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Lake sediment records of persistent organic pollutants and polycyclic aromatic hydrocarbons in Southern Siberia mirror the changing fortunes of the Russian economy over the past 70 years

*Jennifer K. Adams[a*1], César C. Martins[b], Neil L. Rose[a], Alexander A. Shchetnikov[c,d,e], Anson W. Mackay[a]*

[a]Environmental Change Research Centre, Department of Geography, University College London, Gower Street, London WC1E 6BT, UK

[b]Centro de Estudos do Mar da Universidade Federal do Paraná, P.O. Box 61, 83255-000, Pontal do Paraná, PR, Brazil

[c]Institute of the Earth's Crust, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 664033, Russia

[d] Vinogradov Institute of Geochemistry, Siberian Branch of Russian Academy of Sciences, Irkutsk, 664033, Russia

[e] Irkutsk Scientific Center, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 664033, Russia

*Corresponding author e-mail: j.adams@utoronto.ca (J.K. Adams)

[1]Present address: Department of Earth Sciences, University of Toronto, 22 Russell Street, Toronto, Ontario, M5S 3B1, Canada

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Abstract

Persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) have previously been detected in the surface sediments, water, and endemic organisms of Lake Baikal, a UNESCO World Heritage Site. The Selenga River is the primary source of freshwater to Lake Baikal, and transports pollutants accumulating in the Selenga River basin to the lake. Sources of POPs and PAHs in the Selenga River basin grew through the 20th century. In the present study, temporal changes in the concentrations of PAHs and POPs were reconstructed from two lakes in the Selenga River basin over the past 150 years using paleolimnological techniques. Increased concentrations in PAHs and PCBs were recorded initially in the 1930s. The 1940s to 1980s was the period of greatest exposure to organic contamination, and concentrations of dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs), hexachlorocyclohexanes (HCHs) and many PAHs peaked between the 1960s and 1980s in the two lakes. Declines in concentrations and fluxes were recorded for most PAHs and POPs in the 1980s and 1990s. Temporal trends in concentrations of total and individual compounds/congeners of PAH, PCBs, and polybrominated diphenyl ethers (PBDEs) indicate the contribution of both local and regional sources of contamination in the 20th and 21st centuries. Temporal variations in contaminants can be linked to economic and industrial growth in the former USSR after World War II and the economic decline of Russia in the late-1980s and early-1990s, as well as global trends in industrialization and development during the mid-20th century.

Capsule

Regional and local sources of pollution in southern Siberia were key contributors during peak period of organic contamination, exposing the Lake Baikal ecosystem to low to moderate toxicity conditions.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs), such as halogenated organic compounds (HOCs), are characterized by their toxicity to humans and wildlife, persistence in the environment, and a tendency to bioaccumulate and biomagnify in the food web. In the last two decades, global legislation has mandated restrictions on the use and production of many of these organic pollutants worldwide, including the 2001 UNEP Stockholm Convention, and the 1998 Aarhus Protocol on POPs (UNEP, 2001). HOCs are anthropogenically sourced and have been produced since the early-20th century for their use in pesticides and industrial applications. PAHs may be produced from both natural and anthropogenic organic matter combustion, however much of the global PAH production during the last century has been attributed to anthropogenic sources (Fernandez *et al*., 2000; Yang *et al*., 2016). Following production and use, HOCs and PAHs may volatilise and be transported atmospherically and deposited either locally or far from source. This allows for accumulation in remote regions (e.g. Wania, 2003; Grimalt *et al*., 2004), although PAH concentrations tend to decrease with increasing distance from their source (Maliszewska-Kordyback, 1999; Halsall *et al.,* 2001). Once deposited they may transfer from terrestrial sources to freshwaters via run-off and within aquatic systems by sediment transport.

The properties of PAHs and HOCs, and their ubiquity in the environment may result in harm to aquatic ecosystems. The hydrophobic nature of most PAHs and HOCs, and high affinity for organic matter, generally results in accumulation in the environment (Kanzari *et al.,* 2014), and deposition and retention in aquatic systems during sedimentation and burial processes (Kelly *et al.,* 2007; Wu *et al.,* 2009; Deribe *et al.,* 2011). Moreover, HOCs and PAHs may be taken up from particulate organic matter in lake water and bottom sediments by organisms and incorporated into the aquatic food web. HOCs, such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) may biomagnify in the food web, increasing in concentration with trophic level (Wu *et al.,* 2009; Driebe *et al*., 2011). Consumption of aquatic organisms, such as fish, or terrestrial organisms which feed on aquatic organisms, may then expose humans to organic contaminants (Lee *et al*., 2014; Zhao *et al*., 2014).

Lake Baikal, located in the Republic of Buryatia in southeast Siberia, is a UNESCO World Heritage site due to the unique ecosystem created by the lake's extreme age, depth, and volume, resulting in very high rates of endemism and biodiversity (Kozhova and Izmest'eva, 1998). The Selenga River contributes over 60% annual inflow as the primary tributary to Lake Baikal, and enters the lake through the Selenga Delta, a Ramsar site (Scholz and Hutchinson, 2000). The Selenga River basin comprises over 80% of the Lake Baikal watershed (Figure 1) (Nadmitov *et al*., 2015). Early POPs studies of Lake Baikal focussed near suspected sources of pollution, detecting benzo(*a*)pyrene and organochlorines in bottom sediments near the Baikalsk Pulp and Paper Mill (BPPM) in the 1980s (e.g. Maatela and Paasivirta, 1990; Nikanorov *et al*., 2012). Higher concentrations (1-2 orders of magnitude) of PCBs and DDT have consistently been observed in the sediments, water, and biota of the southern Baikal basin, Selenga River estuary, and regions closer to industry, relative to the northern and central basins (Iwata *et al*., 1995; Kucklick *et al*., 1996; Mamontov *et al*., 2000). Industrial towns in the Selenga basin (e.g. Selenginsk) recorded regionally high levels of atmospheric PCBs in the 1980s (7.3 $\mu g\ m^{-3}$), while high surface water PCB concentrations (0.036-0.240 ng L^{-1}) in southern Lake Baikal in the early-1990s indicated likely local sources of PCBs rather than long-range transport, and primary delivery of contaminants to Lake Baikal through rivers and tributaries (Iwata *et al.,* 1995). Historically, the former USSR has been a globally dominant producer/user of POPs, and between 1950 and 1990 was the second greatest user of technical hexachlorocyclohexanes (HCHs) (Li, 1999). Recent studies have found that while low concentrations of $\sum_{209}$PCBs (17.8-116.8 ng g^{-1}), $\sum_{16}$PAHs (219.8-1255/6 ng g^{-1}), and $\sum_{40}$PBDEs (0.181-1.155 ng g^{-1}) are observed in Lake Baikal sediments, there are signals of recent contamination to the lake (Ok *et al.,* 2013). PCBs have been observed as a dominant contaminant in Lake Baikal's endemic top predator *Pusa siberica*, the world's only exclusively freshwater seal, at levels of up to 3,600 ng g^{-1} for dioxin-like-PCBs and 35,000 ng g^{-1} for non-dioxin-like-PCBs (Tanabe *et al.,* 2003; Tsydenova *et al.,* 2004; Imaeda *et al.,* 2009).

