

Historical Changes in Levels of Organic Pollutants in Sediment Cores from Brno Reservoir, Czech Republic

E. Franců · J. Schwarzbauer · R. Lána · D. Nývlt · S. Nehyba

Received: 11 May 2009 / Accepted: 14 August 2009 / Published online: 2 September 2009
© Springer Science + Business Media B.V. 2009

Abstract Results of a comprehensive study are presented on the spatial and depth-related distribution of persistent organic pollutants (POPs) in sediments of the Brno reservoir, Czech Republic. Based on sedimentological observations, three major historic phases were identified related to the evolution of the depositional environment, flow rate, and material input. Data on organic carbon, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides showed specific distribution patterns in a 3-m-deep core. The analysis of the depth trends of the geochemical data combined with sedimentology made it possible to distinguish between remote sources of the pollutants, early weathering alterations of POPs, transport by river associated with organic matter as sorbent on one

hand, and local sources weakly related to lithology on the other hand. The integrated sedimentological and environmental geochemical archive provided an improved dynamic view of the pollution in historical terms.

Keywords PCBs · PAHs · Organochlorine pesticides · Sediment profile

1 Introduction

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are incessantly being found in water, sediments, and biota throughout the world despite the fact that their production and usage have been restricted since the 1970s (Konat and Kowalewska 2001; Sapozhnikova et al. 2004; Covaci et al. 2006). POPs are known to have a strong affinity to particles, and thus, river and lake sediments represent an important sink for these contaminants (Zennegg et al. 2007). Many authors have successfully used undisturbed sediment cores as pollution archives to restore the historical changes in the levels and patterns of POPs in aquatic environments (e.g., Hong et al. 2003; Frignani et al. 2005; Heim et al. 2005; Evenset et al. 2007; Kim et al. 2007).

The bulk analysis of POPs is often extended to more precise information on the pollution sources

E. Franců (✉) · R. Lána · D. Nývlt
Czech Geological Survey,
Leitnerova 22,
65869 Brno, Czech Republic
e-mail: eva.francu@geology.cz

J. Schwarzbauer
Institute of Geology and Geochemistry of Petroleum and Coal, Aachen University of Technology (RWTH),
Lochnerstr. 4-20,
52056 Aachen, Germany

S. Nehyba
Department of Geological Sciences,
Masaryk University of Brno,
Kotlarska 2,
61137 Brno, Czech Republic

and their fate in the environment using more detailed analysis, e.g., by isomer- or congener-specific analyses of PCBs, OCPs, or PAHs (e.g., Götz et al. 2007; Zennegg et al. 2007). The multicomponent analysis of different substance classes provides a basis for a comprehensive assessment of relationships among different types of contaminants and their sources.

Owing to an intensive agricultural and industrial production in past few decades, in particular, river and reservoir sediments in the Czech Republic are loaded with POPs and their levels are only slowly decreasing (Holoubek et al. 2000, 2003, 2007). In contrast to soil contamination monitored regularly in the Czech Republic since the late 1970s (Svobodova et al. 2003), there are very limited data available on POPs in sediment cores, especially no data prior to the 1970s (e.g., Bábek et al. 2008). This makes it difficult to assess the historical trends in the amounts of POPs entering the aquatic environment and to evaluate the effect of implementation of legal measures toward the POPs reduction on their real occurrence.

A great number of papers published during the past decade present valuable data on the pollutant distribution in surface sediments and cores (e.g., Dsikowitzky et al. 2002; Yunker et al. 2002; Navarro et al. 2006; Li et al. 2009). In many papers, however, there is a limited analysis of the sedimentological features of the pollutant distribution, which may play a key role in distinguishing among the different sources, transport processes, and state of preservation of the contaminants in the specific environment (Eyre and McConchie 1993; Pereira et al. 1999; Lüder et al. 2006).

Brno reservoir is an important artificial lake within the southern Moravian water management system. It was built on the Svatka River in 1936–1939 and filled in the early 1940s (Bayer et al. 1954). This type of basin provides a unique opportunity to study an undisturbed sedimentary sequence not only to illustrate the spatial distribution in the reservoir but also describe depth trends in POPs. For this purpose, more comprehensive analysis comprising congener- and isomer-specific analyses as well as multicomponent approaches have been applied together with sedimentological characteristics of the sediment cores to document a sedimentation period from the 1920s to the construction of the Brno reservoir and its evolution until present time.

2 Sampling and Methods

2.1 Sampling

A preliminary sampling campaign was performed to explore an optimal location for drilling a deep core. Therefore, 12 shallow cores were collected (Fig. 1) using a hand-coring device. Each core was cut into slices of about 5 cm; the total cored depth interval ranged from less than 100 to 250 cm. Based on these results, a 292.5-cm-deep core (BP4) was drilled in March 2008 using Makita vibration hammer and Eijkelpamp coring tubes (Fig. 1). The drilling site of the BP4 core is located in the upper part of the Brno reservoir below the Veveří Castle, where the Svatka River has incised meandering fluvial pattern. The core was placed in a plastic sleeve and divided immediately into two equal parts. One part was frozen and stored and the other one was photo documented, lithologically described, and divided into 121 subsamples, each about 2.5 cm thick.

2.2 Bulk Characterization

The samples were dried, pulverized, homogenized, and sieved through a 1-mm mesh. All samples were subjected to elemental analysis of total organic (TOC) and inorganic carbon using a Metalyt CS 1000 S apparatus (ELTRA GmbH, Neuss, Germany). Environmental magnetic susceptibility (MSS) was measured as mass susceptibility (χ) in $10^{-9} \text{m}^3 \text{kg}^{-1}$ dividing the volume susceptibility by material density using the MFK1-FA Kappabridge at the magnetic field of 200 A m^{-1} in the AGICO, Ltd. For further summary of magnetic parameters and terminology, see Evans and Heller (2003).

