest OI values at 56–53 cm. In contrast, the
270 HI values increased progressively from 203 in unit II to 426 mg HC g⁻¹ TOC in this
271 unit, with maximum HI values observed at 55–53 cm. The C/N ratio was higher than
272 those of units I and II (average value 9.5).

273 Unit IV (10–5 cm) was composed of dark brown silty sands. In this unit, the water
274 content (50%) and TOC values (2.7%) were similar to unit II, and the TOC value was
275 approximately half that measured in unit III. The MinC average values were similar to
276 those in unit III (2.70%). The C/N average values were the highest in this unit (~11).

277 Finally, unit V, the uppermost sediments (from 5 cm to surface) featured light brown
278 silts, with 73% silt, a water content of 50%, and 2.3% TOC (average values). The
279 MinC increased again at the surface (uppermost cm), reaching a value of 3.2%. The

HI and OI values continued to decrease and increase, respectively, without reaching the initial values recorded in unit I. The C/N ratio was low.

3.2. Age model

The chronology of the Vidy Bay sequence was based on ^{137}Cs and VMS dating. Two activity peaks were detected in the ^{137}Cs profile, reaching 121 and 231 Bq kg $^{-1}$ at 61 and 29 cm depth, respectively (Fig. 2b). These two peaks corresponded to the maximum ^{137}Cs deposition from radioactive fallout from nuclear weapon tests in the atmosphere (1963/64) and the Chernobyl accident (1986), respectively, allowing absolute dates to be assigned (Appleby, 2001). We also considered the first traces of ^{137}Cs deposition in 1954 for the age model. The first maximum gradient observed in VMS profile (Fig. 2b) is a reliable chronological marker because it corresponded to the implementation of the FeCl_3 treatment in the WWTP in 1971 (Loizeau et al. 2003). The detection of ^7Be (77 ± 17 Bq kg $^{-1}$) in the uppermost sample indicates that the water-sediment interface was preserved during coring operation and subsequent sampling. The age-depth model was based on the linear interpolation between these five tie points. Based on the sharp water content and grain size changes in unit IV (Fig. 2a), we assumed that the sediment deposited in centimeters 5 to 10 corresponded to resuspended or deposited particles from the transfer work of the WWTP outlet pipe, corresponding to the year 2001. Considering all this, the age model that we propose features four different SARs: in the 1954–1964 section, the SAR was 0.68 ± 0.13 g cm $^{-2}$ y $^{-1}$; in the 1964–1986 section, the SAR was 0.64 ± 0.04 g cm $^{-2}$ y $^{-1}$; in the 1986–2001 section, the SAR was 0.66 ± 0.08 g cm $^{-2}$ y $^{-1}$; and in the 2001–2010 section, the SAR was 0.33 ± 0.07 cm $^{-2}$ y $^{-1}$ (Fig. 2b). From extrapolation of the older SAR, the bottom of the sediment core is estimated to correspond to 1915.

Following the age model, unit I (103–94 cm) corresponded to years ~1915 to ~1930; unit II (94–60 cm) to years ~1930 to 1964; unit III (60–10 cm) to years 1964 to 2001; unit IV (10–5 cm) to 2001; and unit I (5–0 cm) to between 2001 and 2010. However, the dating corresponding to the bottom ~10 cm is doubtful due to the lack of time markers older than 1954. Moreover, the sharp transition in water content between unit I and unit II (Fig. 2a) may suggest a sediment hiatus between these two units. For the purpose of this study, this uncertainty is not an issue because this section clearly remains at background levels with respect to Lake Geneva sediment contamination, and no detailed discussion focuses on this time period in the sediment core.

