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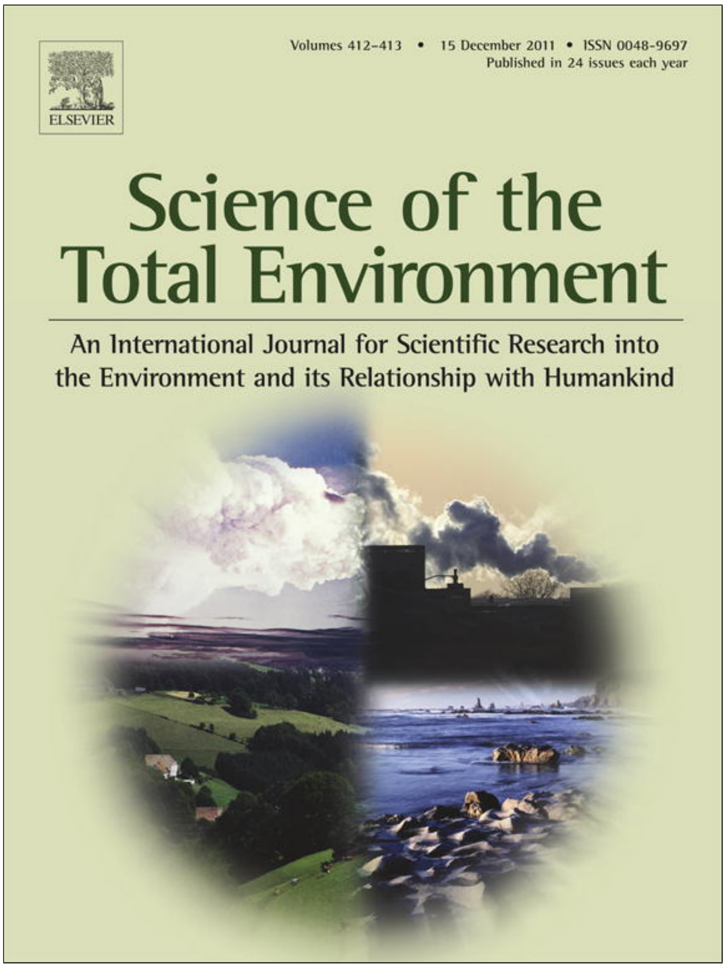
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Local to regional scale industrial heavy metal pollution recorded in sediments of large freshwater lakes in central Europe (lakes Geneva and Lucerne) over the last centuries

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ABSTRACT

This research first focuses on the spatial and temporal patterns of heavy metals from contrasting environments (highly polluted to deepwater sites) of Lake Geneva. The mercury (Hg) and lead (Pb) records from two deepwater sites show that the heavy metal variations before the industrial period are primarily linked to natural weathering input of trace elements. By opposition, the discharge of industrial treated wastewaters into Vidy Bay of Lake Geneva during the second part of the 20th century, involved the sedimentation of highly metal-contaminated sediments in the area surrounding the WWTP outlet pipe discharge. Eventually, a new Pb isotope record of sediments from Lake Lucerne identifies the long-term increasing anthropogenic lead pollution after ca. 1500, probably due to the development of metallurgical activities during the High Middle Ages. These data furthermore allows to compare the recent anthropogenic sources of water pollution from three of the largest freshwater lakes of Western Europe (lakes Geneva, Lucerne, and Constance). High increases in Pb and Hg highlight the regional impact of industrial pollution after ca. 1750–1850, and the decrease of metal pollution in the 1980s due to the effects of remediation strategies such as the implementation of wastewater treatment plants (WWTPs). However, at all the studied sites, the recent metal concentrations remain higher than pre-industrial levels. Moreover, the local scale pollution data reveal two highly contaminated sites (>100 μg Pb/g dry weight sediment) by industrial activities, during the late-19th and early-20th centuries (Lake Lucerne) and during the second part of the 20th century (Vidy Bay of Lake Geneva). Overall, the regional scale pollution history inferred from the three large and deep perialpine lakes points out at the pollution of water systems by heavy metals during the last two centuries due to the discharge of industrial effluents.

1. Introduction

Anthropogenic toxic heavy metals that accumulate in the environment and in the food chain, are threatening the world's freshwater resources used for drinking and recreational purposes (Vörösmarty et al., 2010). Lake sediments offer a unique opportunity for reconstructing the heavy metal pollution history of our environment, and for evaluating the impacts of remediation for natural water quality protection. Indeed, the enrichment of heavy metals in depositional areas such as lacustrine sediments can provide a long-term history of changes in natural and anthropogenic trace element input, and the possibility to evaluate the recent metal contamination in comparison to the natural level (background; Eades et al., 2002). Freshwater lakes not only receive atmospheric (anthropogenic) pollutant emissions, but also the natural (lithogenic) heavy metals discharged by rivers. In Europe, anthropogenic atmospheric heavy metal source has dominated over the geogenic source since industrialization (Schotyk et al., 1998; De Vleeschouwer et al., 2007), but major issues remain about the sources of pollutant metals into aquatic environment. Moreover, some sediment deposits highly contaminated by past human activities (e.g., municipal and industrial waste sediment from wastewater treatment plants (WWTPs)) can present a potential health risk to a population through the possible remobilization of pathogens and inorganic pollutants at the sediment-water interface under the influence of chemical (e.g., changing redox conditions; Pearson et al., 2010) or physical (e.g., mass movement event or dam flushing; Girardclos et al., 2007; Wildi et al., 2004) processes.