2.3 Extraction and Fractionation

n-Pentane, *n*-hexane, *n*-heptane, and dichloromethane (DCM; all of residue analysis grade) as well as silica gel were purchased from Merck (Darmstadt, Germany); anhydrous sodium sulfate for analysis (activated at 600°C for 6 h prior use) was obtained from Penta (Chrudim, Czech Republic). Sample aliquots of 5 g were mixed with a portion of activated Na_2SO_4 and spiked with 25 μL of surrogate recovery standard solution containing 2,4,5,6-tetrachloro-*m*-xylene, PCB 209, d10-

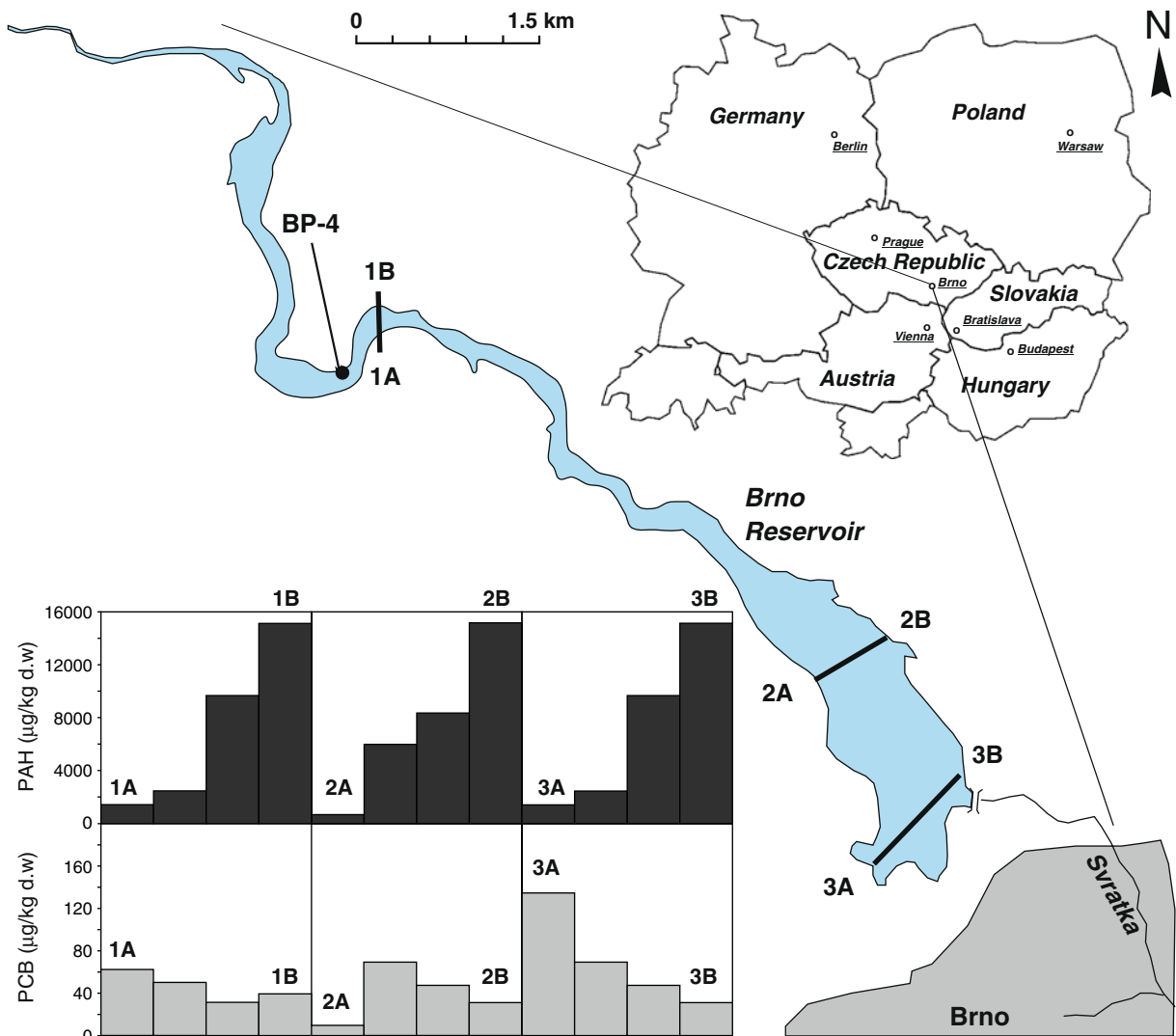


Fig. 1 Sampling locations and PCB and PAH concentrations for surface sediments in Brno reservoir

anthracene and d12-chrysene. Extraction was performed with *n*-hexane/acetone (1:1) by accelerated solvent extraction on a ASE 100 system (Dionex, USA). The extractions were performed at 100°C and 2,000 psi with two static extraction cycles (4 min each), then the extraction cell was flushed with solvent (60%) and purged with nitrogen (2 min). The raw extracts were reduced to 0.5 mL using a gentle stream of nitrogen, and the volume was adjusted to 10 mL with *n*-hexane. For analysis of halogenated compounds, an aliquot of 2 mL of the extract was taken to a vial, 2 mL of *n*-heptane together with 50 µL of internal standard containing octachloronaphthalene (to control the cleanup step, 1 ng/µL in

n-heptane) was added, and after concentration to 0.5 mL and readjustment to 2 mL with *n*-heptane, activated powder copper was added in order to remove sulfur (overnight). The cleanup was carried out on a glass column with 0.5 g of activated silica, 0.5 g of silica impregnated with AgNO₃, 0.5 g of silica impregnated with NaOH, another 0.5 g cm of silica, then 1.5 g of silica impregnated with 96% H₂SO₄, and finally 0.5 g of silica. The target analytes were eluted with 28 mL of pentane, evaporated to 0.5 mL using nitrogen, transferred to a gas chromatography GC vial, and the volume was adjusted to 1 mL with *n*-heptane. For the PAH analysis, an extract aliquot of 2 mL was placed on a

silica gel column to separate the aliphatic and aromatic hydrocarbon fractions by liquid chromatography using *n*-hexane and DCM as eluents; powder copper was added in order to remove elemental sulfur (overnight).