3.3 Geochemistry of detrital elements

Depth profiles for all detrital elements Al, Si, Ca, Ti, K, Zr, Rb and Sr were measured using the XRF technique (Fig. 3), and some were also measured via ICP-MS. The element concentration signals measured by the two techniques showed similar patterns (Fig. S1 in supplementary material). A key application of XRF core scanning is the use of lithogenic element ratios as indicators, for instance, of the relative changes in particle grain size, authigenic carbonate production, detrital inputs or redox conditions. As the sediments of Vidy Bay are clearly affected by the activity of the WWTP, most of the ratios studied in the literature under natural conditions cannot be applied in this peculiar setting. Thus, based on Croudace and Rothwell (2015), four ratios are shown in Fig. 3 to better identify i) the particle grain size variations emphasized by Si/Al and Ti/K ratios, high Al/Si suggesting fine silts and clays (Van Daele et al. 2014) and a decrease in Ti/K implying a reduction in grain size (Marshall et al. 2011); ii) the in-lake carbonate precipitation by Ca/Ti ratio (Kylander et al. 2011); and iii) diatoms settling increase by Si/Ti ratio (Kylander et al. 2011). Si/Al and Ti/K

profiles did not show significant changes in units I and II. In unit III the ratios importantly increased until unit IV and V. In the latter, values tend to reach the initial values observed in the deepest units. In contrast, Si/Ti values decreased in unit III compared to unit II that registered the highest values. Ca/Ti profile did not show clear trends along the sediment core, only short-term variations can be observed. In addition, a correlation matrix of all the major elements measured by XRF is provided in supplementary material, Table S1.

3.4 Anthropogenic trace elements

The quantitative (ICP-MS) and the semi-quantitative (XRF) results are complementary and comparable (Supplementary material, Fig. S2). Similarly to detrital elements, the profiles of trace metals obtained by both techniques are analogous, providing a robust dataset. The concentration profiles of Pb, Cu, Zn, Cd, Ni, Cr, Co, Ag, Bi, Hg, Fe, P, and S are shown in Fig. 4, and the data are described in Table 1 by stratigraphic unit. Considering that the aim of this study was to highlight the direct impact of the WWTP in sediments, the non-normalized data closely reflected the contamination of heavy metals in the sediment. The trends in anthropogenic trace metal concentrations measured by either XRF or ICP-MS were similar. However, only the ICP-MS data are shown in Fig. 4 because this technique provided more trace metals. Some metals presented similar behavior along the sediment core. Following similarities found in the profiles of Fig. 4, and the high correlation values (supplementary material, Table S1), Pb, Cd, Cu and Zn are described together. They showed the lowest concentrations in unit I (ca. 1915–1930), followed by a progressive increase in unit II (Fig. 4 and table 1). The highest values occurred in 1964 and 1979. Since 1979, concentrations of these elements decreased gradually, reaching values similar to those observed before 1964 in unit IV (2001).

355 The Ni, Cr, and Co concentration profiles differed from the four previously described.
356 Although Ni, Cr, and Co also reached the highest values in unit III, their general
357 increase was more gradual. Recent values have decreased, reaching levels similar to
358 the oldest concentrations in ~1979. The Ag and Bi ($r = 0.89$, Table S1)
359 concentrations did not show any increasing trend until 62 cm (~1964), where they
360 increased dramatically (Fig. 4 and Table 1). High concentrations were observed over
361 a longer time interval in the Ag profile than in the Bi profile, although in both profiles
362 recent sediments also approached initial values. The Hg concentration in the
363 sediment core did not closely follow the same trend as the other trace metals. In unit
364 I, Hg concentrations were 10 times lower than the current concentration (top of the
365 sediment core) (Table 1). Up to 63 cm, the concentration gradually increased,
366 following a trend similar to those of Pb, Cd, Cu, and Zn. Before 1964, the sediments
367 were already contaminated, with 2.6 mg kg^{-1} of Hg, rising to 4.6 mg kg^{-1} in 1964.
368 Then, these concentrations remained quite stable with small-scale fluctuations up to
369 33 cm. The highest Hg value was observed at 32 cm (1986), whereas the other
370 metals did not peak at this depth (Fig. 4). Since the 1990s, the concentration of Hg
371 has gradually decreased. Fe concentrations in the sediments of Vidy Bay recorded
372 different events than the other metals. No increase in Fe was observed from the
373 bottom of the core, ca. 1915, up to 53 cm. Between 53 and 55 cm (1971), Fe
374 concentration suddenly increased, reaching its highest values (Fig. 4). Finally, S
375 exhibited a slight increase from 60 cm up to the top of unit IV.