More than the two thirds of the Swiss population live in urban areas, which are mainly located on the Swiss Plateau, extending from Lake Geneva in the southwest to Lake Constance in the northeast (altitude ranging from about 350 to 550 m a.s.l.) (Fig. 1). Many foreland lakes were formed after the retreat of the ice margin from the Alpine foreland following the Last Glacial Maximum (after ca. 17.5 ka; Ivy-Ochs et al., 2004). Today, Switzerland is the source of many major Europeans rivers, such as the Rhône and the Rhine. In this study, we first investigate the pollutant deposition history from deepwater sites of Lake Geneva (which is fed by the Rhône River; Fig. 1). We then consider the contaminated sediments of Vidy Bay

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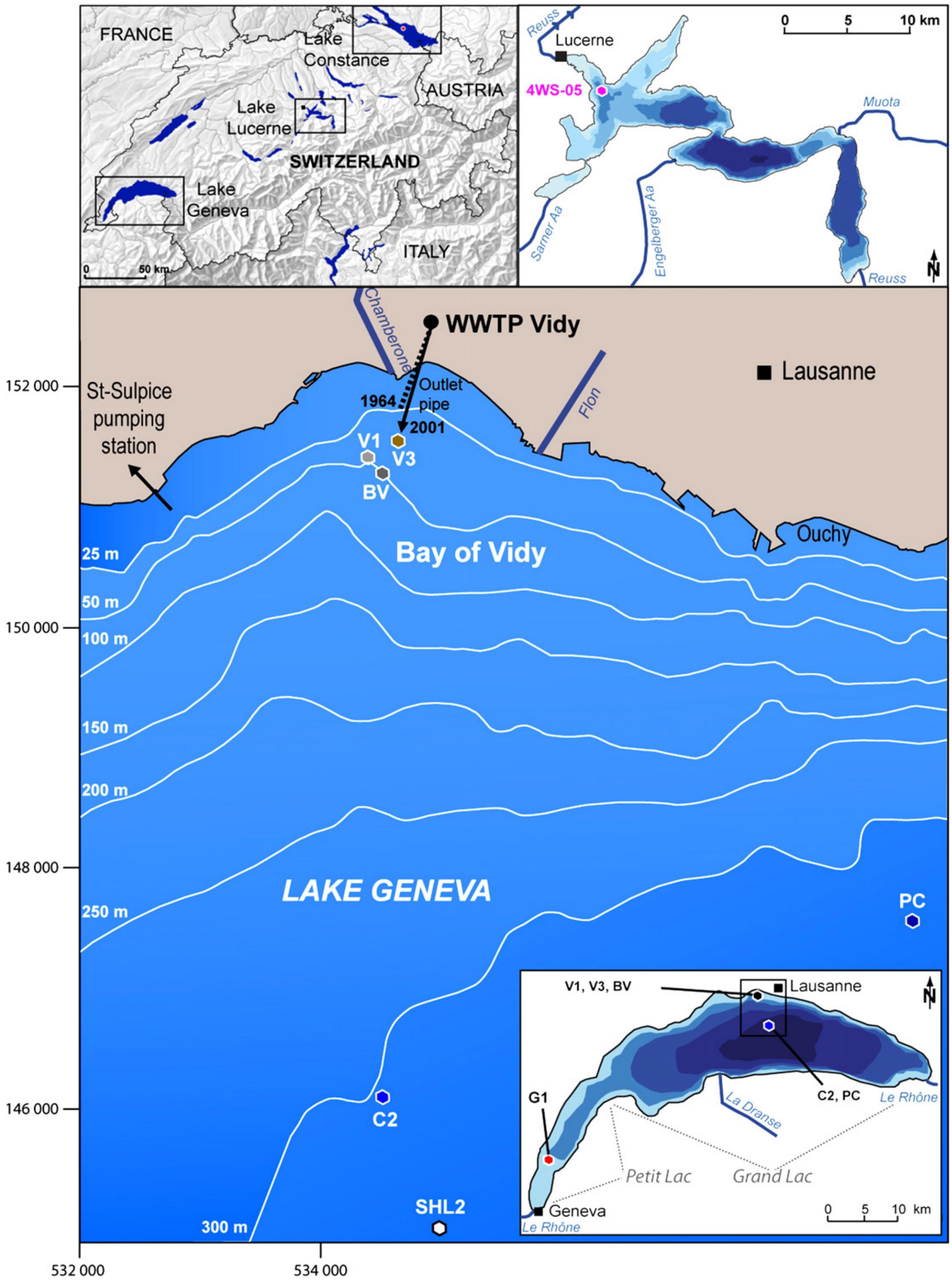

Fig. 1. (Top left) Map of Switzerland with the largest Swiss lakes indicated, and the location of the three Swiss lakes mentioned in the text. (Upper right) Bathymetric map of Lake Lucerne showing the location of the city of Lucerne situated on the outflow River Reuss and core 4WS-05 (bathymetric contour interval is 40 m). (Bottom right) Bathymetric map (bathymetric contour interval is 50 m) of Lake Geneva showing the location of the city of Geneva situated on the outflow River Rhône and the studied areas. (Centre) Bathymetric map of Vidy Bay close to the wastewater treatment plant (WWTP) of the city of Lausanne; also showing the location of the cores from the deepest part of Lake Geneva (C2, 304 m) and from Vidy Bay (V1 and V3).

of Lake Geneva (Fig. 1), where the treated wastewaters from the Vidy treatment plant (WWTP) have been discharged since 1964. This site was previously investigated to evaluate the impact of the discharge of municipal and industrial waste sediments from the WWTP. High concentrations of heavy metals (Monna et al., 1999; Loizeau et al., 2004), high microbial activities (Poté et al., 2008; Thevenon et al., 2011a), and the spreading of pharmaceutical and hormonal micropollutants (Perazzolo et al., 2010) occurred in the sediment.

Here, we present new lead (Pb) records from Vidy Bay and from the deepest parts of the Grand Lac (Large Lake; ~300 m) and the Petit Lac (Small Lake; ~50 m) (Fig. 1), in order to evaluate i) pre-industrial variations in concentrations of heavy metals in Lake

Geneva, and ii) recent anthropogenic heavy metal emissions in sites with different natural inputs (based on normalization to a conservative, lithogenic element).

We provide a broader understanding of the sources of heavy metals and evaluate the recent contamination of European lakes, a major issue for large freshwater lakes such as Geneva and Constance (Monna et al., 1999; Bollhöfer et al., 1994; Kober et al., 1999). We compare the Lake Geneva Pb record to that of Lake Lucerne, which was highly impacted by different fossil fuel combustion products during the late-19th and early-20th centuries (Thevenon and Anselmetti, 2007). A new stable Pb isotope record from this site is compared to published records from lakes Geneva and Constance, in order to discriminate the anthropogenic sources of heavy metal pollution and to assess the recent contamination of these major European drinking water resources.

