Blast from the Past: Melting Glaciers as a Relevant Source for Persistent Organic Pollutants

CHRISTIAN BOGDAL,*†‡, PETER SCHMID,† MARKUS ZENNEGG,‡ FLAVIO S. ANSELMETTI,§ MARTIN SCHERINGER,† AND KONRAD HUNGER BÜHLER†

Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland, Empa, Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, CH-8600 Dübendorf, Switzerland

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In this study, the hypothesis that melting Alpine glaciers may represent a secondary source of persistent organic chemicals is investigated. To this end, a dated sediment core from a glacier-fed lake (Lake Oberaar, Switzerland) was analyzed for a wide range of persistent organic pollutants, organochlorine pesticides, and synthetic musk fragrances. Input fluxes of all organochlorines increased in the 1950s, peaked in the 1960s–1970s, and decreased again to low levels in the 1980s–1990s. This observation reflects the emission history of these compounds and technical improvements and regulations leading to reduced emissions some decades ago. The input of synthetic musks remained at a high level in the 1950s–1990s, which is consistent with their relatively constant production throughout the second half of the 20th century. Since the late 1990s, input of all compound classes into the high-Alpine Lake Oberaar has increased sharply. Currently, input fluxes of organochlorines are similar to or even higher than in the 1960s–1970s. This second peak supports the hypothesis that there is a relevant release of persistent organic chemicals from melting Alpine glaciers. Considering ongoing global warming and accelerated massive glacier melting predicted for the future, our study indicates the potential for dire environmental impacts due to pollutants delivered into pristine mountainous areas.

Introduction

Global warming is one of the major global issues at present, implying many social, economic, environmental, and health-related impacts (1). Glaciers, which cover large parts of the Polar regions and also mountainous areas such as the Alps, represent the largest reservoir of fresh water on Earth and are predicted to undergo massive melting in the future (1). Glacial ice may contain significant amounts of chemicals deposited in earlier times that have been stored in the deeper layers of the ice during the last decades. Accelerated glacier ablation may result in a substantial release of chemicals from this kind of reservoir. Of particular concern are persistent, bioaccumulative, and toxic organohalogens, which are ubiquitous environmental pollutants occurring even in remote areas, where they have never been produced or used (2). Hence, pristine ecosystems may be affected by the delayed release of environmental contaminants whose emissions were high in the past (2–5).

The aim of this study is to investigate the hypothesis of a possible release of legacy pollutants from melting Alpine glaciers and to assess the relevance of this process. For a wide range of contaminants, we reconstructed a concentration time series using a dated sediment core from the high-Alpine Lake Oberaar, Switzerland, which is mainly fed by meltwater from rapidly receding glaciers (6, 7). Target compounds include several persistent organic chemicals such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), as well as dichlorodiphenyl trichloroethane (DDT) and its main transformation products (dichlorodiphenyl dichloroethene DDE and dichlorodiphenyl dichloroethane DDD). Additional organochlorine pesticides or their transformation products (hexachlorobenzene HCB, γ-hexachlorocyclohexane γ-HCH, dieldrin, and heptachlor epoxide HPEX), as well as the poorly studied synthetic nitro and polycyclic musk fragrances were also measured. An accurate and reliable sediment dating method (6), long time period covered (1953–2006), and comprehensive selection of organohalogens for which environmental pollution is currently expected to be declining (2–4, 8) provide a unique opportunity to investigate the “delayed release hypothesis”.

Materials and Methods

Sampling Site. Figure 1 shows the location of Lake Oberaar and three low-altitude lakes in Switzerland, which will be discussed for comparison later in this study. Two sediment cores (OAR06-1 and OAR06-2) from Lake Oberaar were...
retrieved at the same site in the lake in 2006 by using a percussion piston corer. Lake Oberaar (46°33′ N, 8°16′ E) is a hydroelectric proglacial reservoir lake (surface area: 1.5 km²; maximum depth: 83 m; lake catchment area: 18 km²) located at 2303 m above sea level in Central Switzerland. The lake is fed by meltwater from the Oberaar Glacier. The Oberaar Glacier has been monitored for the last century and decreased significantly in size during this time (Figure 1). Since 1930, the glacier tongue has shrunk by 1.6 km (7). The water of Lake Oberaar drains into Lake Grimsel, which is also a glacier-fed lake. Since 1980, Lake Oberaar has also received glacial water from Lake Grimsel through a pump—storage operation between the two lakes.

**Sediment Dating and Preparation.** Prior to our study, the first half of the material from the two sediment cores from Lake Oberaar was analyzed in a separate study (6); the second half of the sediment material was used in the present study. The combination of the two cores defines a complete master section providing sediment material covering the entire period from 1953 to 2006 (6). The recomposed sediment section was dated by counting the annual sediment layers (varves). After dating, the recomposed sediment core was divided into 2–5 year intervals, and the sediment was freeze-dried, pestled, homogenized, and stored in the dark prior to analysis. Further details of the sediment dating are provided in the Supporting Information.

