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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 effect concentration" (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 Vidy Bay represent a major contaminant legacy that constitutes a potential threat to the lake biota in the case of sediment remobilization.

1. Introduction

Lake sediments are archives of climatic variations and pollution in the environment. Trace, minor and major element signals recorded in sediments allow the reconstruction of historical events, both natural and anthropogenic in origin. Detrital trace metals are discharged through watershed runoff (directly or from fluvial inputs) into lakes. Heavy metal emissions by anthropogenic activities have been shown to increase local, regional, and global fluxes to the atmosphere since the beginning of metallurgy (Nriagu, 1996; Vesely, 2000). Thus, trace metals are widely distributed in the environment. Nevertheless, sewage waters and sludge directly discharged by wastewater treatment plants (WWTP) also represent major sources of contamination in lakes. Heavy metals accumulate in sediments via several mechanisms, such as adsorptive attachment to fine-grained particles (Sholkovitz and Price, 1980), precipitation of discrete metal compounds, coprecipitation of metals by Mn- and Fe-oxyhydroxides and carbonates, and association with organic molecules (Förstner, 1982). The mobility and bioavailability of trace metals in lake sediments depend on their speciation and

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stability (Calmano et al., 1993), which are controlled by chemical conditions such as the sediment redox potential, pH, organic matter content, and Mn- and Fe-oxyhydroxides. Sediment contamination can harm benthic infauna and epifauna through superficial contact with polluted sediments and pore water, as well through direct ingestion of sediments and detritus (Lawrence and Mason, 2001; Reynoldson, 1987). Moreover, in case of sediment remobilization, trace metals are likely released into the water column and may enter the aquatic life, which is deleterious to organisms because they accumulate in food, leading to damage in human organs and severe diseases (Alissa and Ferns, 2011; Hu, 2000; Ibrahim et al., 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 sediments 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 Poté, 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 km^2, a volume of 89 km^3 and an average depth of 152.7 m (maximum depth: 309 m). The Lake Geneva catchment area (including the lake) is 7999 km^2, and the Rhône River is the major tributary (75% of the total water input), with a mean inflow of 185 $m^3\ s^{-1}$ and a mean outflow of 250 $m^3\ s^{-1}$. 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 $m^3\ s^{-1}$) 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 $m^3\ s^{-1}$ 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-$NH_4\ L^{-1}$) (Margot et al., 2013).

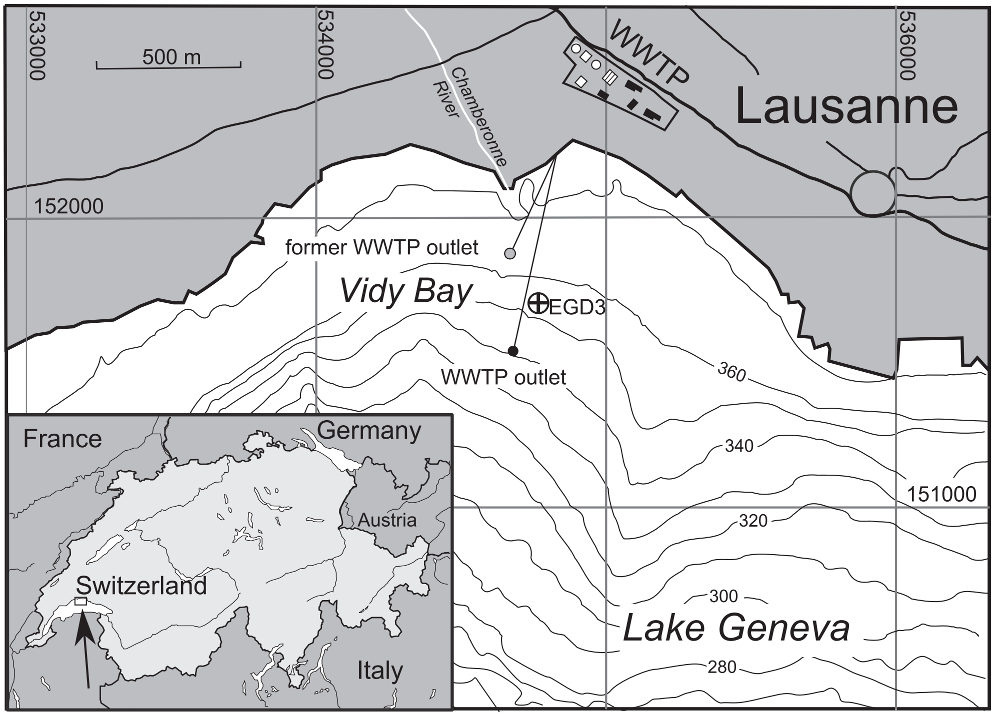

Fig. 1. Location of Vidy Bay shown on a bathymetric map of the study area in Lake Geneva. EGD3 represents the site were the studied sediment core was retrieved.