2.4 Quantification of PCBs and OCPs

PCBs and OCPs were determined using a Hewlett-Packard 6890 gas chromatograph, equipped with an electron capture detector and a HP-5ms fused silica capillary column (60 m×0.25 mm i.d.×0.25 μm, J&W Scientific, USA). Hydrogen was used as the carrier gas (constant flow 1.1 mL/min), and the GC oven temperature was programmed as follows: initial temperature 50°C held for 2 min—increase to 150°C at a rate of 50°C/min—final increase to 300°C at 5°C/min and held for 11 min. The following halogenated organic contaminants were analyzed: seven PCB congeners (28, 52, 101, 118, 138, 153, and 180), dichlorodiphenyltrichloroethane (DDT) and selected metabolites (*o,p'*- and *p,p'*-DDT, *o,p'*- and *p,p'*-dichlorodiphenyldichloroethylene (DDE), and *o,p'*- and *p,p'*-dichlorodiphenyldichloroethane (DDD)) as well as hexachlorobenzene (HCB). All reference standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany), and quantification was based on an external eight-point calibration (0.5–500 ng/mL of each component in *n*-heptane).

2.5 Quantification of PAHs

Determination of 16 EPA PAHs including naphthalene (N), acenaphthylene (Ayl), acenaphthene (Aen), fluorene (F), phenanthrene (P), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo[*a*]anthracene (BaA), chrysene (Ch), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IP), dibenzo[*a,h*]anthracene (DahA), and benzo[*ghi*]perylene (BghiP) was carried out using a Hewlett-Packard 6890N gas chromatograph connected to a HP 5973N MSD quadrupole mass spectrometer (MS) operated in the electron impact mode (EI⁺, 70 eV) with a source temperature of 270°C and single ion monitoring. The chemical identity of PAHs was checked both by retention time match and by using selected qualifier ions. The following ions were used for qualification and quantification (in italic form) of the target PAHs (*m/z*): N (127, 128, 129), Ayl

(151, 152), Aen (152, 153, 154), F (165, 166, 167), P + An (176, 178, 179), Fl + Py (200, 202, 203), BaA + Ch (226, 228, 229), BbF + BkF + BaP (126, 252, 253), IP + BghiP (274, 276), and DahA (276, 278).

A volume of 1 μL was injected splitless (splitless time 60 s, injection temperature 100°C, then increase to 300°C at 720°C/min) onto a HP-5ms capillary column (30 m×0.25 mm i.d.×0.25 μm). Separation was carried out using helium at a constant flow of 1.2 mL/min with the following oven temperature program: 50°C (held for 1.2 min), then at 10°C/min to 170°C and at 6°C/min to the final temperature of 315°C (held for 3 min). The PAH quantification was also based on an external four-point calibration with authentic reference material.

2.6 Quality Control

The identification of all PCBs and OCPs was verified by the analyses of selected samples using GC/MS (method described above). Blank samples were prepared by submitting pure solvent to the whole analytical procedure with activated Na₂SO₄ instead of sample material (at least with each set of ten samples). Analytical blanks had levels of high-chlorinated PCB congeners (138, 153, 180) and HCB below method detection limits; no other compounds were detected. The analyte recoveries were determined by analyzing certified reference material (Metranal™ 2—River sediment, ANALYTIKA Ltd., Prague, Czech Republic) and for PCBs and OCPs, and PAHs were in the range of 61–100.8% and 70.8–128.9%, respectively. Those samples with recoveries below 50% were not used for quantification. The detection limits, calculated from the calibration solution with the lowest concentration within the linear range of the detector used, were 0.7 μg kg⁻¹ for PCBs and OCPs and 1 μg kg⁻¹ for PAHs.

3 Results and Discussion

3.1 Spatial Distribution of POPs

For a preliminary insight into the pollution level of Brno reservoir sediments, three horizontal profiles (A to B), perpendicular to the Svratka River flow, at three different locations (1 to 3) were sampled and analyzed for sum of PAHs and PCBs (Fig. 1). The quantitative

distribution of the selected contaminant groups in the upper 5 cm below the surface along the three horizontal profiles revealed low amounts indicating an only negligible contamination of the Brno reservoir. Interestingly, total PAH concentrations (between 448 to 15,170 $\mu\text{g kg}^{-1}$ dry weight (dw)) increased from right to left bank in all three profiles (Fig. 1, top) and suggested that local sources, such as numerous small furnaces in recreational weekend houses cumulated on the left bank, prevail over the PAH transported by the Svratka River. On the contrary, the PCB concentrations occurred close to or slightly above the value of 20 $\mu\text{g kg}^{-1}$ dw. They show a rather flat distribution along the three profiles (Fig. 1, bottom) with gentle increase from the left to the right bank, i.e., in the opposite direction to the increasing trend of the PAHs. The maximum amounts of all contaminants are observed in the SW bay in the lower end of the reservoir. The slightly elevated values coincide with the location close to the marina and electric boat harbor.

3.2 Depth Trends

The BP4 core provides the most complete set of sedimentological, geochemical, and physical data in the studied area, which document the principal phases of evolution by three depth intervals with characteristic depth trends of the measured parameters. The data include lithological profile and facies (Fig. 2), TOC content, and MSS (Fig. 3). They reflect the oscillation in the water level, seasonal and annual variations.

3.2.1 Fluvial Succession

The lower part of the core (218.5–292.5 cm) is built mainly by medium- to coarse-grained sands with variable bed thickness up to 29 cm. Sands are usually poorly sorted. The very low TOC content ranging from 0.17% to 1.5% is associated with high magnetic susceptibilities (MSS mostly $>250 \cdot 10^{-9} \text{m}^3 \text{kg}^{-1}$), which exhibit several local maxima (300, 257.5, and 240 cm) and gradual upward decrease (Figs. 2 and 3). The increased MSS values are associated with higher proportion of ferromagnetic minerals delivered from amphibolites, scarns, and schists of the Moravicum unit (Svoboda 1963) by the main stream of the Svratka River and their deposition in the sand- and gravel-rich sediments. This lowermost part of the