**Sediment Analysis.** Sediment was Soxhlet extracted, and aliquots of the extract were used for further analysis. A first aliquot was used for the analysis of PCDD/Fs, PCBs, and PCNs, while a second aliquot was used for the analysis of organochlorine pesticides and synthetic musk fragrances. Aliquots were first spiked with isotope-labeled internal standards. For PCDD/Fs, PCBs, and PCNs, purification and fractionation were performed with concentrated sulfuric acid treatment, gel permeation chromatography, and sequential chromatography through silica gel, alumina, and activated carbon. For organochlorine pesticides and synthetic musks, purification included gel permeation and silica gel chromatography. To all final fractions an isotope-labeled recovery standard was added. All compounds were analyzed by gas chromatography coupled to electron ionization high-resolution mass spectrometry. The method is described in detail in the Supporting Information.

**Quality Assurance.** Very reliable dating based on the identification of annual sediment varves (6), high resolution of this recomposed sediment core, and large sample amount (20–30 g for each sample) provides a good basis for sound data interpretation. Analytical quality assurance included repeated analyses of blank samples, a check for recovery of internal standards, analysis of a deep sediment sample from preindustrial times as a procedural blank, and analysis of a spiked sediment sample from preindustrial times. The limit of detection (LOD) for each individual analyte was set equal to the maximum blank value or was based on a signal-to-noise ratio >3 in the reconstructed ion chromatogram, whichever was greater. Concentrations of the target compounds are generally higher than 10 times LOD. Only for some PCDD/F congeners, some dioxin-like PCB congeners, γ-HCH, HPEX, and some musk fragrances, sediment levels are below or close to the LOD in the least concentrated samples. These cases are mentioned separately in the discussion. The detailed quality assurance procedure and processing of nondetects are presented in the Supporting Information.

**Data Presentation.** In this publication, ΣPCDD/F refers to all 17 of the 2,3,7,8-chlorosubstituted PCDD/Fs. ΣPCB denotes the sum of the coplanar dioxin-like PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189 and the six indicator PCBs 28, 52, 101, 138, 153, and 180. ΣPCN denotes the sum of tetra-CN to octa-CN. ΣDDT denotes the sum of p,p’-DDT and o,p’-DDT and their main metabolites (p,p’-DDE, o,p’-DDE, p,p’-DDD, and o,p’-DDD). ΣMusks denotes the sum of nitro musks (musk ambrette, musk xylene, musk muskene, musk tibetene, and musk ketone) and polycyclic musks (crysolide ADH1, phantolide AHMI, fixolide AHTN, traseolide ATIL, and galaxolide HHCB). In one single sample from 1972, levels of ΣMusks were higher by a factor of 10 than in all other samples from the 1950s–1990s. Considering the relatively constant use of synthetic musks as fragrances throughout the second half of the 20th century (9, 10), this single outlier cannot be explained. Although in this sample all individual musks compounds had elevated concentrations and blank levels were always low, an analytical artifact cannot be ruled out. Therefore, this sample was omitted from our data set. Abbreviations, congener numbering, and calculation of toxic equivalents (TEQs) from concentrations of PCDD/Fs and coplanar dioxin-like PCBs are further described in the Supporting Information.

Our data are not blank corrected and are presented as fluxes into the sediment, which are more representative of the input into lakes than concentrations. Fluxes are obtained by combining the measured concentrations of the target analytes with the sedimentation rate of the corresponding sediment section. Concentrations of the target analytes in sediment from Lake Oberaar are provided in the Supporting Information.

**Results**

Fluxes into sediment from Lake Oberaar are presented in Figure 2; they reveal a consistent trend for all persistent organochlorines. Four episodes in their input fluxes into Lake Oberaar sediment can be distinguished.

**Low Fluxes in the 1950s.** Fluxes of compounds were low in the deepest sediment sample from the early 1950s. However, apart from γ-HCH and HPEX, the fluxes were already above LOD in the early 1950s.

**First Peak in the 1960s–1970s.** In the 1950s–1960s, fluxes rapidly increased to reach a peak in the 1960s–1970s for most target compounds. Only for ΣPCN, this first peak is less distinct, and ΣMusks have a constant flux throughout these decades. The highest fluxes determined for this period are 0.4, 25, 1.1, 13, 24, 0.6, 1.4, 0.2, and 56 µg/m²/y for ΣPCDD/F, ΣPCB, ΣPCN, ΣDDT, HCB, γ-HCH, Dieldrin, HPEX, and ΣMusks, respectively.

**Low Levels in the 1980s–1990s.** The declining input in the 1970s–1980s resulted in low fluxes in the 1980s–1990s, similar to fluxes in the 1950s. For HCB and γ-HCH, fluxes in the 1980s–1990s were low, but they did not decrease to the low-background levels from the 1950s. ΣMusks still had a constant input flux in this period.