The Selenga River and Selenga Delta are crucial components of the Lake Baikal ecosystem (Chalov *et al.,* 2016). Very little work has been undertaken to date to investigate the historic levels of organic contamination within the Selenga River basin, despite the existence of local and regional sources of contamination. In this study, we use a paleolimnological approach to assess the temporal and spatial variation in the concentrations of PAHs and HOCs (including DDT, PCBs, PBDEs, HCHs, and chlordanes) from two locations within the Selenga River basin in southeast Siberia during the past 150 years. By comparing sediment records from two shallow lakes within the Selenga River basin, our study will assess the importance and contributions of local vs. regional sources, production, and use of organic contaminants within southern Siberia. Additionally, we provide an assessment of the period of peak contamination and risk to the Lake Baikal ecosystem from organic contaminants.

Materials and methods

Study sites

Two lakes within the Selenga River basin were selected for study (Figure 1). The first site is not officially named, and so here is called SLNG04 (Table S1). SLNG04 is a shallow lake on the northeast side of the Selenga Delta, with surface flow connections to both the Selenga River and Lake Baikal (Figure 1). The northeast perimeter of the Selenga Delta is heavily utilized for agricultural lands, which increased in intensity beginning in the 19th century (Bazhenova and Kobylkin, 2013). SLNG04 is located approximately 30 km from the town of Selenginsk in the Kabansy district. Selenginsk is a relatively young town, founded in 1961, while the district of Kabansky was formed in 1927, with a population of 30,800 in 1939 (first census) (Government of Buryatia Statistics; http://burstat.gks.ru/wps/wcm/connect/rosstat_ts/burstat/ru/statistics/population/). Selenginsk contains the Selenginsk Pulp and Cardboard Mill (SPCM), which began operations in 1974, and was an open system until 1990 (Nomokonova et al., 2013), at that time discharging wastewater at a rate of 40,000 m3 day-1 into the Selenga River (Kozhova and Silov, 1998).

The second study site, Chernoe Ozero or “Black Lake” (site code BRYT) is a shallow lake located within the Selenga River basin, approximately 200 km upstream of the Selenga Delta (Figure 1; Table S1). Black Lake is located close (13 km) to the industrial city of Gusinoozersk in the Selenginskii District of Buryatia. Selenginskii was formed in 1923 with a population of 25,000 (1926 census), and Gusinoozersk was formed as a mining town in 1939, and gained city status in 1953 (Figure 1) (Government of Buryatia Statistics, http://burstat.gks.ru/wps/wcm/connect/rosstat_ts/burstat/ru/statistics/population/). Mining in and around Gusinoozersk became established in the 1940s and intensified in the 1960s with the construction of the Gusinoozersk State Regional Power Plant (SRPP) (Pisarsky et al., 2005).

Sediment core collection and sample preparation

Sediment cores were collected from both lakes in March 2014 with an *Uwitec* gravity corer (UWITEC Ltd., Austria; http://www.uwitec.at/html/corer.html) fitted with a 6.3 cm internal diameter Perspex® tube. Two sediment cores were extracted from each site, and labelled as B or C (Table S2). Sediment core A was also collected, but was not used in this study. Cores were collected from within a 5 m^2 area while lakes were ice-covered. A gas-powered auger was used to drill a hole in the ice, with the final 10 cm of ice drilled by hand to avoid potential contamination. All collection and extruding equipment were also protected during drilling. A new hole was drilled into the ice for each new sediment core. All sediment cores were collected from the deepest point in the lake, as determined through previous surveys. Sediment cores B were collected for POP and PAH analyses. These were collected in hexane-cleaned Perspex® tubes and extruded using hexane-cleaned equipment at 0.5 cm intervals into hexane-cleaned aluminum foil. The sealed foil packets containing sediments were then placed into plastic sample bags for ease of labelling and storage. In this way, sediments were never in contact with the plastic bags. Sediment cores C were used for radiometric dating (Table S2). Sediment samples were stored at -20°C. Following transport back to the UK, sediments were freeze-dried in Thermo Modulyo D and Edwards Modulyo freeze-driers.

Radioisotope dating and cross-correlation of chronologies

Radiometric techniques were used to date sediment cores SLNG04-C and BRYT02-C (Table S2). Freeze-dried sediment samples were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay in the Environmental Radiometric Facility at UCL, using ORTEC HPGe GWL series well-type coaxial low background intrinsic germanium detectors. ^{210}Pb chronologies for the sediment cores were constructed using the constant rate of supply (CRS) dating model (Appleby and Oldfield, 1978; Appleby, 2001), and independently verified using ^{137}Cs and ^{241}Am. The final chronologies for the cores were derived from a combination of all these data. Due to the truncated chronologies, approximate dates were extrapolated beyond the dating provided by ^{210}Pb CRS model, using an average of the pre-1980 sedimentation rates from the dated portion of BRYT-C, and the pre-1990 sedimentation rates from SLNG04-C, to achieve an estimate of background sedimentation rate for older sediments.

To obtain dates for the undated cores (core B) loss-on-ignition (LOI) at 550°C and 950°C was conducted on all collected sediment cores using standard techniques (Heiri *et al*., 2001; Table S2). LOI_{550} and LOI_{950} profiles from both B and C cores were examined for distinct features (i.e. tie-points) present in profiles from both cores. The radiometric dates for the tie-points were then cross-correlated between the dated and undated profiles. Dates were then interpolated between tie-points. A minimum of three tie-points were confirmed between cores to construct the cross-dated age-models.

Sample extraction and instrumental analysis

Nineteen parent PAHs, six alkyl PAHs, and two biogenic/diagenetic PAHs (perylene and retene) were analyzed. See Table S3 for full list of PAH compounds analysed. Concentrations reported for total PAHs include all low molecular weight (LMW), high molecular weight (HMW) and alkyl PAHs. A total of 50 PCB congeners, four HCH congeners, two chlordane congeners, four PBDE compounds, and DDT and its degradation products (DDE and DDD) were also investigated. See Table S4 for full list of HOC congeners analysed. Total concentrations for major HOC types were calculated and are reported as the summative concentrations of 1) PCB congeners (∑PCBs), 2) DDT plus degradation products (∑DDT), 3) HCH congeners (∑HCH), 4) chlordane congeners (∑chlordane), and 5) PBDE compounds (∑PBDEs).