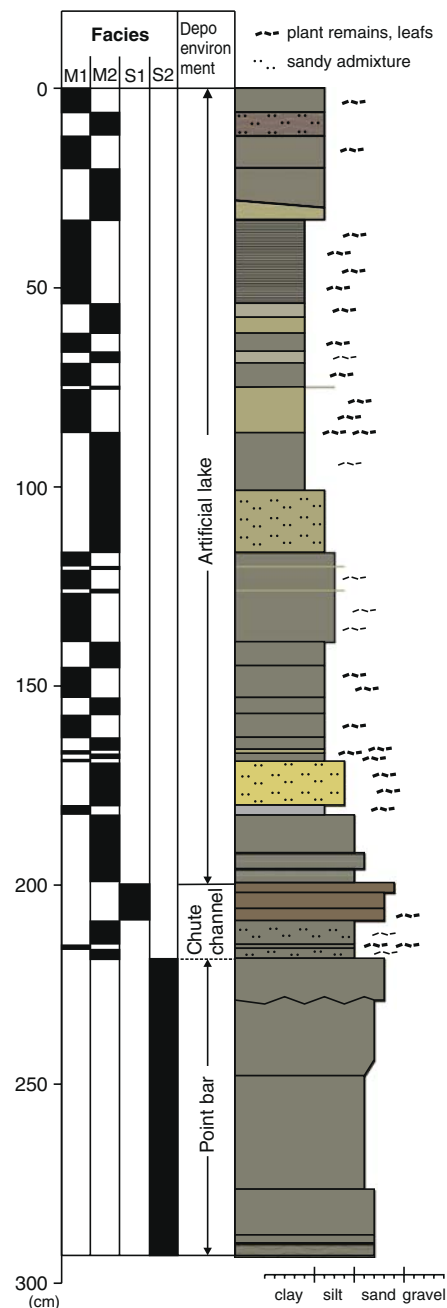


Fig. 2 Lithological profile, depositional environment, and facies in the BP4 borehole. The graphic log on the *right-hand side* presents macroscopically described sedimentological data. Log gives a visual impression of vertical changes in the studied section, including color, sedimentary texture (i.e., grain-size), sedimentary structures, lithology, and nature of bed contacts. The grain size of individual beds is expressed by its thickness—the wider the column, the coarser the sediment. For further explanation of sedimentological logging, see Tucker (1988, 2003)

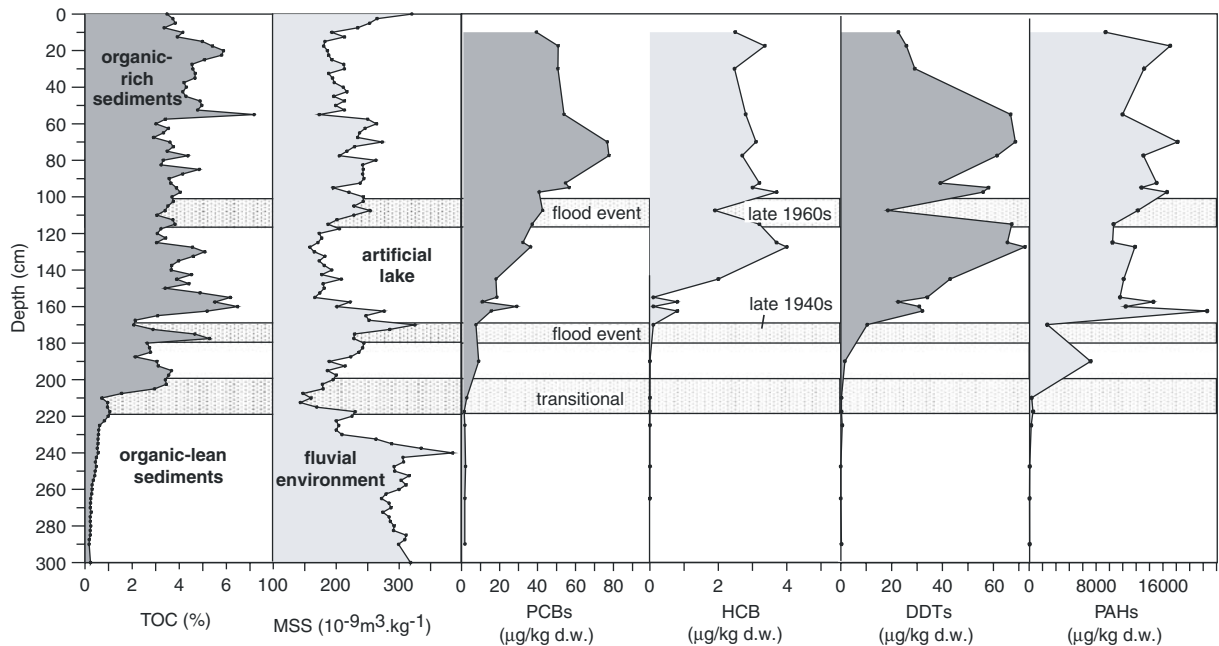


Fig. 3 Total organic carbon (TOC), magnetic susceptibility (MSS), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), DDTs, and hexachlorobenzene (HCB) in the BP4 profile

succession is interpreted as S2 facies formed in fluvial environment by lateral accretion of the sandy material in the meander point bar associated with the migration of the flow line toward the right cut bank of the Svatka River in this part of the valley.

3.2.2 Transitional Interval

The above-laying transitional interval (199.5–218.5 cm) is formed by thinner (<5 cm) sandy beds (S1 facies) alternating with sandy–silty laminas of M2 and M1 facies (Fig. 2), the latter being highly enriched in plant remains. It is characterized by sudden upward increase both in TOC up to 3.55% and MSS down to $155 \times 10^{-9} \text{m}^3 \cdot \text{kg}^{-1}$. These sediments formed most probably by avulsion (redeposition) associated with possible meander chute channeling during a flood event and reservoir filling in 1939 followed by partial water outflow during the years 1939–1940, which is manifested in the coarsening-upward trend at this part of the succession (Fig. 3).

3.2.3 Artificial Lake Succession

The upper part of the core profile (0–199.5 cm) consists of dark clayey silts, silty clays, and some

sandy silt interlayers occurring in the lower part of the succession. The muddy facies with rhythmical bedding, bed thickness of 10–30 cm, and rich or slightly enriched in plant detritus (M1 and M2 subfacies, respectively, Figs. 2 and 3). The organic-rich layers are notably darker and typically more clayey. The predominantly muddy material of the upper part of the profile was deposited in the artificial lake environment. The lithological variations and presence of several intercalated sandy silt layers, e.g., at depth of 101–116.5 and 169–180 cm, are interpreted as natural and/or anthropogenic forcing to the reservoir deposition associated with flood events when coarser material was deposited even in the lateral position off the main water flow line through the reservoir. In contrast to the transitional interval, there is a clear negative correlation between TOC and MSS. High TOC occur in medium–fine-grained silt and clay, where the amount of magnetic minerals is decreased while peak MSS values correlate with drops in the TOC in the sandy–silty layers.