**Second Peak Starting in the Late 1990s.** From the late 1990s until 2005, the fluxes of all compound classes clearly increased again. For ΣPCDD/F, ΣPCB, ΣDDT, and dieldrin fluxes steadily increase toward the upper sediment layer from 2005. For ΣPCN, HCB, γ-HCH, HPEX, and ΣMusks, fluxes are higher in the upper sediment sections than in the 1980s, although in 2005 they are leveling off or slightly decreasing. The highest fluxes determined in this period are 0.4, 25, 2.4, 65, 40, 2.1, 0.5, 0.1, and 172 µg/m²/y for ΣPCDD/F, ΣPCB, ΣPCN, ΣDDT, HCB, γ-HCH, dieldrin, HPEX, and ΣMusks, respectively. Throughout the time period covered, fluxes into the sediment of Lake Oberaar are highest for ΣMusks, followed by the organochlorine pesticides ΣDDT, HCB, γ-HCH, and by ΣPCB. ΣPCDD/F, ΣPCN, dieldrin, and HPEX have the lowest fluxes. For PCDD/Fs and PCBs, the fluxes converted into TEQ closely follow the trend of the concentration-based fluxes. TEQ-based fluxes also peaked in the 1960s–1970s, with a contribution from PCDD/Fs being one order of magnitude higher (23 ng WHO98 TEQ/m²/y) than that from PCBs (2.0 ng
WHO98 TEQ/m²/y). In the recent sediment layers, TEQ-based fluxes increase again for PCDD/Fs (14.3 ng WHO98 TEQ/m²/y) and PCBs (1.4 ng WHO98 TEQ/m²/y).

Discussion

Historical Peak of Persistent Organic Chemicals in the 1960s–1970s. The first culmination of organochlorine levels in Lake Oberaar sediment as well as the steady flux of synthetic musks is consistent with the known global production, usage, emission, and regulatory history of these compound classes.

PCDD/Fs. Unintended anthropogenic emissions of PCDD/Fs due to combustion or chemical processes involving organochlorine precursors considerably increased at the beginning of the 20th century in parallel to industrialization and reached high levels after World War II (5). Since the early 1980s, improved solid waste disposal technologies resulted in sharply decreasing emissions in Switzerland (8). Also on a continental scale, significantly decreasing emissions in Europe since the 1970s were reported (4).

PCBs and PCNs. PCNs were forerunners of PCBs, with similar applications and with production starting in the 1920s. Later, PCNs were progressively substituted by PCBs as dielectric fluids, plasticizers, and flame retardants (11). The global production of PCBs started in the 1930s and increased until the 1960s–1970s (3). PCBs were banned in Switzerland for open applications in 1972. In 1986, a complete ban for all applications was established for PCBs and PCNs (12).

Organochlorine Pesticides. Usage and associated emissions of the organochlorine pesticides analyzed in this study decreased in Europe and Switzerland during the last decades (4). DDT was the first organochlorine pesticide to be banned in Switzerland in 1972, while HCB, γ-HCH, chlordrin, and hexachlor (i.e., the precursor of HPEX) were banned in 1986 (12).

Synthetic Musk Fragrances. Synthetic musks, the less expensive substitutes of natural musk, are widely used fragrances for body care products and household detergents. Nitro musks, the first generation of synthetic musks, were introduced into the world market at the beginning of the 20th century and were followed by polycyclic musks after the 1950s (9). Since the late 1980s, total world production of synthetic musks has remained stable, though nitro musks have gradually been replaced by polycyclic musks (10). The peak of legacy organochlorines in Lake Oberaar in the 1960s–1970s provides further confidence in the applied age model of our recomposed sediment core because it is in line with previous studies reconstructing time trends of ΣPCDD/F, ΣPCB, and ΣDDT in low-altitude lakes in the region (Figure 3). Maximum PCDD/F levels in sediment in the 1960s–1970s have been reported for Lake Greifen (13) and Lake Constance (14), which are both located in highly urbanized areas in northern Switzerland (Figure 1). PCB levels in sediments peaked in the 1960s in Lake Greifen (13) as well as in peri-alpine Lake Thun (15), which is a low-altitude lake situated at a linear distance of only 45 km from Lake Oberaar (Figure 1). For DDT, maximum levels in sediment occurring already in the 1950s were observed in the low-altitude lakes in Switzerland (15, 16).

In Lake Greifen, maximum fluxes in the 1950s–1970s of ΣPCDD/F (2 μg/m²/y), ΣPCB (185 μg/m²/y), and ΣDDT (54 μg/m²/y) were up to 1 order of magnitude higher than in Lake Oberaar (0.4, 25.1, and 13 μg/m²/y for ΣPCDD/F, ΣPCB, ΣPCN, and ΣDDT, respectively). In Lake Thun, historical fluxes in three dated sediment cores of ΣPCB (6–34 μg/m²/y), ΣPCN (3–8 μg/m²/y), and ΣDDT (42 μg/m²/y) have been reported (15). Thus, fluxes of these chemicals into the sediment of the remote Lake Oberaar are lower than in the urban Lake Greifen but similar to those in

FIGURE 2. Input fluxes of (A) ΣPCDD/F, (B) ΣPCB, (C) ΣPCN, (D) ΣDDT, (E) HCB, (F) γ-HCH, (G) chlordrin, (H) HPEX, and (I) Musks from the high-Alpine Lake Oberaar into the lake sediment. Open circles indicate data points below LOD. LOD was converted into a flux on the basis of a typical sample amount and sedimentation flux. Error bars on the x-axis indicate the time span covered by the corresponding samples. For ΣMusks, the curve is interrupted where an outlier was removed.

