THE HAUNTING LEGACY: SEDIMENT RECORD OF PERSISTENT ORGANIC POLLUTANTS IN THE GLACIER-FED LAKE TSCHEPPA, SWITZERLAND

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Abstract

The goal of this study is to investigate whether melting glaciers may represent a secondary source for persistent organic pollutants (POPs). Therefore, a dated sediment core from a high-Alpine lake (Lake Tscheppa, Switzerland) was analyzed for POPs, including PCDD/Fs, PCBs, PCNs, and DDTs. In the 1990s, Lake Tscheppa was mainly fed by meltwater from the adjacent glacier, which melted off rapidly and ultimately disappeared in 2003 due to climate warming.
Input fluxes of POPs into Lake Tscheppa increased in the 1980s and peaked between 1985 and 2005. A recent increase of the direct input into Lake Tscheppa through atmospheric deposition is unlikely. Therefore, the observed time trend in this glacier-fed lake is probably a consequence of the release of legacy POPs from the melting glacier.

Introduction

The occurrence of persistent organic pollutants (POPs) at high latitudes or in remote mountain areas can result from global distillation, i.e. volatilization from warm source regions and condensation in cold areas[1]. Atmospheric transport of particulate matter and high precipitation rates can also result in the enhanced deposition of POPs in mountain areas. In cold regions, glaciers can accumulate atmospherically-derived contaminants that deposit on the ice surface[1].
In Alpine regions, water resources are expected to undergo major changes as a consequence of global warming[2]. Next to the impact on water balances, climate change may significantly affect water quality. In particular, the release of pollutants stored in Alpine glaciers is conceivable.

The aim of the present study is to investigate the possible release of POPs from melting Alpine glaciers. Historical trends of POPs in sediment from Lake Tscheppa, Switzerland, which was significantly fed by a melting glacier during the last decades, have been reconstructed. We analyzed polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), as well as dichlorodiphenyl trichloroethane (DDT) and its main metabolites (dichlorodiphenyl dichloroethene DDE and dichlorodiphenyl dichloroethane DDD) in a dated sediment core from this remote high-altitude lake.

Materials and Methods

Sampling Site
Lake Tscheppa (46°27'N, 9°45'E) is a small lake (0.076 km^2, max. depth 32 m) located at 2616 m a.s.l. in South-Eastern Switzerland. Formerly, the Crasta-Tscheppa Glacier, which melted off completely in 2003, represented the major water source for the lake. Currently, Lake Tscheppa is only fed by runoff water from its small non-glaciated catchment (1 km^2).

Sampling and Dating
A sediment core of 50 cm in length was sampled in 2007 at a depth of 27 m by using a gravity corer. Dating of our sediment core was based on the identification of characteristic varves in a reference core, which was dated itself based on ^{137}Cs and ^{210}Pb measurements and extensively analyzed in a previous study[3]. After dating, sediment sections representing 10 years of sediment deposition were prepared.

Sediment analysis
Homogenized and freeze-dried sediment was Soxhlet extracted. Aliquots of the extracts were spiked with isotope labeled internal standards ($^{13}C_{12}$-labeled PCDD/Fs, $^{13}C_{12}$-labeled PCBs, $^{13}C_{10}$-labeled PCNs, $^{13}C_{12}$-labeled DDT, and $^{13}C_{12}$-labeled DDE), purified and fractionated. Detection and quantification was performed with gas-chromatography coupled to high resolution mass spectrometry. Target analytes included all 17 2,3,7,8-chlorosubstituted PCDD/Fs, dioxin-like PCBs (congeners number 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), di-*ortho*-chlorosusbstituted PCBs (congeners number 28, 52, 101, 138, 153, and 180), tetra- to octa-chlorosubstituted PCNs, and DDTs (p,p'-DDT, o,p-DDT, p,p'-DDE, o,p-DDE, p,p'-DDD, and o,p-DDD).