The average accumulation rate estimated from the sediment thickness and total time since the first reservoir filling was $\sim 3 \text{ cm year}^{-1}$ with a gently upward decreasing trend and probable fluctuations manifested by uneven layer thickness. Assuming the

mentioned rate, the two flooding events in the core might be deposited in the late 1940s and late 1960s of the past century. Precise sediment dating of this profile would be dealt with elsewhere.

3.3 General Trends in POPs in the Core

3.3.1 PCBs

Concentrations of PCBs (sum of PCB congeners 28, 52, 101, 118, 138, 153, and 180) in the whole profile ranged from <LOQ to $77.6 \mu\text{g kg}^{-1}$ dw (Fig. 3). The occurrence of PCBs in the sedimentary layers in a depth below 220 cm representing the pre-industrial period of time before the filling of the reservoir (1930s and older) may be explained by either molecular diffusion or bioturbation, similar to, e.g., the case described by Evenset et al. (2007). From 220 cm upward, the amount of PCBs increased from 2.74 to 76.7 and $77.6 \mu\text{g kg}^{-1}$ dw, the maximum PCB levels within the profile were at 77.5–70 cm, respectively. Above this depth, the PCBs declined to the value of $39.4 \mu\text{g kg}^{-1}$ dw in the top layer of the recent age. This value fits very well with the data obtained from the surface sediment samples (see Section 3.1). Noteworthy, a PCB peak was observed at a depth of 160 cm, which coincided with an increase in the TOC.

The PCB production began in the early 1930s in the western countries (Breivik et al. 2002). Since the commercial production of PCBs in the former Czechoslovakia started during the early 1960s (Holoubek et al. 2003), PCBs found in core segments representing the periods of time after the 1940s (upward from ca. 200 cm) probably originated from imported foreign PCB products. The maximum PCBs corresponded to the late 1970s–mid-1980s. Decreasing trends in PCBs, observed in subrecent sedimentary layers, reflect the implementation of the legal measures toward the reduction of PCB use during past decades.

3.3.2 Organochlorine Pesticides

DDT contamination level started at a depth of approximately 210–200 cm (Fig. 3) reached two maxima of 72.4 and $68.7 \mu\text{g kg}^{-1}$ dw at depths of 128 and 70 cm, respectively. In contrary to a more stable increase in PCBs, two significant drops at depths of 108 and 93 cm were observed in sandy layers. This might be explained as a result of flood events when sandy

material was selectively deposited whereas the fine-grained fraction was washed further away with DDTs (see Section 3.4.2 for detailed discussion).

The concentration of HCB showed increase within the depth interval from 155 to 115 cm. Toward the surface layers, a relatively uniform HCB level at around $3 \mu\text{g kg}^{-1}$ dw was observed with less significant decrease in recent samples.

3.3.3 PAHs

The evolution trend of the PAHs is similar to that of the PCBs with more abrupt increase from the background values ($41\text{--}62 \mu\text{g kg}^{-1}$ dw) to $236 \mu\text{g kg}^{-1}$ dw at the fluvial-to-transitional environmental boundary (218.5 cm; Fig. 3). The transitional interval is enriched in PAHs by one order of magnitude ($300\text{--}463 \mu\text{g kg}^{-1}$ dw) while in the initial fine-grained artificial lake sediments, the total amount of PAHs reaches the highest value of the entire profile ($21,278 \mu\text{g kg}^{-1}$ dw at 164 cm), which is by three orders of magnitude higher than that in the fluvial S2 facies. The sandy silt layers of the transitional interval and initial artificial lake succession are associated with marked decrease in PAHs. This does not apply to the shallower sandy silt layer at depth of 101–116.5 cm, where the PAHs content does not seem to be controlled by lithology.

3.3.4 Comparison with Similar Studies

Vertical changes in POPs from the Brno reservoir sediment core showed comparable trends with other published studies. Yamashita et al. (2000) observed increasing contamination trends for various organochlorines in a sediment core from Tokyo Bay with a beginning in the early 1900s and a maximum in the early 1980s. The maximum levels of PCBs and PAHs were 150 and $2,000 \mu\text{g kg}^{-1}$ dw, respectively. PCBs (sum of six indicator congeners) in a sediment core from Greifensee, Switzerland, had nearly the same historical trends between the 1930s and 1980s with a maximum of $130 \mu\text{g kg}^{-1}$ dw in the 1960s (Zennegg et al. 2007). Decreasing concentration trends for PCBs from the 1970s were also observed in sediment cores from the Venice Lagoon, Italy (Frignani et al. 2005). Similarly, slightly declining levels of organochlorines were found in recent sedimentary layers from the Teltow Canal, Germany, and in sedimentary

archives from the Lippe and Rhine rivers (Heim et al. 2004, 2005, 2006). Even POPs in sediment cores from remote areas show similar time trend, as demonstrated by Evenset et al. (2007) who found maximum levels of PCBs and DDTs (71.8 and 4 $\mu\text{g kg}^{-1}$ dw, respectively) as back as the mid-1960s with an increase beginning in the 1930s.

3.4 Compound-Specific Distribution of POPs

3.4.1 PCBs

A detailed study of the congener pattern, e.g., by comparing PCB of different degree of chlorination, might be a helpful tool to evaluate changes in PCB application or changes in environmental conditions

(Li et al. 2009). Three predominant congeners in all cores were PCB 138, 153, and 180. The ratio of PCB congeners 28/153, which act as representatives of trichlorinated and hexachlorinated congeners, ranged dominantly from 0.05 to 0.39 with a mean of 0.27 representing a dominance of higher chlorinated congeners (Table 1). Also, the more comprehensive ratio (28+52)/(138+153+180) supported this observation. Higher chlorinated technical formulations are typical constituents in hydraulic fluids or thermostable lubricants, whereas lower chlorinated mixtures are used in less viscous applications. The congener patterns of the investigated PCBs were relatively consistent and without general trend throughout the whole length of the core (Fig. 4). A significant increase of both PCB ratios (up to 1.6 or 0.95,

Table 1 Ratios of the PCB congeners, DDTx metabolites, and selected PAHs—An/(An + P), Fl/(Fl + Py), BaA/(BaA + Ch) in the BP4 core samples