376 The calculated EF for each anthropogenic trace metal (Pb, Cu, Zn Cd, Ni, Cr, Co, Ag,
377 Bi, Hg and Fe) is presented in Fig. 5. Unit V (uppermost sediments) was the least
378 enriched metal interval, corresponding to the “reference” value (unit I). Although Unit I
379 could be slightly affected by anthropogenic activities, trace metal concentrations are

low and comparable to reference values of Lake Geneva (Arbouille et al. 1988) and to crustal rocks (Wedepohl, 1995). Therefore they are used as reference value to calculate the EFs. In unit II, the EFs were slightly higher for all metals, excluding Ag and Bi. Unit III was the most enriched interval for all metals, which is consistent with the results of the metal concentrations (Table 1 Fig. 5). This unit presents extremely high EFs values for all toxic trace metals, i.e. Hg 240; Cd 100; Pb 93; Cu 74 and Zn 43. Bi and Ag also presented elevated EFs (680 and 190 respectively). Compared to the other metals, Cr and Co EFs increased most slightly later at 52–53 cm, and Fe EF sharply increases in 1971. Unit IV exhibited lower metal EFs than in unit III. Generally, the mean EFs values metals between units I, II and V did not vary considerably (Fig. 5).

Discussion

4.1. Physico-chemical parameters

Grain size profiles showed finer sediments in units I and II (Fig. 2a) corresponding to the uncontaminated sediments. From 1930 to 1934 (the base of unit II), the grain size was finer than all of unit I. In addition, the water and TOC contents decreased abruptly during these years, which coincided with the boundary between units I and II. The sudden decrease in these physico-chemical parameters therefore suggested a possible hiatus (at 90–94 cm), likely due to erosion due to underflows and mass movement processes that occur in the lake slopes (Corella et al. 2014, 2016; Lambert and Giovanoli, 1988) and are frequently recorded in the distal basin (Kremer et al. 2015a).

The WWTP contributed to the increase in sand-sized particles in Vidy Bay, with maximum sand values reported between 1964 and 2001 (units III and IV). However,

in the measurements made using the Coulter LS100, it is not possible to distinguish between organic and inorganic coarse particles because both are classed as sand sized (Loizeau et al. 1994). Thus, it is likely that in unit III, the particles classified as sand sized, were a mixture of inorganic sandy particles as suggested by the Si/Al and Ti/K ratios (Fig. 3, section 3.3 and 4.4) and organic matter (Fig. 2a). However, coarse grains were observed in unit IV. The TOC and grain size relationship was not present between 2001 and 2010 (unit IV). Therefore, we assume that the sandy silts deposited in unit IV were related to the WWTP outlet pipe relocation work.

4.2. Total organic carbon and mineral carbon

Maximum MinC concentrations characterized the base of the sediment core (unit I), reflecting endogenic calcite precipitation and detrital carbonates from the catchment. The effluent of the WWTP was rich in TOC and this was reflected in the sediments from 1964 on. From this year, TOC gained importance over MinC in the bay, corresponding to the increase of trace metal concentration in these sediments. The high levels of TOC in the sediments of Vidy Bay in unit III, while creating favorable geochemical conditions to sequester trace metals, are not the driving factor of the metal content increase since both TOC and metals are released by the WWTP effluent. The TOC amounts measured in recent sediments (units IV and V) were slightly above the initial values found in units I and II (higher MinC and lower TOC than unit III) as a result of the relocation of the WWTP outlet pipe.

