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RESEARCH ARTICLE

Source apportionment of polycyclic aromatic hydrocarbons in Lake Baikal water and adjacent air layer

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ABSTRACT
The composition of polycyclic aromatic hydrocarbons (PAHs) in Lake Baikal water and adjacent air layer and PAH emission composition profiles of possible sources were investigated. Analysis of emission composition data showed that the source profiles could not be grouped by fuel type or pyrogenic/petrogenic origin. Because of the similarity of source PAH profiles, the drawing of 3D mixing diagrams was the only way to check whether some of the potential PAH sources were the true sources. The mixing diagrams showed that the sources of air pollution were paper mills and wood burning and that the sources of water pollution were coal-fired and oil-fired boilers. The common source for both air and water was only oil and petroleum products. To determine the locations of PAH sources, their contributions to air and water pollution were calculated and mapped. Based on the results, air and water were polluted from both local and regional sources. The location of the zone influenced by a particular source was conditioned by physical properties of source emission, direction of air/water flows that transfer PAHs and temperature differences between mixing air/water flows.

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KEYWORDS
Polycyclic aromatic hydrocarbons; Lake Baikal; water; air; sources; contributions; spatial distribution

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of complex organic chemicals composed of carbon and hydrogen that have a fused ring structure containing at least two benzene rings [1]. PAHs are known mutagens and carcinogens or are precursors to carcinogenic daughter compounds. PAHs can originate from natural processes; however, most of these compounds are anthropogenic: coal and wood combustion, petrol and diesel oil combustion, and industrial processes [2]. PAHs are ubiquitous pollutants detected in all environmental compartments, including water, air, soil, and bottom sediments. However, PAH contamination of freshwaters is of special interest because the primary use of this resource is to sustain life. The problem of PAH contamination of water is particularly important for sustainable water use in the Lake Baikal region [3]. Lake Baikal is the largest freshwater lake by volume in the world, containing roughly 20% of the world's unfrozen surface freshwater. Most importantly, the lake is the source of drinking

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water for thousands of villages and towns located along the Angara River, which is the only outflow from Lake Baikal. Despite numerous studies devoted to PAH contamination of the lake and its tributaries [4–7], the sources and the pathways of PAH transport to the lake remain poorly understood. The PAH sources closest to Lake Baikal or located upstream of the lake are assumed to be primary contributors of PAHs to the lake. This problem is not typical only for Lake Baikal, and numerous studies concern pollution of freshwater [3,8] and freshwater sediments [9,10] worldwide. In spite of these studies, all that has been determined with certainty about the migration of PAHs is that surface flow is the mechanism of transport of wet and dry PAH deposition from soil surface to water bodies [11,12] in dissolved [13,14] or particulate form [15,16]. This is particularly evident during storm events [17,18] in impervious urban areas [19,20].

Revealing the pathways of PAH transport into water begins with identification of PAH sources [8,14]. The relative molecular concentration ratios (diagnostic ratios or DRs) are often considered a signature of a given emission source. The DR method is based on a comparison between the ratio of selected PAH isomers measured in the object of study and the ratio measured in the sources or that obtained from the literature [21–23]. The most complex DR is the 'Pyrogenic Index' (PI) proposed by Wang et al. [24] as a quantitative indicator for identification of pyrogenic PAHs and for differentiation of pyrogenic and petrogenic PAHs. The PI is defined as the ratios of the totals of five target alkylated PAH homologues to the totals of the other EPA priority unsubstituted 3–6 ring PAHs. However, whereas DRs are indicative of intrasource variability, they are also indicative of intersource similarity [25]. The other approach to identify sources is to apply multivariate statistical techniques such as principal component analysis (PCA) [25,26], cluster analysis [27–29] and factor analysis [9,30]. Multivariate techniques use an orthogonal transformation to convert a set of observations of possibly correlated variables (PAHs) into a set of values of linearly uncorrelated variables called principal components (PCs) or factors. Each PC is assumed to represent a source [10,31], characterised by a certain group of PAHs (source profiles). This principle also underlies the self-modeling curve resolution method used in the UNMIX model [32]. One problem with using multivariate techniques is that each PC is only a line that runs in the direction of highest variability of input data and can be the combination of several source profiles [3]. Another problem is that these reconstructed sources (PCs) are unknown. The only way to identify sources properly is to use detailed source profiles directly measured in manufacturing facilities. These profiles can be used as source signatures for source apportionment of PAHs in various environmental compartments, including water [3]. Unfortunately, the detailed literature data on emission profiles are scarce.

Source identification of PAHs in Lake Baikal water and adjacent air layer was the primary objective of this research. To achieve this objective, the most likely PAH sources were selected and the spatial distributions of their contributions to pollution were assessed. The secondary objective of the study was to determine key factors that affected the spatial distribution of source contributions.

2. Materials and methods

2.1. Study area

The study was conducted at Lake Baikal (Eastern Siberia, Russia) in May 2015 right after snowmelt. The study area is a mountainous region characterised by boreal climate and coniferous vegetation. A total of 365 rivers flow into Baikal, but the Angara River in the southern basin is the only outflow. Water and air were sampled near shore (in front of some river deltas) and at deep sites from north to south (Figure 1). The area is not densely populated and consequently is characterised by low to moderate levels of PAH accumulation in environmental compartments. However, because of the huge square area (450,000 km^2), numerous anthropogenic PAH emission sources are located in the Lake Baikal catchment. These sources are aluminium plants, oil-fired and spreader stoker coal-fired central heating boilers, residential wood and coal combustion, oil refineries, woodworking plants, pulp and paper mills, and asphalt plants, among others [33,34]. Natural PAH sources such as forest fires and oil seepages also occur in the area [35,36].

