

Contrasting temporal trends and relationships of total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in rural low-altitude and remote high-altitude lakes†

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Historical records of total organic carbon (TOC), black carbon (BC), and polycyclic aromatic hydrocarbons (PAHs) were reconstructed in dated sediment cores from four nearby lakes in central Switzerland. In the sub-Alpine Lake Thun, located at 558 m a.s.l., the proximity to anthropogenic emission sources is reflected in higher input of BC and PAHs into sediments with fluxes only slightly decreasing during the last decades. PAH/BC ratios are relatively high and correlation between levels of total PAHs and BC is almost inexistent in Lake Thun, probably due to the presence of less condensed forms of the BC spectrum (char BC) that is underestimated with the chemothermal oxidation method applied in this study. The sediment profiles of TOC, BC, and PAHs are noticeably different in the mountain lakes located around 2000 m a.s.l. In Lake Engstlen, the PAH/BC ratios, as well as the correlation between PAHs and BC, point towards appreciable amounts of predominantly light soot particles. Light soot particles have higher mobility and can, therefore, be efficiently transported to this remote site. The proglacial Lake Oberaar is shown to be a receptor of BC and PAHs released by the fast melting adjacent glacier acting as a secondary source for these conservative species temporarily stored in the glacier ice. Finally, Lake Stein is in strong contrast to all other lakes. High flux of BC into Lake Stein, combined with constant temporal evolutions of BC and PAHs, and in particular BC/TOC ratios approaching 100% are all strong indications for a geogenic presence of graphite in its catchment area.

Introduction

Anthropogenic activities involving fossil fuel and biomass burning, together with natural forest fires, lead to the unintentional formation of carbonaceous particles collectively termed black carbon (BC) and pollutants such as polycyclic aromatic hydrocarbons (PAHs). BC particles have a three-dimensional structure, are composed of stacked sheets, and are in the nm to μm range.¹ As a result of its emission by incomplete combustion, BC is ubiquitous in soils and sediments.^{2,3} It accounts for 9% (median of about 300 worldwide samples) and 4% (median of 90 samples) of the total organic carbon (TOC) in sediments and soils, respectively.⁴ PAHs consist of two or more fused aromatic rings, have a planar structure, and pose significant

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Environmental impact

This study reports on temporal trends of organic carbon, black carbon, and polycyclic aromatic hydrocarbons in sediment from four close-by lakes in Switzerland. The investigated lakes include a sub-Alpine lake located in a rural area and three high-altitude lakes located in remote background regions. The presented dataset provides an improved comprehension about the sources and the environmental fate of combustion-derived anthropogenic air pollutants, as well as the interaction between these species.

environmental and health concerns as some of them are carcinogens and mutagens.⁵ PAHs and BC are also linked by the considerably increased sorption of PAHs to BC as compared to bulk organic matter, thus having implications for the bioavailability and toxicity of PAHs.^{4,6,7}

To track temporal trends of environmental pollution by conservative species, such as BC and PAHs, dated sediment cores with discrete layers have successfully been employed.^{8–18} Reconstructing historical profiles of pollutants in dated sediment cores enable to evaluate the effectiveness of reduction efforts and regulatory actions initiated to decrease environmental contamination by hazardous pollutants. Thus, the significant reduction of environmental contamination by persistent organic pollutants in Europe, North America, and Japan has been documented in analyses of sediment cores.^{8,16–18} Sediment cores are also valuable archives supporting investigations of processes governing the environmental fate of pollutants. Recently, it has been shown that melting Alpine glaciers that incorporate various aerosols such as BC^{19,20} also represent a secondary source of persistent organic pollutants that were previously deposited on glaciers and are now released back to the environment due to the accelerated melting of glaciers induced by global warming.^{9,14} This process has been verified in proglacial lakes fed by glacial meltwater in the Swiss Alps for persistent halogenated chemicals, but not for BC or PAHs.

In lake sediments, TOC is often considered as a non-specific indicator of the primary productivity of the overlying water column. Thus, TOC allows quantification of the trophic status of aquatic ecosystems.^{21,22} While technical improvements aiming at limitation of nutrient release and reduction of environmental emissions of combustion-derived pollutants have been made, regulatory actions have also been taken. PAHs are included in the United Nations Economic Commission for Europe (UNECE) protocol on persistent organic pollutants. Recently, the European Union (EU) set a threshold value for ambient air concentrations of benzo[*a*]pyrene (BaP), representing the most potent carcinogenic PAH.

Here we present a comprehensive analysis of historical evolutions of TOC, BC, and PAHs in sub-Alpine and high-Alpine lakes. Remote high-altitude sites embody particularly sensitive ecosystems. We analyzed three sediment cores from Lake Thun (denoted thereafter: TH), Switzerland, representing a rural lake located at low altitude. Additionally we analyzed sediment cores from a high-Alpine lake (Lake Engstlen: ENG) and proglacial lakes (Lake Oberaar: OAR and Lake Stein: ST). All these remote lakes are located in central Switzerland very close to each other in the same catchment.

Materials and methods

Study sites

Lake Thun (TH) is a sub-Alpine lake located at 558 m a.s.l. in the Bernese Oberland. The lake's vicinity includes urbanized areas in the east (city of Interlaken) and west (city of Thun) with mainly private residential occupation. Industry located in the area includes mainly small to medium size commerce. Thus, ongoing anthropogenic activities in the Lake Thun region are potential diffuse sources of environmental contaminants. Three

sediment cores from three different sampling sites from TH (TH1, TH2, TH3, see Fig. 1) were analyzed, covering the whole 20th century.

Lake Engstlen (ENG) is a high-Alpine lake located at 1850 m a.s.l. in the Bernese Oberland. Its catchment area is mostly composed of limestones with a few sandstones that are partially covered by Quaternary deposits, pasture, forest, and to a small extent glacier. The catchment area of ENG is comparatively well covered by vegetation. In the region only a few touristic accommodation facilities are potential sources of environmental contaminants, such as recreational fireplaces and wood stoves by one nearby hotel open in winter and summer during the touristic season. ENG is exempt from waste water input. A sediment core including sediment from 1963 to 2008 was analyzed.

Lake Oberaar (OAR) and Lake Stein (ST) are proglacial lakes, *i.e.* formed by natural or artificial damming after the retreat of a melting glacier, located in the Bernese Oberland at 2303 m a.s.l. and 1930 m a.s.l., respectively. Their catchment areas are mainly composed of crystalline rocks covered to a large degree by glaciers and also by moraines, as well as some soil with fairly low organic matter content. Anthropogenic activities in the vicinity include hiking trails and military exercises, which are potential sources of contaminants. The sediment cores from OAR and ST cover the periods 1956–2004 and 1961–2006, respectively.

Sediment sampling, dating, and preparation

Sediment cores from TH were sampled in the inlet (TH1: 46°40'N, 7°49'E, 60 m depth), middle (TH2: 46°40'N, 7°44'E, 217 m depth) and outlet areas (TH3: 46°44'N, 7°38'E, 18 m depth) of the lake. Sediment cores from ENG (46°46'N, 8°21'E, 49 m depth) and ST (46°43'N, 8°26'E, 20 m depth) were sampled in the deep basin floor of the lakes. In OAR a sediment core was sampled at intermediate depth (46°33'N, 8°16'E, *ca.* 10 m depth). These sediment cores were all analyzed in previous studies, where the sampling and dating procedures were described in detail.^{8,9,14} Briefly, sediment cores were sampled in 2005 (TH), 2009 (ENG), 2006 (OAR), and 2009 (ST) using gravity corers (TH, ENG) or percussion-piston corers (OAR, ST). After sampling, the sediment cores were opened lengthwise and photographed. Cores from TH and ENG were dated by ¹³⁷Cs measurements enabling the identification of the peaks of 1963 (atmospheric nuclear bomb testing) and 1986 (Chernobyl accident) fallouts. Dating of cores from OAR and ST was performed by counting annual sediment layers (varves) and verified by ¹³⁷Cs measurements. After dating, the sediment cores were divided into individual samples that were freeze-dried, pestled, homogenized, and stored in the dark prior to analysis.

The temporal resolution of sediment cores was adapted to the available sediment material due to the different sedimentation rates in the investigated lakes (Table 1). The cores were divided into samples of intervals of 1–3, 2–7, 2–5, and 1–2 years for TH, ENG, OAR, and ST, respectively. The possible dating error of individual sediment samples is expected to lie within ±5 years in TH and ENG.^{8,14} The very clear identification of individual sediment varves in OAR and ST enables to exclude a dating error.^{9,14}

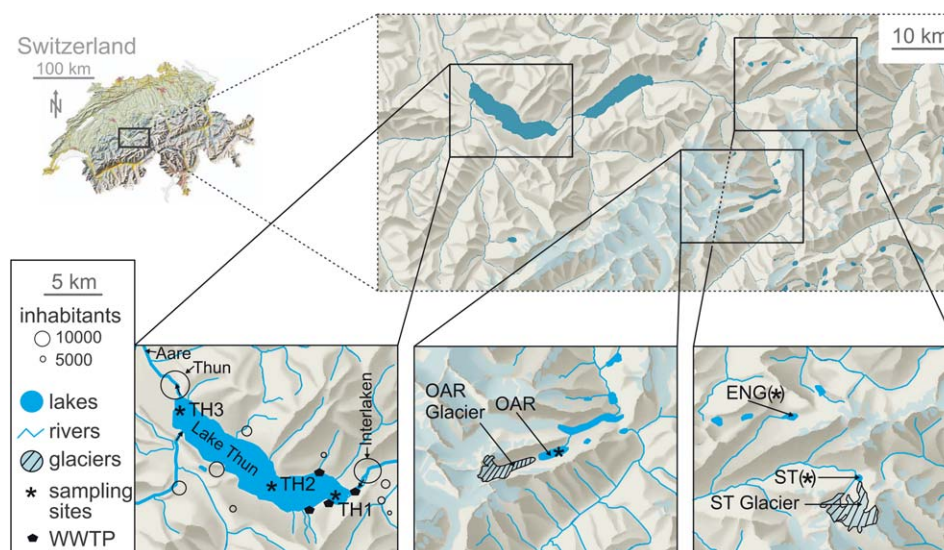


Fig. 1 Map of Switzerland and enlargement of the regions of the study sites considered in this study, including the catchment areas of Lake Thun (TH), Lake Oberaar (OAR), Lake Engstlen (ENG), and Lake Stein (ST). WWTP indicates locations of waste water treatment plants.

Analysis of TOC and BC

The analysis protocol followed previous work,^{23,24} with some slight modifications. The method used to determine BC content in sediments is commonly referred to as the chemothermal oxidation method at 375 °C (CTO-375).²⁴ Briefly, 10–20 mg of sediment were weighed in Ag-capsules and placed in a tube furnace, in which the samples were combusted for 24 h under a continuous airflow. The temperature was programmed to

increase with 10 °C min⁻¹ to 350 °C, then with 1 °C min⁻¹ to 375 °C to avoid temperature overshoot.²³ Every third series of analysis, the furnace was heated to 600 °C overnight, to avoid memory and cross-contamination effects. Carbonates were removed by fumigation using fuming concentrated HCl (37%) in an excicator²⁵ and treated with 50 µL of deionized water to remove remaining HCl. The samples were then dried in a sand bath at 105 °C before elemental analysis. The carbon content in

Table 1 Major characteristics of the lakes investigated in this study

	Lake Thun (TH)	Lake Engstlen (ENG)	Lake Oberaar (OAR)	Lake Stein (ST)
Altitude/m a.s.l.	558	1850	2303	1930
Surface area/km ²	47.7	0.46	1.46	0.11
Max. depth/m	219	49	90	20
Typical sedimentation rate at coring sites/cm a ⁻¹	0.4	0.2	1.7	2.5
Catchment area/km ²	2451	7.8	19.4	8.5
Max. catchment altitude/m a.s.l.	4272	3034	3631	3600
Trophic status	Oligo-mesotrophic	Oligo-mesotrophic	Oligotrophic	Oligotrophic
Lake formation	Natural lake formed after last ice age	Natural lake formed after last ice age	Artificial proglacial reservoir lake dammed in 1953	Natural proglacial moraine-dammed lake formed in the 1940s
Precipitation rate/mm a ⁻¹	1281 (site: Hondrich), 1174 (site: Interlaken)	1604 (site: Gadmen)	2094 (site: Grimsel Hospiz)	1604 (site: Gadmen)
Catchment geology	Limestones, marls, sandstones, crystalline silicate rocks	2/3 limestone, 1/3 sandstone	Crystalline silicate rocks	Crystalline silicate rocks
Catchment coverage	Rocks, Quaternary deposits, glaciers, pasture, agriculture, forest, and urban area (95 000 inhabitants in the catchment). TH is downstream of Lake Brienz. Lake Brienz is downstream of Lake Grimsel, which is downstream of OAR.	Rocks, Quaternary deposits, pasture, forest, and to a small extent glacier	Rocks, Quaternary deposits, and glacier (26%)	Rocks, Quaternary deposits, and glacier (70%)

the sediment samples before (TOC), and after combustion (BC), was determined with an elemental analyzer. Prior to elemental analysis, the Ag—capsules were placed in Sn—capsules to facilitate combustion of the sample. The method precision (expressed as relative standard deviation of quintuple analyses) on the elemental analyzer for TOC measurements in a same sample varied between 1% and 4%. Reported data for BC are mean values ($n = 2-5$) with a median relative standard deviation of 23%.