Depth (cm)	PCB28/ PCB153	PCB (28 + 52)/PCB (138 + 153 + 180)	2,4-/4, 4-DDE	2,4-/4, 4-DDD	2,4-/4, 4-DDT	An/ (An + P)	Fl/ (Fl + Py)	BaA/ (BaA + Ch)
10	0.16	0.11	N/A	3.27	N/A	0.05	0.57	0.46
17.5	0.18	0.13	N/A	3.47	N/A	0.06	0.57	0.46
30	0.18	0.12	N/A	4.75	N/A	0.05	0.57	0.46
55	0.39	0.24	0.02	2.09	0.14	0.06	0.57	0.45
70	0.15	0.10	N/A	0.68	0.09	0.07	0.57	0.46
77.5	0.20	0.13	0.02	1.3	0.12	0.06	0.57	0.45
92.5	1.13	0.71	0.04	3.99	0.43	0.07	0.57	0.49
95	1.60	0.95	0.03	0.91	0.14	0.07	0.57	0.45
97.5	0.27	0.17	0.04	1.49	0.14	0.07	0.57	0.49
107.5	0.07	0.06	N/A	2.71	N/A	0.08	0.57	0.48
115	0.16	0.11	0.03	0.67	0.44	0.07	0.56	0.45
125	0.13	0.10	0.03	1.25	0.2	0.08	0.56	0.48
127.5	0.15	0.12	0.05	0.58	0.28	0.09	0.55	0.45
145	–	–	0.06	0.89	0.39	0.08	0.57	0.45
155	–	–	0.10	0.82	N/A	0.08	0.58	0.46
157.5	0.27	0.24	0.12	1.15	N/A	0.09	0.58	0.50
160	0.09	0.08	0.11	1.04	N/A	0.09	0.58	0.46
162.5	0.21	0.24	0.10	0.72	N/A	0.09	0.58	0.51
170	–	–	N/A	1.00	N/A	0.10	0.58	0.45
190	–	–	N/A	N/A	N/A	0.09	0.57	0.46
210	–	–	N/A	N/A	N/A	0.08	0.57	0.40
217.5	–	–	N/A	N/A	N/A	0.09	0.57	0.41
225	–	–	–	–	–	0.09	0.57	0.41
247.5	–	–	–	–	–	0.13	0.57	–
265	–	–	–	–	–	–	–	–
290	–	–	–	–	–	–	–	–

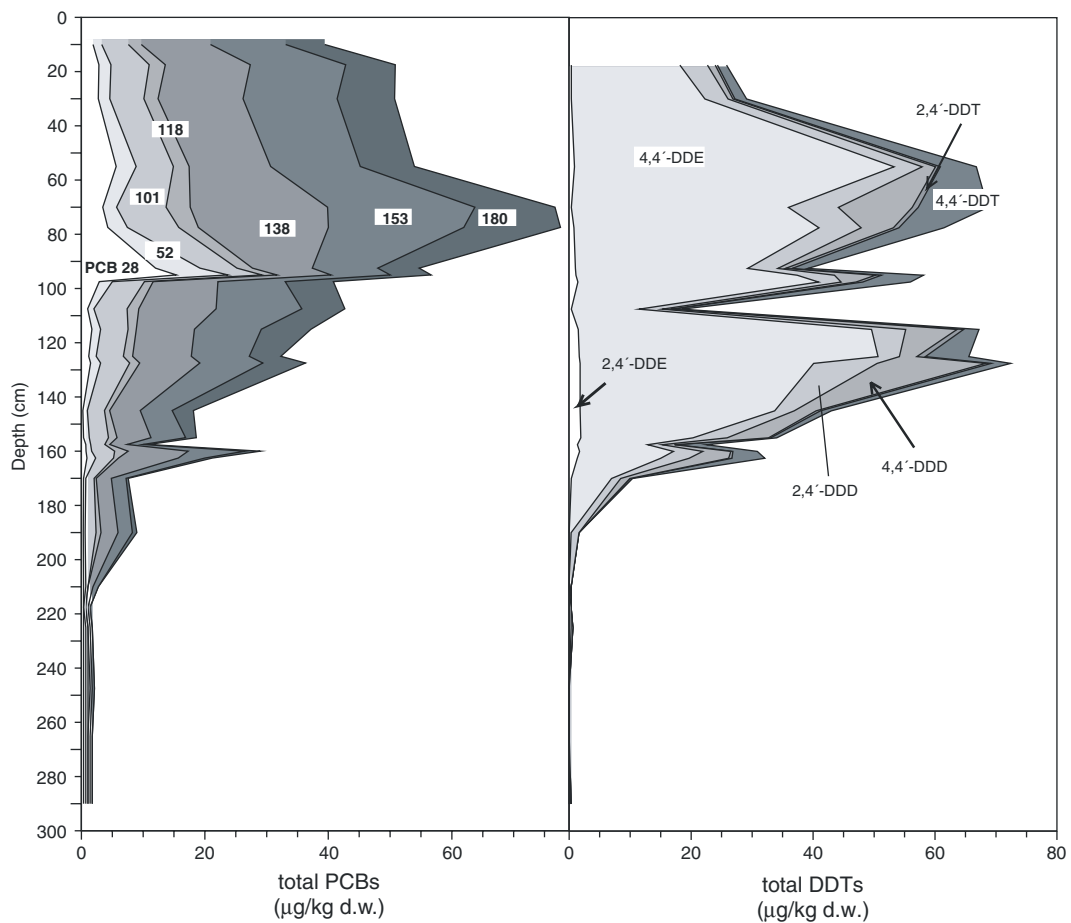


Fig. 4 PCB congener patterns and DDT homologous in the BP4 sediment core (Brno reservoir 2008)

respectively), at depth 95 cm, may suggest a temporary input of technical PCB mixtures with higher content of low chlorinated PCB congeners. An accidental leakage from a former manufacture of transformers and capacitors utilizing a low chlorinated technical mixture of Delor 103 (similar to Aroclor 1242) and situated upstream from the reservoir has been documented for this time period and might, therefore, be the reason for the excursion of the congener pattern. Hence, the PCB ratio excursion illustrates the superimposition of diffuse and constant contamination by a local emission event.