2.2. Chemical determinations

We used the concentration data for individual PAHs in lake water and air samples to identify PAH sources. Thirty-nine samples of riverine water and 36 samples of atmospheric air

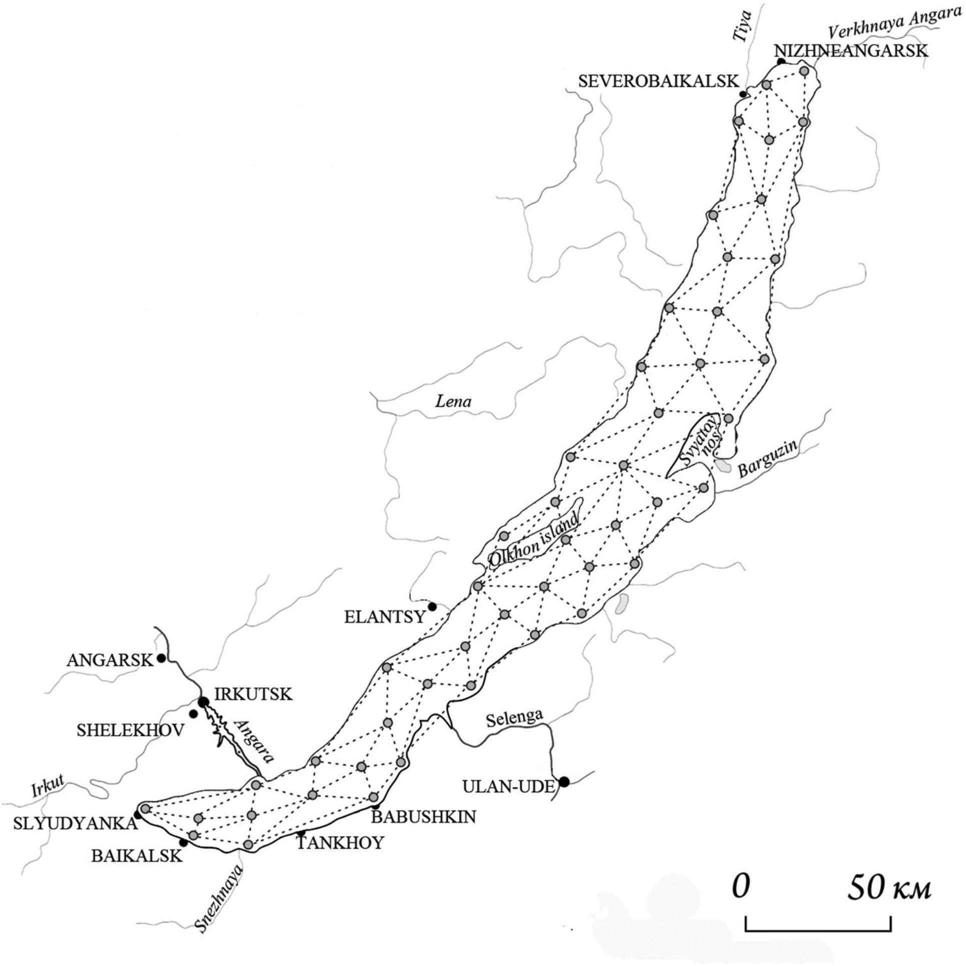


Figure 1. Sampling locations connected with lines for which perpendicular bisectors were drawn to create Voronoi polygons.

were collected in total. For the lake water, all the solutes were measured in unfiltered water samples. The PAHs were extracted with hexane, and the extracts were filtered through 0.45-µm Advantec (Tokyo, Japan) membrane filters. The samples were concentrated and adjusted to a volume of 0.1–0.2 mL using a rotary evaporator. Atmospheric air was sampled isokinetically using a PAH sampling system, which was equipped with a sampling probe, glass cartridge, pump, flow meter and control computer. A tube-type glass fibre filter was used to collect particulate matter and particle-phase PAHs. A glass cartridge packed with XAD-16 resin and supported by a polyurethane foam (PUF) plug was used to collect the gas-particle phase PAHs. PAHs from the cartridges and from the filters were extracted and measured as described below. Twelve PAHs were analysed, including phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), benzo[g,h,i]perylene (BghiP), and indeno [1,2,3-c,d]pyrene (IcdP). The PAH emission composition profiles of various sources used in this study were derived from the literature [37,38].

To control the analysis quality, all samples were spiked with 100 µL of PAH surrogate standards (EPA 525 Fortification solution B) before extraction. The standard solution was a mixture of acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} dissolved in acetone; the concentration of each compound was 5 µg mL^{-1}. The samples were analysed using an Agilent GC/MS system (Santa-Clara, CA 95051, USA) consisting of an Agilent Model 6890N gas chromatograph (GC) and an Agilent Model 5973 mass selective detector (MSD). The GC/MS was calibrated at six concentration levels (0.04, 0.4, 1, 4, 6, and 10 µg/mL) to determine the linearity of the responses before sample analysis. The GC temperature was held at 50°C for 0.5 min and increased to 300°C at 20°C min^{-1}. Separation of the analytes was achieved using a DB-5 ms column (30 m × 250 µm) operating under isocratic regime conditions. The injector temperature was maintained at 290°C. The injection volume was 2 µL. The MSD was run in selected ion monitoring mode (SIM) for optimum sensitivity. Identification of individual PAHs was based on the retention times of target ion peaks. Identified PAHs were quantified based on an internal standard calibration procedure.