4.3. Hydrogen Index, Oxygen Index and C/N ratio

Units I and II were characterized by high OI values and low HI values, indicating that sediments were dominated by allochthonous terrestrial organic matter (Ariztegui et al. 2001; Espitalié et al. 1985a, 1985b; Jaccard et al. 2009; Montero-Serrano et al. 2015;

428 Steinmann et al. 2003). Such inverse HI and OI trends were also observed in the
429 most recent sediments (units IV and V). However, in Vidy Bay and since 1964 (base
430 of unit III), the inverse HI and OI tendencies have behaved similar to autochthonous
431 (algal) material (Fig. 6). Nevertheless, it is not likely that this signal results from a
432 sudden and massive increase in productivity due to the nutrient load but rather to the
433 settling of organic-rich particles released by the WWTP. To our knowledge there are
434 no studies in the literature investigating the HI and OI behavior of lacustrine
435 sediments affected by treated and untreated waste water sewage. Only in the
436 Mediterranean Sea a similar HI and OI behavior in sludge deposit sediments has
437 been observed as a product of sewage discharges (Kruge et al. 2010). For the first
438 time, the combination of TOC, MinC, C/N, HI and OI results obtained in the present
439 work permitted to characterize the “algal-type” signal obtained in unit III (Fig. 6) as
440 anthropogenic, organic-rich particles instead of algal or autochthonous sediments.
441 Moreover, the Si/Ti ratio supports that, although the HI/OI ratio seems algal, these
442 sediments did not record a diatom-rich algal bloom in this period (see section 4.4).
443 The topmost part of Unit V (Fig. 2a) showed the recovery of the sediment through
444 increasing values of HI and decreasing values of OI toward values similar to those of
445 natural, freshly deposited, sediments. However, the HI/OI values measured in this
446 unit (Fig. 6) fall in-between the algal and terrestrial end members, suggesting higher
447 productivity in the recent sediments than those deposited before 1964. The C/N ratio
448 in unit III featured somewhat higher values than in units I, II and V (Fig. 2a), which
449 would indicate increased terrestrial organic matter input, thus contradicting *a priori*
450 the HI and OI results. However, as explained by Tyson (1995), the slightly more
451 terrestrial appearance of the organic matter in unit III, as suggested by the C/N ratio,
452 is due to the particular location of these sediments, i.e., close to the WWTP outlet

pipe. Therefore, they are affected by degraded organic matter released by the sewage effluent.

4.4. Detrital inputs in sediments

The WWTP gathered up the urban runoff containing different substances and released them after treatment into the lake, likely changing the natural processes delivering sediment into the lake. Thus only a limited number of detrital ratios as proxies of natural changes in the sediment geochemistry can be used. In this context, Fe increases are related to use of FeCl_3 in the wastewater treatment and thus, ratios such as Fe/Ti, Zr/Fe, and Fe/Mn cannot be used as indicators of grain size, reducing conditions, or flood layers.

The increase of Si/Al ratio in unit III can be related to an increase of coarse particles brought by the WWTP effluent (Van Daele et al. 2014), excluding (broken) diatoms since the ratio Si/Ti decrease dismissing algal productivity blooms (Kylander et al. 2011). Similarly to Si/Al ratio, Ti/K ratio increased in unit III, indicating also increases in grain size (Marshall et al. 2011) (Fig. 2a). A proxy of the importance of the in-lake CaCO_3 precipitation is the Ca/Ti ratio (Kylander et al. 2011). The relatively stable profile of Ca/Ti ratio suggested that the authigenic carbonate precipitation was not affected by the WWTP effluent (Fig. 3). Some elements presented abrupt peaks between 10 and 20 cm, presumably due to alterations on the surface of the split sediment core used for XRF analyses, differences on physical properties such as density and water content could interfered with the signal (Tjallingii et al. 2007).