Freeze-dried sediments (15 g) were analysed based on the procedure for organic contaminants analysis from the United Nations Environmental Programme (UNEP, 1992) with minor modifications (Bícego *et al.,* 2006). Sediments were individually extracted in a Soxhlet apparatus for 8 hours with 80 mL of a 50% mixture of *n*-hexane in dichloromethane (DCM) (1:1, v/v). A surrogate standards mixture of five deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}; Z-014J, AccuStandard, New Haven, CT, USA) and two polychlorinated biphenyls (PCB-103 and PCB-198; C-103N and C-189N, AccuStandard, New Haven, CT, USA) was added to each blank (Table S5). The resulting extract was concentrated to 4 mL in a rotary vacuum evaporator and divided into two portions of 2 mL. The extracts were purified and fractionated by liquid chromatography on a 30 cm x 1 cm i.d. glass column. The first portion was cleaned using 3.2 g of 5% deactivated alumina. HOC elution was performed with 20 mL of a DCM/n-hexane (3:7, v/v) mixture and the eluate concentrated to 0.5 mL under a gentle gas stream of purified nitrogen. TCMX (tetrachloro-m-xylene; M-8082-SS-10X, AccuStandard, New Haven, CT, USA) was added as internal standard prior to the gas chromatograph analysis. The second portion was fractioned and cleaned with 5% deactivated alumina (1.8 g) and silica (3.2 g). The hydrocarbons were removed by eluting 10 mL of *n*-hexane through the column, followed by the addition of 15 mL of a 30% mixture of DCM in n-hexane. The second fraction, containing the PAHs, was concentrated to 0.5 mL in a rotary vacuum evaporator. An internal standard (benzo[b]fluoranthrene-d12; Sigma Aldrich, Darmstadt, Germany) was added prior to the gas chromatograph analysis.

The identification and quantification of the organic contaminants were performed by analyzing 2 mL of the final extracts in a gas chromatograph (Agilent 7890A GC) coupled to a mass spectrometer (Agilent 5975C inert MSD with Triple-Axis Detector). A capillary column (Agilent 19091J-433) of fused silica coated with 5% diphenyl-dimethyl siloxane (30 m length, 0.25 mm internal diameter and 0.25 mm thick film) was used. Helium was used as the carrier gas (flow: 1.5 mL min-1). For PAHs, the oven temperature was programmed to heat from 40° C to 60° C at 20° C min-1, then to 250°C at 5°C min-1, and finally to 300°C at 6°C min-1 where it remained constant for 20 min. For the HOCs, heating was from 75° C to 150° C at 15° C min-1, then to 260°C at 2°C min-1, and finally to 300°C at 20°C min-1 where it remained constant for 10 min. The injector (splitless mode) was conditioned at 280°C, the interface with the detector at 300°C and the ion source at 230°C.

The data were acquired in the SIM (selected ion monitoring) mode. The organic compounds were identified by matching the retention times and the mass/charge of ion fragments with those obtained from a mixture of external standards (PAHs - Z-014G-FL; PCBs - C-WNN and C-WCFS; organochlorine pesticides and individual BDEs - AE-00010; all from AccuStandard, New Haven, CT, USA). The calibration curve for PAH quantification ranged from 0.10 to 2.00 ng µL-1. For the quantification of HOCs, calibration curve concentrations varied from 1 to 200 pg μL^{-1}. The individual compound concentrations were based on the integration of the main fragment peak area for each compound using the HP Chemstation program (G2070 BA). Pesticide identifications were confirmed by the injection of extracts in the Agilent 7890A (GC) with electron capture detection (ECD) at the same capillary-fused silica column and ramping programme used in the GC coupled to a mass spectrometer (Tables S5-S8).

Analytical control

Quality assurance procedures included analyses of procedural blanks, matrix spikes, surrogate standards recoveries (Wade and Cantillo, 1994), five replicates per sample, and the use of certified reference materials (IAEA-408) from the Marine Environment Laboratory of the International Atomic Energy Agency (IAEA, Vienna, Austria) (Villeneuve et al., 2000). The complete results for analytical control evaluation are presented in the Supplementary Material (Tables S5, S9-S14). Procedural blanks were performed for each extraction series of 10 samples. The limit of detection (LD) for HOCs was 0.05 ng g^{-1} HOCs and 0.50 ng g^{-1} for PAHs. The organic contaminant concentrations in the blanks were sufficiently low (<three times LD) and did not interfere with the analyses of the target compounds.

Data analysis

Ratios were calculated between several of the PAH compounds to assess shifts in potential PAH sources (Yunker *et al*., 2002):

i. Anthracene / Phenanthrene + Anthracene (Ant/178) is indicative of petroleum (< 0.1) or combustion source (> 0.1);

ii. Fluoranthrene / Fluoranthrene + Pyrene (Fl/Fl+Py) indicates petroleum combustion (< 0.5) or biomass burning and coal combustion (> 0.5);

iii. Benzo(*a*)anthracene / Benzo(*a*)anthracene + chrysene (BzA+228) is indicative of either pure petroleum (< 0.2), mixed sources (> 0.2 < 0.35) or combustion sources (> 0.35);

iv. Indeno(1,2,3-*c,d*)pyrene / Indeno(1,2,3-*c,d*)pyrene + benzo(*g,h,i*)perylene (IP/IP+B*ghi*) is indicative of pure petroleum (< 0.4), petroleum combustion (> 0.4 < 0.5), or biomass burning and coal combustion sources (> 0.5);

v. Phenanthrene / Phenanthrene + C1-Phenanthrene (C_0-P/(C_0+C_1)-P) indicates biomass burning and coal combustion sources (> 0.5).

vi. Retene / Fluoranthrene + Pyrene (Retene/Fl+Py) where high values indicate wood burning and lower values indicate coal combustion.

Fluxes of PAHs and HOCs were calculated using the sediment accumulation rate (SAR) of the radiometrically dated cores. Principal components analysis (PCA) was performed on PAH and HOC data from each site, to explore temporal trends in concentrations, while breakpoint analysis was performed on the PCA axis 1 scores to determine points of major change. Breakpoint analysis for HOCs was conducted only from the point at which contaminants are detected above the limits of detection. PCA was performed using Canoco5 (ter Braak and Šmilauer, 2014), and breakpoint analysis was performed in R, using the segmented package (R. v.3.2.4, 2016). Stratigraphical plots were constructed using C2 v.1.7.6 (Juggins, 2014).

Results

Radioisotope dating and cross-dating

SLNG04

Well resolved peaks in ^{137}Cs and ^{241}Am activity at 23.75 cm in SLNG04-C, confirmed a date of 1963 from the peak in fallout from atmospheric nuclear weapons testing. This was used to correct the ^{210}Pb chronology. The LOI$_{550}$ profiles between SLNG04-C and SLNG04-B were nearly identical, which, given confidence limits in ^{210}Pb-derived dates, eliminated the need for specific tie-points between profiles (Figure S1a). An age-depth model was created for SLNG04-B based on the correlation with the ^{210}Pb-dated CRS model established for SLNG04-C (Figure S1b).

Black Lake

A well resolved peak in ^{137}Cs activity occurred at 32.25 cm in BRYT02-C, and detection of ^{241}Am at 33.75 cm indicates that this ^{137}Cs peak was derived from the 1963 maximum fallout of nuclear weapons testing. Again, these were used to correct the ^{210}Pb chronology. The profiles of LOI$_{550}$ and LOI$_{950}$ matched well between BRYT02-C and BRYT02-B, indicating good potential for cross-correlation. Three tie-points were determined through the dated portion of BRYT02-C with BRYT02-B, based on a combination of LOI$_{550}$ and LOI$_{950}$ (Figure S2a, Table S2, Table S15). An age-depth model was created for BRYT02-B based on cross-correlation with the ^{210}Pb-dated CRS model established for BRYT02-C (Figure S2b).