To ensure that the expected levels of quality were reached, detection limits, precision and accuracy of measurements and recovery efficiency of the analytical method were assessed [39]. To assess the recovery, five replicate filters, PUF plugs and distilled water samples were spiked with standard solutions as described above. The spiked sample substrates were extracted and analysed. The average recovery was 99 ± 11%, similar to that recommended for GC–MS analyses of PAHs [40]. The recovery values were calculated as part of the QA/QC protocols, but no further correction was applied to the results. The recovery levels calculated for PUF samples were consistent with recovery results calculated from filters and water samples. Sample detection limits for waterborne PAHs varied widely, from 0.02 ng L^{-1} for FLU to 0.001 ng L^{-1} for ANT. Detection limit for all airborne PAHs was 0.05 ng m^{-3}. Precision ranged from 2.1% to 20.3%, although most values were better than 10%, and accuracy ranged from 2.7% to 13.4% and therefore was very good.

2.3. Identification of PAH sources and evaluation of their contributions to pollution

The PAH composition of water and air was considered a mixture of PAHs from multiple sources. The number of sources was determined using PCA. A PCA was performed to find eigenvalues and eigenvectors of the correlation matrix calculated from PAH measurement data. Eigenvalues reflect the quality of the projection from the N-dimensional initial table (samples are rows and the columns are variables) to a reduced number of dimensions. Each eigenvalue corresponds to eigenvector called a PC, and each PC corresponds to one dimension. A PC is a linear combination of the initial variables (PAHs), and all the PCs are uncorrelated. The eigenvalues and the corresponding PCs are sorted by descending order of how much of the initial variability they represent (converted to %). To determine the number of meaningful PCs that should be retained for interpretation, the Kaiser criterion [41] is usually applied. With this approach, any PC with an eigenvalue greater than 1.00 accounts for more variance than that contributed by one initial variable and therefore is retained and interpreted. Such a component accounts for a meaningful amount of variance and should be retained. For simplicity, the number of retained PCs is assumed to explain in total at least 90% of the data set variability [42]. For a mixture arising from a convex combination of $m+1$ linearly independent end-member sources, m PCs are required to explain the variation in the data when the matrix is centred before eigenvectors extraction [42]. Thus, the number of PAH sources will be one more than the number of retained PCs.

Sources were identified using such an end-member mixing approach [3]. The identification procedure was based on plotting the samples with potential end-member sources on the same mixing diagram using coordinates of source tracer concentrations. The sums of PAHs with the same molecular weight were used as tracers. The rule used to identify tracers and sources was to determine whether most samples could be bound by a polygon formed by potential sources. When a point was inside a polygon, all the sources contributed to sample pollution, whereas when a point was outside a polygon, only two neighbouring sources (vertices) contributed to pollution [3]. Another rule was that the number of sources was one more than the number of tracers. This rule arose from a system of linear equations that were solved to obtain source contributions:

$$\begin{cases} \mathrm{f}_1 + f_2 + \ldots + \mathrm{f}_n = 1 \\ T_1^1 \cdot \mathrm{f}_1 + T_2^1 \cdot \mathrm{f}_2 + \ldots + T_n^1 \cdot \mathrm{f}_n = T_{\mathrm{mix}}^1 \\ T_1^2 \cdot \mathrm{f}_1 + T_2^2 \cdot \mathrm{f}_2 + \ldots + T_n^2 \cdot \mathrm{f}_n = T_{\mathrm{mix}}^2 \\ \ldots\ldots\ \ldots\ldots\ \ldots\ldots\ldots\ \ldots\ \ldots\ldots\ \ldots\ldots\ldots\ \ldots \\ T_1^{\mathrm{m}} \cdot \mathrm{f}_1 + T_2^m \cdot \mathrm{f}_2 + \ldots + T_n^m \cdot \mathrm{f}_n = T_{\mathrm{mix}}^m, \end{cases}$$

where T is the tracer, f is the contribution of the specified source; superscripts denote tracer number, subscripts denote source number and the subscript mix denotes mixture or environmental compartment.

Source contributions obtained for sampling points (Figure 1) were interpolated over the entire lake area using the nearest neighbour method. The method uses Voronoi polygons to define areas of influence around each input (i.e. measured) data point [43]. Voronoi polygons have boundaries that define the area that is closest to each point relative to all other points, and this property is defined by the perpendicular bisectors of the lines between all input data points (Figure 1). Therefore, in this case, the value of the nearest measurement point is assigned to every unsampled location. Adjacent polygons with similar contribution values were joined, and the lines bounding these polygons were smoothed.

3. Results and discussion

3.1. Identifying the PAH sources

The highest concentrations in both air and water were observed for the six light PAHs, PHE, ANT, FLU, PYR, BaA, and CHR. The high concentrations were most likely due to the high volatility and high solubility of these PAHs. These three pairs of PAH isomers were used to analyse the differences in literature-derived source profiles (Figure 2). However, sources could not be grouped by fuel type or pyrogenic/petrogenic origin. As shown in Figure 2, the composition of PAH emissions from diesel engines was similar to that from wood burning, the composition of PAHs emitted by asphalt plants was similar to that emitted by coal-fired boilers, and the PAH profile from food processing facilities matched that from iron and steel industry. The unique combination of fuel origin, intensity of industrial production, equipment manufacturer, and degree of equipment deterioration, among other factors, caused the absence of an association between source profiles and particular combustion processes. This result indicated why possible pollution sources of lake water and adjacent air should be selected carefully, accounting for the similarity between PAH compositions of environmental samples and those of source emissions.