Quality assurance
With each batch of five sediment samples, a procedural blank was simultaneously analyzed. The most concentrated blank sample represented 29% of PCDD/Fs, 22% of PCBs, 16% of PCNs, and 16% of DDTs, compared to the least concentrated sediment sample that was above the limit of detection (LOD). Recovery of isotope labeled internal standards was 52%-96%, 58%-108%, 59%-98%, and 50%-98% for PCDD/Fs, PCBs, PCNs, and DDTs, respectively. A deep sediment sample corresponding to pre-1900 was analyzed for PCDD/Fs, PCBs, and PCNs. The detected amounts of these analytes were below blanks. A deep sediment sample corresponding to pre-1900 was spiked with 400 pg of native PCDD/Fs and 5000 pg of native PCBs. The analysis of this sample revealed a recovery of these native analytes of 85%-109% and 88%-115%, for PCDD/Fs and PCBs, respectively.

Results

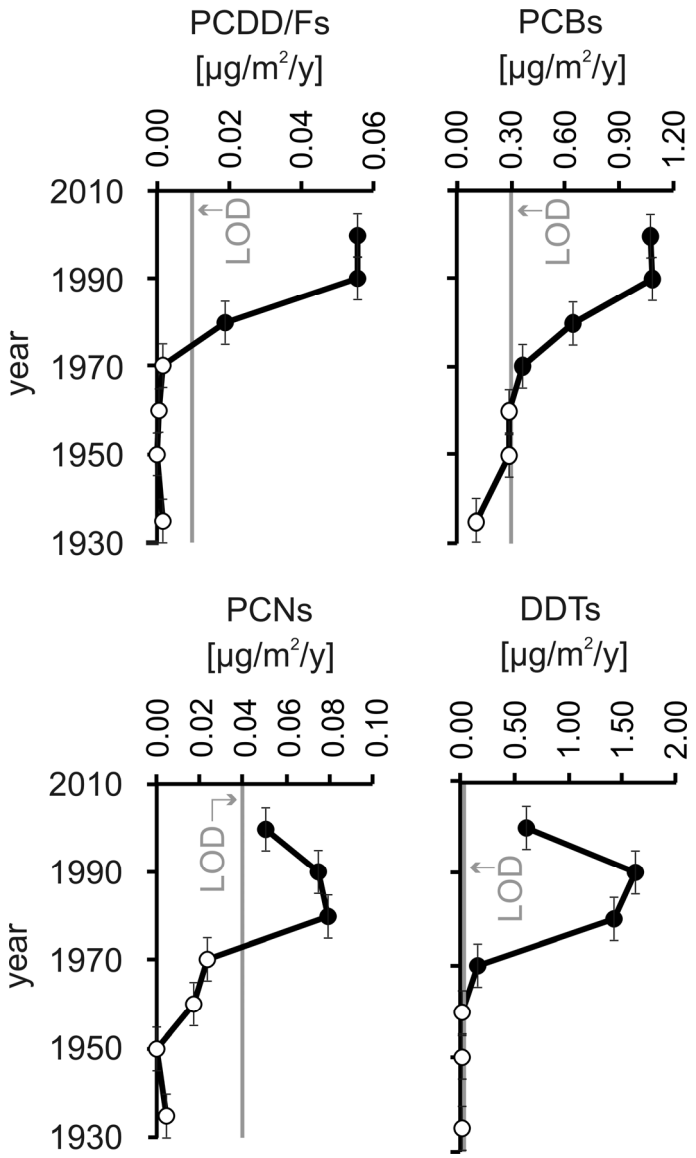

Figure 1. Fluxes of PCDD/Fs, PCBs, PCNs, and DDTs into sediment from the high-Alpine Lake Tscheppa (black curves). The error bars on the y-axis indicate the time span (10 years) covered by the corresponding samples. LOD were converted into a flux, based on a typical sample amount and sedimentation flux. Open circles indicate data points below LOD.