4.5. Historical reconstruction of pollutants in Vidy Bay in the 20th century

The probable effect concentration (PEC) is a consensus-based sediment quality guideline (SQG) that provides a reliable basis for assessing sediment quality

477 conditions in freshwater ecosystems (MacDonald et al. 2000). These values provide
478 a basis for predicting sediment toxicity. Prior to ca. 1930 (unit I), the sediments have
479 the lowest concentrations of all the anthropogenic trace metals, which were always
480 below the PEC values (Fig. 4). After this period, the sediments featured a slow
481 increase in some trace metal concentrations (Pb, Cu, Zn, Cd, and Hg), coinciding
482 with intensified industrial activities. Following World War I, coal combustion and
483 heavy metal ore smelting released particulate contamination into the atmosphere,
484 and this contamination was subsequently deposited in freshwater bodies. Cu and Zn
485 ($r = 0.91$, Table S1) experienced a significant increase in concentration starting in ca.
486 1930 and 1946 respectively and exceeded the PEC values in Vidy Bay (Fig. 4). The
487 anthropogenic increase of Cu in the sediments near the city of Lausanne has been
488 related to the roofs and catenaries of trains and trolleybuses, and car brakes. This Cu
489 enters the urban water through stormwater (880 kg y^{-1}), reaching the lake through
490 combined sewage overflows and WWTP effluent. The water column of Vidy Bay is
491 estimated to receive 1500 kg y^{-1} of Cu, and around 910 kg settled every year in the
492 sediments (Chevre et al. 2011). Fig. 3 shows an increase of Cu from the 1930's
493 corresponding to the evolution of the public transport of the city. The first trolleybus
494 line in Lausanne started in 1932 and this type of transport increased progressively
495 during the following decades.

496 The Pb, Cu, Zn, Cd and Hg concentrations increased significantly in 1964 due to the
497 implementation of the WWTP in Vidy Bay (Fig. 4, Table 1). Most of the trace metal
498 concentrations studied in the present work (for which a PEC value exists) exceeded
499 the PEC threshold in unit III (Fig. 4). The most flagrant exceedances involved Pb, Hg,
500 Zn, Cu and Cd that presented respectively about 30, 10, 20, 10, and 5 times higher
501 the established PEC threshold, and this is of major concern in case of remobilization

of sediments, works or mass movements in the affected area. Although, Co concentrations did not appear to be much affected by the WWTP (Fig. 3), the EF calculated for this metal (Fig. 4) showed a clear contamination a few years after 1964.

The maximum values in this contaminated unit were (in mg kg⁻¹ dry weight) as follows: Pb 4000, Cd 23, Cu 1200, Zn 8600, Hg 11, Ni 140, and Cr 270. To our knowledge, Vidy Bay is the only reported lacustrine site where such a contamination history related to WWTP sewage discharge is recorded in the sediment. To compare and discuss our results, we have chosen other water bodies polluted with trace toxic metals from sources other than municipal wastewater treatment plants. The Malter Reservoir, located close to a mining and industrial area in Germany, contains lower concentrations (in mg kg⁻¹) of Pb (740), Cu (240), and Zn (1900) (Muller et al. 2000) than Vidy Bay. The mean EFs in sediments of Vidy Bay during the most contaminated period (Fig. 4) were close to those of Malter Reservoir for Co and Pb. In contrast, Cu was 3 to 4 times greater in Vidy than in this mining area, and Cd was lower than in Malter Reservoir (Muller et al. 2000). Compared to sediments that received urban effluents in Rhodes Harbour, Greece (Angelidis and Aloupi, 1995), the mean EFs of Cd, Cr, Cu, Fe, Pb and Zn in the sediments of Vidy Bay deposited during the period when the WWTP effluent was directly influencing the sediments (unit III) (Fig. 5), were much higher than those found by Angelidis and Aloupi (1995). The maximum EF values (Fig. 5) were extremely high compared to other study areas, such as Koumoundourou Lake, Greece (Karageorgis et al. 2009). After reaching the maximum concentrations and EF values, the release of heavy metals and other compounds has progressively decreased from 35–37 cm (1982–1983) to the present. The general reduction of global atmospheric, industrial and domestic

emissions of trace metals during the last decades is reflected by a drop in all the heavy metals shown in Fig. 4. In 2010, after the return to 1964 conditions resulting from the relocation of the WWTP outlet pipe in 2001, the Vidy Bay surface sediments exhibit lower amounts of metals than in the underlying unit III (e.g., Pb 160 mg kg⁻¹, Cu 76 mg kg⁻¹, Zn 230 mg kg⁻¹ and Cd, 0.94 mg kg⁻¹). However, the concentrations in unit V were still higher than the reference values of the lake (Pb 30, Cu 30, Zn 60 and Cd 0.2 mg kg⁻¹; Arbouille et al. (1988)).