To evaluate and validate the CTO-375 setup in our laboratory, twelve standard materials of various origin and nature (environmental matrices, lab-produced BC materials, potentially interfering materials) from the BC interlaboratory comparison²⁶ were analyzed for TOC and BC and compared with the results of four other groups using CTO-375. The data comparison showed that for all materials our own data were within 95% confidence interval of the means of the other laboratories using CTO-375. Additionally, the oxygen supply was sufficient to avoid charring, which was specifically tested by analyzing samples containing high amounts of amorphous organic carbon but no soot. No soot was quantified in these samples with CTO-375. Furthermore, standard addition experiments with Standard Reference Material (SRM) 2975 (NIST, Gaithersburg, MD) to sediment core materials revealed recoveries of 37–84%, which is comparable to numbers reported previously (51–78%).²³ Reasons for such seemingly rather mediocre recoveries are given in the specialized literature.^{23,26}

Analysis of PAHs

Sediment analysis of PAHs was conducted as described before.²⁷ Briefly, 16 PAHs representative of this compound class, often referred to as the 16 EPA-PAHs and including naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BPE) were targeted. PAHs were Soxhlet extracted from 1–2 g of sediment with activated copper in *n*—hexane for 36 h. The extracts were cleaned by *N,N*-dimethylformamide–Milli-Q water (9 : 1, v/v) liquid–liquid partitioning and over water-deactivated silica gel. PAHs were separated and detected by gas chromatography coupled to mass spectrometry, and quantified using the internal standard method. For each of the 16 PAHs, 200 ng of a deuterated analogue was added as surrogate standard to the samples prior to extraction. The analysis of the characteristic ratio of methylanthracenes and methylphenanthrenes to phenanthrene ((mANT and mPHE)/PHE), methylfluoranthenes and methylpyrenes to pyrene ((mFLT and mPYR)/PYR), and 1,7- to 1,7- and 2,6-dimethylphenanthrene (1,7-(1,7- and 2,6-)DmPHE) as well as of the molecular markers retene (RET) and perylene (PER) was carried out as described previously.²⁷ Prior to gas chromatography injection, 200 ng of indeno[1,2,3-*cd*]fluoranthene was added to the extracts as a recovery standard. Recovery of surrogate standards ranged from 24% for NAP to 128% for BPE. Note that the use of isotope labeled surrogate standards implies that presented data are directly corrected for

recovery rates. Method blanks consisting of Soxhlet thimbles with activated copper were analyzed in parallel with the samples. Based on a typical sample amount, blank concentrations for PAHs were on average 11 $\mu\text{g kg}^{-1}$ ($n = 18$), with NAP (50%), PHE (19%), and ANA (8%) contributing most to the blank concentrations. In sediment samples from TH, blank levels of PAHs can be considered as unproblematic, as on average blank levels contributed to 3% of sediment concentrations. In sediment from ENG, OAR, and ST, on average blank levels of PAHs corresponded to 25% of sediment concentrations. Although blank levels appear to be close to sediment concentrations, the small variability among blank samples of ENG, OAR, and ST (relative standard deviation of PAHs in blank samples 20%) shows that measured sediment concentrations are affected by a constant background level and can, therefore, be considered as acceptable. Limit of detection (LOD) for each individual PAH was either 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. LOD for PAHs was on average 11 $\mu\text{g kg}^{-1}$. The reliability of the analytical procedure was confirmed by a quadruple analysis of PAHs in the sample from 2001 in OAR, providing a relative standard deviation of 5.7%. The regular participation at the International Sediment Exchange for Tests on Organic Contaminants (SETOC) of the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL)²⁸ was the measure for external quality control.

Data presentation

Since concentrations of minor sediment components may be affected by varying the input resulting in dilution of the major detrital matter, data are presented as input fluxes into sediment. Input fluxes of PAHs into sediment (Flux_{PAH}) are calculated by multiplying the concentrations measured in a sediment sample (C_{PAH}) with the sediment mass accumulation rate of the corresponding sediment layer (S) according to:

$$\text{Flux}_{\text{PAH}} [\text{mg m}^{-2} \text{a}^{-1}] = (C_{\text{PAH}} [\mu\text{g kg}^{-1}] \times S [\text{g m}^{-2} \text{a}^{-1}]) \times 10^{-6}$$

Fluxes of TOC and BC were calculated analogously. All raw data are provided in the ESI†. For reasons of clarity and to avoid producing artificial data, presented data are not blank corrected; all blank levels are provided in the ESI†. Unless otherwise specified, in this publication PAHs denotes the sum of the 16 PAHs analyzed. Light PAHs include NAP, ANY, ANA, FLU, and PHE. Heavy PAHs include ANT, FLT, PYR, BaA, CHR, BbF, BkF, BaP, IPY, DBA, and BPE.

Results

Evolution of fluxes of TOC, BC, and PAHs in Swiss lake sediments

Fig. 2 shows the evolution of fluxes of TOC, BC, the ratio BC/TOC, fluxes of light and heavy PAHs, and the ratio PAH/BC in the sub-Alpine TH (TH1, TH2, and TH3), in the natural remote high-Alpine ENG, and in the remote proglacial lakes OAR and ST. Note the different scales in the panels of Fig. 2.

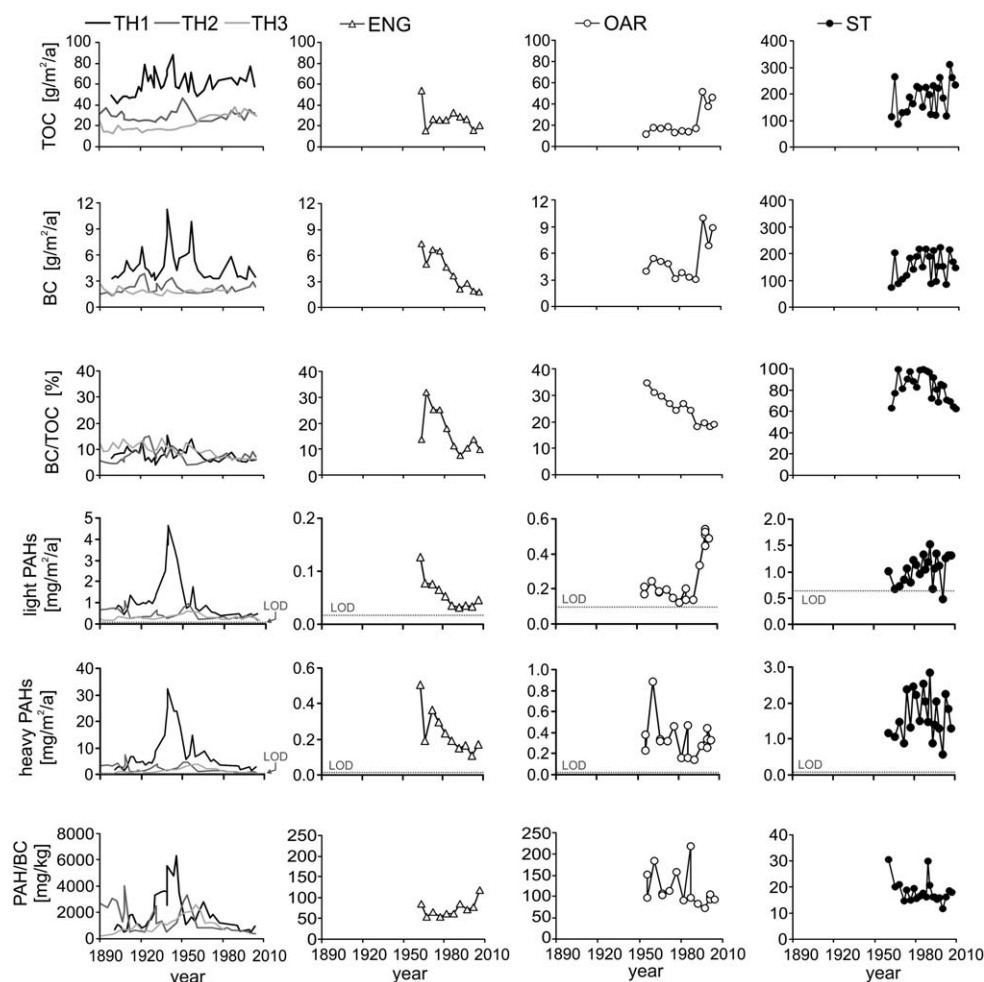


Fig. 2 Evolutions of input fluxes of total organic carbon (TOC), input fluxes of black carbon (BC), the ratio BC/TOC, input fluxes of light polycyclic aromatic hydrocarbons (PAHs), input fluxes of heavy PAHs, and the ratio PAH/BC in sediments from Lake Thun (TH1, TH2, and TH3), Lake Engstlen (ENG), Lake Oberaar (OAR), and Lake Stein (ST). Limit of detection (LOD) of PAHs was converted into a flux, based on the mean sample amount and the mean sedimentation rate in the corresponding site. Note the different scales in the plots.

TOC. Fig. 2 shows that TOC fluxes in the three sediment cores from TH ($10\text{--}88\text{ g m}^{-2}\text{ a}^{-1}$) varied only little during the 20th century. In TH1, TOC increased during the early 20th century and remained stable afterwards. In TH2, TOC remained almost at the same level. In TH3, TOC increased steadily throughout the 20th century, meeting TH2 fluxes since the 1960s. In the high-Alpine ENG, TOC fluxes were highest in the oldest sample from 1963 ($54\text{ g m}^{-2}\text{ a}^{-1}$), followed by constant fluxes in the more recent years ($16\text{--}38\text{ g m}^{-2}\text{ a}^{-1}$). In the proglacial OAR, fluxes remained constant in the 1950s–1990s ($11\text{--}18\text{ g m}^{-2}\text{ a}^{-1}$), whereas fluxes increased in the latest samples ($38\text{--}51\text{ g m}^{-2}\text{ a}^{-1}$). In the proglacial ST, TOC fluxes showed important fluctuations and were considerably higher ($87\text{--}312\text{ g m}^{-2}\text{ a}^{-1}$) than in the other lakes.

BC. BC fluxes in TH remain in a range of $1\text{--}11\text{ g m}^{-2}\text{ a}^{-1}$ with two maxima in TH1 around 1940 and 1960. Again, TH1 fluxes were higher than those of TH2 and TH3. In ENG, fluxes were similar to TH ($2\text{--}7\text{ g m}^{-2}\text{ a}^{-1}$), but indicate a decrease since the 1960s. Also BC fluxes in OAR were similar ($3\text{--}9\text{ g m}^{-2}\text{ a}^{-1}$), but highest in the most recent samples. In ST, BC fluxes were up to

two orders of magnitude higher than in the other investigated lakes ($72\text{--}223\text{ g m}^{-2}\text{ a}^{-1}$).

BC/TOC. The ratio BC/TOC in TH sediment cores does not indicate a clear trend and lies within 4–17%. In ENG and OAR, because both BC and TOC fluxes were similar to those in TH; their BC/TOC ratio is also similar (7–32%), and decreasing over time. In ST, however, BC/TOC ratios were considerably higher (63–99%).