FIGURE 3. Historical trends of (A) ΣPCDD/F, (B) ΣPCB, and (C) ΣDDT in sediment from Lake Oberaar and from low-altitude lakes in Switzerland. Input fluxes of ΣPCDD/F, ΣPCB, and ΣDDT in sediments from Lake Greifen and Lake Thun and concentrations of ΣPCDD/F in sediments from Lake Constance are from literature (references in the figure key). All trends are normalized relative to their maximum historical peaks.
the rural Lake Thun. This comparison shows that historical inputs in the 1950s–1970s into peri-Alpine Lake Thun and high-Alpine Lake Oberaar were similar, although the latter is located in a rather pristine environment.

The ubiquitous occurrence of organochlorines and synthetic musks in the Alpine environment was observed in a previous study about fish from mountain lakes in Switzerland (17). Concentrations of synthetic musks in fish from remote lakes were similar to or even higher than organochlorine pesticides. In Lake Oberaar, the sediment trend of synthetic musks shown in Figure 2 indicates a steady atmospheric deposition input from the 1950s until the late 1990s at a high level similar to that of ΣDDT and HCB. This uniform flux of synthetic musks into Lake Oberaar is consistent with their relatively constant production throughout the second half of the 20th century (9, 10).

**Melting Glaciers as a Relevant Source for Legacy Pollutants to Aquatic Ecosystems.** The increase of fluxes of persistent organic chemicals into the sediment of glacial-fed Lake Oberaar since the late 1990s is in strong contrast to the sediment record in low-altitude Lake Thun (15). In Lake Thun, the sediment record extended to 2004 and did not reveal any sign of a recent increase of legacy organochlorines (Figure 3). Considering emission, usage, and regulatory history of these legacy organochlorines in Switzerland (3, 4, 8, 12), a recent input of large amounts into high-Alpine lakes through direct atmospheric deposition is unlikely. Therefore, release of chemicals from melting glaciers is regarded as a possible source for this considerable recent increase of input of legacy pollutants into such glacial-fed lakes. According to this hypothesis, the glacier trapped and accumulated large amounts of atmospherically deposited pollutants in the 1950s–1970s and is now releasing these chemicals at historically high rates. Also, in contrast to low-altitude lakes, the rate of decline in input fluxes into Lake Oberaar slowed between the 1970s and the mid-1990s and fluxes achieved an almost constant level. This ongoing input of persistent organic chemicals, which is particularly observable for ΣPCDD/F (Figure 3), at a time when environmental emissions decreased (8) is another indication of substantial release from the glacier. Moreover, for all substances, without any exception, we observed a coherent trend in our sediment analysis.

Compared to the considerable increase of input fluxes into sediment during the past decade (Figure 2), the concurrent reduction in size of the Oberaar Glacier might appear to be relatively small (Figure 1). However, a large amount of melted ice is not a sufficient condition for an important release of pollutants from a glacier. Primarily, the pollutant load of the ice is responsible for increasing fluxes into a glacier-fed lake. Generally, glaciers undergo a flow of ice from their upper alitudinal zone to their lower part (18). This flow results in a delayed release of pollutants carried by the ice. Thus, a relatively small amount of ice, formed in a period when environmental pollution was high, can represent an important reservoir of contaminants and result in an important release when this ice melts. Conversely, a large amount of ice, originating from a period when environmental levels of pollutants were low, contains no or only small amounts of pollutants and does not represent an important reservoir of pollutants. In the case of Lake Oberaar, the observed sediment fluxes indicate that since the late 1990s the Oberaar Glacier has probably dispensed ice that was loaded with persistent organic chemicals.

The presumption of melting glaciers as a source of pollutants that had accumulated in the ice has already been expressed in earlier studies. Such investigations revealed higher concentrations of organochlorines in glacier meltwater than in nonglacial surface water, e.g., for PCBs and organochlorine pesticides in the Italian Alps (19, 20) and also for organochlorine pesticides in the Canadian Rockies (21). In another study, melting glaciers were considered as a possible reason for the observed increase in DDT concentrations in zebra mussels from the peri-Alpine Lakes Como and Iseo, Italy, by a factor of 150 between 2003 and 2005 (22). However, measurements of PCBs in the same samples did not support the DDT data. Furthermore, the considerable increase of DDT appeared in a surprisingly short period of time.