2. Materials and methods

2.1. Study sites and samples

2.1.1. Lake Geneva cores (V1, V3, G1, and C2)

Lake Geneva (Lac Léman) is the largest lake of Switzerland and one of the largest European lakes, with a surface area of 581 km^2, a volume of 89 km^3, and a maximum depth of 309 m. The lake is located on the south-western part of the Swiss Plateau at an elevation of 372 m a.s.l. The Rhône and the Dranse rivers are the major tributaries to the lake (Fig. 1). Lake Geneva is a monomictic lake, with intense vertical mixing rarely affecting the entire water column (complete turnover favored by cold weather; Livingstone 1997). It is now a mesotrophic lake, but was originally oligotrophic before World War II, while a period of sub-anoxic conditions (eutrophication) occurred between ca. 1960 and 1980.

Approximately 700,000 people are supplied with water from Lake Geneva, which is the largest freshwater reservoir in Western Europe. The pumping station of St.-Sulpice that provides about 60% of drinking water to the city of Lausanne (the largest city on the lakeshore) is located at less than 4 km from Vidy Bay (Fig. 1). Vidy Bay is the most contaminated area of Lake Geneva due to the release of treated domestic and industrial wastewaters into the bay (Pardos et al., 2004; Poté et al., 2008). Lausanne generates large volumes of domestic and industrial wastewaters which are released into Vidy Bay i) through the outlet pipe of the WWTP built in 1964, ii) via the Flon River which collects surface and wastewater from the western part of the city, and iii) from the Chamberone River which collects surface runoff waters from its natural drainage basin and urban runoff waters from the city of Lausanne (Fig. 1). The WWTP, initially set up with mechanical and biological treatments for 216,000 equivalent inhabitants, was expanded in 1976, but its effluents were still being discharged 300 m from the lakeshore at depth of 15 m. The outlet pipe was eventually extended to 700 m from shore, at 35 m depth, in 2001.

In 2009 and 2010, two sediment cores were retrieved from the Bay of Vidy: a 32 cm-long core V1 (Swiss coordinates: 534.426/151.512), and a 36 cm-long core V3 (534.682/151.538), which is the coring location closest to the WWTP outlet pipe discharge (Fig. 1). Two additional cores were collected in the deepest parts of Grand and Petit lakes: i) a 60 cm-long core G1, at 51 m water-depth in the center of the Petit Lac (502.613/122.938), and ii) a 130 cm-long core C2, at 304 m water-depth in the center of the Grand Lac (534.504/146.178).

2.1.2. Lake Lucerne core (4WS05)

Lake Lucerne (Vierwaldstättersee) has a surface area of 116 km^2 and is located at an elevation of 434 m a.s.l., at the northern Alpine front in Central Switzerland (Fig. 1). Its maximum depth is 214 m, and the lake encompasses four steep-sided basins separated by moraine ridges, and has four inlet alpine rivers (Reuss, Muota, Engelberger Aa and Sarner Aa; Fig. 1). Lake Lucerne is monomictic, with one complete overturn every six years generally preceded by a significant rise of the hypolimnic temperature. The lake underwent a period of moderate eutrophication from 1960 to 1979 (Bührer and Ambühl, 2001).

In 2005, a 163 cm-long core (4WS05, Fig. 1) was collected in the middle of the Chrüztricher Basin (669.397/209.079) at 110 m water depth. This core has been previously analyzed for combustion residues (Thevenon and Anselmetti, 2007) and trace element concentration (Thevenon et al., 2011b).

2.2. Sediment dating and trace elements analysis

2.2.1. Cesium (^{137}Cs)

Specific ^{137}Cs activities of the recent sediments were determined by gamma spectroscopy using HPGe well detectors (Ortec, GWL series, USA). Efficiency of the detector was obtained by measurement in the same geometry of the soil reference material (IAEA-375). Detection limit is better than 1 Bq/kg.

2.2.2. Advanced mercury analysis (AMA)

Total mercury (Hg) was determined by cold vapor atomic absorption spectrometry after thermal decomposition of the sample using an automatic solid analyzer (Altec®, model AMA-254). The detailed procedure is described in Cossa et al. (2002). The detection limit (3 SD blank) was 0.005 mg/g and the reproducibility better than 5%. The method is known as standard method N 7473 of the US-EPA. The accuracy of the determination for Hg concentrations was estimated using BEST-1 (National research Council Canada); the repeated analyses never exceeded the published concentration range (0.092 ± 0.009 mg/g).

2.2.3. Sediment digestion

Around 5–7 mg of sediment powder was completely digested using pure acids in Teflon bombs and heated using a glass ceramic hotplate, in a four-step procedure: 2 ml HNO_3 (suprapur, 65%), a mixture of 1 ml of $HClO_4$ (suprapur, 70%) with 1 ml HF (suprapur, 40%), and two treatments with 1 ml of HNO_3 (suprapur, 65%). The samples were evaporated between each step of the procedure, and finally diluted to 10 ml with 1% HNO_3 solution for chemical analysis. For the samples from the Vidy Bay, the trace element analysis on the leached fraction (HNO_3 extraction) follows the digestion of additional sediment sample in Teflon bombs heated in analytical grade 2 M HNO_3 (Loizeau et al., 2004).

2.2.4. Trace elements

The trace elements' concentration (including scandium (Sc), titanium (Ti), and Pb) was measured in the digested solution using quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS, Agilent®, model HP 4500). Multi-element standard solutions at different concentrations (0, 0.02, 1, 5, 20, 100 and 200 ppb) were used for the calibration. Total variation coefficients of four replicate measurements were less than 10%. Results are expressed in mg/g dry weight sediment.