PAHs. Fluxes of PAHs in sediment from TH spread over a wide range with a predominance of heavy PAHs ($0.1\text{--}32\text{ mg m}^{-2}\text{ a}^{-1}$) compared to light PAHs ($0.1\text{--}5\text{ mg m}^{-2}\text{ a}^{-1}$). The temporal evolution is similar for light and heavy PAHs with a peak in TH1 in the 1940s, whereas TH2 and TH3 show a constant trend. In ENG, fluxes of PAHs have decreased since the 1960s and heavy PAHs (up to $0.5\text{ mg m}^{-2}\text{ a}^{-1}$) dominated compared to light PAHs (up to $0.1\text{ mg m}^{-2}\text{ a}^{-1}$). In OAR, in the 1960s heavy PAHs (up to $0.9\text{ mg m}^{-2}\text{ a}^{-1}$) outweighed light PAHs (up to $0.2\text{ mg m}^{-2}\text{ a}^{-1}$). Since the 1990s, the trend of light PAHs in OAR has differed considerably from heavy PAHs. Whereas

fluxes of heavy PAHs remained stable between 0.1 and 0.4 mg m⁻² a⁻¹, fluxes of light PAHs increased sharply to peak around 0.5 mg m⁻² a⁻¹. Finally in ST, fluxes are four times higher than in other mountain lakes (0.5–1.5 mg m⁻² a⁻¹ for light PAHs and 0.6–2.9 mg m⁻² a⁻¹ for heavy PAHs) with no systematic trend. Characteristic PAH ratios and molecular markers providing indications about sources of PAHs are shown in the ESI†(Fig. S1 and S2) and discussed below.

PAH/BC. The ratio PAH/BC is highest in sediment from TH1 (452–6325 mg kg⁻¹) with a peak in the 1940s, simultaneous to the peak of PAHs. TH2 and TH3 have ratios ranging from 112 to 4055 mg kg⁻¹. In ENG (55–120 mg kg⁻¹) and OAR (73–217 mg kg⁻¹) the ratio is within a similar range and has been stable since the 1950s. In ST, PAH/BC is also stable, but lowest among all lakes (12–30 mg kg⁻¹).

Correlation between TOC, BC, and PAHs in Swiss lake sediments

Fig. 3 plots fluxes of BC *versus* TOC, light and heavy PAHs *versus* TOC, as well as light and heavy PAHs *versus* BC for the low-altitude TH and the high-altitude lakes ENG, OAR, and ST.

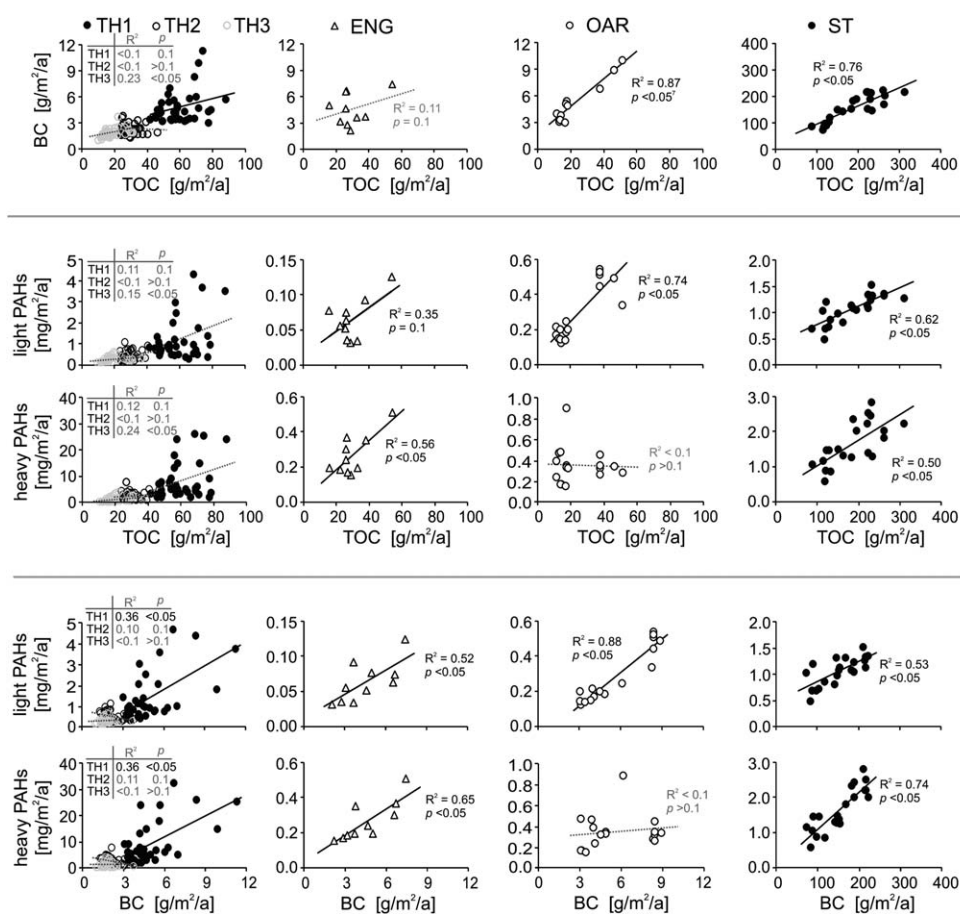


Fig. 3 Correlations between black carbon (BC) and total organic carbon (TOC), light polycyclic aromatic hydrocarbons (PAHs) and TOC, heavy PAHs and TOC, light PAHs and BC, and heavy PAHs and BC in sediments from Lake Thun (TH1, TH2, and TH3), Lake Engstlen (ENG), Lake Oberaar (OAR), and Lake Stein (ST). R^2 and p denote the coefficient of determination and the significance level p -value, respectively.

BC vs. TOC. In TH, almost no correlation is observed between BC and TOC. In ENG, the correlation is also inexistent, whereas in the proglacial lakes a very clear correlation exists.

PAHs vs. TOC. In the three sediment cores from TH, neither light nor heavy PAHs are correlated with TOC. In all mountain lakes, light PAHs are correlated with TOC. Heavy PAHs are correlated with TOC in ENG and ST, whereas in OAR no correlation exists.

PAHs vs. BC. In TH, light and heavy PAHs are correlated with BC only in sediment core TH1, but not in TH2 and TH3. In the mountain lakes, the same picture is observed as for the correlation with TOC, that is: light PAHs correlate with BC in all lakes; heavy PAHs correlate with BC in ENG and ST, but not in OAR.

Discussion

Table 2 provides a summary about fluxes and ratios of TOC, BC, and PAHs in sediments from sub-Alpine as well as mountain lakes in the Alps. Table 2 includes the lakes investigated here, as well as for comparison data from previous studies monitoring at least two of the target species from this study.

Table 2 Summary of data collected in the literature as well as data from this study about fluxes and concentrations of total organic carbon (TOC), fluxes and concentrations of black carbon (BC), ratio BC/TOC, fluxes and concentrations of polycyclic aromatic hydrocarbons (PAHs), ratio PAH/BC in sediments from sub-Alpine lakes, mountain lakes, and proglacial lakes

	Altitude/ m a.s.l.	TOC flux/g m ⁻² a ⁻¹ (concentration/mg g ⁻¹)	BC flux/g m ⁻² a ⁻¹ (concentration/mg g ⁻¹)	BC/ TOC (%)	PAHs flux/mg m ⁻² a ⁻¹ (concentration/ng g ⁻¹)	PAH/BC (mg kg ⁻¹)	Reference
<i>Sub-Alpine lakes</i>							
Lake Thun (TH) (Switzerland)	558	10–88 (4.0–32)	1.0–11 (0.4–3.1)	4–17	0.2–37 (86–12 219)	112–6325	This study
Lake Bourget (France)	232	ca. 42–83 ^a (0.8–1.5)			ca. 0.2–5.0 ^a (328–3745)		29
Lake Bled (Slovenia)	475	29–53 ^{bc} (23–47)	1.7–6.2 ^b (1.8–4.9)	6–12			11
<i>Mountain lakes</i>							
Lake Engstlen (ENG)	1850	16–54 (10–30)	2.1–7.4 (1.5–3.3)	7–32	0.2–0.6 (140–245)	55–120	This study
Lake Krisko Sup. (Alps, Slovenia)	2150	44 ^b (69–111)	3.0 ^b (6.0–8.3)	7–9			11
Lake Krn (Alps, Slovenia)	1383	n.a. (10–47)	n.a. (0.7–1.5)	5–11			11
Lake Ledvica (Alps, Slovenia)	1830	5.8–21 ^{bc} (66–157)	0.3–1.3 ^b (3.6–9.2)	6–7			11
Lake Planina (Alps, Slovenia)	1430	31–250 ^{bc} (68–168)	1.6–11 ^b (3.3–10.5)	3–7	<0.01 to 2.8 (120–9500)	250–2000 ^b	12
Lovrensko Lake (Alps, Slovenia)	1520	31–33 ^{bc} (400–460)	1.3–1.5 ^b (14–24)	3–5			11
Zgornje Kriško jezero (Alps, Slovenia)	2150		2.8–6.0 (6.1–8.3)				13
Jezero v Ledvicah (Alps, Slovenia)	1830		0.3–1.3 (3.5–9.3)				13
Jezero na Planini pri Jezeru (Alps, Slovenia)	1430		1.5–11.2 (3.7–10.4)		0.05–3.0 (116–9532)	28–1702	13
Lake Noir (Alps, France)	2750	2.3–4.3 (n.a. ^d)			<0.01 to 0.09 (92–1200)		10
Schwarzsee above Sölden (Alps, Austria)	2799	3.0–16 (n.a. ^d)			<0.01 to 0.1 (30–870)		10
Gossenkölle (Alps, Austria)	2417	7.0–20 (n.a. ^d)			<0.01 to 0.07 (100–890)		10
<i>Proglacial lakes</i>							
Lake Oberaar (OAR)	2303	11–51 (0.8–1.5)	3.0–10.0 (0.2–0.3)	18–35	0.3–1.1 (18–57)	73–217	This study
Lake Stein (ST)	1930	87–312 (1.7–4.4)	72–223 (1.2–3.0)	63–100	1.0–4.4 (28–52)	12–30	This study

^a Fluxes not published, only concentrations published. Fluxes are estimated based on concentrations, water content, sedimentation rate, and assuming a sediment core diameter of 5.6 cm as in this study. ^b BC fluxes only published for some sediment samples. ^c Calculated based on BC fluxes and the BC/TOC ratio. ^d n.a. = not available.

Sub-Alpine Lake Thun (TH)

Next to primary production in the water column of TH, runoff from the mixed urban and rural catchment area, as well as waste water discharge, are probably also sources of TOC, reflected in the higher TOC fluxes in core TH1 compared to TH2 and TH3. TH1 is located close to the urban area around Interlaken, whereas urban runoff from the city of Thun flows into the Aare downstream of TH (see Fig. 1). Moreover, all waste water treatment plants discharging into TH are located in the area east of TH1. Nutrient input from waste water discharges may lead to enhanced primary production in the TH1 region and, thus, to higher TOC fluxes. The absolute levels of TOC in TH are similar to previous studies monitoring sub-Alpine lakes (Table 2) and also similar to a recent study about TH.³⁰ Unlike in the current study, evolutions of TOC in the study by Wirth and coworkers indicated higher concentrations in the 1960s–1980s as a result of intensive anthropogenic activities leading to high nutrient input and associated eutrophication. Probably the location of the

sampling sites explains this difference. Whereas in Wirth *et al.* all six sediment cores were sampled in the deep basin floor of the lake where partial anoxic conditions prevailed during eutrophication,³⁰ the three sediment cores from the present study originated from different areas of the lake. Eutrophication took place in TH, although it remained moderate. Since the beginning of the 20th century, the nutrient level in the lake water has increased and peaked in the 1960s with a total phosphorus concentration in water around 12–21 µg l⁻¹.³¹ In contrast, lakes in Switzerland located in densely populated areas with extensive agricultural activities have considerably higher nutrient levels. For instance in Lake Greifen, a small (8.5 km²) and shallow (31 m depth) lake situated in a densely populated urban area in Northern Switzerland (total population in its catchment area around 100 000 inhabitants), the total phosphorus concentration in lake water reached up to 500 µg l⁻¹ in the 1960s and is currently still noticeably higher (40 µg l⁻¹ in 2009)³¹ than in Lake Thun (5 µg l⁻¹ in 2009).³² Note that TOC is more labile than other organic

indicators, such as for instance PAHs and, therefore, concentrations of TOC measured in sediment and the resulting fluxes do not necessarily reflect the entire initial input into the water column. The gross primary production in the water column in TH was determined recently and accounts for a TOC production of $95 \text{ g m}^{-2} \text{ a}^{-1}$.³³ Compared to the TOC flux into surface sediment for the three sites in TH ($30\text{--}50 \text{ g m}^{-2} \text{ a}^{-1}$), it appears that approximately one third of TOC ended up in the surface sediment. In the 1980s, the primary TOC production was $200 \text{ g m}^{-2} \text{ a}^{-1}$, whereas in sediment from the 1980s, the TOC flux was on average $37 \text{ g m}^{-2} \text{ a}^{-1}$. This tentative comparison confirms that organic matter biosynthesized in the photic zone of the lake or introduced into the lake from the catchment area undergoes rapid remineralization during the sinking of particulate matter and in the bioturbation surface layer of sediments.^{21,22} The constant TOC flux in the deeper sediment layers, thus, represents only the fraction of organic matter that is recalcitrant to decomposition processes and is conserved in deep sediment.