The Ag and Bi concentration and EF profiles (Figs. 4 and 5) were directly related to the WWTP effluent. The Ag contamination in the Vidy Bay is related to waste produced by the Kodak S.A. photograph industry, established in Lausanne and connected to the WWTP in 1963. Although the EF in this period (Fig. 4) is similar to the Ag EF reported in Malter Reservoir sediments (Muller et al. 2000), the maximum Ag concentration measured in Vidy Bay reached 130 mg kg⁻¹, almost 5 times higher than in Malter Reservoir (Muller et al. 2000). The expansion of the Kodak factory in 1986 matched with a second peak in Ag concentrations (104 mg kg⁻¹) located at 28–29 cm depth. The provenance of the Bi trace metal remains unclear. Ferrari et al. (2000) and Karlsson et al. (2007) carried out studies on natural and anthropogenic atmospheric sources of Bi. However, only a few studies have focused on Bi from sewage sludge in lakes. Bismuth Active Substances have been found in different sewage of municipal WWTPs (Amneklev et al. 2015b; Fuerhacker et al. 2001; Wagner, 1978; Zoller, 1993). Bi is generally present in household products, such as cosmetics and plastics, as well as in industries and, to a lesser extent, in hospitals (Amneklev et al. 2015a; 2015b; Fuerhacker et al. 2001). In this study, twelve municipalities with several industries related to the pharmaceutical industry, human health activities and chemical product manufacturing are connected to the Vidy

WWTP. Thus, the high levels of Bi found in the Vidy Bay sediments coinciding with the implementation of the WWTP and the absence of this metal during the previous decades (Fig. 3) could be explained by the use of this element by the industries and domestic wastes of the Swiss municipalities linked to the WWTP. Indeed, Bi concentrations reached an extremely high value of 310 mg kg^{-1} compared to the 37 mg kg^{-1} present in the Malter Reservoir (Muller et al. 2000). Additionally, the Bi EF reached 770 in Vidy Bay, whereas the maximum value was approximately 100 in Malter Reservoir.

The decrease in trace metal concentrations from the late 1970s was likely due to the improvements in the efficiency of the WWTP, such as the introduction of a physico-chemical treatment that significantly increased the water treatment capacity (details in section 1.2. in this paper)

The effect of mercury emissions started to be evident in sediments dated to the 1920s (Fig. 3). Later on, since 1964, an important increase in Hg occurred in Vidy Bay. Local chemical and pharmaceutical industries developed products containing Hg (antifungal pesticides, antibacterial mercurochrome® and vaccines) (Ball et al. 2001; Deflora et al. 1994; Mukherjee et al. 2004). These products were the main Hg sources to the WWTP, and Hg was subsequently released into the bay. However, contrary to the other heavy metals in this study, the maximum Hg concentration of 11.4 mg kg^{-1} was observed at 32 cm, corresponding to the year 1984. This value is the highest concentration of Hg ever found in Lake Geneva and is 300 times higher than the lake sediment background level (Arbouille et al. 1988). This Hg maximum did not correspond to any other measured heavy metal maximum (Fig. 3), implying that the WWTP outflow did not increase at that time. The lack of correlation with other metals suggests that there was some increase in the use or mercury wastes in some

industries (or hospitals) in the catchment area during these years. This is of major concern because slope instabilities have already been recorded in the sediments of Lake Geneva (Corella et al. 2014, 2016; Kremer et al. 2014, 2015b). In case of mass movements, the contaminated sediments could be resuspended, causing ecotoxicological damage to the lake ecosystem.

