

Supporting Information

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

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

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

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

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

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

Contents

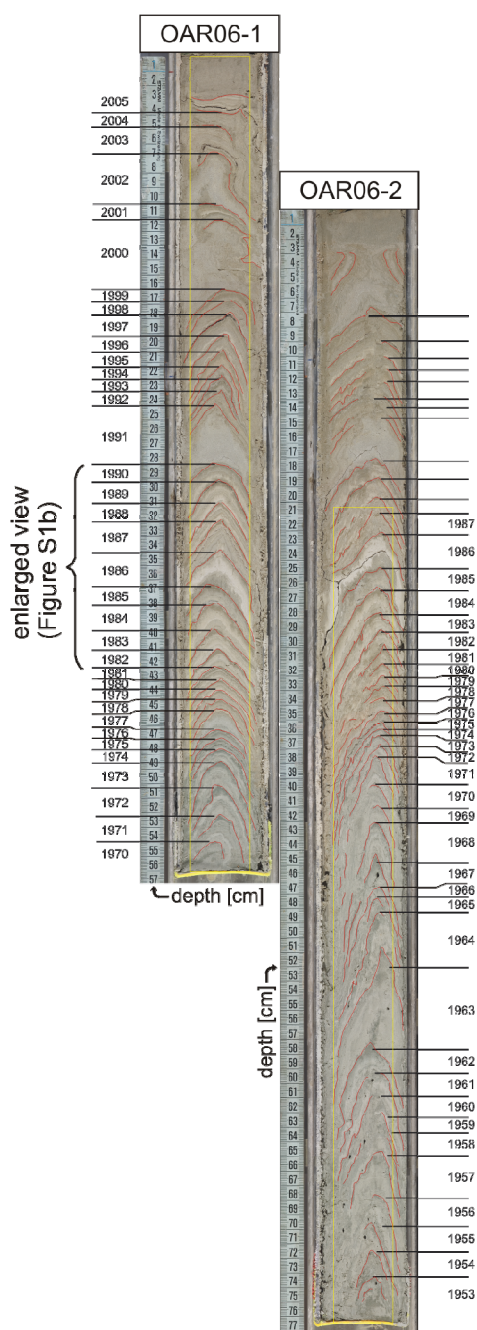
Text, Figure S1	Sediment Dating	Pages S3-S4
Text	Sediment Preparation	Page S5
Text	Sediment Analysis	Pages S5-S9
Text	Sediment Analysis	Pages S9-S10
Figure S2	Sediment Concentrations	Page S11
Text	Abbreviations, congener numbering, and TEQ calculations	Pages S12-S13
Text	References	Page S14

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.

(a)

varved lithology of sediment cores
(OAR06-1 and OAR06-2) from Lake Oberaar



(b)

enlarged view of varved lithology of 28-43 cm section of
sediment core OAR06-1 from Lake Oberaar

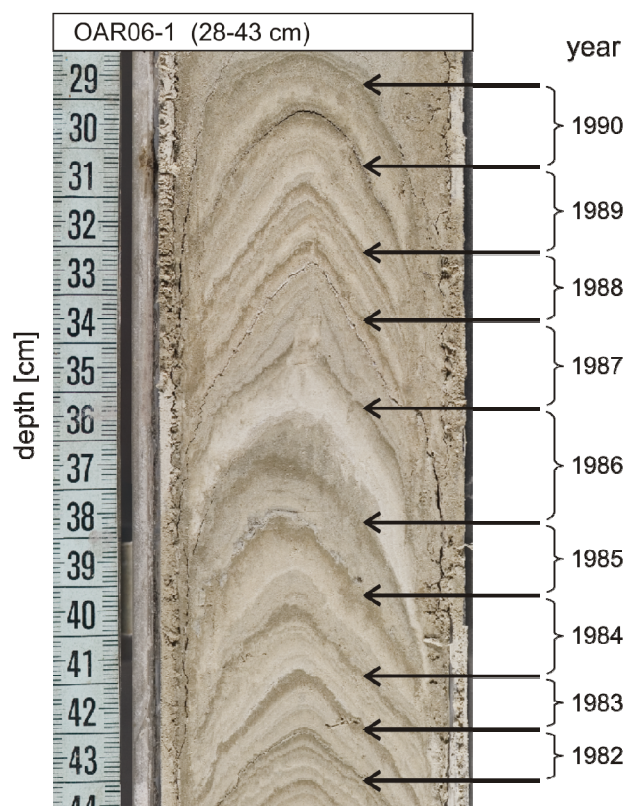


Figure S1. (A) Picture of Lake Oberaar sediment cores (OAR06-1 and OAR06-2) with varved lithology (annual layers) providing the age model employed in this study. Dark layers, which are indicated by the arrows, contain finest grain size and represent sedimentation under the frozen lake surface during 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