The historical record of POPs in the sediment core from the high-Alpine Lake Tscheppa is presented in Figure 1. PCDD/Fs, PCBs, and PCNs exceeded the LOD in the two upper sediment sections corresponding to 1985-2005 by a factor of five, four, and two, respectively. Among DDTs, p,p'-DDT, p,p'-DDE, and o,p-DDE were detected and their sum exceeded clearly the LOD in sediments from 1975 on. For all the analyzed compounds, a clear increase of fluxes into sediment from Lake Tscheppa is observed in the sediment section corresponding to 1975-1985, followed by a maximum in 1985-1995. In the period of 1995-2005, fluxes leveled-off for PCDD/Fs and PCBs, while fluxes decreased by 30% for PCNs and 70% for DDTs. Maximum fluxes are 0.06, 1.10, 0.08, and 1.62 μg/m^2/y for PCDD/Fs, PCBs, PCNs, and DDTs, respectively. For PCDD/Fs and PCBs, the fluxes converted in TEQ using the WHO98 TEF, or the NATO I-TEF, closely follow the trend of the concentration based fluxes. TEQ based fluxes also peaked in the period 1985-1995, with a contribution of one order of magnitude higher for PCDD/Fs (2.3 ng WHO98 TEQ/m^2/y) than for PCBs (0.4 ng WHO98 TEQ/m^2/y).

Discussion

Anthropogenic emissions of PCDD/Fs in Switzerland have sharply decreased since the early 1980s as a result of improved solid waste incineration technologies[4]. PCBs were banned in Switzerland in open applications in 1972, followed by a complete ban and mandatory disposal in 1986[5]. PCNs were also added to the list of banned hazardous substances in 1986[5]. The usage of DDT as an insecticide ceased in the 1960s and since 1972 it has been banned in Switzerland[5]. Worldwide, the Stockholm Convention, which includes PCDD/Fs, PCBs and DDT, has been in force since 2004[6].

Thus, the observed time trend of PCDD/Fs, PCBs, and DDT in sediment from the high-Alpine Lake Tscheppa is in opposition to the production, usage, emission, or regulatory history of these compounds. Decreasing concentrations of POPs during the last decades in dated sediment cores from various low-altitude lakes in Switzerland have previously been reported[7-9].

A significant release into water of formerly accumulated pollutants from melting glaciers is a likely reason for the considerable recent increase of the input of legacy pollutants into Lake Tscheppa. The Crasta-Tscheppa Glacier was located some 700 m above Lake Tscheppa, had a maximal extension around 1850, melted off during the last 150 years, and ultimately disappeared in 2003[3]. In earlier times, the glacier represented the major water source for Lake Tscheppa, whereas currently the lake is only fed by surface runoff. Thus, the input of all investigated pollutants in sediment from Lake Tscheppa during the period 1985-2005 occurred concurrently with the melting process. According to this hypothesis, in the 1950s-1980s, airborne pollutants that were deposited on the glacier surface were incorporated into the ice mass at that time and were released from the ice matrix during the rapid melting process. The sediment record (Figure 1) reveals that the release of POPs from the glacier attained its maximum in the period 1985-1995. In the recent period 1995-2005, the input into Lake Tscheppa leveled-off for PCDD/Fs and PCBs, and it decreased for PCNs and DDTs. This difference may be due to the different deposition history of these pollutants on the glacier. PCNs have been introduced to the world market one decade prior to PCBs and had probably earlier emissions than PCBs[10]. DDT was also phased out in Switzerland earlier than PCBs. So, the release of PCNs and DDTs from the glacier may have peaked earlier due to the melting of older ice, while PCBs and PCDD/Fs may have been released later in 1995-2005.

As a conclusion, our study provides indications of a possible release of various legacy POPs from a melting Alpine glacier. This secondary source of persistent, bioaccumulative and toxic organochlorine chemicals deserves further attention regarding its ecotoxicological relevance.

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