Fe and P concentrations reflected the water treatment history. The dephosphatation process was introduced in 1971 in the WWTP and involved adding FeCl_3 to precipitate phosphorous in the sludge and subsequently eliminating it from the sewage water. A clear increase in P and Fe values occurred in 1971, surely related to the beginning of the dephosphatation process (Fig. 4). This confirms that the addition of FeCl_3 since 1971 in the WWTP processes led to enrichments in P in the sewage sludge, which was subsequently released into the lake (see the concentrations in Table 1). An important decrease in both Fe and P was observed during the late 1970s, which was likely due to the use of new treatments and more efficient techniques in the WWTP. Fe and P are thus considered anthropogenic elements. The Fe geochemistry in Vidy Bay is mainly influenced by dissimilatory microbial iron oxide reducers that transform Fe(III) into Fe(II) (Percak-Dennett et al. 2013). The subsequent Fe(II) -rich sediments in presence of P involved precipitation of mineral phases, such as vivianite, or sorption of phosphates to ferrous hydroxides. The Fe(II) -P phases represented a significant portion of the reactive Fe in the Vidy Bay sediments. The PCA suggests that Bi, Cu, Zn, Co, Ni, Cr, Pb and Cd covaried in a very similar manner and exhibited a different behavior than Fe, Ag, Hg and P.

Finally, S is primarily bound to organic matter. Accordingly, S showed a slight increase from 1964 on; therefore, it is considered to be linked to anthropogenic inputs. Moreover, under anoxic conditions, S can form sulfidic compounds that act as

fixative agents for chalcophile elements, such as Zn, Cd, Cu, Cr, Hg, Ag, Bi, and Fe (Goldschmidt, 1937).

4. Conclusions

Our multiproxy study of the sedimentary archives in Vidy Bay provides an opportunity to investigate the evolution of sediment contamination from pre-industrial times to the present, the environmental response to strong anthropogenic contamination and the timing and tempo of the recovery following the perturbation. The trace metal record (Pb, Cd, Cu, Zn and Hg) highlights the regional impact of industrial pollution starting in ca. 1930 and the high metal contamination starting in 1964 in the sediments surrounding the outlet pipe discharge. The parallel changes observed in grain size, TOC, MinC, HI and OI are in agreement with the trace metal results regarding the origin of the contamination. The WWTP discharges modified the natural ratios of detrital elements, and the OM characteristics of the sediments, producing algal-like characteristics (e.g., higher HI values). The particular conditions created by sewage water release entirely modified the environmental conditions of the affected area and therefore the geochemistry of sediments, making this sedimentological environment of special interest and incomparable to pristine lakes or lakes contaminated by different types of sources. The long-term geochemical evolution of both the clastic elements and trace metal pollution recorded in Vidy Bay exemplifies the need for paleolimnological studies to further understand the environmental consequences of human activities in lacustrine systems. This study helps to define target limnological conditions and management strategies in aquatic ecosystems and shows the need for high-resolution records and multiproxy studies to make correct assessments of pollution in lake systems.

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863 Tables

864 Table 1. Mean metal concentrations $\pm$ standard error and the concentration ranges
865 per stratigraphic unit.

866

867 Figure captions

868 Fig. 1. Location of Vidy Bay shown on a bathymetric map of the study area in Lake
869 Geneva. EGD3 represents the site where the studied sediment core was retrieved.

870 Fig. 2. A) From left to right: EGD3 core image; sedimentary units; grain size and
871 water content (white line); TOC: total organic carbon and MinC: mineral carbon; OI:
872 Oxygen index and HI: Hydrogen index; and C/N ratio. B) The age-depth model based
873 on ^{137}Cs radiometric dating and Volume Magnetic Susceptibility (VMS).