$^{13}\text{C}_{12}$ -labeled PCDD/Fs (all 17 2,3,7,8-chlorosubstituted PCDD/Fs), $^{13}\text{C}_{12}$ -labeled 1,2,7,8-TCDF, $^{13}\text{C}_{12}$ -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), $^{13}\text{C}_{12}$ -labeled PCB-70, $^{13}\text{C}_{12}$ -labeled PCNs (congeners CN-27, 42, 52, 67, 73, and 75), $^{13}\text{C}_{12}$ -labeled p,p'-DDE, $^{13}\text{C}_6$ -labeled γ -HCH, and $^{13}\text{C}_{12}$ -labeled Dieldrin were purchased from Cambridge Isotope Laboratories, Andover, MA, USA. $^{13}\text{C}_{12}$ -labeled p,p'-DDT and $^{13}\text{C}_6$ -labeled HCB and $^2\text{H}_3$ -AHTN (Fixolide) was purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany. $^{15}\text{N}_3$ -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 (¹³C₁₂-labeled PCDD/Fs, ¹³C₁₂-labeled PCBs, and ¹³C₁₂-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-*ortho*-PCBs, di-*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-*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).

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 γ -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; $[M-CCl_3]^+$ and $[M-CHCl_2]^+$ for DDT and DDE; $[M-Cl]^+$ for HCH, Dieldrin, and HPEX; $[M-CH_3]^+$ for polycyclic musks ADBI, AHMI, AHTN, and HHCB; $[M-C_3H_7]^+$ 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'-DDD, o,p'-DDE, p,p'-DDE, and DDMU) and the labeled internal standards ($^{13}\text{C}_{12}$ -labeled p,p'-DDT and $^{13}\text{C}_{12}$ -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 $^{13}\text{C}_{12}$ -labeled Dieldrin; and between native synthetic musks and the labeled internal standards ($^{15}\text{N}_3$ -musk xylene and $^2\text{H}_3$ -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 $\mu\text{g}/\text{m}^2/\text{y}$, 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