According to the PCA results obtained for air and lake water, the maximum possible proportion (100%) of data variability was explained by two PCs; thus, three sources of PAHs contributed to both water and air pollution. Based on cluster analysis, the source rich in PHE was common to both environmental components (Figure 3) and was most likely oil and petroleum products. For the other two sources of PAHs in water, three possible candidates were available: coal-fired boilers, oil-fired boilers and wood burning (Figure 4(a)). As shown in Figure 3(a), the wood burning was too far from the array of data points and therefore was an unlikely source of PAHs in water. The same relation

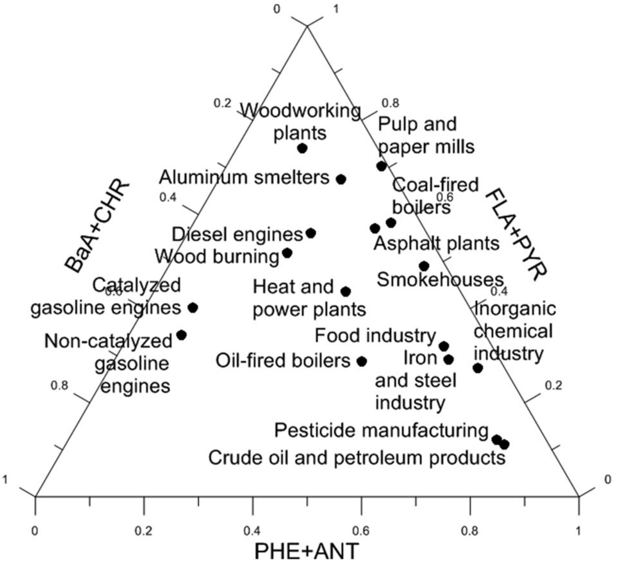


Figure 2. Ternary diagram illustrating the composition of PAH emissions from anthropogenic and natural sources in the Lake Baikal area.

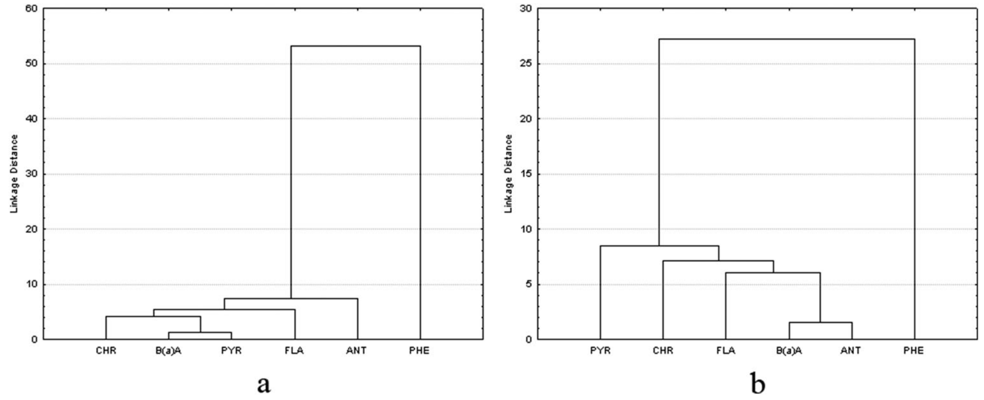


Figure 3. Hierarchical dendograms for six PAHs in Lake Baikal water (a) and in adjacent air layer (b).

was observed when sources and samples were plotted in coordinates of PC scores (Figure 5(a)). Other than the source of oil and petroleum products shared with water, three candidates were available for the two other sources of PAHs in air: pulp and paper mills, aluminium smelters, and wood burning (Figure 4(b)). Remarkably, heating boilers were not included among the sources of air pollution at the end of spring and conclusion of the heating season. In contrast to water, both the paper mills and aluminium smelters could be eligible sources because they are located close to one another (Figures 4(b) and 5(b)). The triangle formed by oil, wood burning, and paper mills bounded more samples than the triangle formed by oil, wood burning, and aluminium smelters (Figure 4(b)). Thus, according to the source identification rule, the paper mills were a more appropriate source than the aluminium smelters. Nevertheless, to determine the number of PAH sources that actually contributed to air pollution and to ensure that wood burning was certainly not a fourth source of PAHs in water, pseudo-3D mixing