Analyses of ΣDDT (p,p′-DDT and p,p′-DDE) in penguins from Antarctica and comparison of observed levels to previous measurements revealed that currently penguins are exposed to old rather than new sources of ΣDDT (23). These observations were attributed to melting glaciers as a probable source of DDT to the Antarctic marine ecosystem. However, this study has been disputed because of limited data and the simplifying assumptions regarding glacier dynamics and the feeding areas of penguins (24, 25).

Melting glaciers have not only been considered as a possible source for organic compounds but also for inorganic species. In high-Alpine lakes in Austria, an 18-fold increase in electrical conductivity in water since the 1990s has been observed (26). As this finding could not be attributed to the geology of the catchment, solute release, including sulfate, calcium, and magnesium, from melting glaciers was mentioned as a possible explanation.

**Significance of the Glacier Hypothesis.** In contrast to the previous studies mentioned above (19, 20, 22, 23, 26), our investigation provides a unique opportunity to reconstruct the chronological sequence over a long period of time. The covered time span and use of identical analytical techniques for all samples enable us to directly compare historical levels of environmental contaminants to current levels.

For all compounds, except ΣDDT and γ-HCH, the current input flux is similar to the peak flux from the 1960s–1970s (Figure 2). For ΣDDT and γ-HCH, the current input even exceeds the past maximum flux by a factor of five and two, respectively. Accordingly, the current rate of release of legacy pollutants from the Oberaar Glacier is comparable to the former direct atmospheric input, when these compounds were still in use or before emission reduction measures were established. Table 1 shows the sediment burden of the measured compounds in Lake Oberaar for the periods 1953–1997, when the input is assumed to be mainly due to direct atmospheric input and glacier melting, and the period 1997–2005, when direct atmospheric deposition is decreasing and the input is suspected to be boosted by release of the pollutant inventory of the melting glacier.

### Table 1. Total Accumulation of Persistent Organic Chemicals in Sediment of Lake Oberaar

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<tr>
<td>ΣPCDD/F</td>
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<td>mg WHO98-TEQ</td>
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<td>g</td>
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<td>ΣPCN</td>
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<td>ΣDDT</td>
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<tr>
<td>γ-HCH</td>
<td>3660 mg</td>
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<td>1437 mg</td>
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*TEQ calculation procedure is described in the Supporting Information.
The burden of pollutants in Lake Oberaar sediment due to glacier melting is already in the same range as the earlier accumulation from direct atmospheric input. The undiminished increase of the fluxes of many organohalogens into the sediment of Lake Oberaar (Figure 2) does not yet prefigure an exhaust of the glacial inventory of these contaminants.

Alpine regions present some peculiarities that may become of concern. First, ice and snow melting in mountainous areas occurs in a relatively short period of time in late spring and early summer, possibly leading to short but intense pulses of pollutants to the surrounding environment. Second, some typical Alpine activities such as the use of glacier meltwater as drinking water in Alpine huts, irrigation facilities supplied by meltwater, artificial snow production with glacier meltwater, as well as fishing in mountain lakes may result in increased specific exposure of humans and wildlife to hazardous compounds.

At this stage, our study indicates that accelerated glacier melting due to global warming may also account for enhanced release of legacy organic pollutants at historically high levels. Since 1999, the 1500 glaciers in the Swiss Alps have shrunk by 12% (27). A more comprehensive and quantitative evaluation of the relevance of melting glaciers as a secondary source of organohalogens requires, however, additional consideration of glacier dynamics. The recent accelerated mass loss of Alpine glaciers leads to enhanced release of chemical species from surfacial ice layers, which would have been retained much longer in the glacier under stationary climate conditions. The coupling of glacier dynamics and pollutant cycling is a complex topic (23–25) and represents a poorly studied research field. Ongoing work in this field may provide additional insight into the fate of persistent organic pollutants in the Alpine environment.

Acknowledgments
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Supporting Information Available
Sediment dating procedure, analytical methods, quality assurance issues, abbreviations, TEQ calculations, and congener numbering. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

Blast from the past: Melting glaciers as a relevant source for persistent organic pollutants

Christian Bogdal\textsuperscript{1,2,*}, Peter Schmid\textsuperscript{2}, Markus Zennegg\textsuperscript{2}, Flavio S. Anselmetti\textsuperscript{3},
Martin Scheringer\textsuperscript{1}, Konrad Hungerbühler\textsuperscript{1}

\textsuperscript{*} Corresponding author, phone: +41 44 632 5951, email: christian.bogdal@chem.ethz.ch

\textsuperscript{1} Institute for Chemical and Bioengineering, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland

\textsuperscript{2} Empa, Swiss Federal Laboratories for Materials Testing and Research, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

\textsuperscript{3} Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, CH-8600 Dübendorf, Switzerland