3.4.2 DDTs

With respect to the sediment core investigated, an unusual distribution of DDT metabolites was detected. Relative abundances of DDT isomers (Fig. 4) were found to be in order DDE \gg DDD $>$

DDT in almost all layers of the core. Particularly, the concentration of *p,p'*-DDE accounted for 49.9–81.7% of total Σ DDT concentrations. This was a somewhat unusual observation in dominantly strict anaerobic reservoir sediments where, consequently, a predominance of the *p,p'*-DDD was expected. The observations may indicate an input of highly weathered DDT, as already published by, e.g., Evensen et al. (2007). In our case, the principal source of DDT was agricultural activities upstream to the reservoir during past decades and the following aerobic degradation of DDT on soil that have been then transported to an anaerobic sedimentary environment. The mean ratio of *p,p'*-DDT/*p,p'*-DDE, used to estimate the “age” of DDT inputs, was 0.13 in our core (Table 1). According to Strandberg et al. (1998), the ratio of 0.33 or less in sediments is considered as an aged mixture and this suggests that current input of DDT into the reservoir are of little importance.

3.4.3 PAHs

Source indicative PAHs were used for calculation of the ratios Fl/(Fl + Py), BaA/(BaA + Ch), 1,7-DMP/(2,6 + 1,7-DMP) ratios introduced by Budzinski et al. (1997) and (Yunker et al. 1999). These parameters are used to distinguish the dominant emission source and the associated emission pathways of PAH, in particular its petrogenic or pyrolytic origin. This approach was also applied to the sediment samples of the Brno reservoir. The most significant ratios Fl/(Fl + Py) and BaA/(BaA + Ch) were higher than 0.5 and indicated combustion processes as main PAH source (Table 1; Yunker et al. 2002). Accordingly, the PAHs seem to derive dominantly from diffuse emissions of contaminated airborne particles or from soil erosion also polluted by pyrogenic material.

4 Conclusions

Based on sedimentological and screening analysis, the investigated core profile can be divided into three major sections with different depositional history and pollutant distribution. The lowest interval (218.5–292.5 cm) was deposited in a fluvial environment with low organic carbon and POPs content. Depletion in contamination might probably not reflect lower emission rates but might be the result of rather higher flow rates washing away the fine-grained and normally higher polluted particles. The lower sorption capacity of the accumulated coarser sedimentary material is suspected to be the reason for the low pollution level in the lower core section.

The intermediate interval represented the initial flooding process of the Brno reservoir (218.5–199.5 cm). It was marked by a sudden increase in TOC and with the amounts of analyzed POPs associated with upward coarsening of sediments. This was interpreted as a result of extensive sediment redeposition during one flooding event.

The upper segment deposited in the reservoir environment (199.5–0 cm) was rich in clays and silts, and two sandy layers evidenced two major flood events in the late 1940s and late 1960s. The clay-rich interval was characterized by a pronounced increase in all POPs in contrast to sandy interlayers with low amounts of DDTs and HCB. Surprisingly, these were associated neither with decrease in PCBs nor in

PAHs. This discrepancy could be explained by a different input of the mentioned pollutant groups into the reservoir. DDTs and HCB were washed down dominantly from upstream agricultural influenced area and corresponding soils, adsorbed on clays and organic matter, and transported into the reservoir by the Svatka River. During the flood events with elevated flow rates, the sandy material was deposited selectively while the fine-grained fraction was washed away and the associated DDT and HCB contaminants were probably mobilized. Based on the fact that the PCBs and PAHs did not show decrease in the sandy intervals, it might be deduced that they were brought into the reservoir dominantly by precipitation from the air and short distance sheet runoff from the surrounding slopes by means of transport which was less sensitive to grain size fractionation and thinning during floods.

Acknowledgments Special thanks to F. Hrouda and M. Chlupáčová (Agico Ltd.) for magnetic susceptibility measurement. This study was funded by The Czech Ministry of Environment (grant no. SP/1b7/156/07).

References

- Bábek, O., Hilscherová, K., Nehyba, S., Zeman, J., Famera, M., Francu, J., et al. (2008). Contamination history of suspended river sediments accumulated in oxbow lakes over the last 25 years. *Journal of Soils and Sediments*, 8, 165–176.
- Bayer, M., Mencl, V., & Pelikán, V. (1954). Erozivní zjevy na březích nádrže na řece Svatce v Kníničkách. Sbor. VŠ Stav. IV, 293–302.
- Breivik, K., Sweetman, A., Pacyna, J. M., & Jones, K. C. (2002). Towards a global historical emission inventory for selected PCB congeners—a mass balance approach: 1. Global production and consumption. *The Science of the Total Environment*, 290, 181–198.
- Budzinski, H., Jones, I., Bellocq, J., Pierard, C., & Garrigues, P. (1997). Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry*, 58, 85–97.
- Covaci, A., Gheorghe, A., Hulea, O., & Schepens, P. (2006). Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta, Romania. *Environmental Pollution*, 140, 136–149.
- Dsikowitzky, L., Schwarzbauer, J., & Littke, R. (2002). Distribution of polycyclic musks in water and sediments of the Lippe River (Germany). *Organic Geochemistry*, 33, 1747–1758.
- Evans, M. E., & Heller, F. (2003). *Environmental magnetism. Principles and applications of enviromagnetics. International Geophysics Series 86*. San Diego: Academic.