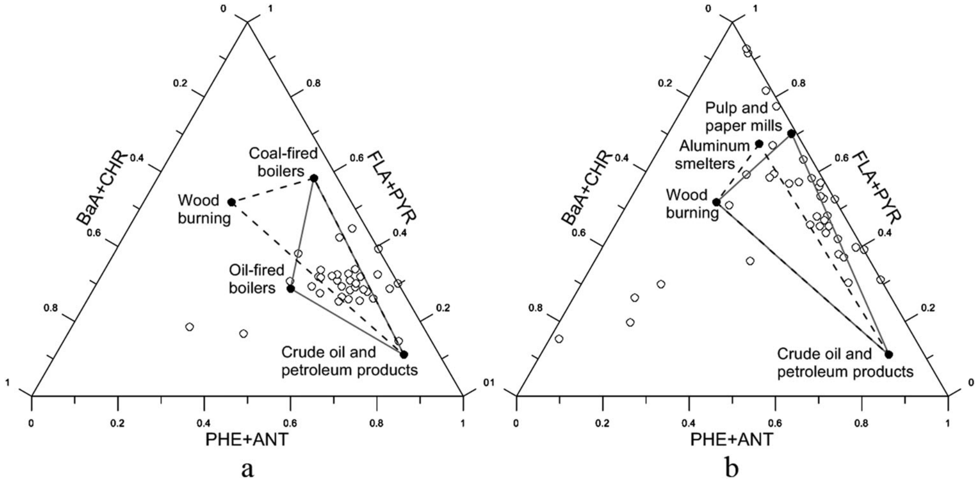
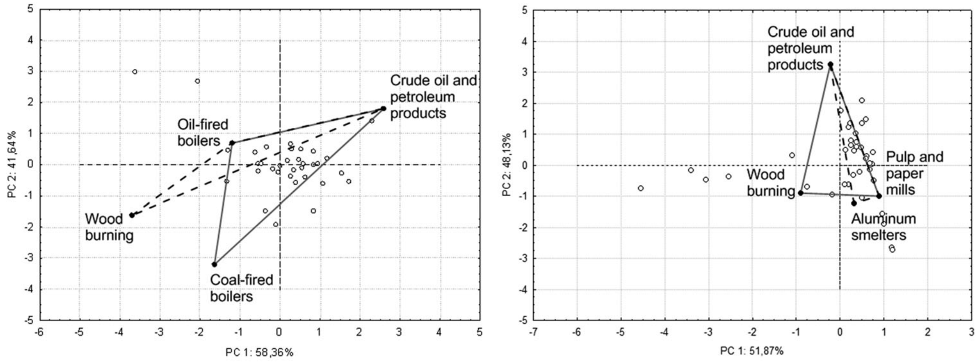


Figure 4. Ternary diagrams illustrating the mixing of PAHs from potential sources in Lake Baikal water (a) and in adjacent air layer (b).



a

b

Figure 5. PCA biplots illustrating the mixing of PAHs from potential sources in Lake Baikal water (a) and in adjacent air layer (b).

diagrams were created (Figure 6). All the data points in the 3D diagrams were apparently outside the mixing spaces, with the shape of unsymmetrical tetrahedral pyramids. To ensure that all the data points were outliers, we drew one more pyramid on each figure using one of the sample points (grey points in Figure 6(a,b)) as the apex of each new pyramid. Because most of the sample points were outside the mixing spaces, wood burning was not the fourth source of PAHs in water (Figure 6(a)), and only three PAH sources contributed to air pollution (Figure 6(b)).

The differences in PAH sources between air and water could not exactly explain the differences in distribution of sample points on the mixing diagrams. As shown in Figures 4–6, the water samples were grouped within the mixing triangle exhibiting similar composition, whereas air sample points were scattered along the hypotenuse of the mixing triangle exhibiting variable composition of airborne PAHs. Similar PAH composition of water in different locations might partly result from a common PAH fractionation pattern during the long-range transport through the watershed and riverine network. For example, the remoteness from emission sources explains the fractionation pattern of polychlorinated biphenyls in the Northern Hemisphere [44]. Similar PAH composition of lake water at different locations might also be due to large-scale advective exchange of water masses [45]. By contrast, variable composition of air samples might be caused by the predominance of vertical diffusion over horizontal advection at the time of day when the air was sampled [46]. If air were sampled continuously for 24 h, the composition of PAH samples collected from different locations would be more similar due to horizontal movement of air at night.

3.2. Determining the PAH source locations

To identify the locations of possible PAH sources the values of source contributions to pollution were calculated using PAH compositions of samples projected in PCA space coordinates as tracers. For the compositions of water samples, the differences were more evident for source contributions than for PAH concentrations. For most of the surface layer (above the deep water region), water was equally polluted by all identified sources (Figure 7(a)). The contribution of coal-fired boilers was lower than expected, because coal is the most

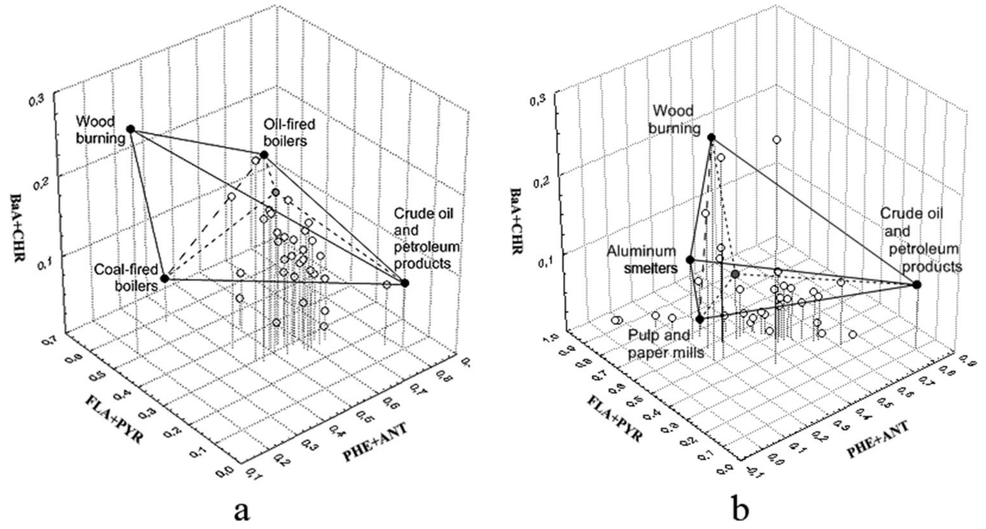


Figure 6. Pseudo-3D diagrams illustrating the mixing of PAHs from potential sources in Lake Baikal water (a) and in adjacent air layer (b).