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S2
Sediment Dating

Two sediment cores (OAR06-1 and OAR06-2) from Lake Oberaar were retrieved at the same site, using a percussion-piston corer. Prior to our study, half of sediment material from Lake Oberaar was analyzed in a previous study to investigate the effects of Alpine hydropower dams on particle transport and lacustrine sedimentation [1]. The second half of the sediment material was used in our study. The correlation and combination of both cores defined a complete mastersection providing sediment material covering the entire period from 1953 to 2006 [1]. The cores showed 53 clearly visible proglacial layers (‘varves’), e.g. an regular intercalation of dark winter layer consisting of the finest grain size, with light-colored coarser multi-graded layers that reflect a succession of strong runoff events during summer and fall months (Figure S1). The abrupt downcore change into gravel-rich layers representing the former proglacial river plain correspond to the year 1953, when the hydropower dam was constructed and the plain became flooded. The identification of these varves and the recognition of the 1953-layer enabled a very accurate and reliable age model of the master sediment section. Figure S1a shows the annual varves of the two corresponding sediment cores. Figure S1b shows an enlarged view of one section of the yearly varves in one Lake Oberaar sediment core. Due to the percussion-piston coring method, the originally horizontal varves became curved during sampling.
**Figure S1.** (A) Picture of Lake Oberaar sediment cores (OAR06-1 and OAR06-2) with varved lithology (annual layers) providing the age model employed in this study. Dark layers, which are indicated by the arrows, contain finest grain size and represent sedimentation under the frozen lake surface during winter. The yellow rectangles mark the sections of each sediment core that were sampled; (B) enlarged view of the section 28-43 cm from sediment core OAR06-1 covering the period 1990-1982.
Sediment preparation

After dating, the sediment core was divided in intervals representing 2-5 years of sediment deposition. Wet sediment was filled in pre-heated and pre-rinsed glass jars. Sediment was further freeze-dried, pestled, homogenized, and stored in the dark prior to analysis.

Sediment analysis

Reference materials and chemicals

$^{13}$C$_{12}$-labeled PCDD/Fs (all 17 2,3,7,8-chlorosubstituted PCDD/Fs), $^{13}$C$_{12}$-labeled 1,2,7,8-TCDF, $^{13}$C$_{12}$-labeled PCBs (dioxin-like congeners 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189, and the six indicator congeners 28, 52, 101, 138, 153, 180), $^{13}$C$_{12}$-labeled PCB-70, $^{13}$C$_{12}$-labeled PCNs (congeners CN-27, 42, 52, 67, 73, and 75), $^{13}$C$_{12}$-labeled p,p’-DDE, $^{13}$C$_{6}$-labeled γ-HCH, and $^{13}$C$_{12}$-labeled Dieldrin were purchased from Cambridge Isotope Laboratories, Andover, MA, USA. $^{13}$C$_{12}$-labeled p,p’-DDT and $^{13}$C$_{6}$-labeled HCB and $^2$H$_3$-AHTN (Fixolide) was purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. $^{15}$N$_3$-musk xylene was synthesized in our laboratories. Reference DDD, DDE, and DDT (o,p’-DDD, p,p’-DDD, o,p’-DDE, p,p’-DDE) were purchased from National Institute of Standards and Technology, Gaithersburg, MD, USA. Native HPEX (heptachloro-exo-epoxide isomer B 98.9 %, Pestanal) was purchased from Riedel-de Haën. Native nitro musks (musk ambrette, xylene, moskene, tibeten, and ketone were generously given by Givaudan Roure) and polycyclic musks (Crysolide ADBI, Phantolide AHMI, Fixolide AHTN, Traseolide ATII, and Galaxolide HHCB) were obtained from LGC Promochem GmbH. All solvents that were employed were of pesticide grade.
for residue analysis. Sodium sulfate, silica gel, alumina, and activated carbon were of high purity and baked out overnight prior to use.

**Glassware preparation**

All glassware was washed in a glassware washer and immersed in a detergent bath for 12 hours. Then glassware was heated to 450°C overnight. Prior to use, all glassware was rinsed twice with acetone and once more with n-hexane.

**Extraction**

Sediment samples (20-30g) were Soxhlet extracted for 24 hours using acetone/n-hexane (1:1 v/v).

**Extract treatment**

Extracts were adjusted to a fixed volume and aliquots were used for the further analysis. A first aliquot was used for the analysis of PCDD/Fs, PCBs, and PCNs, while a second aliquot was used for the analysis of organochlorine pesticides and synthetic musk fragrances.