In contrast to TOC, the input of conservative chemical species can be inferred from measured concentrations in the sediment. Note that, although BC is largely resistant to environmental degradation, the CTO-375 quantification method applied in this study is a harsh method, in which an oxidation of the less condensed forms of the BC spectrum (char BC) takes place, resulting in an underestimation of the total BC present in the sediment.^{23,34,35} However, more inert fractions of the BC continuum, specifically soots, are well captured with this method. Fluxes of BC in TH are in the same range as previously measured in sub-Alpine lakes (Table 2). Fluxes of BC from the atmosphere to open oceans with no population have been shown to be considerably smaller. Measurements of deposition of BC in South Atlantic sediments showed fluxes of $<0.08 \text{ g m}^{-2} \text{ a}^{-1}$.³⁶ Modeled BC fluxes on open oceans worldwide were estimated at $0.04 \text{ g m}^{-2} \text{ a}^{-1}$.³⁷ Interestingly, the variability and absolute numbers of BC/TOC in TH were smaller in 1960–2000 (5–9%) than in 1830–1960 (4–17%). This could be due to a small fraction of TOC still degraded in deep sediment layers. The median BC/TOC ratios in sediment from TH (8.5%) is very close to the 9% reported for 300 sediment samples from all around the world⁴ and similar to Lake Bled in the Slovenian Alps, where median ratios of 8.7% were reported.¹¹ The BC/TOC ratio in sediment are usually higher than in soils, as soils have typically higher TOC levels.⁴ In soils in Switzerland, ratios of 1–9% (median of 105 samples: 3%) were reported.³⁸

Combustion related air pollutants, such as BC and PAHs, probably originate to a large extent from anthropogenic activities in the catchment area of TH. The peak of BC and PAHs in sediment from TH in the 1940s–1950s may be the result of a local event of increased organic matter burning. In the early 1940s, energy production by wood and wood char combustion in Switzerland rose from 10 to 30%; in the late 1940s, wood and wood char contribution was again reduced to 10%.³⁹ Simultaneously, coal and fossil fuel combustion dropped from 55% and 10% to 40% and 1%, respectively. For the last few decades, possibly, increased use of fossil fuel as an energy source has been partly compensated by improvements in combustion technologies, resulting in the slightly decreasing PAHs in TH1 and stable fluxes elsewhere. Current fluxes of PAHs in TH are comparable to values from Lake Bourget, France.²⁹ The temporal evolutions

of light and heavy PAHs are similar. Heavy PAHs make up on average 85%, 80%, and 64% of the total of PAHs in TH1, TH2, and TH3, respectively. The prevalence of heavy PAHs in TH reflects the proximity of sources of PAHs, particularly in TH1.

In contrast to BC, fluxes of PAHs determined in this study are clearly highest in sediments from TH, probably due to its proximity to emission sources, particularly in TH1. Also the correlation between PAHs and BC observed in TH1 indicates common sources of these two species in this area. Conversely, no correlation is observed in TH2 and TH3. Possibly, the correlation is lost due to the presence of an appreciable fraction of BC that is not resistant to the CTO-375 method applied in this study. The PAH/BC ratio in TH points also towards a labile fraction of BC that is not assessed here, but that has initially been emitted with PAHs by combustion sources.

Further, sources of PAHs that do not contribute to BC emissions, such as petrogenic PAHs, natural formation of PAHs, or PAHs emitted from road pavements, could be a reason for the elevated PAH/BC ratio. With up to 6000 mg kg^{-1} , the PAH/BC ratio in TH is high when compared to other sites described in the literature. In a small lake south of Stockholm, Sweden, PAH/BC was lower ($40\text{--}1400 \text{ mg kg}^{-1}$).⁴⁰ Jonker and Koelmans³⁴ determined in various types of soot the sum of 11 PAHs, which make up 60–90% of PAHs in our study. In different soots, 11PAH/BC ranged from 60 to 800 mg kg^{-1} , showing that the PAH/BC ratio in TH is high. Again, the presence of a labile fraction of BC in sediment from TH, which is oxidized (*i.e.* lost) during the CTO-375 treatment procedure, is probably a reason for this high ratio.

Measurements of characteristic PAH ratios and molecular markers (see the ESI†) allowed to further investigate possible sources of PAHs in TH. The ratio of characteristic combustion PAHs (Fig. S1†, Comb-PAHs/PAHs) in TH was generally in the range indicating the relevance of combustion as a source for PAHs. Though, some sediment layers had a lower ratio, which casts the reliability of this ratio into doubt, as petrogenic origin of PAHs in TH is unlikely.²⁷ Earlier critical evaluations of characteristic ratios already showed that this ratio is probably less consistent, whereas FLT/(FLT and PYR) and IPY/(IPY and BPE) were reported to be more reliable.⁴¹ Indeed, as expected from earlier soil investigations, FLT/(FLT and PYR) and IPY/(IPY and BPE) point both towards combustion as a dominant source of PAHs in sediments from TH. This conclusion is further corroborated by the fact that (mANT and mPHE)/PHE and (mFLT and mPYR)/PYR (0.3–1.0 and 0.4–0.8, respectively) were close to the numbers indicative for pyrogenic sources (0.5 and 0.3, respectively, see Fig. S2†).⁴¹ Specific ratios of PAHs determined at their respective sources allow identifying the relevance of different fuel types to the PAH load produced by combustion. FLT/(FLT and PYR) and IPY/(IPY and BPE) are possible markers for the distinction between grass, coal, and wood combustion and fossil fuel combustion.^{27,41,42} In Lake Thun both ratios revealed a relevant contribution of grass, coal, and wood combustion to the PAH load (Fig. S1†). Vehicle emissions, fossil fuel combustion, and biomass burning can be distinguished by dialkylated PAH ratios. 1,7-/(1,7- and 2,6-)DmPHE may reveal vehicle emissions (ratio <0.45) and mixed combustion of fossil fuel (0.45–0.7).⁴² Throughout the investigated time period, 1,7-/(1,7- and 2,6-)DmPHE remained below 0.7, indicating mixed combustion sources (Fig. S1†). In TH3 before 1900, 1,7-/(1,7- and 2,6-)DmPHE was close to 0.45. A ratio below 0.45 points towards an increased contribution

of vehicle emissions. This would, however, be rather unlikely considering the almost complete absence of combustion engines at that time. Accordingly, 1,7-(1,7- and 2,6-)DmpHE was earlier identified as a typical example for a ratio that should be interpreted with care when source apportionment of PAHs is performed.⁴¹

As the formation of PAHs by combustion of wood may be identified by RET,⁴³ the ratio RET/(RET and CHR) was calculated here. From the 1900s until the 1980s the relevance of wood combustion decreased, as indicated in Fig. S1†, by a decreasing RET/(RET and CHR) in all three cores. After 1980, RET/(RET and CHR) raised again, suggesting increasing emissions from wood combustion. In the survey about Swiss soils, wood combustion has also been identified as a likely source for PAHs.⁴¹ In Switzerland the use of wood as a heating source increased by 9.5% from 1990–2006.⁴⁴ In some Alpine valleys, heating by wood produces an important fraction of the total particulate matter and BC emissions.⁴⁵ The augmenting demand for wood heating systems is a probable explanation for the observed increase in PAHs from wood combustion. Recently, in Sweden indoor air levels of PAHs were shown to be three- to five-fold higher in homes using wood burning for heating, compared with homes without wood-burning appliances.⁴⁶ In Europe small wood combustion processes were indicated as the major BaP source, followed by coal combustion, metal refining activities and vehicle emissions.⁴⁷ The latter study indicated that emissions of BaP by the different sources are expected to decrease in the future, although reductions are expected to be less important for wood combustion.⁴⁷

Among the different PAHs derived during early diagenesis, PER is a specific indicator, that was identified in sediments from Lake Lucerne, Lake Zurich, and Lake Greifensee, Switzerland, and Lake Washington, United States.⁴⁸ In TH PER/(PER and PYR) increased towards deeper sediments (Fig. S2†). This trend is different from that of the other PAHs formed by anthropogenic activities. These observations are in line with previous studies showing that microbially mediated formation of PER in deeper sediments can occur within a few decades.^{48,49} Thus, Lake Thun provides the required conditions for such formation processes of specific PAHs.

Alpine Lake Engstlen (ENG)

Fluxes of TOC in ENG are similar to TH, although, mountain lakes are expected to have lower primary production. Whereas in sub-Alpine lakes decomposition of organic material may occur to a certain extent, such as addressed for TH, in colder mountain areas it may be considerably reduced. Probably, lower temperatures and, therefore, reduced degradation of organic matter contribute to an enhanced conservation of TOC. Particularly during the period of ice coverage in mountain lakes, darkness added to cold temperatures can lead to significantly reduced biological activity and, therefore, to enhanced conservation of TOC.⁵⁰ Further, the core from ENG was sampled in the deep basin floor of the lake where partial anoxic conditions may exist, supporting the conservation of TOC. Also in soils of Switzerland, increasing levels of TOC with altitude have been observed.³⁸ Fluxes of TOC in ENG are comparable to other oligomesotrophic Alpine lakes (Table 2). Only in Lake Planina (Slovenia), which is an eutrophic lake located at lower altitude, reported fluxes are clearly higher.¹¹ The decrease of TOC fluxes prior to the 1960s and the stable fluxes afterwards is in line with previous studies

of TOC in Alpine lakes. In Lake Noir, France, TOC fluxes varied within a factor of 2 throughout the 20th century with no clear trend.¹⁰ In the Austrian lakes Gossenkölle and Schwarzsee above Sölden, TOC has decreased by a factor of 3 and 8 since the 1930s and 1900s, respectively.¹⁰ In Gossenkölle, modifications of the trophic status of the lake and/or in the watershed were provided as reasons for the TOC decrease. In Schwarzsee, changes in sedimentation rates were at the origin of the observed TOC reductions.

Fluxes of BC in ENG are in a similar range as in TH and the previously monitored mountain lakes. BC decreases by a factor of 3 during the 1960s–1990s and is stable afterwards. Hammes *et al.*²⁶ showed that the forms of BC that are resistant to the CTO-375 method are predominantly small and light fractions. Thus, in mountain lakes, such as ENG, BC may also be composed of small and light forms of BC that are efficiently transported to such remote areas and may result in these relatively high levels of BC, compared to sub-Alpine lakes located considerably closer to source areas. The decreasing trend of BC/TOC observed in ENG during the last few decades results almost entirely from the decreasing BC flux. The highest BC/TOC ratio (>30%) is clearly higher than ratios in TH (Fig. 2) and those reported in other mountain lakes (Table 2). BC and in particular the light and small soot particles, which are effectively captured and accurately determined by the CTO-375 method applied here, may be transported at considerable distances, leading to a rather constant burden for all lakes. Local emissions are likely of additional relevance in TH and apparently double the background BC flux. The decrease in BC flux in ENG and OAR is probably a result of improved combustion techniques.