2.2.5. Pb isotopic analysis

The Pb isotopic composition was only determined for the Lake Lucerne core, because similar data existed for sediments of lakes Geneva and Constance (Fig. 5). Pb was purified by anion exchange chromatography using an AG-MP1-M resin in hydrobromic medium and small volume columns (0.08 ml). Pb was subsequently loaded on Re filaments using the silica gel technique (Gerstenberger and Haase, 1997). All samples (as well as the SRM981 standard) were measured in static mode at a pyrometer-controlled temperature of 1220 °C on a multicollector Thermo TRITON mass spectrometer at the Department of Mineralogy of Geneva (Switzerland). Pb isotope ratios were corrected for instrumental fractionation by a factor of 0.1% per amu based on more than 100 measurements of the SRM981 standard and using the standard values of Todt et al. (1996). External reproducibility (2σ) of the standard ratios are 0.05% for $^{206}Pb/^{204}Pb$, 0.08% for $^{207}Pb/^{204}Pb$, 0.10% for $^{208}Pb/^{204}Pb$, 0.006% for $^{206}Pb/^{207}Pb$, 0.007% for $^{208}Pb/^{207}Pb$ and 0.008% for $^{208}Pb/^{206}Pb$. Total procedural blanks were ≤120 pg.

3. Results

3.1. Core dating

3.1.1. Lake Geneva age models

Similarly to Lake Lucerne, we limited radiocarbon (^{14}C) dating to the only sample containing leaf remnants, which are brittle vegetal fragments and are therefore unlikely to have been reworked or redistributed before deposition in contrast to wood fragments or total sedimentary organic matter. One ^{14}C date (ETH-40161) was performed on a leaf found at 78 cm depth in core C2 (130 cm long), yielding a radiocarbon age of 365±30 years BP (before present = 1950). Calibration using OxCal v3.10 program (Bronk Ramsey, 2001) gives a calendar age of 1540±53 years, according to the statistical uncertainties of the calibration curve (Fig. 2).

Age models for cores C2 and G1 are based on the coring year and on the depth of the peak attributed to the 1963 maximum ^{137}Cs emissions (Fig. 2). The cores PC and BV, analyzed at higher resolution (0.5 and 1 cm, respectively) by Monna et al. (1999) exhibit two distinct peaks of ^{137}Cs activity, allowing an absolute dating of both 1963/64 and 1986 layers. It is meaningful to note i) the absence of the Chernobyl ^{137}Cs peak in our sequences from the deepwater sites of Lake Geneva (C2 and G1) probably due to the low sampling resolution (2 and 3 cm, respectively), and ii) the absence of the 1963/64 maximum radionuclide fall-out in our records of the Vidy Bay (V1 and V3) which indicates that these sediments were deposited after the WWTP implementation in 1964.

3.1.2. Lake Lucerne age model

The age model for core 4WS05 is described in detail in Thevenon et al. (2011b). For the upper part of the core (Fig. 2), the age model is based on the linear interpolation between four tie points: the coring year (2005), two distinct ^{137}Cs peaks attributed to the Chernobyl accident in 1986 and to the maximum radionuclide fall-out from atmospheric nuclear tests in 1963/64 (at 4 and 11 cm, respectively; Fig. 2), and one ^{14}C date (ETH-31562; Thevenon et al., 2011b) obtained on a leaf founded at 53 cm downcore (ca. 1394±70 calendar years).

3.2. Trace element records from Lake Geneva (deepwater sites and Vidy Bay)

In order to compare the Lake Geneva's Pb data with former ones measured on HNO_3 leached solution (cores PC and BV; Monna et al., 1999), the new leached Pb records of Lake Geneva (cores V1, V3, G1, and C2) are plotted in Fig. 4. The Pb concentration of core C2, which has been analyzed by the two different methods (HNO3 leached solution and HF digestion), demonstrates that both methods produce similar Pb concentrations for Lake Geneva's sediments (Fig. 3). Finally, Fig. 5 compares the concentrations of total Pb (following HF dissolution of the sediment) for lakes Lucerne and Geneva. In order to compare both records by taking into account the differences in sedimentation rate, these concentrations of Pb have been normalized to the conservative crustal element Sc, and expressed as enrichment factors (EF_S) normalized to the background value of each site.

The strong agreement between the concentrations of Pb and Hg within the deepest parts of the Grand Lac (core C2) and the Petit Lac (core G1) reflects a homogeneous temporal and spatial distribution of trace metals to Lake Geneva's floor (Fig. 3). In the Petit Lake (core G1), the Hg concentration significantly increases above background levels (~0.03 μ/g) around the First Industrial Revolution (around 1750), and Pb concentration strongly rises after the Second Industrial Revolution (around 1850). The highest contamination of Lake Geneva deepwater sediments by Pb and Hg occurs during the middle of the twentieth century, as indicated by the vicinity with the 1963/64 peak of ^{137}Cs (crosses in Fig. 3). Such a finding is in agreement with previous high-resolution records of Hg contamination from Lake Geneva, which locate a peak of Hg contamination in 1971 and the maximum value around 1945 (e.g., Dominik et al., 1992).