874 Fig. 3. Si/Al, Ti/K, Si/Ti and Ca/T ratios measured with X-ray fluorescence (XRF).
875 Horizontal short gray dashes represent the limits between lithological units I to V from
876 bottom to top

877 Fig. 4. Trace metals in mg kg^{-1} (analyzed by ICP-MS); Hg in mg kg^{-1} (analyzed by CV-
878 AAS); and S and P in cps (analyzed by XRF). Horizontal short gray dashes represent
879 the limits between stratigraphic units I to V from bottom to top. Vertical dotted gray lines
880 represent the probable effect concentration (PEC) for each element (MacDonald et al.
881 2000).

882 Fig. 5. Enrichment factor (EF) profiles of the anthropogenic elements. Horizontal short gray
883 dashes represent the limits between stratigraphic units I to V from bottom to top.

884 Fig. 6. Hydrogen index (HI) versus oxygen index (OI) for all samples of EGD3. Double-
885 headed arrows indicate the organic matter trends as discussed in the text.

886

887 Supplementary material

888 Table S1. Spearman correlation matrix of detrital elements measured by XRF and
889 trace metals measured by ICP-MS.

890 Fig. S1. Detrital element profile concentrations measured by XRF and ICP-MS.

891 Fig. S2. Trace metal profile concentrations measured by XRF and ICP-MS

892

Table 1

Statigraphic Units		Pb (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Cd (mg kg ⁻¹)	Ni (mg kg ⁻¹)	Cr (mg kg ⁻¹)	Co (mg kg ⁻¹)	Ag (mg kg ⁻¹)	Bi (mg kg ⁻¹)	Hg (mg kg ⁻¹)	Fe (mg kg ⁻¹)
V	mean	140 ± 18	63 ± 4	200 ± 12	0.75 ± 0.08	55 ± 3	24.5 ± 0.9	11.4 ± 0.4	2.3 ± 0.5	1.6 ± 0.1	0.21 ± 0.04	24903 ± 806
	range	118 - 160	53 - 76	175 - 234	0.50 - 0.94	49 - 66	21.9 - 26.4	10.1 - 12.6	1.2 - 3.5	1.2 - 2.1	0.12 - 0.32	22431 - 27367
IV	mean	235 ± 6	95 ± 5	679 ± 197	1.42 ± 0.09	50 ± 4	23 ± 1	9.2 ± 0.1	8.1 ± 0.6	2.8 ± 0.2	0.84 ± 0.09	22916 ± 304
	range	222- 253	83 - 110	279 - 1348	1.17 - 1.75	45 - 65	18 - 25	8.9 - 9.7	5.7 - 9.0	2.4- 3.8	0.66 - 1.12	21904 - 23662
III	mean	1913 ± 155	469 ± 40	2579 ± 246	11.6 ± 0.9	83 ± 4	104 ± 8	11.7 ± 0.4	76 ± 4	99 ± 14	4.2 ± 0.3	38231 ± 1753
	range	236 - 3977	99 - 1166	543 - 8586	1.3 - 23.2	45 - 226	24 - 265	8.5 - 19.5	8 - 126	2 - 309	1.2 - 11.4	20374 - 61856
II	mean	351 ± 49	212	1588 ± 201	2.2 ± 0.3	71 ± 2	56 ± 4	12.7 ± 0.1	4 ± 1	13 ± 4	0.65 ± 0.08	24570 ± 251
	range	1702 - 1621	21 - 459	247 - 3972	0.4 - 8.9	51 - 93	28 - 114	10.2 - 14.1	0.3 - 33	0.7 - 134	0.09 - 2.66	20811 - 27153
I	mean	73 ± 4	22.7 ± 0.4	304 ± 10	0.45 ± 0.08	56.0 ± 0.6	28 ± 1	11.4 ± 0.2	1.2 ± 0.5	0.75 ± 0.04	0.059 ± 0.005	22600 ± 328
	range	63 - 97	21 - 24	242- 347	0.32 - 1.07	53 - 58	23 - 33	10.8 - 12.1	0.2 - 4.6	0.63 - 0.98	0.040 - 0.087	20992 - 22556

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6