PAH concentrations

SLNG04

Total concentrations of PAHs (∑PAH) are lowest at the base of the core at 1.78 ng g^{-1}, and peak just below the surface, at 188.3 ng g^{-1} (~2010 AD) (Figure 2). Retene displays the earliest observed increase in PAHs, c. 1915 (Figure S3). The first observed increase in ∑PAHs above background occurred c. 1930, briefly reaching 67 ng g^{-1}, declining again by 1935 to pre-1930 levels. Breakpoint analysis indicated two points of significant change in the PAH profiles, both occurring in the mid-twentieth century: first, in the late-1950s, and second in the mid-1970s. Correspondingly, the most pronounced shift in PAH concentrations occurred c. 1960, at which time ∑PAHs, ∑HMW PAHs, and ∑alkyl PAH concentrations began to increase (Figure 2). ∑PAHs reached concentrations of approximately 100 ng g^{-1} by the mid-1970s and remained elevated until the mid-1990s. Increases in ∑HMW PAH (and most individual HMW PAH compounds), and ∑alkyl PAH concentrations occurred between the late-1950s and 1980s, peaking in the mid-1980s, after which they declined to the surface (Figures 2 and S3). The early PAH record is dominated by perylene, however this may be of diagenetic origin. The recent PAH record is dominated by the LMW PAHs naphthalene and phenanthrene, which became more dominant in the late-1970s.

Black Lake

Breakpoint analysis identified two significant shifts in PAH concentrations at Black Lake: the early-1930s, and the mid-1970s. ∑PAH concentrations declined from the base of the sediment record to the surface (Figure 3). However, concentrations of the 16 USEPA PAHs ($\sum_{16}$PAHs) increased in concentrations following the mid-1940s, reaching 138 ng g^{-1} by the mid-1970s (Figure 4). Retene also began to increase in the mid-1940s, and peaked c. 1960 (Figure S4). ∑HMW PAHs, and most individual HMW PAH compounds, increased in concentration c. 1945, and peaked in the early-1970s (Figures 3 and S4). Post-1945, the PAH record was dominated by LMW PAHs naphthalene and phenanthrene, which increased in relative abundance in the 1960s. ∑LMW PAH concentrations increased beginning in the mid-1960s due, primarily, to the increase in naphthalene. Concentrations of $\sum_{16}$PAHs and ∑HMW PAHs declined following the mid- to late-1970s.

PAH ratios

Ratios of Fl/Fl+Py and C0-P/C0-C1-P at SLNG04 and Black Lake indicated biomass and coal combustion throughout the record (Figures 4 and 5). An increase in the C0-P/C0-C1-P ratio beginning in the mid-1930s at Black Lake indicated a shift away from biomass burning towards coal combustion (Figure 5). Moreover, retene/Fl+Py at SLNG04 indicated a switch from biomass burning to coal combustion beginning c. 1950, becoming most pronounced by the mid-1960s, concurrent with the brief indication of coal combustion from IP/IP+Bghi at SLNG04 (Figure 4). Petroleum combustion is indicated by IP/IP+Bghi through most of the record at SLNG04, and throughout the record at Black Lake. BzA/228 indicates combustion as the dominant PAH source since the early-20th century at SLNG04, while Bza/228 ratios from Black Lake indicated mixed sources of coal and petroleum combustion throughout the record. Ant/178 is only measured from c. 1970 to the surface in SLNG04 due to an absence of anthracene from the record prior to this time. Since the mid-1960s at Black Lake and c. 1970 at SLNG04, Ant/178 indicated a source of uncombusted petroleum products (Figures 4 and 5).

Halogenated organic compounds

SLNG04

HOCs began to increase in the mid-1950s at SLNG04, with the greatest increase in concentrations for all HOCs occurring c. 1960, and coinciding with a significant breakpoint (Figure 2). Early (c. 1930 to c. 1950) increase in PCBs was attributed mainly to increases in di- and tri-chlorophenyls (Figure S5). PCB concentrations increased through the 1950s and 1960s, reaching maximum concentrations in the mid-1960s. The dominant PCB congeners during this period were octa-chlorophenyl PCB203 (≤ 58% abundance), followed by tetra-chlorophenyl PCB70 (> 10% abundance) (Figure S5). A decline in ∑PCB concentrations began in the mid-1970s, and continued to the surface. However relative abundances of PCB congeners did not change. Non-dioxin-like (NDL) PCBs began to increase c. 1960, around the same time as most other HOCs. ∑HCH (primarily β-HCH) concentrations increased c. 1960, and remained elevated through the 20th century, increasing in the early-21st century to peak c. 2007. ∑PBDE concentrations peaked in the mid-1960s and again in the mid-1970s. Penta-BDE99 was the most common congener throughout the record (Figure S5). Total chlordane concentrations increased in the mid-1960s, and peaked in the mid-

1970s. ∑DDT concentrations increased most markedly between the mid-1960s and early-1970s, after which concentrations show a general decline to the surface (Figure 2).

Black Lake

Concentrations of most HOC compounds began to increase c.1920 (Figure 3), after which breakpoint analysis indicates two significant shifts: the mid-1940s, and c. 1960. ∑PCB concentrations fluctuated from the base of the core to the surface but began a subtle increase c. 1920 (Figure 3), with a mixture of PCB congeners present. Concentrations increased notably from the mid-1940s to late-1950s, with tetra-chlorophenyl PCB70 dominating the record (Figures 3 and S6). Concurrent to the second breakpoint, increases in NDL-PCBs and a change in congener dominance to penta-chlorophenyl PCB105, and NDL-hexa-chlorophenyl PCB138 occurred c. 1960 (Figure S6). Total PCB concentrations continued to be relatively high until the mid-1970s. ∑DDT concentrations increased c. 1950 until the mid-1960s (Figure 3). Declines in ∑DDT concentrations occurred between the mid-1960s and early-1980s. ∑PBDEs increased in concentrations c. 1950 and continued to increase until the early-1960s, with signs of continued presence until the mid-1970s. At all times PBDEs were dominated by BDE100 and BDE28 (Figure S6). HCHs only appeared in the sediment record between the mid-1930s (α-HCH) and late-1940s (β-HCH) (Figure 3). After this point, concentrations of ∑HCHs remained <LD to the surface. Total chlordane concentrations increased in the mid-1950s, remained elevated until the mid-1970s, then declined to the surface (Figure 3).

PAH and HOC fluxes

PAH fluxes tended to follow sediment accumulation rates (SAR), particularly during an increase in SAR in the early-1960s at SLNG04 (Figure S7), and c. 1980 at Black Lake (Figure S8). PAHs at SLNG04 underwent increasing fluxes until the early-1990s, followed by declining fluxes to the surface. The flux of ∑PAHs and ∑LMW PAHs increased c. 2010 at SLNG04. Black Lake ∑LMW PAH fluxes increased in the late-1960s, prior to an increase in SAR. ∑HMW PAH flux followed a similar trend as SAR at Black Lake, however most other PAH fluxes underwent fluctuations and slight declines to the surface which did not follow SAR.