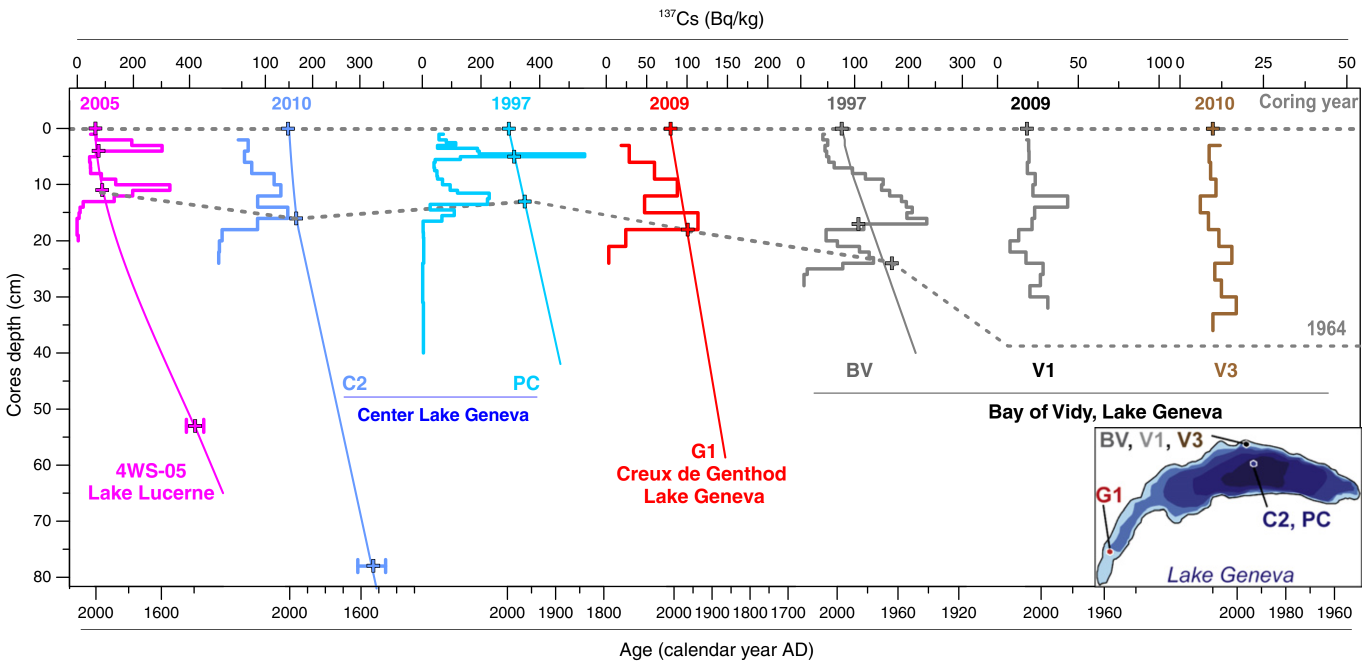

Fig. 2. ^{137}Cs activity profiles plotted versus the cores depth of the cores studied from Lake Lucerne (4WS-05) and Lake Geneva (C2, G1, V1, and V3). Comparison with the ^{137}Cs activity profiles of cores PC and BV from Monna et al. (1999). The crosses mark the maxima of ^{137}Cs activity resulting from nuclear bomb fallout in 1964 and Chernobyl fallout in 1986.

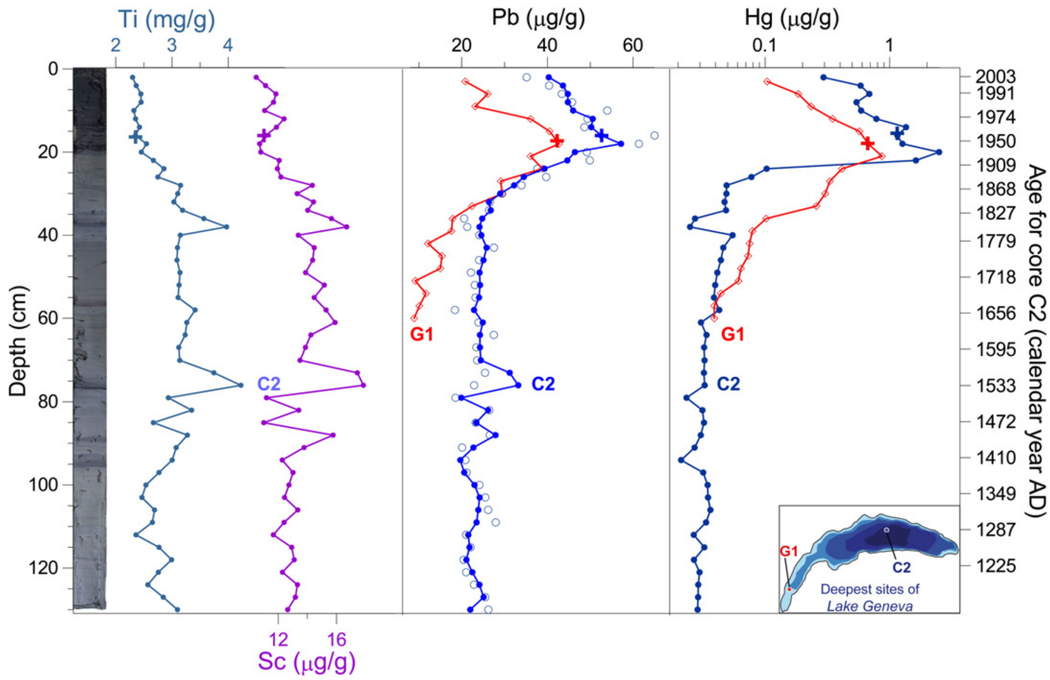

Fig. 3. Core photograph of core C2 from the deepest part of the Grand Lake Geneva. Ti, Sc, and Pb (measured by HF dissolution) and Hg as a function of depth (left axis) for cores C2, with the corresponding age on the right axis. Pb and Hg of core G1 from the deepest part of the Petit Lake Geneva. The crosses mark the maximum of ^{137}Cs activity in 1964. The filled blue points represent the total Pb measured after HF dissolution, while the empty blue points represent the leached Pb measured by HNO_3 treatment of core C2.

Similarly to these previous investigations, the deepwater records from our study show that the anthropogenic metal input declines in the 1980s up to 2010, pointing out the efficiency of implementation of sewage treatment plants.

The agreement between the lithogenic trace elements (Ti and Sc) and Pb and Hg is remarkable for the pre-industrial period, but these proxies strongly differ during the industrial period (core C2 in Fig. 3). Anthropogenic inputs largely override the contribution of the natural source of heavy metal during the industrial period. By comparison, Pb and Hg concentrations in the post-1964 sediments deposited into the Vidy Bay are about ten times higher than those from the central parts of the lake (Fig. 4), whereas human activities