**Analysis of PCDD/Fs, PCBs, and PCNs**

The aliquot was spiked with internal standards (\(^{13}\)C\(_{12}\)-labeled PCDD/Fs, \(^{13}\)C\(_{12}\)-labeled PCBs, and \(^{13}\)C\(_{12}\)-labeled PCNs) and first treated with concentrated sulfuric acid, followed by cleanup with gel permeation chromatography to remove elemental sulfur. Subsequently, column
chromatography was performed. A silica gel column (10% water deactivated and 40% sulphuric acid silica from top to bottom) was eluted with \( n \)-hexane (fraction F1) and 50% dichloromethane in \( n \)-hexane (fraction F2 preserved for other analytes not presented here). The F1 \( n \)-hexane eluate was further passed through a basic alumina column eluted with 4% dichloromethane in \( n \)-hexane (F3 containing mono-\textit{ortho}-PCBs, di-\textit{ortho}-PCB and part of the tetra-CN) and 50% dichloromethane in \( n \)-hexane that was further passed through an activated carbon column eluted with 50% dichloromethane in \( n \)-hexane (F4 preserved for other analytes not presented here) and backflushed with toluene (F5 containing non-\textit{ortho}-PCBs, PCNs and PCDD/Fs). The four fractions were reduced in volume and transferred to gas chromatography vials containing a suitable recovery standard (\( ^{13} \text{C}_{12} \)-labeled PCB-70 for F3 and F5 and \( ^{13} \text{C}_{12} \)-labeled 1,2,7,8-TCDF for F5).

\textbf{Analysis of organochlorine pesticides and synthetic musk fragrances}

The aliquot was spiked with internal standards (\( ^{13} \text{C}_{12} \)-labeled \( p,p' \)-DDT, \( ^{13} \text{C}_{12} \)-labeled \( p,p' \)-DDE, \( ^{13} \text{C}_{6} \)-labeled HCB, \( ^{13} \text{C}_{6} \)-labeled \( \gamma \)-HCH, \( ^{13} \text{C}_{12} \)-labeled Dieldrin, \( ^{15} \text{N}_{3} \)-musk xylene, and \( ^{2} \text{H}_{26} \)-AHTN) and first cleaned up with gel permeation chromatography. Subsequently, a silica gel column (10% water deactivated) eluted with \( n \)-hexane was used. The eluate was reduced in volume and transferred to gas chromatography vials containing a suitable recovery standard (\( ^{13} \text{C}_{12} \)-labeled PCB-70).
Detection and quantification

All compounds were analyzed by gas chromatography coupled to electron ionization high resolution mass spectrometry (GC/EI HRMS). GC/EI HRMS analysis was carried out on a MAT 95 high resolution mass spectrometer (Thermo Finnigan MAT, Bremen, Germany) coupled to a gas chromatograph HRGC Mega 2 series (Fisons Instruments, Rodano, Italy) equipped with an A200S auto sampler (CTC Analytics, Zwingen, Switzerland).

Samples were injected in splitless mode (split valve closed for 20 s) at an injector temperature of 260°C. For GC separation, a self manufactured glass capillary column (20 m × 0.28 mm) coated with a DB-5 analogue stationary phase (PS 086, Fluka, Buchs, Switzerland) with a film thickness of 0.15 µm was used with H₂ at constant pressure as carrier gas (40 kPa for PCDD/Fs, organochlorine pesticides, and synthetic musks; 50 kPa for PCBs and PCNs). The temperature program started at 110°C, held for 1 min, increased to 240°C at 20°C/min, then increased to 280°C at 5°C/min and held for 5 min for PCDD/Fs. It started at 110°C, held for 1 min, increased to 150°C at 20°C/min, then increased to 285°C at 5°C/min and held for 5 min for PCBs and PCNs. It started at 110°C, held for 1 min, increased to 150°C at 20°C/min, then increased to 220°C at 4°C/min, then increased to 260°C at 20°C/min, and held for 5 min for organochlorine pesticides and synthetic musks.

The ion source was operated at 180°C, the electron energy was 70 eV, and the mass spectrometer was tuned to a mass resolution of 10,000. For all compounds, the two most abundant signals of the molecular or fragment ion clusters were recorded (M⁺ for PCDD/Fs, PCBs, PCNs, DDE, HCB, and nitro musks; [M-CCl₃]⁺ and [M-CHCl₂]⁺ for DDT and DDE; [M-Cl]⁺ for HCH, Dieldrin, and HPEX; [M-CH₃]⁺ for polycyclic musks ADBI, AHMI, AHTN, and HHCB; [M-C₃H₇]⁺ for ATII).
For PCDD/Fs, PCBs, HCB, γ-HCH, and Dieldrin for each individual congener or compound, an isotope labeled standard was available for quantification. For PCNs, one or two isotope labeled congeners for each homologue group were available (CN-27 and 42 for tetra-CN, CN-52 for penta-CN, CN-67 for hexa-CN, CN-73 for hepta-CN, and CN-75 for octa-CN). The response of all congeners within a homologue group was assumed identical to the available labeled internal standard. For DDT, the response between all the DDT isomers ((o,p’-DDT, p,p’-DDT, o,p’-DDD, p,p’-DDE, o,p’-DDE, and DDMU) and the labeled internal standards (\(^{13}\)C\(_{12}\)-labeled p,p’-DDT and \(^{13}\)C\(_{12}\)-labeled p,p’-DDE) was determined by the analysis of native DDT isomers and these internal standards. The same was done between native HPEX and \(^{13}\)C\(_{12}\)-labeled Dieldrin; and between native synthetic musks and the labeled internal standards (\(^{15}\)N\(_{3}\)-musk xylene and \(^2\)H\(_3\)-AHTN). With the use of isotope labeled internal standards added to the samples prior to extraction, all presented data are directly corrected for recovery.