With the exception of a brief increase in flux with SAR in the early-1960s, HOC fluxes at SLNG04 remained steady until the 1990s, at which point most fluxes increased briefly (Figure S7). Post-1990, flux of ∑PCBs remained similar to SAR, increasing and remaining steady to the surface, while ∑DDT flux declined to the surface, and ∑HCH flux remained constant until the 21st century, after which time fluxes increased until ~2010, before declining to the surface. HOC fluxes at Black Lake did not appear to follow SAR (Figure S8). ∑DDT flux declined from the 1960s to the surface, while ∑chlordane and ∑PBDE fluxes were low with slight fluctuations in the late-20th and early-21st centuries. ∑PCB fluxes increased from the early-1960s until the early-1980s, after which point fluxes declined and were steady to the surface, with the exception of an increase in the uppermost sample.

Discussion

Mid-20th century peak contamination of the Selenga River basin

The period of most rapid and sustained increases in organic contamination in the Selenga River basin occurred from the 1940s to the 1980s (Figure 2 and 3). PAH and HOC concentrations in both lakes during this period are similar to contemporary concentrations of freshwater systems in remote areas, including lakes of the northern Tibetan Plateau (11-279 ng g^{-1} $\sum_{15}$PAHs), North American Rocky Mountains (31-280 ng g^{-1} $\sum_{16}$PAHs) (Usenko *et al.,* 2007; Wang *et al.,* 2010), and other freshwater deltas, including the Mekong River Delta, Vietnam (<LD – 6.6 ng g^{-1} ∑DDT, <LD – 1.3 ng g^{-1} ∑HCH) (Minh *et al*., 2007). Moreover, concentrations recorded in this study are 1-3 orders of magnitude lower than many highly-contaminated sites, such as those in close proximity or downwind of industrial or urban sources, including urban freshwater river systems (Kanzari *et al.,* 2014), and lakes in European alpine regions (van Drooge *et al.,* 2011). Ecological toxicity of contaminants within this study fall below those concentrations determined to be of possible impact to benthic aquatic organisms (MacDonald *et al*., 2000; Long *et al*., 2006). Therefore, it is likely that even during the period of greatest anthropogenic contamination in the Selenga River basin, the threat to the Lake Baikal ecosystem from organic pollutants was likely low to moderate.

Contaminant concentrations at both SLNG04 and Black Lake peaked in the 1960s and 1970s, with similar trends in PAH concentration observed between lakes, and signs of increased pace of regional development during this time. LMW PAHs naphthalene and phenanthrene dominated the records from both SLNG04 and Black Lake and have also been recorded as the dominant PAHs in Lake Baikal sediments (Ok et al., 2013). Additionally, increases in ∑HMW PAHs in the mid-20th century at both SLNG04 and Black Lake were observed, suggesting regional-scale increases in combustion sources, as heavier PAHs are generally pyrogenic in origin, emitted during high temperature combustion processes, and tend to be deposited more locally to their source due to higher molecular weight (Johnson *et al*., 2005; Huang *et al*., 2012). PAH ratios of C_0-P/(C_0+C_1)-P, Fl/Fl+Py, and retene/Fl+Py may also indicate a shift in energy production away from biomass/wood burning and towards coal combustion in the region between the mid-1930s and 1950s, and an overall increase in energy consumption during mid-20th century. Ratios of IP/IP+Bghi, BzA/228, and Ant/178 are common across both lakes, and indicate petroleum combustion and petroleum usage, and may indicate regional increases in population, and related increases in transportation and vehicular emissions.

Benzo(*a*)anthracene, anthracene, and methylated phentanthrene are labile and prone to photooxidation during long-range transport, potentially altering the composition from its original source (Kamens et al., 1988; Simo et al., 1997; Fernandez *et al*., 2000; Grimalt *et al*., 2004). Moreover, benzo(*a*)anthracene may undergo post-depositional diagenesis in lake sediments (Grimalt *et al*., 2004). Hence the interpretation of PAH isomer ratios must be undertaken with caution. However, since the 1950s local and regional sources of PAHs are present in the Selenga River basin, likely limiting the degradation of PAHs to those undergoing long-range transport. While it is likely that some degree of degradation occurs prior to burial at our sites, proximity to local sources of combustion beginning c. 1950 suggests our results reflect changes to inputs rather than diagenetic processes.

The 1930s and 1940s in the USSR saw the beginning of infrastructure development for the expansion of industries and transportation in Siberia, and led to rapid industrial growth relative to previous decades, with the start of the USSR's five-year plans for economic growth, which stretched from 1928 to 1991 (Dienes, 1987; Khanin, 2003). In particular, the decades following the end of WWII were characterized by great increases in industrial development and population growth in southeast Siberia, coinciding with the Russian economy's recovery to pre-war levels during the fourth to sixth five-year plans (Orlov, 1970). Regional industrial development occurred with the construction and operation of the Baikalsk Pulp and Paper Mill (BPPM) in 1966, Selenginsk Pulp and Cardboard Mill (SPCM) in 1974, and the coal-fired Gusinoozersk State Regional Power Plant (GSRPP) in the 1960s (Pisarsky et al., 2005; Nomokonova et al., 2013). Population censuses taken in the Selenga River basin indicate increasing populations beginning post-WWII across southern Siberia, on republic (Republic of Buryatia; 499,900 people in 1937, 555,800 people in 1950, and 899,400 people in 1979), district (Kabansky district (SLNG04); 30,800 people in 1939, 62,100 people in 1959, 70,800 people in 1968) and municipal scales (Gusinoozersk city (Black Lake); 11,600 people in 1959, 23,500 people in 1979) (Chernykh, 2003). Increases in Selenga River basin contamination linked with increased local and regional development in the mid-20th century was concurrent with increasing global PAH and HOC concentrations associated with global trends in post-war development, population growth, and rapid industrialization in the second half of the 20th century (Bigus *et al*., 2014), termed "The Great Acceleration" (Steffen *et al*., 2015).

Spatial and temporal contrasts between lake sediment records

Spatial differences between HOC records from SLNG04 and Black Lake give evidence for increases in local-scale development in the Selenga River basin since the mid-20th century. Octa-PCB 203 has dominated the SLNG04 PCB record since c. 1950, while this highly chlorinated congener was not found in the record from Black Lake. This suggests a local source of PCBs to SLNG04 since the mid-1950s. Moreover, PCB203 has not been recorded at Lake Baikal since the 1990s (Iwata *et al*., 1995; Ok *et al*., 2013), and octa-PCBs in general have been present in very low abundances, although this does not preclude the possibility of occurrence in Lake Baikal prior to first observational records. As PCB203 has not been found in previous studies in the Lake Baikal region, a definite source is unknown. A potential local PCB source to SLNG04 is the SPCM in the town of Slenginsk, upstream of the Selenga Delta, operating as an open system until 1990 (Nomokonova et al., 2013). However, the SPCM did not begin operations until 1974, leaving an unknown source of PCB203 to SLNG04 during its early record.