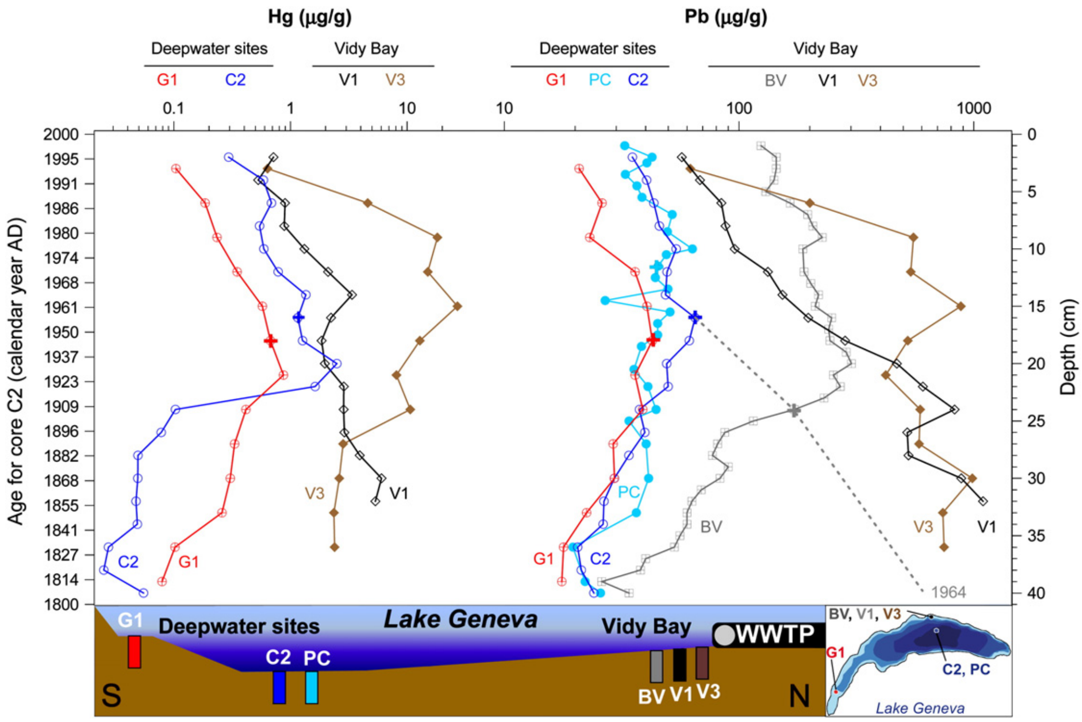

Fig. 4. Left part: Hg records of cores from the deepest sites of Lake Geneva (G1 and C2) and from Vidy Bay (V1 and V3) as a function of depth (right axis). Pb (measured by HNO_3 leaching dissolution) profiles of cores V1, V3, G1, and C2, compare to cores BV and PC (Monna et al., 1999), as a function of depth (right axis), with the corresponding age of core C2 on the left axis. The crosses mark the maximum of ^{137}Cs activity in 1964. Lower part: Diagram (north–south section) showing the location of the studied cores in Lake Geneva.

have increased pre-industrial Pb concentration into the Vidy Bay by about more than 20 times during the middle of the twentieth century (Fig. 4) due to the local release of industrial and domestic wastewaters. Now, the effluents of the WWTP and the runoff inputs from the city of Lausanne preferentially accumulate in the vicinity of the outlet pipe discharge (Poté et al., 2008). Our results agree that the concentration of metal pollutants into Vidy Bay is inversely related to the distance from the WWTP outlet pipe discharge point over the last decades (V3 > V1 > BV > C2; Fig. 4).

4. Discussion

4.1. Regional-scale pollution history inferred from three large freshwater lakes of Central Europe (Geneva, Lucerne, and Constance)

The records of lakes Geneva and Lucerne extend to the 13th century, which coincides with the birth of the Old Swiss Confederation (1291–1797) that established a protective alliance to ensure safety on mountain trade routes. Many cities (e.g., Lucerne, Berne) were founded from the 11th to the 13th centuries, and the regions of Lucerne and Geneva became important links in the trade between northern Europe and the Mediterranean coast, especially after the opening of the Gotthard Pass around 1230. Despite significant human activities, the Pb records for lakes Geneva and Lucerne show very low enrichment in anthropogenic metals before the industrial period (Pb_{EF} < 1.5; Fig. 5). Heavy metal concentrations clearly exceed natural levels only during the European industrial revolution. The subsequent large increase in anthropogenic trace metal concentration in lakes Lucerne and Geneva therefore reflects the rapid and synchronous impact of industrialization on the Swiss Plateau, which coincides with the adoption of the Swiss Federal Constitution in 1848 and the European revolutions. By contrast, the input of geogenic elements Ti and Sc (Fig. 3) from the deepest site of Lake Geneva declines, possibly reflecting the anthroponenic impact on the fluvial sediment input to Lake Geneva during the last century (numerous hydroelectric dams built on tributaries of the Rhône River; Loizeau et al., 1997).

The strong agreement between the sedimentary Pb records from lakes Geneva, Lucerne, and Constance for the last 200 years (Fig. 5), demonstrate the synchronous contamination of the large Swiss freshwater lakes by Pb and Hg during the twentieth century. Hence, the broad temporal variations in inorganic pollutant concentrations across the Swiss Plateau show synchronous variations in pollution related to human activities. During the last decades, the Pb concentration in Lake Constance (core taken at 205 m water-depth near Friedrichshafen; Kober et al. (1999)) decreases towards the pre-industrial level, while it only decreases moderately in lakes Geneva and Lucerne (reaching 30 μg/g and 40 μg/g, respectively).

Our results also highlight the dramatic accumulation of highly contaminated sewage-derived sediments in the Vidy Bay during the late-twentieth century, which constitute a potential hazard for the biota and drinking water quality, considering the action of bottom lake currents and the frequent mass movement events affecting Lake Geneva (Girardclos et al., 2003, 2005; Loizeau et al., 2004). By comparison, the maximum level of pollution at Vidy during the second part of the twentieth century is almost equivalent to the great peak of pollution recorded nearby the city of Lucerne during the early-twentieth century (>100 μg Pb/g dry weight sediment; Fig. 5).