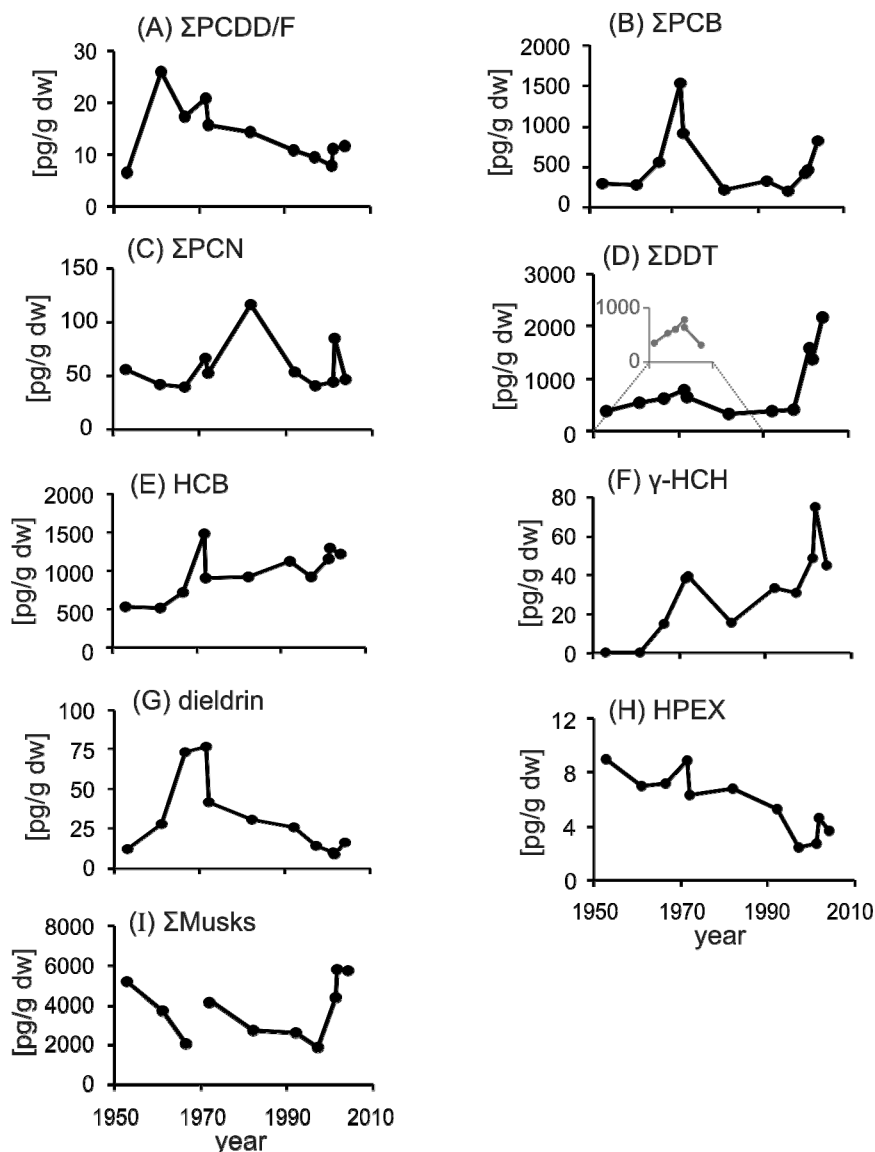


Figure S2. Concentrations of (A) Σ PCDD/F, (B) Σ PCB, (C) Σ PCN, (D) Σ DDT, (E) HCB, (F) γ -HCH, (G) dieldrin, (H) HPEX, and (I) Σ musks in sediment from the high-Alpine Lake Oberaar. Concentrations are given in pg analyte per g dry weight (dw) of sediment. For Σ Musks the curve is interrupted where an outlier was removed.

Abbreviations, congener numbering, and TEQ calculations

List of abbreviations

ADBI	Acetyldimethyl- <i>tert</i> -butylindan (Crysolide)
AHMI	Acetyl-hexamethylindan (Phantolide)
AHTN	Acetyl-hexamethyltetralin (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-hexamethylcyclopenta-benzopyran (Galaxolide)
HPEX	Heptachlor epoxide
HRMS	high resolution mass spectrometry
LOD	limit of detection
musk ambrette	4- <i>tert</i> -butyl-2,6-dinitro-3-methoxytoluene
musk keton	4- <i>tert</i> -butyl-2,6-dimethyl-3,5-dinitroacetophenone
musk tibeten	5- <i>tert</i> -butyl-1,2,3-trimethyl-4,6-dinitrobenzene
musk xylene	1- <i>tert</i> -butyl-3,5-dimethyl-2,4,6-trinitrobenzene
PCBs	polychlorinated biphenyls
PCDD/Fs	polychlorinated dibenzo- <i>p</i> -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

1. Anselmetti, F. S.; Bühler, R.; Finger, D.; Girardclos, S.; Lancini, A.; Rellstab, C.; Sturm, M., Effects of Alpine hydropower dams on particle transport and lacustrine sedimentation. *Aquat. Sci.* **2007**, *69*, 179-198.
2. van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X. R.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T., Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998**, *106*, 775-792.
3. Kutz, F. W.; Barnes, D. G.; Bottimore, D. P.; Greim, H.; Bretthauer, E. W., The international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. *Chemosphere* **1990**, *20*, 751-757.
4. Ballschmiter, K.; Zell, M., Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius. J. Anal. Chem.* **1980**, *302*, 20-31.
5. Wiedemann, T.; Ballschmiter, K., Quantification of chlorinated naphthalenes with GC-MS using the molar response of electron impact ionization. *Fresenius. J. Anal. Chem.* **1993**, *1*, 800-804.