Tetra-PCB 70 was the dominant congener at Black Lake in the mid-20th century, and subordinate congener at SLNG04 since the mid-1950s. Recent (c. 1960 to present) PCB records from Black Lake were dominated by PCB105 and PCB138, also present at up to 10% abundance in SLNG04 since the mid-1950s. PCB70, PCB105 and PCB138 are also common congeners recorded in Lake Baikal (Ok *et al*., 2013), suggesting a common PCB source in the Selenga region. PCB105 and PCB138 are two of the predominant congeners in Sovol, a Russian technical PCB mixture used widely in capacitors, transformers, hydraulic equipment, plasticizers, paints, and plastics. Previous studies in and around Lake Baikal have implicated Sovol as the source of PCBs to snow, soil, and lake sediments in the region (Iwata *et al*., 1995; Mamontov *et al*., 2000; Ok *et al*., 2013), and may have been a source of PCBs to both study sites during the mid-20th century. Furthermore, PCB105 and tetra-PCBs were observed by Ok *et al*. (2013) in sediments adjacent to the BPPM, potentially providing a regional source of PCBs since beginning operations in 1966.

Similarities between the concentration profiles at both sites for PBDEs and PCBs indicate a similar source of the contaminants. PBDE profiles suggest both regional and local sources, with differing BDE compounds dominating between SLNG04 and Black Lake. BDE99 was dominant in SLNG04 throughout the record, but found at lower concentrations in Black Lake. BDE99 was also common in surface sediments of Lake Baikal (Ok *et al*., 2013). Dominance of pentaBDEs in SLNG04 and Black Lake records suggests a source of commercial pentaBDE mixture, which is a major source of BDE99 (Birnbaum and Cohen Hubal, 2006), and has been suggested as a source of PBDEs to Lake Baikal in previous studies (Ok *et al*,, 2013; Tsydenova *et al*., 2007). While manufacture of PBDEs has generally been increasingly prevalent since the 1980s, the addition of PBDEs as flame retardant to a variety of goods, including electrical materials, building materials, foams, and automobiles, has been occurred since the 1960s (Kuryk et al., 2010). Therefore the rapid industrialization and development within the Selenga River basin post-WWII likely provided opportunities for similar sources of PBDEs and PCBs.

Temporal differences were recorded by the onset of increases in contaminant loadings in the mid-20th century at the two sites. Earlier increases in ∑HMW PAH and PCB concentrations were recorded at Black Lake than SLNG04 (Figures 2 and 3) and may indicate temporal differences in the onset of post-WWII industrialization across southeast Siberia. The 1940s brought industrial and mining developments and expansion to the Selenga River basin (Pisarsky *et al.,* 2005), with particularly intensive development occurring in the Gusinoozersk region, which contains Black Lake. It is likely that the earlier increase in contaminant concentrations at Black Lake reflects local industrial and population growth. Gusinoozersk was founded in 1939 as a mining settlement for the local coal industry. The settlement grew rapidly, owing to increased demand for power and industrialization, and in 1953 became the town of Gusinoozersk. Open-cut coal mining began in Gusinoozersk in the 1940s, quickly followed by military installations, the construction of the Trans-Mongolian Railroad, and the construction of the Gusinoozersk State Regional

Power Plant (SRPP), a coal-fired power plant, resulting in increased coal combustion by the 1960s (Pisarsky *et al*., 2005), all of which contributed to increasing PAH production (Figures 3 and 5). Shirapova et al. (2015) found detectable contamination of bottom sediments in Lake Gusinoye by PAHs, with a likely local and pyrolytic source, however concentrations were similar to those in polar regions. Later increases in PCB and PAH concentrations at SLNG04 are likely due to a later onset of intense development nearby SLNG04, with the operations at BPPM in 1966 and SPCM in 1974. Temporal variations between the sites likely indicates the increasing importance of local contaminant sources in the mid-20th century within the Selenga River basin.

Recent trends in organic contamination

Declines in contaminant concentrations into the 21st century at both sites are likely due to discontinued production of HOCs in the Baikal region in the late-20th century, including the halted production of PCBs in Russia between 1990 and 1993 (Tsydenova *et al.,* 2004), but also to the global restrictions on the production and use of POPs and PAHs following the 1998 UNECE Aarhus Protocol, and the 2001 Stockholm Convention (AMAP, 2000; UNEP, 2001). The decline in concentrations of organic contaminants coincided with increased destabilization in the USSR economy in the mid-1980s, and recorded declines in economic and industrial growth (Khanin, 2003), preceding the collapse of the Soviet Union in 1991. The national declines in growth were mimicked in the Selenga River basin, with population declines recorded in Kabansky district, Selenginsk, Gusinoozersk, and Selenginskii district since 1993, 2002, 1997, and 1999, respectively (Chernykh, 2003; Government of Buryatia Statistics, http://burstat.gks.ru/wps/wcm/connect/rosstat_ts/burstat/ru/statistics/population/). Declining concentrations and fluxes of ∑HMW PAHs by the end of the 20th century coincided with declines in concentrations of spheroidal carbonaceous fly-ash particles (SCPs), produced from the high-temperature combustion of fossil-fuels, and mercury at SLNG04 (Adams, 2017). Such declines may be attributed to the declining Soviet economy and resulting declines in local fossil-fuel combustion sources. SCP concentration declines observed in Lake Baikal sediments post-1990 are likely further evidence of reductions in fossil-fuel consumption in southeast Siberia (Rose *et al*., 1998). However, concentrations of PAHs and most reported HOCs remained elevated above pre-1930s concentrations throughout most of the recent record at both sites, indicating either continued production in the region, long-range transport, or possible leaching of legacy contaminants into aquatic systems due to erosional inputs.

Conclusions

Increasing concentrations of PAHs and HOCs are recorded in shallow lakes of the Selenga River basin in southeast Siberia since the 1930s. Temporal variations in organic contaminants are reflective of economic development in Russia since this time. Earliest records of contamination occur pre-WWII, consistent with early economic growth plans within the former USSR, and are recorded as minor concentration increases at both SLNG04 and Black Lake. The period of greatest contamination at both sites was from the 1940s to 1980s, with peak concentrations from the 1960s to 1980s. This period of contamination occurred in conjunction with major industrial and economic growth in Siberia. Spatial differences in congener dominance and presence, and differences in the onset of contamination and PAH ratios between SLNG04 and Black Lake indicates local pollutant production, usage, and combustion sources starting in the 1950s, and may record spatial variability in the onset of mid-20th century industrialization in southeast Siberia. However, similarities in congener presence may reveal sources of regional PCB contamination to SLNG04, Black Lake and Lake Baikal. Evidence for continued contamination of both SLNG04 and Black Lake at present may be due to long-range transport, continued production in the region, or leaching/remobilization of legacy contaminants. Understanding long-term records of contaminant change is crucial to determining the potential burden the region might face in the future with increased mobility of previously contained contaminants. Therefore, the sediment records from these shallow lakes continue to illustrate the impact potential of anthropogenic industrial activities on aquatic ecosystems.