Fluxes of PAHs in ENG are considerably lower than in the sub-Alpine TH, showing that only a fraction of the pollution plume emitted in populated areas reaches such remote sites. The prevalence of heavy PAHs reflects the relevance of atmospheric deposition of these particle-associated compounds in the ENG region. Reported fluxes of PAHs in mountain lakes span over a large range of values (Table 2). In ENG, fluxes are among the higher ones reported. The evolution of PAHs shows that input fluxes leveled off or decreased (in ENG) during the last decades.

PAH/BC in ENG is drastically lower than in all TH sediments, but comparable to ratios observed for other mountain lakes and indicates no particularly strong point source of either PAHs or BC in the vicinity of ENG. We hypothesize that the small soot particles that are resistant to the CTO-375 method, and that lead to appreciable BC levels, carry PAHs with them. The PAH/BC ratio in ENG is matching the ratio measured earlier in small soot particles by Jonker and Koelmans.³⁴ The correlation observed in ENG between PAH and BC is probably due to common sources, and/or sufficient equilibrium time for PAH to sorb to BC already in the atmosphere.⁵¹ The correlation between PAHs and TOC in sediment may indicate equilibrium between PAHs and organic matter. In Swiss soils, only light PAHs were correlated with TOC, but not heavy PAHs.³⁸ The difference may be due to the fact that equilibrium is faster reached in sediment (under water saturated conditions) than in soils. As discussed for TH, characteristic PAH ratios and molecular markers should again be interpreted with care. Particularly for samples with low concentrations of PAHs, interpretations of PAH ratios is strongly limited. Further, in samples from remote sites, PAH ratios are heavily blurred and systematically shifted due to complex

interfering environmental processes that do not affect all PAHs equally, such as for instance atmospheric deposition or degradation. Generally, PAH ratios and molecular markers point towards combustion as the major source of PAHs detected in ENG. Interestingly, RET/(RET and CHR), which is an indicator of wood combustion, is slightly higher than in TH. Possibly, in Alpine valleys, the importance of wood combustion as a source of PAHs compared to traffic is increased.⁴⁵ In previous studies, sediments from remote Alpine lakes, combustion was also identified as a relevant PAH source based on the relative abundance of combustion derived PAHs and ratios of alkylated to nonalkylated PAHs.¹⁰

Like in TH, ENG also provides the required conditions for natural formation of PER, as shown by the appreciable ratio PER/(PER and PYR) (Fig. S2†). In different remote Alpine lakes, PER was also studied over time and revealed that the natural formation of PER in deeper sediments only occurred in some lakes.¹⁰

Proglacial Lake Oberaar (OAR)

The fluxes of TOC and BC in OAR are similar to ENG (Fig. 2) and other mountain lakes (Table 2). It is important to notice that these appreciable fluxes result from high sedimentation rates in this proglacial lake. Absolute concentrations of TOC and BC in sediment from OAR are lower than in other high-altitude lakes (see Table 2 and Table S8 in the ESI†). Similar to ENG, BC/TOC ratio are higher in OAR than in previously monitored mountain lakes. OAR is a highly oligotrophic proglacial lake with very low primary production. Probably surface runoff from the catchment area of OAR provides a TOC source as well. TOC can also originate to some extent from remote sources like BC, after all, 20–40% of TOC is BC. Finally, stable chemicals previously deposited to and incorporated into Alpine glaciers can now be released by fast melting glaciers as a consequence of global warming. This has recently been shown in OAR for highly persistent organic pollutants, including polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs).⁹ It has also been quantified that chemicals incorporated into the Oberaar Glacier are released with meltwater with a delay of two to five decades.⁵² Thus, the adjacent Oberaar Glacier is also expected to be a contemporary source of TOC and BC to the lake.

PAHs, particularly the light PAHs, show a considerable increase during the last decade. This observation is also in line with the possibility of release of pollutants from the Oberaar Glacier.⁹ Probably, light and more volatile PAHs are efficiently trapped on cold spots, such as the glacier surface, resulting in an enhanced storage in the glacier and followed by an enhanced release into the lake some decades ago. Recently, environmental contamination by PAHs (sum of 11 compounds) at high altitude has been reconstructed in a dated ice core from Colle Gnifetti, Swiss/Italian Alps (4450 m a.s.l.).⁵³ The latter study confirmed the efficient trapping of light PAHs on snow surface, resulting in light PAHs making up 85% of PAHs in ice. Like for ENG, characteristic PAH ratios and molecular markers point towards combustion as a relevant source of PAHs in OAR. However, these markers do not allow more detailed source identification. Once again, the applicability of such markers for source apportionment of PAHs is limited with increasing distance from their original sources.⁴¹

Proglacial Lake Stein (ST)

Although having similar characteristics as OAR, ST represents a special case. TOC fluxes are stable and absolute levels are comparable to or higher by about a factor of 2–6 than fluxes determined for TH and ENG or reported in the literature (Table 2). BC fluxes in ST, however, are more than one order of magnitude higher than in comparable sites. The high and constant BC flux in ST throughout the last few decades is a strong indication for a geogenic origin of BC. The ratios of BC/TOC approaching 100% are very remarkable and have so far not been reported for Alpine lake sediments or soils. An input of combustion-derived organic matter with such high BC/TOC is very unlikely. In the catchment of ST, the so-called Aare Massif consists predominantly of crystalline rocks. This massif also contains some graphite layers, where thin units of Mesozoic sedimentary rocks became metamorphosed. In fact, a graphitic zone crosses the Stein Glacier about 1 to 2 km to the south of the lake and is most likely the source of BC observed in sediment from ST.⁵⁴

TOC, BC, and PAHs, including light and heavy PAHs, are highly correlated in ST. This good correlation indicates a common geogenic source for all species in this lake, which prevails over their regular combustion source. Probably also for this reason, the characteristic PAH ratios and molecular markers show only small differences of the pattern in ST. The ratio Comb-PAHs/PAHs is throughout the investigated period on average lower in ENG than in other mountain lakes, pointing towards a reduced relevance of combustion sources. Petrogenic origin of PAHs in ENG is provided by IPY/(IPY and BPE), and ratios of methylated PAHs (*i.e.* (mANT and mPHE)/PHE and (mFLT and mPYR)/PYR), which are lower in ENG (see Fig. S1 and S2†). Compared to the factor of 10–15 between BC fluxes in ST and the other mountain lakes, fluxes of PAHs appear not to be surprisingly high as they are only higher than in other mountain lakes by a factor of 4, resulting in a relatively low PAH/BC ratio. This is consistent with the hypothesis of graphite occurring in the catchment of ST and delivering the high BC fluxes. It has been shown that graphite is resistant to the CTO-375 method applied here, resulting in high BC levels,⁵⁵ but has low contents of PAHs. In the study by Jonker and Koelmans,³⁴ levels of PAHs in graphite samples were below detection limit. Based on Fig. 2, atmospheric fluxes of BC in ENG and OAR are consistently around $5 \text{ g m}^{-2} \text{ a}^{-1}$, whereas geogenic BC fluxes in ST are by a factor of 20 higher around $100 \text{ g m}^{-2} \text{ a}^{-1}$. Also the ratio PAH/BC points towards a predominance of geogenic input in ST compared to the atmospheric input. The PAH/BC ratio is around 20 in ST, whereas ENG and OAR have consistent ratios around 100, thus a factor of 5 higher.

Conclusions

The method applied in this study proved to be efficient for reconstructing temporal developments of environmental contamination by anthropogenic pollutants. After considerable decreases in the mid-20th century, evolutions of BC and PAHs have been almost stable or only slightly decreasing for the last few decades. Thus, improvements of combustion technologies and regulations probably compensated the continuous use of fossil fuel energy sources. Although being close, all the sites investigated in this study show important differences.

Contrasting the sediment profiles BC and PAHs in the sub-Alpine lake TH with the remote mountain lake ENG showed that populated areas, even in rural regions, are direct sources of these pollutants. The proglacial lake OAR confirmed the efficient trapping of lighter PAHs in cold environments, particularly on Alpine glaciers. Finally, the proglacial ST revealed the presence of geogenic graphitic BC in this region.

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Supplementary Information

Contrasting temporal trends and relationships of total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in rural low-altitude and remote high-altitude lakes

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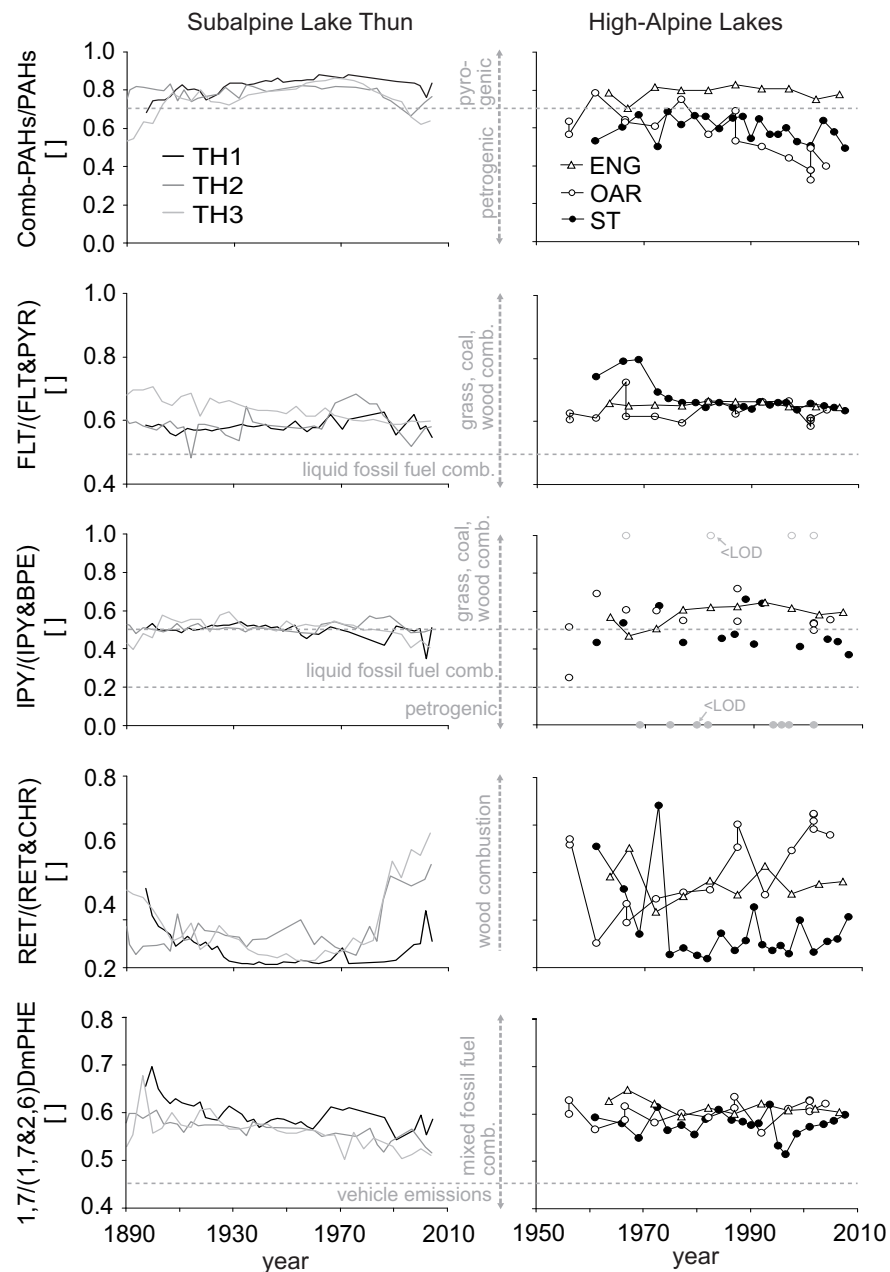


Figure S1. Source-characteristic PAH ratios and molecular markers in three dated sediment cores (TH1, TH2, and TH3) from Lake Thun and sediment cores from mountain lakes (Lake Engstlen ENG, Lake Oberaar OAR, Lake Stein ST).

Rationale

FLT, PYR, BaA, CHR, BbF, BkF, BaP, IPY, and BPE (denoted Comb-PAHs) were stated to be markers for pyrogenic origin¹. The ratio Comb-PAHs / PAHs, where PAHs denotes the 16 EPA PAHs, higher than 0.7 indicates combustion dominated source, whereas a lower ratio points towards petrogenic origin¹.