4.2. Isotopic composition of Pb from Lake Lucerne and the pollution sources of three Swiss freshwater lakes

The long-term history of the $^{206}Pb/^{207}Pb$ ratio of Lake Lucerne (Fig. 5) indicates the continuous decline of the lithogenic Pb contribution relative to the anthropogenic Pb sources after ca. 1500. The

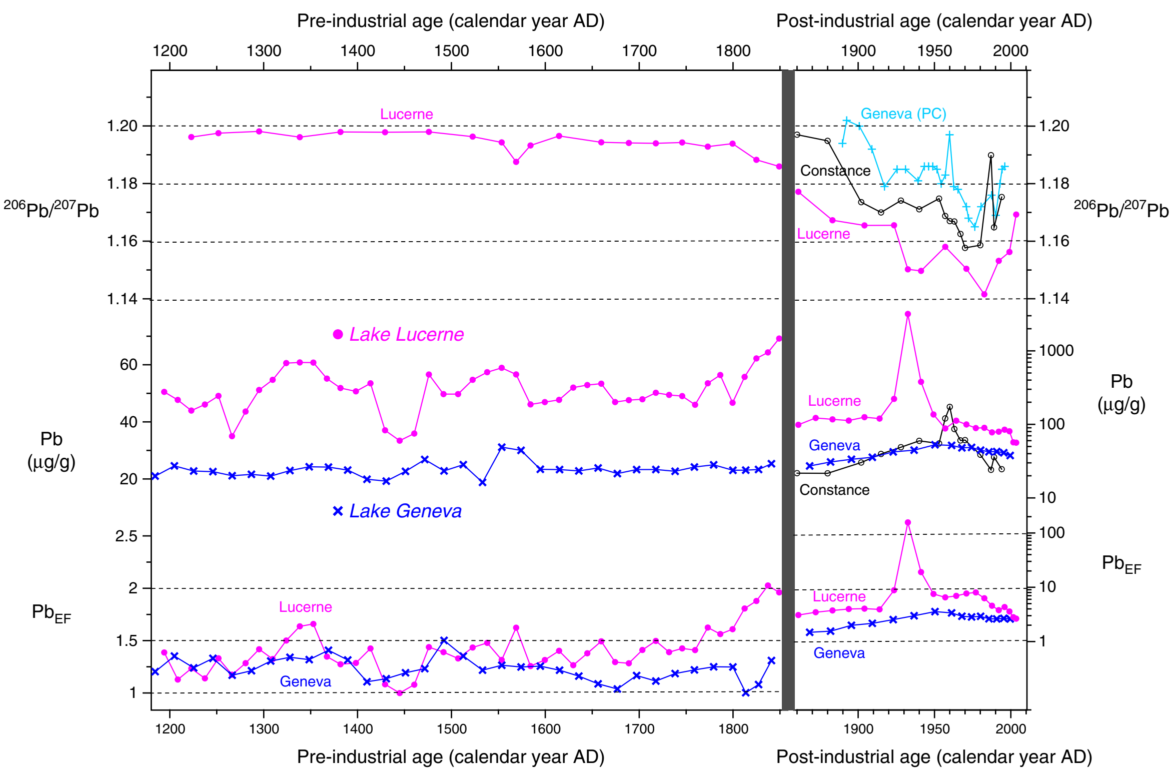

Fig. 5. $^{206}Pb/^{207}Pb$ ratio for Lake Lucerne (this study) compared to Lake Geneva (core PC; Monna et al., 1999) and Lake Constance (Kober et al., 1999) post-industrial data. Pb concentration and Pb_{EF} (normalized to the lowest Pb/Sc value) for lakes Geneva and Lucerne, with the Pb post-industrial record of Lake Constance for comparison.

presence of less radiogenic Pb around 1550 could indicate environmental pollution from mining activities during the High Middle Ages. However, the corresponding anthropogenic Pb is rather low, and according to the uncertainty of the age model, this event could be related to the turbidites deposited in other sub-basins of Lake Lucerne in response to the earthquake that occurred in 1601 (Schnellmann et al., 2004).

Fig. 6 plots the ^{208}Pb/^{207}Pb vs. ^{206}Pb/^{207}Pb isotopes ratios for Lake Lucerne (this study), Lake Constance (Kober et al., 1999), and Lake Geneva (deepest part and Vidy Bay from Monna et al., 1999), and further reports the isotopic compositions of potential lead sources; as well as those of the aerosols collected from a city centre (Ste Clotilde) and a country (Passeiry) station of Geneva (data sources: Monna et al., 1999 and Chiaradia and Cupelin, 2000). The isotope signature of the aerosols displays the maximum anthropogenic contribution at the city centre, while aerosols collected in the country-side display a lower Pb pollutant contribution. The lead isotopic composition of the lowermost sediment samples of the three lakes plots opposite of the modern aerosol signatures (i.e., close to the UCC values; Wedepohl, 1995), ruling out a significant contribution of a low radiogenic anthropogenic source before the industrial period (Fig. 6).

During the last 200 years, both Lake Geneva's sites exhibit significant changes in Pb sources linked to higher anthropogenic lead inputs. The sedimentation of less radiogenic Pb to Vidy Bay (core BV) indicates a higher contribution of anthropogenic components between ca. 1930 and 1965, with mixed values between local lithogenic background and industrial sources (e.g., European coal in Fig. 6). The Pb isotope data from the sediments deposited synchronously in the central part of Lake Geneva are also consistent with a high contribution of fossil fuel combustion (e.g., Geneva coal in Fig. 6). Additionally, the Pb isotopic data from the Vidy Bay (core BV) indicate a marked change in the Pb source precisely when the WWTP started operations in 1964 (upper part of Fig. 6). The Pb content of the highly polluted sediments deposited after 1964 at this site therefore primarily originated from wastewater inputs, as also testified by the $^{206/207}$Pb isotopic signature from the particles from the WWTP effluent sampled in 1997 ($^{206/207}$Pb, 1.146–1.149, n = 3), that are quite similar to those reported for industrial sources in Switzerland and in other countries (Monna et al., 1997). $^{206/207}$Pb ratio of 1.142 measured in 2011 from the WWTP effluent (reported in Fig. 6) furthermore suggests that the Pb isotope composition of the WWTP has remained nearly constant through time and that Pb was primarily derived from industrial sources. The isotopic composition of the sediments of Vidy Bay is also close to