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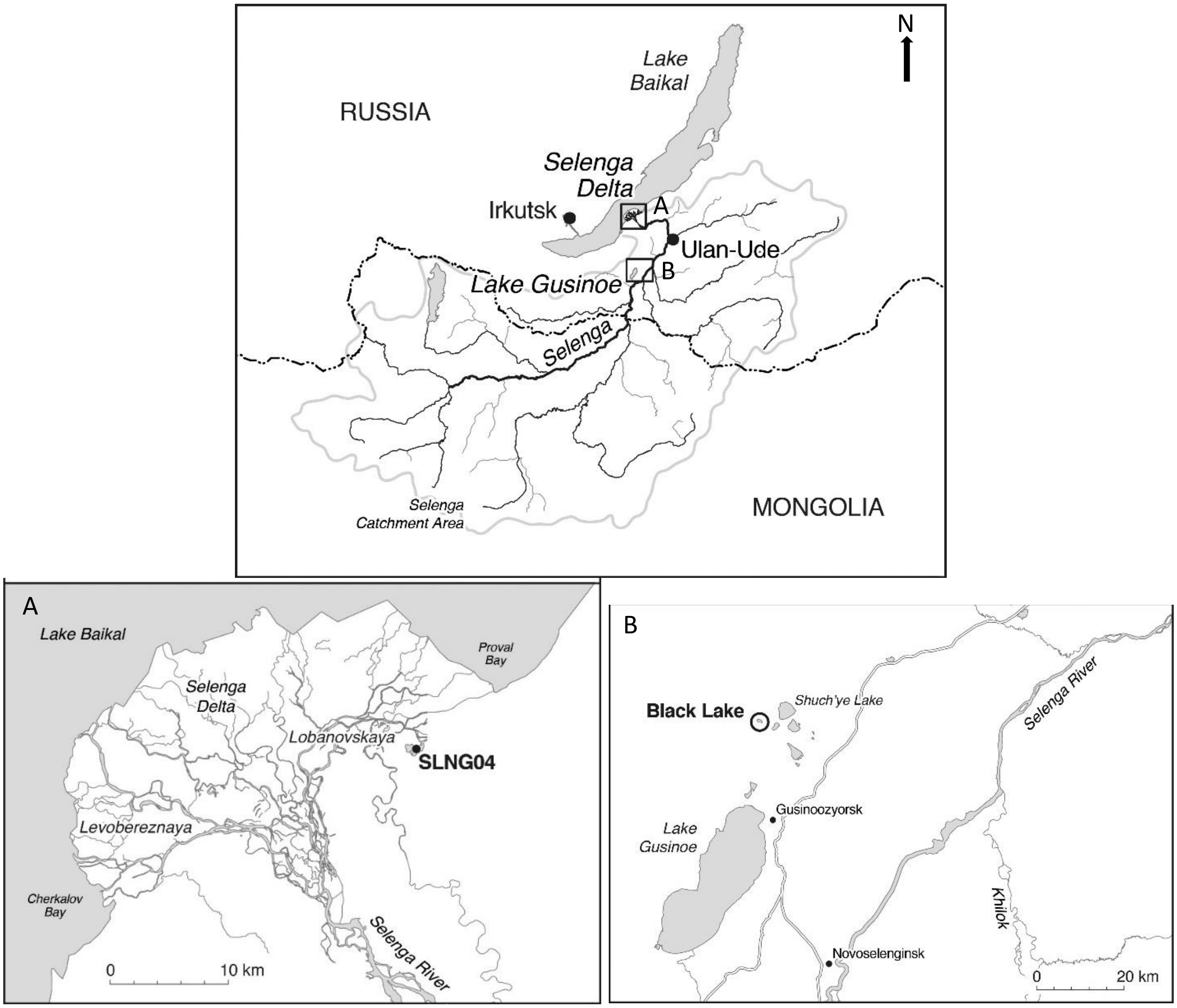
Figure 1. Map of the Selenga River basin in southeast Siberia and northern Mongolia, with major river tributaries and cities labelled. **Subset A.** Map of the Selenga Delta with SLNG04 location indicated. **Subset B.** Location of Black Lake (BRYT) in the Gusinoozersk region.



A

Figure 2. PAH concentrations, sums of PAH groups, and sums of HOC groups for SLNG04. Units of measurements are ng g^{-1}. Radioisotope-derived dates and confidence limits are highlighted on the y-axis. Italicized dates are extrapolated beyond ^{210}Pb radioisotope dating. Note different scales on the x-axes.

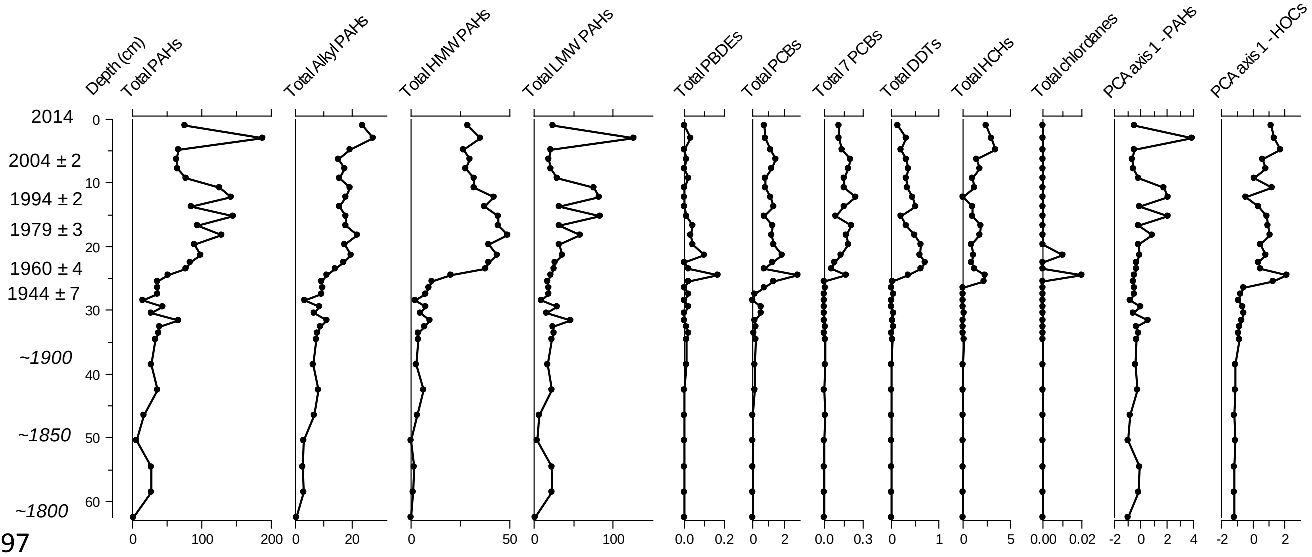


Figure 3. PAH concentrations, sums of PAH groups, and sums of HOC groups for Black Lake. Units of measurements are ng g^{-1}. Radioisotope-derived dates and confidence limits are highlighted on the y-axis. Italicized dates are extrapolated beyond ^{210}Pb radioisotope dating. Note different scales of x-axes.