Other frequently applied ratios are FLT / (FLT&PYR) and IPY / (IPY&BPE). FLT / (FLT&PYR) and IPY / (IPY&BPE) are possible markers for the distinction between grass, coal, or wood combustion, and fossil fuel combustion²⁻⁴.

As the formation of PAHs by combustion of wood may be identified by RET⁵, the ratio RET / (RET&CHR) was calculated.

1,7 / (1,7&2,6)DmPHE may reveal vehicle emissions (ratio <0.45) and mixed combustion of fossil fuel (0.45-0.7)².

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Table S1. Total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in dated sediment core TH1 from Lake Thun.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
2004	3184	21.7	1.3	43	4	7	13	110	18	241
2001	3492	20.3	1.1	19	1	4	7	70	9	78
2000	2570	22.5	1.5	23	8	5	11	108	18	157
1997	2282	24.1	1.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1993	2232	26.4	1.4	20	3	5	10	82	7	175
1991	2215	24.6	1.4	20	3	9	18	152	13	283
1987	2409	26.1	2.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1978	1936	32.4	1.7	22	3	6	15	151	42	331
1973	1887	28.0	1.7	31	7	10	21	191	44	549
1971	2014	29.5	1.5	30	5	11	21	173	31	360
1966	1650	23.5	1.5	37	12	18	32	285	62	764
1962	1895	25.2	2.2	35	8	11	28	233	66	625
1960	2009	22.6	2.3	35	7	11	29	236	56	462
1957	2860	20.3	2.8	41	12	19	34	399	69	672
1955	3012	16.9	2.0	29	6	12	26	214	39	383
1953	2831	22.9	2.0	22	5	12	21	182	25	360
1948	2315	19.7	2.0	59	51	13	50	539	263	1124
1946	2884	20.1	1.5	66	32	43	69	846	112	1775
1944	2684	28.7	1.9	64	35	25	86	950	131	1773
1939	2730	n.a.	2.2	78	57	28	106	1266	150	2475

n.a. = not available

Table S1. continued.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
1939	3744	20.5	3.1	63	33	25	81	833	111	1503
1939	2835	20.0	2.4	64	45	27	90	1047	107	1718
1937	2755	17.2	1.4	44	35	15	54	593	62	974
1935	3168	16.6	1.2	44	35	13	42	471	50	828
1930	3688	22.3	0.9	36	13	10	28	311	49	536
1930	3496	14.9	1.0	35	10	11	24	238	23	354
1928	2806	19.0	1.0	40	5	12	23	188	24	240
1926	3257	16.9	1.1	41	5	12	26	211	54	250
1923	3023	20.7	1.2	38	3	10	25	182	27	197
1921	3304	15.0	1.9	55	6	10	21	184	30	270
1919	3228	16.2	1.4	44	6	11	20	174	27	262
1917	3059	13.7	1.3	45	6	11	23	177	29	266
1914	2987	14.1	1.2	46	8	13	26	234	44	401
1912	3340	12.9	1.3	43	6	16	30	283	51	389
1910	3327	12.5	1.4	31	3	8	16	124	20	157
1908	3552	12.6	1.1	24	2	5	11	76	10	85
1905	3496	11.3	1.0	35	2	8	17	140	17	148
1903	3654	11.2	0.9	42	4	9	21	155	20	172
1901	3588	11.4	0.9	36	4	5	19	116	15	103
1899	4168	12.4	0.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = not available

Table S2. Polycyclic aromatic hydrocarbons in dated sediment core TH1 from Lake Thun.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>] fluoranthene [µg/kg]	benzo[<i>a</i>] pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
2004	200	102	109	87	46	109	85	14	81	1270
2001	55	35	62	42	16	28	26	11	47	511
2000	117	74	100	90	47	101	85	12	83	1037
1997	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1993	108	54	82	65	34	66	57	9	59	836
1991	227	109	154	119	63	119	96	12	88	1483
1987	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1978	197	159	242	218	84	181	139	53	191	2036
1973	359	258	358	323	149	279	232	64	242	3117
1971	268	174	235	247	120	207	219	52	219	2373
1966	470	325	415	403	215	397	342	82	320	4176
1962	457	349	467	473	215	362	345	108	381	4162
1960	340	249	364	316	145	260	247	75	266	3098
1957	516	345	508	522	204	378	382	100	458	4657
1955	278	182	295	271	125	221	241	71	271	2664
1953	243	146	208	204	96	171	190	45	172	2102
1948	852	491	658	607	302	613	546	126	564	6858
1946	1321	660	1006	838	451	785	654	128	619	9403
1944	1307	633	894	709	400	741	563	106	535	8954
1939	1733	890	1262	1013	556	987	769	147	702	12219

n.a. = not available

Table S2. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>]anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>]fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3- <i>c,d</i>]pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
1939	1071	598	822	646	374	681	512	108	484	7945
1939	1236	656	901	662	395	717	528	104	482	8778
1937	694	354	510	409	227	411	328	67	301	5078
1935	578	320	428	362	214	382	338	64	284	4455
1930	394	217	269	236	133	248	223	35	203	2942
1930	261	140	187	149	83	155	135	16	123	1945
1928	180	96	134	109	52	95	103	16	95	1411
1926	190	103	144	117	56	108	110	16	100	1542
1923	147	79	108	77	39	78	77	11	74	1171
1921	204	117	150	125	60	124	117	16	115	1602
1919	197	106	141	120	59	120	116	18	118	1541
1917	196	109	139	121	60	111	114	16	109	1531
1914	310	173	222	193	91	189	163	28	174	2314
1912	315	172	208	171	82	176	151	23	153	2269
1910	124	63	76	64	30	67	58	10	58	907
1908	61	33	48	40	19	40	35	5	35	528
1905	103	56	76	69	32	61	70	10	69	913
1903	125	68	86	65	30	67	76	7	66	1012
1901	73	34	49	36	17	33	41	3	40	626
1899	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = not available

Table S3. Total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in dated sediment core TH2 from Lake Thun.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
2004	1884	13.2	1.0	n.a.	2	8	10	58	3	55
2002	1572	12.6	1.1	30	2	4	11	65	5	72
2000	1904	14.1	1.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1996	1311	13.1	1.1	84	13	6	27	69	15	86
1993	1766	13.4	1.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1989	1575	n.a.	0.8	29	2	5	11	75	5	83
1987	1585	13.7	1.1	32	2	8	13	91	5	114
1983	1183	15.8	1.1	29	3	7	14	101	10	194
1979	1260	18.2	1.4	33	3	9	16	118	9	204
1972	881	15.7	1.2	30	3	8	15	109	11	207
1961	1013	16.0	1.1	29	4	6	14	93	10	161
1954	1308	17.6	0.6	47	6	14	25	261	38	357
1951	1817	15.1	0.7	34	5	11	23	210	33	333
1946	2032	16.5	0.7	21	5	4	11	88	14	155
1943	2565	10.1	1.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1939	1906	10.5	1.2	21	4	4	11	71	9	93
1935	1475	10.5	0.9	25	6	5	16	125	15	183
1931	1276	12.7	1.2	32	6	7	19	143	17	260
1931	1438	11.3	0.9	38	88	3	26	154	177	275

n.a. = not available

Table S3. continued.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [μg/kg]	acenaphthylene [μg/kg]	acenaphthene [μg/kg]	fluorene [μg/kg]	phenanthrene [μg/kg]	anthracene [μg/kg]	fluoranthene [μg/kg]
1926	1703	10.4	0.7	35	8	4	11	79	27	136
1923	1955	7.8	1.2	28	4	4	9	67	11	96
1919	2405	8.1	1.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1915	1661	8.8	0.8	21	3	3	8	66	5	78
1912	2305	8.3	0.8	19	3	3	8	54	4	63
1908	2119	9.7	0.8	93	65	5	25	208	388	351
1908	2266	8.7	0.6	35	9	6	18	148	19	220
1906	2659	10.1	0.5	29	7	3	13	98	10	106
1903	2169	10.7	0.7	32	17	5	19	209	18	344
1899	2160	8.9	0.4	28	10	5	17	156	14	207
1895	2697	9.7	0.5	22	8	5	15	137	16	186
1888	2343	8.7	0.4	27	10	5	15	135	15	198
1884	1935	9.9	0.6	31	19	4	20	184	24	272
1881	2556	7.9	0.9	22	12	3	13	111	16	160
1877	2525	8.4	0.7	22	2	2	7	40	3	39
1873	2751	9.4	0.6	31	3	6	8	40	4	43
1870	2382	9.2	0.7	19	3	2	8	47	5	43
1866	2841	9.1	0.6	29	27	3	17	161	29	221
1862	2923	10.6	0.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = not available

Table S4. Polycyclic aromatic hydrocarbons in dated sediment core TH2 from Lake Thun.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
2004	40	18	36	26	12	30	28	3	28	356
2002	53	24	44	33	15	35	32	4	33	466
2000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1996	80	34	54	36	22	52	30		32	641
1993	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1989	56	24	46	33	18	37	39		29	492
1987	71	36	59	46	24	55	49	4	38	646
1983	104	49	80	70	37	71	69	7	54	898
1979	109	54	87	76	40	77	83	6	62	986
1972	96	51	93	86	53	92	67	7	65	993
1961	85	48	93	89	48	74	76	7	64	902
1954	266	168	193	154	85	219	134	15	119	2101
1951	239	159	180	155	73	199	101	30	110	1894
1946	115	77	80	68	32	93	45	11	48	866
1943	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1939	66	37	62	63	25	61	46	9	45	626
1935	124	70	116	120	52	108	92	16	88	1161
1931	143	86	154	158	66	106	101	21	106	1426
1931	239	126	174	179	82	244	145	24	140	2115

n.a. = not available

Table S4. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
1926	109	55	83	84	37	126	76	12	73	955
1923	71	31	52	49	21	48	40	5	39	575
1919	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1915	54	26	45	41	17	40	29	3	28	469
1912	44	20	37	33	15	34	28	3	24	391
1908	378	164	205	187	95	568	186	29	173	3122
1908	158	78	125	109	47	115	69	9	70	1236
1906	79	31	57	50	23	49	45	5	39	645
1903	232	109	204	199	89	177	118	22	118	1913
1899	144	66	127	119	49	103	70	14	73	1204
1895	140	74	104	90	39	110	62	8	62	1078
1888	142	77	117	114	49	110	79	11	75	1179
1884	184	103	173	173	77	147	107	19	116	1653
1881	111	70	96	87	40	95	57	10	52	956
1877	23	10	19	17	6	15	15		13	233
1873	28	12	19	17	7	20	14		12	264
1870	28	14	18	14	7	15	10	1	14	248
1866	165	98	108	79	43	102	78	10	69	1237
1862	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

n.a. = not available

Table S5. Total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in dated sediment core TH3 from Lake Thun.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
2005	1954	11.7	n.a.	27.53	1.20	5.06	8.87	35.73	1.88	36.51
2000	1917	n.a.	n.a.	43.60	1.42	7.84	10.67	41.90	2.28	46.86
1996	2236	11.1	n.a.	31.43	1.32	5.53	9.57	41.47	2.16	50.39
1993	2304	10.8	n.a.	28.29	1.84	3.08	8.16	43.03	3.97	64.96
1989	1921	11.9	n.a.	32.24	1.82	8.85	11.71	60.42	4.23	95.21
1985	2123	12.3	0.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1982	2006	12.2	0.8	22.35	1.90	5.73	11.03	51.25	3.17	86.22
1978	2028	12.2	0.8	21.69	3.01	3.97	10.13	59.95	6.51	116.40
1975	2096	12.0	0.8	24.20	4.64	4.39	10.92	70.53	8.54	146.53
1971	2417	11.6	0.8	23.30	4.38	4.67	12.32	70.52	11.27	157.57
1968	2252	11.4	0.9	20.75	4.08	4.91	11.42	78.01	8.75	168.52
1964	2069	10.6	0.7	27.49	8.69	4.52	16.03	119.56	15.73	286.75
1960	2378	8.5	0.6	30.23	9.37	6.28	18.26	150.61	17.01	306.66
1957	2296	7.2	0.7	26.22	10.91	4.44	16.44	141.05	16.51	261.16
1953	2602	5.6	0.5	24.29	10.94	3.43	16.38	125.26	13.21	211.80
1950	2595	7.3	0.6	27.11	14.37	2.63	16.84	132.56	13.39	215.72
1946	2372	7.1	0.7	29.41	12.25	5.24	16.58	110.90	12.01	186.11
1943	2622	6.4	0.7	27.87	8.04	4.29	15.37	106.73	10.51	169.87
1939	2106	6.3	0.8	33.14	9.03	3.48	14.05	89.25	15.69	150.95