abundant heating fuel in the watershed of the Selenga River [33,34], which is a major tributary of Lake Baikal, occupying 82% of its watershed [45,47]. The low contribution of coal-fired boilers was most likely due to long-range transport of submicron and ultrafine soot particles typical for emission from oil-fired boilers [48], leading to an underestimation of the contribution of coal-fired boilers. The highest contributions of oil-fired boilers were found in a narrow strip of water along almost the entire coast that coincided with the area of shallow water [49]. In the spring, the shallow water region of the lake is separated from the deep water region by a thermal bar [47]; thus, the chemical composition of shallow waters was to a sufficient extent inherited from that of lake tributaries fed by snowmelt runoff. The similar PAH composition of riverine waters in different parts of the watershed was most likely also due to long-range transport of soot particles typical for emissions from oil-fired boilers, which is a hypothesis supported by the fact that long-range transport of polychlorinated biphenyls to Lake Baikal has been recently recorded [50]. The highest contributions of oil and petroleum products to water pollution were observed in the central basin of Lake Baikal (Figure 7(a)). Slightly reduced PAH contributions from oil and petroleum products were typical for northern and southern basins and for the Maloye More Strait separating Olkhon Island from the mainland. The clearly identifiable shape and the small size of 'oil' contours indicated that the pollution originated from nearby point sources. In the central basin, these sources were most likely natural oil seeps located south of Olkhon Island and in the Gulf of Barguzin [35]. In the northern and southern basins in which the coastal areas are densely populated, these sources were most likely anthropogenic spills of petroleum products directly into the lake or tributary streams. In Maloye More Strait, the most probable sources of oil-derived PAHs were recreational activities such as boating and camping [50]. Oil and petroleum products might also result in underestimation of the contribution of coal-fired boilers to pollution of lake water.

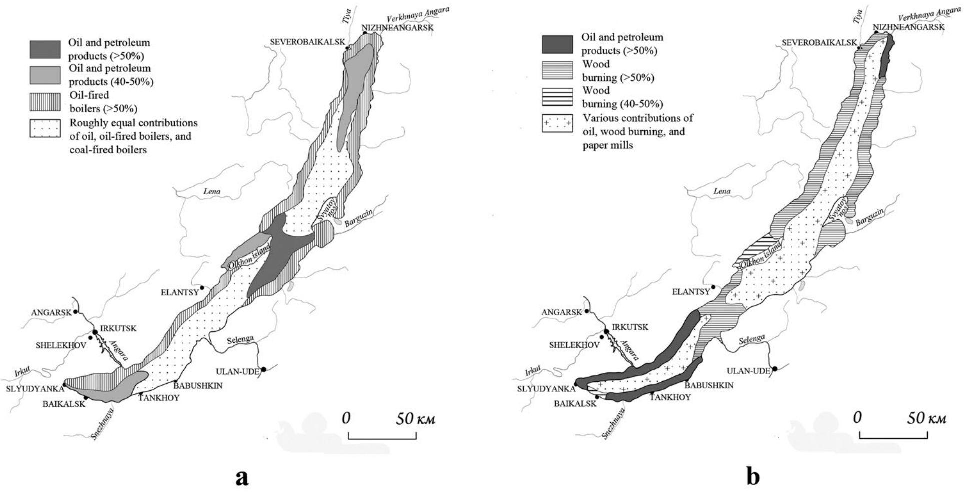


Figure 7. Spatial distribution of PAH source contributions to pollution of Lake Baikal water (a) and adjacent air layer (b).

The spatial distribution of source contributions to air pollution was most likely affected by the temperature differences between the land and water that affected wind direction. During the day, the spatial distribution of PAH source contributions to air pollution above the offshore lake area was unclear (Figure 7(b)), because as the lake breeze flowed inland, the sources of the pollutants remained out of the mixing layer, and the ascending flow at the lake breeze front prevented the pollutants from entering the mixing layer [46]. The only exception was the area in front of the Selenga River mouth at which the air masses from the Selenga River valley met the air masses from the opposite coast. Both air fluxes contained PAHs produced by forest fires that were observed around Baikal in spring 2015 [36,51]. The highest contributions of wood burning were also observed along the coasts of northern and central basins, except for the small area between the deltas of the Selenga and Bargusin rivers. The PAH emissions from the Selenginsk pulp and paper mill (SPPM) located northeast of the Selenga River mouth were likely masked by large forest fires [34]. The highest contributions of oil and petroleum products to air PAHs were observed along the southern coast and along a small part of the northeastern coast (Figure 7(b)). Air pollution near the southern coast was most likely due to both human activity on the coast and transport of air pollution from upwind of the Angarsk oil refinery plant [52]. Air masses travel along the Angara River towards Baikal, and when these masses reach the lake, they become saturated with water above the lake surface and pass as a narrow front along the southern shore. Thus, air pollution from remote sources was very probable in this area. On the northeastern coast, *in situ* volatilisation of petroleum products most likely caused the air pollution by PAHs.

4. Conclusions

The applied set of source apportionment techniques helped answer three basic questions concerning PAH pollution of Lake Baikal water and adjacent air layer: (1) How many sources contributed to the pollution? (2) What were these different sources? (3) How much did each source contribute to the pollution? Because of the similarity of source PAH profiles, the creation of 3D mixing diagrams was the only way to check whether some of the potential PAH sources were the true sources. The applied source apportionment mapping showed the locations of these sources. The data on source locations determined the key factors affecting the spatial distribution of source contributions. Spatial heterogeneity of source contributions to air pollution resulted primarily from different meteorological conditions at different sites that affected the relative importance of transboundary versus domestic emissions. Distribution of source contributions to water pollution during the sampling period was controlled mostly by the thermal bar that separated a shallow body of water located alongside the coast from a large body of deep water. The spatial distribution of source contributions to both air and water pollution was also conditioned by physical properties of emissions from different sources. PAHs associated with soot particles emitted from oil-fired boilers and vapour-phase oil-derived PAHs spread over long distances, whereas PAHs associated with coarse ash particles emitted from wood and coal burning emissions were deposited close to the source area.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Ravindra K, Sokhi R, Vangrieken R. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ. 2008;42:2895–2921.