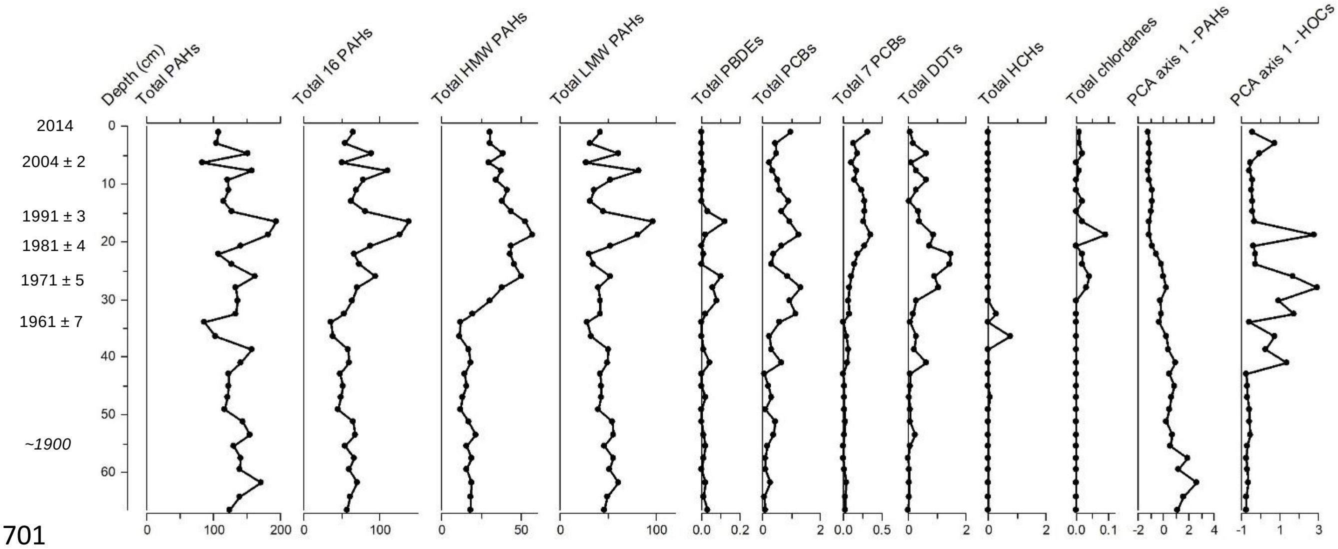


Figure 4. PAH ratios for SLNG04. Radioisotope-derived dates and confidence limits are highlighted on the y-axis. Italicized dates are extrapolated beyond ^{210}Pb radioisotope dating.

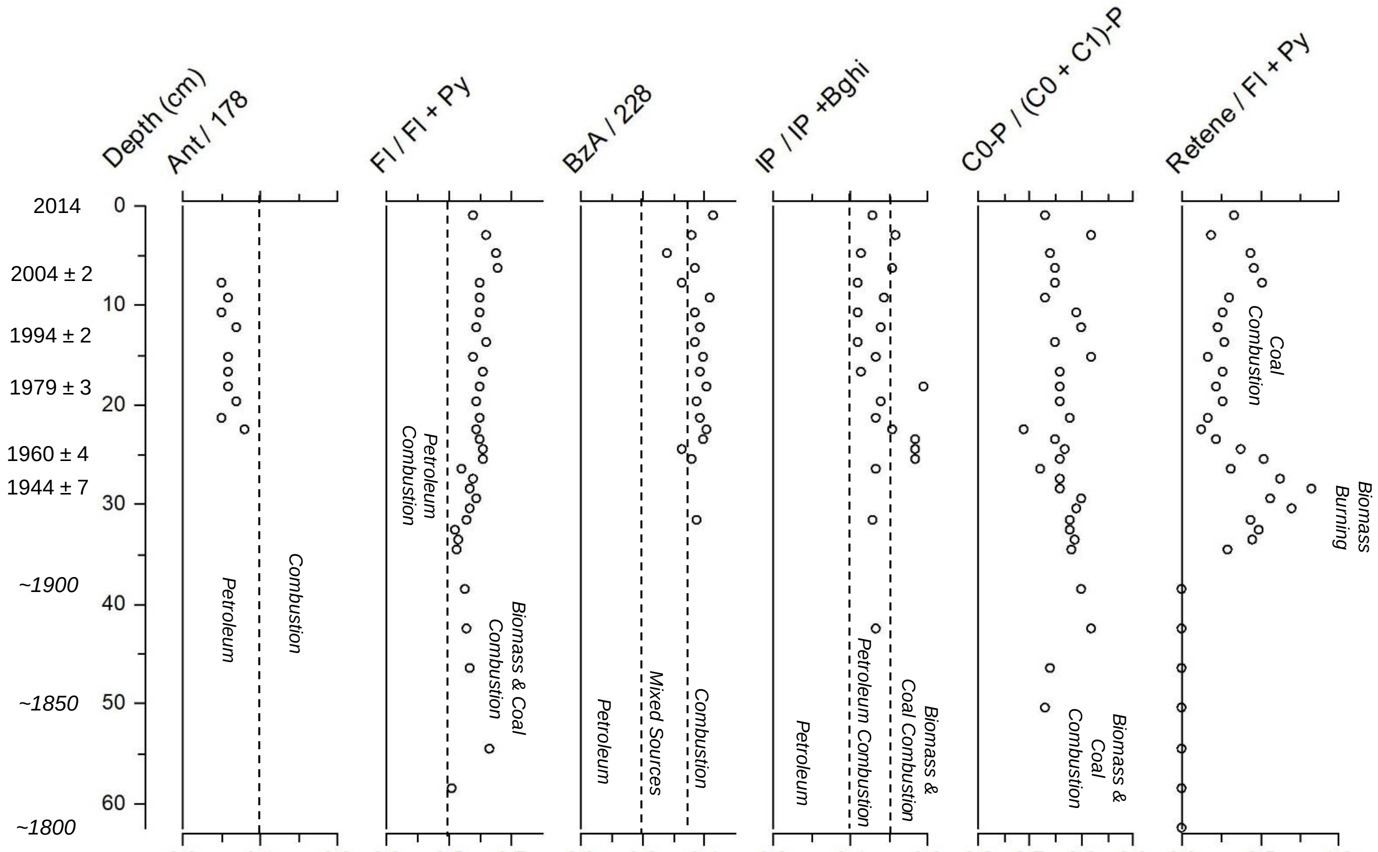


Figure 5. PAH ratios for Black Lake. Radioisotope-derived dates and confidence limits are highlighted on the y-axis. Italicized dates are extrapolated beyond ^{210}Pb radioisotope dating.