n.a. = not available

Table S5. continued.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
1936	3047	6.5	0.5	27.77	3.55	3.76	11.43	77.92	8.89	122.38
1932	2570	6.5	0.5	27.42	2.95	3.43	9.70	64.72	5.41	94.65
1928	2430	6.1	0.6	24.30	2.13	2.93	8.59	51.45	3.45	69.82
1925	2876	6.1	0.6	23.69	3.89	2.54	10.15	55.85	6.17	76.30
1921	2344	5.3	0.7	27.28	2.66	3.12	10.18	63.70	6.31	93.05
1918	2180	6.8	0.7	25.08	3.29	4.33	11.17	85.59	13.53	150.92
1914	3280	6.2	0.6	20.33	1.92	2.48	7.98	56.81	5.14	78.51
1911	2596	6.3	0.6	20.46	1.55	3.16	8.20	60.04	4.90	86.83
1907	2376	6.2	0.8	24.20	1.87	4.16	9.19	80.80	6.78	116.22
1904	2951	5.8	0.7	21.24	2.08	3.65	8.61	59.65	4.52	75.44
1900	2546	6.1	0.6	19.79	1.83	2.48	7.25	43.46	2.45	44.40
1896	2305	6.3	0.8	19.38	1.54	2.93	7.73	42.39	2.39	37.13
1893	2302	5.9	0.8	22.66	1.72	3.26	8.31	40.58	1.93	29.62
1889	3208	6.7	0.7	18.18	1.68	2.46	6.86	33.58	1.95	21.91
1886	2583	5.7	0.7	20.97	2.07	2.68	7.38	33.44	2.05	19.15
1882	3148	6.0	0.6	21.73	2.33	2.74	7.56	35.30	1.89	17.49
1879	3334	4.6	0.4	23.18	2.05	3.01	7.22	31.09	1.51	13.37
1875	3139	4.3	0.6	19.47	1.87	2.73	6.44	28.35	1.04	13.28
1871	3935	4.2	0.7	18.19	1.34	2.57	5.09	24.70	0.62	10.81
1868	3763	4.0	0.5	17.45	1.26	2.25	4.49	21.88	0.41	8.24

Table S5.continued.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [μg/kg]	acenaphthylene [μg/kg]	acenaphthene [μg/kg]	fluorene [μg/kg]	phenanthrene [μg/kg]	anthracene [μg/kg]	fluoranthene [μg/kg]
1864	3421	4.2	0.5	21.08	1.40	2.68	5.24	22.68	0.44	8.39
1861	3405	4.3	0.4	19.79	1.64	2.36	4.92	21.28	0.53	9.73
1857	3783	4.3	0.6	19.18	1.44	2.05	4.00	17.57	0.44	8.63
1854	3551	4.7	0.7	18.85	1.46	2.17	4.84	21.50	0.47	9.91
1850	3492	4.7	0.6	21.37	1.44	1.81	4.95	18.24	0.51	7.23
1847	3659	4.3	0.6	19.66	1.22	2.03	4.79	21.35	0.45	10.14
1843	2690	4.7	0.5	20.77	1.29	1.93	5.08	24.85	0.58	13.60
1839	3370	4.7	0.5	18.49	1.27	2.06	5.05	24.95	0.66	14.72
1836	3099	4.9	0.4	34.00	1.23	3.03	4.27	20.86	0.49	11.47
1832	3066	4.2	0.6	19.43	1.10	2.04	4.17	18.63	0.44	9.63
1829	3134	5.8	0.5	16.76	1.09	2.22	5.20	22.51	0.55	12.70

Table S6. Polycyclic aromatic hydrocarbons in dated sediment core TH3 from Lake Thun.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
2005	24.47	9.56	16.14	16.99	6.11	10.67	9.91	0.94	14.45	226.03
2000	31.95	11.76	20.58	20.49	7.68	12.99	12.67	1.68	15.86	290.21
1996	33.69	12.07	20.62	19.40	7.49	11.72	10.37	1.04	15.09	273.38
1993	45.31	17.62	28.04	29.13	10.99	22.86	20.78	3.03	22.91	353.99
1989	66.38	25.61	41.21	41.62	16.93	31.95	28.00	2.97	29.24	498.37
1985	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1982	56.90	27.73	43.77	49.65	23.40	31.50	39.72	5.04	39.10	498.46
1978	78.16	40.78	62.62	71.36	33.88	47.78	51.48	4.76	52.00	664.46
1975	97.56	51.98	79.53	100.49	48.05	69.65	78.95	6.96	71.79	874.71
1971	101.09	55.26	85.73	115.42	57.27	82.01	88.83	10.66	79.27	959.55
1968	105.41	59.40	94.08	117.46	55.76	73.60	94.73	8.10	78.53	983.50
1964	161.89	86.15	131.64	153.61	68.97	100.33	103.93	15.34	95.34	1395.98
1960	192.88	105.12	157.18	176.67	86.75	127.80	130.07	23.85	119.91	1658.64
1957	164.44	90.09	135.24	142.40	67.19	108.93	104.43	14.92	92.99	1397.38
1953	116.26	58.50	103.54	102.91	48.76	68.62	76.03	11.23	71.41	1062.56
1950	132.04	61.18	100.05	105.33	46.91	81.92	82.25	13.46	68.77	1114.53
1946	109.56	54.26	86.42	92.98	42.18	64.25	58.83	7.88	60.24	949.09
1943	98.81	49.35	75.13	79.84	38.13	56.44	56.05	6.52	54.53	857.47
1939	87.62	44.38	67.99	73.11	32.90	54.30	56.67	6.45	53.49	792.50

n.a. = not available

Table S6. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
1936	69.27	34.14	52.38	55.16	24.86	29.71	37.60	2.57	38.06	599.45
1932	51.19	22.82	39.00	40.40	22.46	20.47	28.31	1.72	24.59	459.23
1928	35.42	15.97	28.94	29.31	15.89	12.49	20.66	0.00	14.14	335.49
1925	40.10	18.69	31.37	33.96	17.78	16.50	29.02	0.00	21.36	387.38
1921	45.89	25.01	39.19	39.16	17.32	18.87	24.27	1.79	25.49	443.28
1918	94.50	52.52	62.58	65.22	33.38	43.25	48.03	3.82	38.26	735.45
1914	36.17	17.62	30.10	32.87	15.24	17.15	30.01	1.51	24.29	378.14
1911	41.52	20.57	32.04	36.50	16.49	18.77	31.40	2.24	27.07	411.74
1907	63.09	36.14	47.37	49.29	53.50	27.82	40.34	2.77	32.25	595.80
1904	39.00	18.94	29.00	30.15	15.76	15.03	25.69	1.40	18.75	368.91
1900	18.48	7.71	16.54	15.62	6.26	4.66	7.41	0.45	8.81	207.60
1896	16.24	6.80	14.83	13.39	17.31	5.47	11.64	0.93	12.51	212.61
1893	12.99	5.39	12.21	10.95	4.95	2.72	6.39	n.a.	9.69	173.38
1889	10.68	4.03	9.52	7.67	3.05	3.83	5.59	n.a.	6.90	137.89
1886	10.56	2.97	7.72	5.57	2.23	2.97	3.90	n.a.	5.76	129.42
1882	10.51	3.08	7.83	5.12	2.86	2.00	n.a.	n.a.	4.34	124.77
1879	8.63	2.50	7.25	5.36	1.40	2.55	n.a.	n.a.	6.35	115.45
1875	7.05	1.94	6.02	4.10	1.33	1.66	n.a.	n.a.	4.31	99.59
1871	5.78	1.73	5.33	3.96	1.12	1.36	n.a.	n.a.	3.76	86.36
1868	5.11	1.16	4.08	2.69	0.81	1.10	n.a.	n.a.	2.84	73.75

n.a. = not available

Table S6. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
1864	5.07	1.47	4.27	3.07	1.09	1.28	n.a.	n.a.	2.94	81.10
1861	5.11	1.31	4.07	2.59	1.00	0.84	n.a.	n.a.	2.40	77.57
1857	4.64	1.37	3.95	2.90	0.84	1.34	n.a.	n.a.	2.59	70.95
1854	6.23	1.46	5.27	3.81	1.41	0.81	n.a.	n.a.	3.77	81.96
1850	4.45	1.00	3.96	2.38	1.09	0.57	n.a.	n.a.	1.84	70.85
1847	5.34	1.37	5.11	3.23	1.12	0.69	n.a.	n.a.	2.49	78.99
1843	6.74	1.90	5.97	4.69	1.60	1.33	n.a.	n.a.	4.15	94.45
1839	6.94	2.11	6.15	4.72	2.36	1.08	n.a.	n.a.	4.21	94.78
1836	5.90	1.41	4.68	3.07	1.25	0.57	n.a.	n.a.	2.24	94.48
1832	5.26	1.27	4.47	3.20	1.28	0.67	n.a.	n.a.	3.39	74.98
1829	6.51	1.77	5.41	3.85	1.28	0.85	n.a.	n.a.	3.11	83.82

n.a. = not available

Table S7. Total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in dated sediment core from Lake Engstlen.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
2007	1239	15.2	1.5	10.20	0.48	1.44	2.85	22.08	1.06	25.52
2002	1042	13.2	1.8	9.09	0.36	1.16	2.57	19.53	0.80	19.29
1997	1093	24.5	2.6	8.73	0.56	1.06	2.56	19.96	1.00	27.13
1992	976	29.5	2.2	8.09	0.42	1.16	2.59	20.04	1.09	27.65
1987	1338	24.6	2.7	6.10	0.55	0.75	2.03	16.50	0.97	27.36
1982	1540	16.8	3.0	8.09	0.55	1.20	2.60	21.32	1.08	30.38
1977	1988	13.1	3.3	7.58	0.38	1.10	2.44	20.78	1.42	27.99
1972	2182	12.2	3.1	11.24	0.59	1.41	2.52	18.47	1.07	31.87
1967	1567	10.0	3.2	26.70	0.66	2.01	3.05	17.38	1.00	23.33
1964	2579	21.0	2.9	17.79	0.95	2.16	3.47	24.44	1.38	37.69

Table S7. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
2007	14.11	6.85	21.65	28.84	9.51	5.01	15.51	1.77	10.58	177.45
2002	10.54	5.14	14.60	21.30	7.14	4.82	12.86	1.34	9.28	139.82
1997	14.82	7.14	19.38	29.57	10.05	8.01	20.68	2.35	12.96	185.98
1992	14.05	6.97	17.59	29.49	10.33	8.54	25.08	2.91	13.83	189.82
1987	13.85	7.22	19.27	29.27	10.19	6.72	17.15	2.04	10.20	170.19
1982	15.25	7.50	18.13	27.13	9.61	7.95	21.13	2.80	12.88	187.60
1977	15.02	8.73	18.00	25.96	9.60	8.01	19.51	2.98	12.53	182.05
1972	17.02	7.89	23.46	33.64	10.84	6.60	17.18	1.52	16.52	201.86
1967	12.54	5.90	15.79	24.84	8.27	4.95	12.72	1.18	14.31	174.63
1964	19.52	9.18	24.51	40.92	13.37	5.44	24.01	2.08	18.06	244.96