[2] Tobiszewski M, Namieśnik J. PAH diagnostic ratios for the identification of pollution emission sources. Environ Pollut. 2012;162:110–119.

[3] Semenov MY, Marinaite II, Bashenkhaeva NV, et al. Polycyclic aromatic hydrocarbons in a small eastern siberian river: sources, delivery pathways, and behavior. Environ Earth Sci. 2016;75 (11):441.

[4] Kirso U, Irha N, Paalme L, et al. Levels and origin of PAHs in some big lakes. Polycycl Aromat Comp. 2002;22(3–4):715–728.
[5] Nikanorov AM, Reznikov SA, Matveev AA, et al. Monitoring of polycyclic aromatic hydrocarbons in the Lake Baikal basin in the areas of intensive anthropogenic impact. Russ Meteorol Hydrol. 2012;37(7):477–484.
[6] Nikonorov AM, Matveev AA, Reznikov SA, et al. Results of multiyear studies on the dynamics of pollution of lake Baikal by polycyclicaromatic hydrocarbons in the area waste water discharge from the Baikal pulp and paper plant. Dokl Earth Sci. 2012;443(1):361–364.
[7] Reznikov SA, Adzhiev RA. Persistent organic pollutants in bottom sediments in the north of Lake Baikal in the area of the Baikal-Amur mainline impact. Russ Meteorol Hydrol. 2015;40 (3):207–214.
[8] Bouloubassi I, Saliot A. Composition and sources of dissolved and particulate PAH in surface waters from the Rhone delta (NW Mediterranean). Mar Pollut Bull. 1991;22(12):588–594.
[9] Bzdusek PA, Christensen ER, Li A, et al. Source apportionment of sediment PAHs in Lake Calumet, Chicago: application of factor analysis with nonnegative constraints. Environ Sci Technol. 2004;38(1):97–103.
[10] Malik A, Verma P, Singh AK, et al. Distribution of polycyclic aromatic hydrocarbons in water and bed sediments of the Gomti River, India. Environ Monit Assess. 2011;172:529–545.
[11] Chen BL, Xuan XD, Zhu LZ, et al. Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. Water Res. 2004;38:3558–3568.
[12] Meyer T, Lei YD, Wania F. Transport of polycyclic aromatic hydrocarbons and pesticides during snowmelt within an urban watershed. Water Res. 2011;45:1147–1156.
[13] Doong R, Lin Y. Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. Water Res. 2004;38:1733–1744.
[14] Luo X, Mai B, Yang Q, et al. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River delta in South China. Mar Pollut Bull. 2004;48:1102–1115.
[15] Fernandes MB, Sicre M-A, Boireau A, et al. Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. Mar Pollut Bull. 1997;34(11):857–867.
[16] Prokeš R, Vrana B, Komprdová K, et al. Annual dynamics of persistent organic pollutants in various aquatic matrices: a case study in the Morava River in Zlin district, Czech Republic. J Soil Sediment. 2014;14:1738–1752.
[17] Ngabe B, Bidleman TF, Scott GI. Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina. Sci Total Environ. 2000;255:1–9.
[18] Menzie CA, Hoeppner SS, Cura JJ, et al. Urban and suburban storm water runoff and polycyclic aromatic hydrocarbons (PAHs) to Massachusetts estuarine and coastal environments. Estuaries. 2002;25(2):165–176.
[19] Motelay-Massei A, Garban B, Tiphagne-larcher K, et al. Mass balance for polycyclic aromatic hydrocarbons in the urban watershed of Le Havre (France): transport and fate of PAHs from the atmosphere to the outlet. Water Res. 2006;40:1995–2006.
[20] Oros DR, Ross JRM, Spies RB, et al. Polycyclic aromatic hydrocarbon (PAH) contamination in San Francisco bay: a 10-year retrospective of monitoring in an urbanized estuary. Environ Res. 2007;105:101–118.
[21] Gschwend PM, Hites RA. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. Geochim Cosmochim Ac. 1981;45:2359–2367.
[22] Dickhut RM, Canuel EA, Gustafson KE, et al. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake bay region. Environ Sci Technol. 2000;34:4635–4640.
[23] Yunker MB, Macdonald RW, Vingarzan R, et al. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem. 2002;33:489–515.
[24] Wang ZD, Fingas M, Shu YY, et al. Quantitative characterization of PAHs in burn residue and soot samples and differentiation of pyrogenic PAHs from petrogenic PAHs – the 1994 Mobile burn study. Environ Sci Technol. 1999;33:3100–3109.

[25] Galarneau E. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos Environ. 2008;42:8139–8149.

[26] Yunker MB, Macdonald RW. Composition and origins of polycyclic aromatic hydrocarbons in the Mackenzie River and on the Beaufort Sea shelf. Arctic. 1995;48:118–129.

[27] Liu Y, Chen L, Huang Q, et al. Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Huangpu River, Shanghai, China. Sci Total Environ. 2009;407:2931–2938.

[28] Hu NJ, Huang P, Liu JH, et al. Source apportionment of polycyclic aromatic hydrocarbons in surface sediments of Bohai Sea, China. Environ Sci Pollut Res. 2013;20:1031–1040.