- Evenset, A., Christensen, G. N., Caroll, J., Zaborska, A., Berger, U., Herzke, D., et al. (2007). Historical trends in persistent organic pollutants and metals recorded in sediment from Reservoir Ellasjøen, Bjørnøya, Norwegian Arctic. *Environmental Pollution*, *146*, 196–205.
- Eyre, B., & McConchie, D. (1993). Implications of sedimentological studies for environmental pollution assessment and management: Examples from fluvial systems in North Queensland and Western Australia. *Sedimentary Geology*, *85*, 235–252.
- Frignani, M., Bellucci, L. G., Favotto, M., & Albertazzi, S. (2005). Pollution historical trends as recorded by sediments at selected sites of the Venice Lagoon. *Environment International*, *31*, 1011–1022.
- Götz, R., Bauer, O. H., Friesel, P., Herrmann, T., Jantzen, E., Kutzke, M., et al. (2007). Vertical profile of PCDD/Fs, dioxin-like PCBs, other PCBs, PAHs, chlorobenzenes, DDX, HCHs, organotin compounds and chlorinated ethers in dated sediment/soil cores from flood-plains of the river Elbe, Germany. *Chemosphere*, *67*, 592–603.
- Heim, S., Schwarzbauer, J., Kronimus, A., Littke, R., Woda, C., & Mangini, A. (2004). Geochronology of anthropogenic pollutants in riparian wetland sediments of the Lippe River (Germany). *Organic Geochemistry*, *35*, 1409–1425.
- Heim, S., Ricking, M., Schwarzbauer, J., & Littke, R. (2005). Halogenated compounds in a dated sediment core of the Teltow Canal, Berlin: Time related sediment contamination. *Chemosphere*, *61*, 1427–1438.
- Heim, S., Hucke, A., Schwarzbauer, J., & Littke, R. (2006). Geochronology of anthropogenic contaminants in a dated sediment core of the Rhine River (Germany): Emission sources and risk assessment. *Acta Hydrochimica et Hydrobiologica*, *34*, 34–52.
- Holoubek, I., Ansorgova, A., Kohoutek, J., Korinek, P., & Holoubkova, I. (2000). The regional background monitoring of POPs (PAHs, PCBs, OCPs) in the Czech Republic. *Organohalogen Compounds*, *46*, 387–390. ISSN 1026-4892.
- Holoubek, I., Adamec, V., Bartoš, M., Černá, M., Čupr, P., Bláha, K., et al. (2003). Úvodní národní inventura persistentních organických polutantů v České republice. Projekt GF/CEH/01/003: Enabling activities to facilitate early action on the implementation of the Stockholm convention on persistent organic pollutants (POPs) in the Czech Republic. TOCOEN, s.r.o., Bmo v zastoupení Konsorcia RECETOX—TOCOEN & Associates, TOCOEN REPORT No. 249, Bmo, srpen. Internet: <http://www.recetox.muni.cz/>.
- Holoubek, I., Klanova, J., Jarkovsky, J., Kubik, V., & Helesic, J. (2007). Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part II. Aquatic and terrestrial environments 1996–2005. *Journal of Environmental Monitoring*, *9*, 564–571.
- Hong, S. H., Yim, U. H., Shim, W. J., Oh, J. R., & Lee, I. S. (2003). Horizontal and vertical distribution of PCBs and chlorinated pesticides in sediments from Masan Bay, Korea. *Marine Pollution Bulletin*, *46*, 244–253.
- Kim, Y. S., Eun, H., Katase, T., & Fujiwara, H. (2007). Vertical distributions of persistent organic pollutants (POPs) caused from organochlorine pesticides in a sediment core taken from Ariake Bay, Japan. *Chemosphere*, *67*, 456–463.
- Konat, J., & Kowalewska, G. (2001). Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea—trends and fate. *The Science of the Total Environment*, *280*, 1–15.
- Li, A., Rockne, K. J., Sturchio, N., Song, W., Ford, J. C., & Wie, H. (2009). PCBs in sediments of the Great Lakes—distribution and trends, homolog and chlorine patterns, and in situ degradation. *Environmental Pollution*, *157*, 141–147.
- Lüder, B., Kirchner, G., Lücke, A., & Zolitschka, B. (2006). Palaeoenvironmental reconstructions based on geochemical parameters from annually laminated sediments of Sacrower See (northeastern Germany) since the 17th century. *Journal of Paleolimnology*, *35*, 897–912.
- Navarro, A., Tauler, R., Lacorte, S., & Barceló, D. (2006). Chemometrical investigation of the presence and distribution of organochlorine and polyaromatic compounds in sediments of the Ebro River Basin. *Analytical and Bioanalytical Chemistry*, *385*, 1020–1030.
- Pereira, W. E., Hostettler, F. D., Luoma, S. N., Geen, A., Fuller, C. H. C., & Anima, R. J. (1999). Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Marine Chemistry*, *64*, 99–113.
- Sapozhnikova, Y., Bawardi, O., & Schlenk, D. (2004). Pesticides and PCBs in sediments and fish from the Salton Sea, California, USA. *Chemosphere*, *55*, 797–809.
- Strandberg, B. O., van Bavel, B., Rergqvist, R.-A., Broman, D., Ishaq, R., Näf, C., et al. (1998). Occurrence, sedimentation and spatial variations of organochlorine contaminants in settling particulate matter and sediments in the northern part of the Baltic Sea. *Environmental Science & Technology*, *32*, 1754–1759.
- Svoboda, J. (Ed.) (1963). Geological map of ČSSR. Sheet M-33-XXIII Česká Třebová, scale 1:200,000. ÚÚG Praha.
- Svobodova, Z., Zlabek, V., Randak, T., Machova, J., Kolarova, J., Hajslova, J., et al. (2003). Profiles of persistent organic pollutants (POPs) in tissues of marketable common carp and in bottom sediments of selected ponds of South and West Bohemia. *Acta Veterinaria Brno*, *72*, 295–309.
- Tucker, M. E. (1988). *Techniques in sedimentology*. Oxford: Blackwell. 408 pp.
- Tucker, M. E. (2003). *Sedimentary rocks in the field* (3rd ed., p. 234). Chichester: Wiley. ISBN 0-470-85123-6.
- Yamashita, N., Kannan, K., Imagawa, T., Villeneuve, D. I., Hashimoto, S., Miyazaki, A., et al. (2000). Vertical profile of polychlorinated dibenzo-p-dioxins, dibenzofurans, naphthalenes, biphenyls, polycyclic aromatic hydrocarbons, and alkylphenols in a sediment core from Tokyo Bay, Japan. *Environmental Science & Technology*, *34*, 3560–3567.
- Yunker, M. B., Macdonald, R. W., Goyette, D., Paton, D. W., Fowler, B. R., Sullivan, D., et al. (1999). Natural and anthropogenic inputs of hydrocarbons to Strait of Georgia. *Science of the Total Environment*, *225*, 191–209.
- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, H., Goyette, D., & Sylvestre, S. (2002). PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH. *Organic Geochemistry*, *33*, 489–515.
- Zennegg, M., Kohler, M., Hartmann, P. C., Sturm, M., Gujer, E., Schmid, P., et al. (2007). The historical record of PCB and PCDD/F deposition at Greifensee, a lake of the Swiss plateau, between 1848 and 1999. *Chemosphere*, *67*, 1754–1761.