Table S8. Total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in dated sediment core from Lake Oberaar.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
2004	30020	1.5	0.3	9.80	0.15	0.96	0.68	4.71	0.08	2.94
2001	28380	1.3	0.2	9.77	0.13	1.02	0.95	6.09	0.11	2.46
2001	28381	n.a.	n.a.	8.65	0.10	1.07	1.15	8.03	0.18	2.83
2001	28382	n.a.	n.a.	12.27	0.11	0.86	0.77	4.48	0.08	2.32
2001	28383	n.a.	n.a.	7.15	0.10	0.73	0.90	6.76	0.11	3.08
1997	34507	1.5	0.3	5.21	0.09	0.53	0.52	3.38	0.05	2.09
1992	11841	1.4	0.3	5.46	0.16	0.56	0.66	4.90	0.09	3.08
1987	12071	1.1	0.3	5.79	0.25	0.65	0.87	8.99	0.22	7.41
1987	12072	n.a.	n.a.	8.34	0.15	0.32	0.41	2.40	0.05	2.93
1982	11291	1.3	0.3	5.78	0.23	0.54	0.48	3.71	0.10	3.70
1977	11344	1.1	0.3	8.20	0.30	0.37	0.45	3.92	0.11	9.11
1972	16460	1.1	0.3	5.76	0.21	0.57	0.65	4.87	0.16	4.68
1967	16460	1.1	0.3	5.45	0.25	0.56	0.55	4.19	0.33	4.64
1967	16461	n.a.	n.a.	7.81	0.18	0.31	0.42	2.46	0.08	3.71
1961	19797	0.9	0.3	4.90	0.28	0.62	0.75	5.75	0.00	7.30
1956	14825	0.8	0.3	7.96	0.28	0.70	0.65	4.74	0.26	5.56

n.a. = not available

Table S8. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>]fluoranthene [µg/kg]	benzo[<i>a</i>]pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
2004	1.68	0.73	1.63	2.29	0.68	0.05	0.48	0.00	0.38	27.23
2001	1.74	0.70	1.54	2.24	0.68	0.13	0.77	0.00	0.65	28.99
2001	1.85	0.64	1.45	2.07	0.60	0.24	1.04	0.11	0.90	30.89
2001	1.48	0.53	1.38	2.04	0.66	0.00	0.56	0.00	0.00	27.54
2001	1.96	0.96	2.09	2.97	0.95	2.12	0.62	0.00	0.62	31.12
1997	1.06	0.47	1.36	1.93	0.56	0.00	0.31	0.00	0.00	17.57
1992	1.57	0.63	2.43	3.21	0.96	0.00	0.00	0.00	0.00	23.72
1987	3.94	1.69	5.27	7.59	2.42	5.34	3.26	0.34	1.27	55.30
1987	1.76	0.64	2.08	2.29	0.77	1.90	0.48	0.00	0.40	24.89
1982	1.89	0.87	2.51	3.75	1.17	0.00	0.34	0.00	0.00	25.07
1977	6.16	3.13	5.44	5.68	2.37	5.33	1.61	0.00	1.30	53.46
1972	2.91	1.38	3.34	4.44	1.52	0.00	0.43	0.00	0.29	31.21
1967	1.77	1.08	3.57	5.24	1.78	0.00	2.26	0.00	0.00	31.67
1967	2.30	1.01	3.02	3.38	1.26	3.25	0.83	0.00	0.54	30.57
1961	4.64	2.28	5.90	8.29	2.86	8.80	3.22	0.00	1.43	57.00
1956	3.62	2.17	3.42	4.65	1.87	0.00	1.08	0.00	3.23	40.19

Table S9. Total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in dated sediment core from Lake Stein.

year	sediment flux [g/m ² /y]	total organic carbon [mg/g]	black carbon [mg/g]	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]
2008	70242	3.3	2.1	8.30	0.13	1.18	1.23	7.70	0.19	4.81
2006	64672	4.1	2.6	8.97	0.16	1.11	1.33	8.73	0.26	6.82
2004	71391	4.4	3.0	7.73	0.17	1.01	1.13	7.54	0.00	7.18
2001	31495	3.7	2.6	8.85	0.12	0.77	0.95	4.60	0.09	4.71
1999	75156	2.4	2.0	6.28	0.11	0.80	1.01	6.73	0.15	4.61
1997	94359	2.8	2.4	7.91	0.12	0.75	0.88	4.61	0.10	5.47
1995	82816	2.7	1.8	7.32	0.10	0.74	0.74	4.01	0.08	4.61
1994	54045	2.2	1.8	6.91	0.11	0.68	0.75	3.98	0.05	4.64
1992	107962	2.1	2.0	6.92	0.16	0.65	0.78	5.51	0.15	7.04
1990	74097	1.7	1.2	5.92	0.10	0.88	1.11	7.96	0.18	4.77
1989	97699	2.0	1.9	5.24	0.10	0.50	0.64	4.13	0.09	4.67
1987	106341	2.1	2.1	5.68	0.10	0.52	0.74	5.38	0.15	5.38
1984	55447	2.7	2.7	6.31	0.15	1.00	1.21	8.71	0.22	7.01
1982	88354	2.5	2.5	6.28	0.15	0.63	0.76	4.94	0.16	6.33
1980	85491	2.7	2.2	6.66	0.16	0.60	0.89	6.01	0.17	8.04
1977	55545	2.9	2.6	6.60	0.14	0.78	0.92	5.74	0.17	6.77
1975	71233	2.6	2.6	6.59	0.17	0.55	0.94	6.68	0.19	9.15
1973	61139	2.2	1.9	5.65	0.20	0.64	0.96	6.42	0.13	4.84
1969	55876	2.3	1.9	5.63	0.24	0.40	0.85	5.74	0.07	8.53
1966	33067	2.6	2.6	7.50	0.83	0.49	1.30	10.26	0.20	13.15
1961	52218	2.2	1.4	6.72	0.45	0.91	1.33	10.08	0.14	8.61

Table S9. continued.

year	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]	benzo[<i>b</i>] fluoranthene [µg/kg]	benzo[<i>k</i>] fluoranthene [µg/kg]	benzo[<i>a</i>] pyrene [µg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [µg/kg]	dibenzo[<i>a,h</i>]anthracene [µg/kg]	Benzo[<i>g,h,i</i>]perylene [µg/kg]	sum 16 PAHs [µg/kg]
2008	2.78	0.77	2.73	3.54	0.88	0.51	0.78	0.00	1.33	36.87
2006	3.74	1.16	4.33	6.01	1.46	0.72	1.71	0.00	2.18	48.68
2004	3.87	1.25	4.94	6.82	1.66	0.99	2.12	0.00	2.56	48.98
2001	2.45	0.74	3.39	2.90	1.33	2.17	0.00	0.00	0.46	31.07
1999	2.62	0.74	2.73	3.18	0.80	0.38	0.76	0.00	1.09	31.98
1997	2.81	1.18	4.94	4.30	1.92	0.25	0.00	0.00	0.61	35.87
1995	2.38	0.72	3.27	2.56	0.99	2.04	0.00	0.00	0.35	29.92
1994	2.46	0.82	3.62	3.06	1.19	0.16	0.00	0.00	0.31	28.74
1992	3.57	1.27	5.97	5.00	1.93	0.18	0.86	0.00	0.48	40.47
1990	2.68	0.83	3.07	3.93	1.00	0.51	1.17	0.17	1.56	35.84
1989	2.56	1.07	4.16	4.49	1.54	0.33	1.27	0.00	0.64	31.42
1987	2.96	1.08	4.63	5.18	1.75	0.38	1.11	0.00	1.21	36.27
1984	3.63	1.02	4.07	5.33	1.26	0.61	1.63	0.16	1.92	44.24
1982	3.47	1.32	5.60	5.49	1.97	0.15	0.00	0.00	0.79	38.03
1980	4.13	1.44	6.30	5.82	1.96	0.19	0.00	0.00	0.67	43.06
1977	3.50	1.03	4.21	4.53	1.20	0.38	0.85	0.17	1.11	38.10
1975	4.43	1.55	7.63	6.65	2.55	0.18	0.00	0.00	0.92	48.19
1973	2.13	0.57	2.70	2.79	0.66	0.08	0.26	0.00	0.15	28.18
1969	2.18	0.75	7.40	5.56	1.21	0.26	0.00	0.00	0.29	39.10
1966	3.49	0.60	7.13	6.14	0.88	0.08	0.14	0.00	0.12	52.33
1961	3.00	0.77	4.76	3.81	0.76	0.03	0.24	0.09	0.31	42.02

Table S10. Polycyclic aromatic hydrocarbons in blank samples based on a typical sample amount.

sample	naphthalene [µg/kg]	acenaphthylene [µg/kg]	acenaphthene [µg/kg]	fluorene [µg/kg]	phenanthrene [µg/kg]	anthracene [µg/kg]	fluoranthene [µg/kg]	pyrene [µg/kg]	benzo[<i>a</i>] anthracene [µg/kg]	chrysene [µg/kg]
blank TH1-1	2.18	<0.01	0.55	0.27	1.16	<0.01	1.07	2.25	<0.01	<0.01
blank TH1-2	2.33	<0.01	0.78	0.46	1.66	<0.01	0.62	0.45	<0.01	<0.01
blank TH1-3	2.18	0.11	0.59	0.30	1.06	<0.01	0.27	<0.01	<0.01	<0.01
blank TH1-4	6.30	0.26	1.20	0.96	2.59	<0.01	0.65	0.56	<0.01	<0.01
blank TH2-1	6.30	0.26	1.20	0.96	2.59	<0.01	0.65	0.56	<0.01	<0.01
blank TH2-2	3.45	0.13	0.41	0.32	1.49	<0.01	0.52	<0.01	<0.01	<0.01
blank TH2-3	2.84	0.09	0.36	0.27	1.48	<0.01	0.65	0.75	<0.01	<0.01
blank TH2-4	2.29	0.06	0.38	0.23	1.06	<0.01	0.55	0.73	0.39	<0.01
blank TH3-1	14.07	0.17	2.31	1.17	2.83	<0.01	0.65	<0.01	0.55	0.20
blank TH3-2	22.43	<0.01	2.42	1.70	3.45	<0.01	1.16	<0.01	<0.01	<0.01
blank TH3-3	7.06	<0.01	0.64	0.38	1.45	<0.01	0.45	<0.01	<0.01	<0.01
blank TH3-4	4.31	<0.01	0.87	0.63	1.82	<0.01	0.43	<0.01	<0.01	<0.01
blank TH3-5	4.05	0.14	1.18	0.70	2.23	<0.01	0.55	<0.01	<0.01	<0.01
blank TH3-6	4.57	0.13	0.76	0.46	2.13	<0.01	1.10	1.46	0.78	<0.01
blank ENG	9.22	0.05	0.30	0.30	0.47	0.01	0.17	0.15	<0.01	<0.01
blank OAR-1	4.59	0.04	0.41	0.60	4.40	0.10	0.70	0.65	<0.01	<0.01
blank OAR-2	4.48	<0.01	0.37	0.27	0.89	<0.01	0.19	0.10	0.12	0.17
blank ST	4.73	0.03	0.53	0.57	3.69	0.08	0.67	0.58	0.16	0.09

Table S11. Polycyclic aromatic hydrocarbons in blank samples based on a typical sample amount.

sample	benzo[<i>b</i>] fluoranthene [μg/kg]	benzo[<i>k</i>]fluoranthene [μg/kg]	benzo[<i>a</i>]pyrene [μg/kg]	indeno[1,2,3, <i>c,d</i>] pyrene [μg/kg]	dibenzo[<i>a,h</i>]anthracene [μg/kg]	Benzo[<i>g,h,i</i>]perylene [μg/kg]	sum 16 PAHs [μg/kg]
blank TH1-1	<0.01	0.23	<0.01	<0.01	<0.01	<0.01	7.70
blank TH1-2	0.18	0.59	<0.01	<0.01	<0.01	<0.01	7.07
blank TH1-3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	4.51
blank TH1-4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	12.52
blank TH2-1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	12.52
blank TH2-2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	6.31
blank TH2-3	<0.01	<0.01	<0.01	2.24	<0.01	1.88	10.58
blank TH2-4	1.21	<0.01	<0.01	<0.01	<0.01	<0.01	6.90
blank TH3-1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	21.96
blank TH3-2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	31.16
blank TH3-3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	9.98
blank TH3-4	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	8.05
blank TH3-5	0.20	0.32	<0.01	<0.01	<0.01	<0.01	9.36
blank TH3-6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	11.39
blank ENG	<0.01	<0.01	<0.01	<0.01	<0.01	0.11	10.78
blank OAR-1	<0.01	<0.01	<0.01	<0.01	<0.01	0.21	11.69
blank OAR-2	0.15	0.16	0.16	<0.01	<0.01	0.17	7.22
blank ST	0.16	0.03	0.12	<0.01	<0.01	<0.01	11.43