[29] Lai I, Chang Y, Lee C, et al. Source identification and characterization of polycyclic aromatic hydrocarbons along the southwestern coastal of Taiwan – with a GMDH approach. J Environ Manage. 2013;115:60–68.

[30] Chen HY, Teng YG, Wang JS. Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Rizhao coastal area (China) using diagnostic ratios and factor analysis with nonnegative constraints. Sci Total Environ. 2012;414:293–300.

[31] Hu NJ, Huang P, Liu JH, et al. Characterization and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in sediments in the Yellow River Estuary, China. Environ Earth Sci. 2014;71:873–883.

[32] Henry RC. Multivariate receptor models – current practice and future trends. Chemometr Intell Lab. 2002;60:43–48.

[33] Saneev BG, Ivanova I, Maisyuk EP, et al. Energeticheskaya infrastructura tsentralnoy ecologicheskoy zony Baikalskoi prirodnoy territorii: vozdeystviye na prirodnuyu sredu i puti ego snizheniya [The power generation infrastructure in the central ecological zone of the Baikal natural territory: the environmental impact and ways to mitigate it]. Geogr Natural Res. 2016;5:218–224. Russian.

[34] Obolkin VA, Potemkin VL, Makukhin VL, et al. Long-range transport of plumes of atmospheric emissions from regional coal power plants to the South Baikal water basin. Atmospheric and Oceanic Optics. 2017;30(4):360–365.

[35] Kontorovich AE, Kashirtsev VA, Moskvin VI, et al. Petroleum potential of Baikal deposits. Russ Geol Geophys. 2007;48:1046–1053.

[36] Laing JR, Jaffe DA, Hee JR. Physical and optical properties of aged biomass burning aerosol from wildfires in Siberia and the Western USA at the Mt. Bachelor observatory. Atmos Chem Phys. 2016;16(23):15185–15197.

[37] Belykh LI, Malykh Y, Penzina EE, et al. Istochniki zagryazneniya atmosphery politsiklicheskimi aromaticheskimi uglevodorodamy v promyshlennom pribaikalye [Sources of atmosphere pollution by polycyclic aromatic hydrocarbons in industrial Transbaikalia]. Atmospheric and Oceanic Optics. 2002;10:944–948. Russian.

[38] Khatmullina RM, Safarova VI, Safarov AM. Emissiya politsiklicheskikh aromaticheskikh uglevodorodov v okruzhayushcuyu sredu [Emission of polycyclic aromatic hydrocarbons to environment]. Safety of Life Activity. 2014;11:34–37. Russian.

[39] Sloan CA, Brown DW, Ylitalo GM, et al. Quality assurance plan for analyses of environmental samples for polycyclic aromatic compounds, persistent organic pollutants, fatty acids, stable isotope ratios, lipid classes, and metabolites of polycyclic aromatic compounds. U.S. Dept. Commer. 2006 (NOAA Tech. Memo. NMFS-NWFSC-77).

[40] Delgado-Saborit JM, Alam MS, Godri Pollitt KJ, et al. Analysis of atmospheric concentrations of quinones and polycyclic aromatic hydrocarbons in vapour and particulate phases. Atmos Environ. 2013;77:974–982.

[41] Kaiser HF. The application of electronic computers to factor analysis. Educ Psychol Meas. 1960;20:141–151.

[42] Christophersen N, Hooper RP. Multivariate analysis of stream water chemical data: The use of principal component analysis for the end-member mixing problem. Water Resour Res. 1992;28:99–107.

[43] Klein R. Abstract Voronoi diagrams and their applications. Lecture Notes in Computer Science. 333. Springer-Verlag; 1989. p. 148–157.

[44] von Waldow H, Macleod M, Jones K, et al. Remoteness from emission sources explains the fractionation pattern of polychlorinated biphenyls in the northern hemisphere. Environ Sci Technol. 2010;44:6183–6188.

[45] Ravens TM, Kocsis O, Wüest A, et al. Small-scale turbulence and vertical mixing in Lake Baikal. Limnol Oceanogr. 2000;45(1):159–173.

[46] Kondo H, Gambo K. The effect of the mixing layer on the sea breeze circulation and the diffusion of pollutants associated with land-sea breezes. J Meteorolog Soc Japan. 1979;57 (6):560–575.

[47] Shimaraev MN, Granin NG, Zhdanov AA. Deep ventilation of Lake Baikal waters due to spring thermal bars. Limnol Oceanogr. 1993;38(5):1068–1072.

[48] Rogge WF, Hildemann LM, Mazurek MA, et al. Sources of fine organic aerosol. 8. Boilers burning. No. 2 distillate fuel oil. Environ Sci Technol. 1997;31:2731–2737.

[49] Sherstyankin PP, Alekseev SP, Abramov AM, et al. Computer-based bathymetric map of Lake Baikal. Doklady Earth Sci. 2006;408(4):564–569.

[50] Samsonov DP, Kochetkov AI, Pasynkova EM, et al. Levels of persistent organic pollutants in the components of the Lake Baikal unique ecosystem. Russ Meteorol Hydro. 2017;42(5):345–352.

[51] Balin YuS., Klemasheva MG, Kokhanenko GP, et al. Vertical structure of the aerosol fields of the atmosphere in the period of forest fires over Lake Baikal in 2015. Proceedings of SPIE 10035, 22nd International Symposium on Atmospheric and Ocean Optics: Atmospheric Physics, 100354D; 2016 November 29; Tomsk Russian Federation.

[52] Semenov M, Khodzher TV, Obolkin VA, et al. Assessing the acidification risk in Lake Baikal region. Chem Ecol. 2006;22(1):1–11.