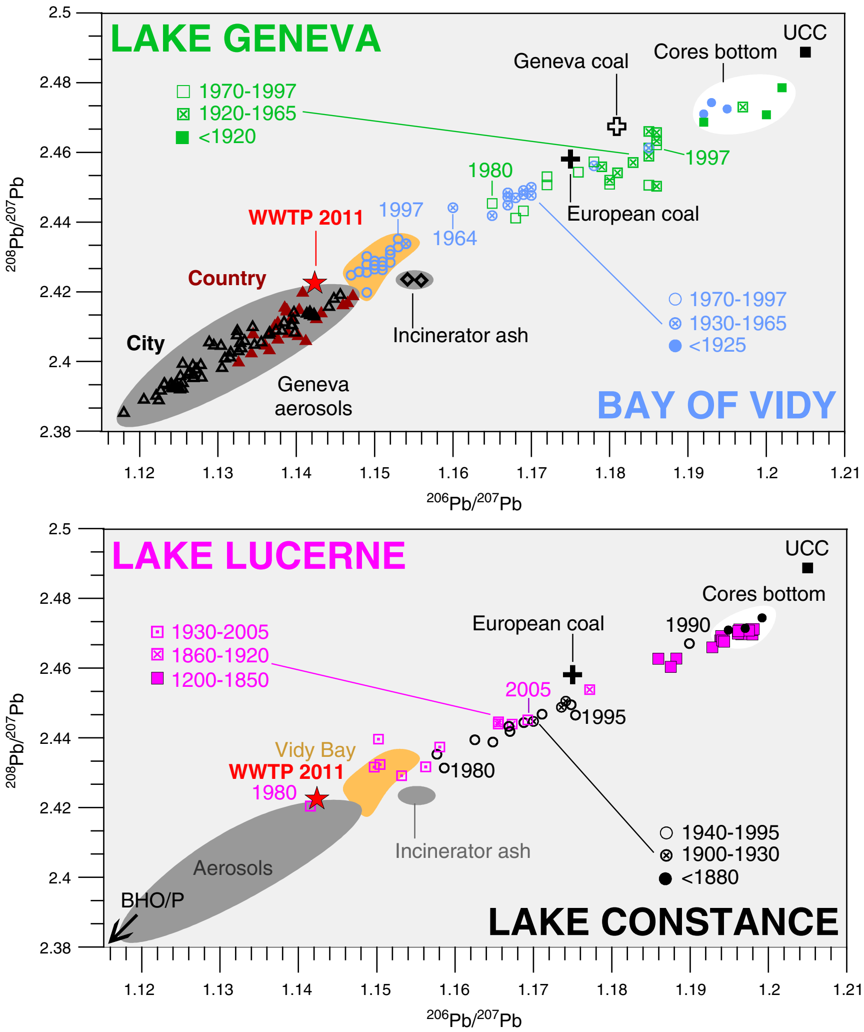

Fig. 6. ^{208}Pb/^{207}Pb ratios as a function of ^{206}Pb/^{207}Pb ratios for lakes Geneva, Lucerne, and Constance. (upper part) Lake Geneva deepest part (core PC) and Vidy Bay (core BV) isotope systematic (Monna et al., 1999). (lower part) Lake Lucerne (this study) and Lake Constance (Kober et al., 1999) isotope systematic. The Pb isotope compositions of European coal and incinerator fly ash (Kylander et al., 2005), Vidy Wastewater Treatment Plant (WWTP) effluent (this study), Geneva coal and aerosols from two Geneva stations (Chiaradia and Cupelin 2000) are reported for comparison. The isotope signatures of the Broken Hill Mine Ore (BHO) and leaded petrol (P) plot off the graph. The records are divided into different chronologic units.

that of the waste incineration (fly ash from a power plant incinerator, Fig. 6), which was in 2000 the main source of atmospheric lead in Geneva, together with petrol (Chiaradia and Cupelin, 2000). The Pb isotope fingerprint observed in the wastewater sediment deposited at Vidy Bay is also close to the recent contaminated sediments from Lake Lucerne (lower part of Fig. 6) that contain abundant fly ash particles formed by fossil fuel combustion (Thevenon and Anselmetti, 2007). These results suggest that industrial activities have been the main pollutant source during the last 200 years in these large freshwater lakes. It is however important to note that the most recent sediments of Lake Geneva analyzed (deposited around 1997; upper part of Fig. 6) encompass more radiogenic Pb, suggesting a significant decrease of anthropogenic Pb pollution towards the end of the twentieth century in Lake Geneva's waters. A similar trend is inferred for lakes Lucerne and Constance, where the uppermost sediment analysed (deposited around 2005 and 1995, respectively) show a growing relative contribution of lithogenic sources with regard to industrial Pb sources (lower part of Fig. 6).

5. Conclusions

The leachable Pb in sediments of Lake Geneva is almost equivalent to total Pb in the bulk sediment, indicating that the Pb components hosted in the silicate phases of the sediment are negligible. Before the industrialisation of the Swiss Plateau, the trace metal (Pb and Hg) distribution of Lake Geneva deepwater sites shows a relatively similar pattern of variation of geogenic elements (Sc and Ti), reflecting natural weathering sources and processes within catchment. This situation contrasts with the industrial period, when anthropogenic sources of Pb and Hg dominate. The anthropogenic Pb contribution to sediments of lakes Geneva, Lucerne, and Constance, demonstrates the regional pollution of their ecosystems around the middle of the 19th century, with pollution maxima in the middle of the 20th century. Lead isotope data from the three large lakes further highlight the growing synchronous contribution of low radiogenic Pb attributed to industrial sources. The regional metal pollution decreases during the 1970s in the large freshwater lakes of the Swiss Plateau, certainly resulting from an increase in the number of sewage plants.

In addition to the regional-scale pollution trends, maximum pollution concentrations (~1 mg Pb/g dry weight sediment) are recorded: i) in Lake Lucerne during the first part of the 20th century due to industrial coal combustion, and ii) in Lake Geneva during the second part of the 20th century due to the discharge of industrial sewage wastewaters into Vidy Bay. The polluted sediments deposited at 500 m from the pipe outlet have heavy metal contents about fifty times more than pre-industrial values measured in the deepest parts of the lake. The highly contaminated sediment from the municipal WWTP has accumulated in the coastal area of Lake Geneva, where highly populated centers draw their supply of drinking water. Further investigations are needed to assess the impact of the anthropogenic micropollutants entrapped in these polluted sediments, and to evaluate their behavior towards climate and human-induced changes to the aquatic environment.

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