**Quality assurance**

The limit of detection (LOD) for each individual analyte was set equal to the maximum blank value or it was based on a signal-to-noise ratio \(>3\) in the reconstructed ion chromatogram, whichever was greater. Analytes with a concentration below LOD were neither excluded nor substituted by a fraction of the LOD, to avoid an artificial fabrication of data. Nondetects were therefore included in the calculation of the sum of a compound class.

With each batch of 5 sediment samples, a blank was simultaneously analyzed. The blank consisted of empty Soxhlet thimbles extracted together with sediment samples and further treated identically to field samples. Detected amounts of Σ PCDD/F, Σ PCB, Σ PCN, Σ DDT, and Σ Musks were 30, 600, 120, 120, and 6000 pg respectively. Based on a typical sample amount and
a typical sediment flux, these blank levels correspond to fluxes of approximately 0.01, 0.3, 0.04, 
0.04, and 2 μg/m²/y, for Σ PCDD/F, Σ PCB, Σ PCN, Σ DDT, and Σ Musks, respectively. For 
HCB, γ-HCH, Dieldrin, and HPEX, the signals of blank samples were below three fold noise 
signals.

Recovery of isotope labeled internal standards was 48%-92%, 60%-105%, 40%-85%, 52%- 
105%, 30%-65%, 35%-58%, 75%-98%, and 45%-62%, for PCDD/Fs, PCBs, PCNs, DDT/DDD, 
HCB, γ-HCH, Dieldrin, and musk xylene/AHTN, respectively.

A deep sediment sample from another high-Alpine lake (Lake Tscheppa, Switzerland) 
corresponding to pre-1900 time was analyzed for PCDD/Fs, PCBs, and PCNs. The detected 
amounts of these analytes were below LOD.

A deep sediment sample from another high-Alpine lake (Lake Tscheppa, Switzerland) 
corresponding to pre-1900 time was spiked with 400 pg of native of Σ PCDD/F and 5000 pg of 
native Σ PCB. The analysis of this sample revealed a recovery of these native analytes of 85%- 
109% and 88%-115%, for Σ PCDD/F and Σ PCB, respectively.
Sediment Concentrations

![Graphs showing concentrations of various compounds over time](image)

**Figure S2.** Concentrations of (A) ΣPCDD/F, (B) ΣPCB, (C) ΣPCN, (D) ΣDDT, (E) HCB, (F) γ-HCH, (G) dieldrin, (H) HPEX, and (I) Σmusks in sediment from the high-Alpine Lake Oberaar. Concentrations are given in pg analyte per g dry weight (dw) of sediment. For Σmusks the curve is interrupted where an outlier was removed.
Abbreviations, congener numbering, and TEQ calculations

List of abbreviations

ADBI  Acetyldimethyl-\textit{tert}-butylindan (Crysolide)
AHMI  Acetyl-hexamethylindan (Phantolide)
AHTN  Acetyl-hexamethytetralin (Fixolide)
ATII  Acetyl-tetramethyl-isopropyl-dihydroindene (Traseolide)
DDD   dichlorodiphenyl dichloroethane
DDE   dichlorodiphenyl dichloroethene
DDT   dichlorodiphenyl trichloroethane
EI    electron ionization
GC    gas chromatography
HCB   hexachlorobenzene
HCH   hexachlorocyclohexane
HHCB  Hexahydro-hexamethycyclopenta-benzopyran (Galaxolide)
HPEX  Heptachlor epoxide
HRMS  high resolution mass spectrometry
LOD   limit of detection
musk ambrette 4-\textit{tert}-butyl-2,6-dinitro-3-methoxytoluene
musk keton 4-\textit{tert}-butyl-2,6-dimethyl-3,5-dinitroacetophenone
musk tibeten 5-\textit{tert}-butyl-1,2,3-trimethyl-4,6-dinitrobenzene
musk xylene 1-\textit{tert}-butyl-3,5-dimethyl-2,4,6-trinitrobenzene
PCBs   polychlorinated biphenyls
PCDD/Fs polychlorinated dibenzo-\textit{p}-dioxins and dibenzofuranes
PCNs   polychlorinated naphthalenes
POPs   persistent organic pollutants
TCDF  tetrachloro dibenzofurane
TEF    toxic equivalent factor
TEQ    toxic equivalent
**TEQ calculations**

WHO98-TEQ designates TEQ based on the TEFs for PCDD/Fs and PCBs published by the World Health Organization (WHO) in 1998 [2].

I-TEQ designates TEQ based on the TEFs for PCDD/Fs published the North Atlantic Treaty Organization (NATO) in 1990 [3].

**Congener numbering**

PCB congeners were numbered according to Ballschmiter and Zell [4]. PCN congeners were numbered according to Wiedemann and Ballschmiter [5].
References


