Polyaromatic Hydrocarbons in the Snow Cover of the Northern City Agglomeration

Aleksandr Kozhevnikov (akozhevnikov@mail.ru)
Northern (Arctic) Federal University
Dmitry Kosyakov
Northern (Arctic) Federal University
Danil Falev
Northern (Arctic) Federal University
Sergey Sypalov
Northern (Arctic) Federal University
Irina Kozhevnikova
Northern (Arctic) Federal University

Research Article

Keywords: environmental monitoring, PAH, HPLC, Snow cover, emission, toxic equivalent

Posted Date: January 23rd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-148443/v1

Abstract

The 13 priority PAHs were qualitatively and quantitatively assessed in snow samples collected at 46 the crossroads of a large city in northern Europe - Arkhangelsk. The HPLC analysis revealed that the range of Σ13PAH concentrations detected in snow. The average, maximum and minimum values were respectively 167.7; 664.5 and 16.0 ng / kg snow. The average toxic equivalent quantity varied is 3.6 ng / kg, which is three times less than the established maximum permissible concentration. The sources of pollution origin were assessed using PAHs markers. The urban agglomeration of Arkhangelsk is not contaminated with anthropogenic PAHs. The markers identified pyrogenic sources of emission. Regression analysis was carried out to find correlations between the presence of benzo(a)pyrene and other PAHs in snow samples. We found that benzo(a)pyrene has a very high correlation with high molecular weight PAHs and has no correlation with low molecular weight PAHs. The quality of the snow polluted is satisfactory.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are highly toxic organic compounds that enter the environment during incomplete combustion of fuel, including when using internal combustion engines. For these reasons, they are typical contaminants of the atmosphere of urban agglomerations. [1–3]. This has an extremely high level of impact on biological organisms. This compounds are included in the group most dangerous for human health due to their high mutagenic and carcinogenic activity. Exposure of women to PAHs during pregnancy is a risk factor for adverse neurobehavioral outcomes. [4]. PAHs are listed as a priority pollutant by the United States Environmental Protection Agency (US EPA), the European Commission, and the Russian Federation. It has been shown that 15 PAHs are important for environmental monitoring. [5, 6].

Precipitation is the main cause of PAH distribution [7]. In addition to directly studying the air environment, information on the quality of the atmosphere can be obtained by analyzing atmospheric precipitation. PAHs drop out of the atmosphere during snowfall and remain in seasonal snow cover. Thus, PAHs in fresh snow and snow cover may reflect PAHs levels in the atmosphere. [8]. Snow is a good deposition matrix for the accumulation and subsequent analysis of the chemical compounds present in it.

Snow accumulates a wide variety of substances deposited from the atmosphere over several months, which makes it possible to assess the long-term pollution of the territory in the northern countries. Snow is easily sampled for subsequent analysis to determine inorganic and organic substances. [9, 10].

The average concentration of the total PAHs content in the snow in the area of the Moscow (ring road) is at the level of 2899 ng / kg of snow. [10]. The total PAHs concentrations in fresh snow and snow cover in Changchun city ranged from 26.6 to 36.9 μg L^{-1} and from 40.3 to 105.9 μg L^{-1}, respectively. [8]. The concentration range of the total PAHs (13 compounds) found in snow collected in the area of the city of Khabarovsk is in the range between 42.83 and 441.13 and 43.00–695.73 ng / L [3]

Arkhangelsk is a large city in the north of Russia with a population of about 350 thousand people and a large number of vehicles (more than 144 thousand vehicles). It is the northernmost city in the world with so much population and transport, where snow cover persists for a long time.

The purpose of our work is to reveal the pollution of the atmosphere of the urban agglomeration of Arkhangelsk, the amount of total PAHs through the assessment of their content in the snow cover.

Results

Figure 1 shows data on sampling sites in the snow cover of Arkhangelsk. Average, maximum and minimum values were respectively 167.7; 664.5 и 16.0 ng/kg PAHs in snow.

The maximum concentration $\sum_{13} PAH$ is found at point 36 in the area of one of the bridges over the river Northern Dvina where there is a large congestion of road transport, traffic jams and the main railway runs. The minimum concentrations of $\sum_{13} PAH$ are observed in areas of the city where there are no traffic flows.

Next, we carried out an identification assessment of the origin of PAHs [2]. We have calculated the values of the ratio (PYR + BaP) / (PHE + CHR);, (PYR + BaP + BghiP) / (PHE + CHR); ANT / ANT/(ANT + PHE); FLT / (FLT + PYR); BaA / (BaA + Chr) (Table 1). Also we calculated ratio between high molecular weight (HMW) / and low molecular weight (LMW) PAHs (Table 1).

Table 1
The modulus ratio of individual PAH inputs into the snow cover

Point N	(PYR + BaP)/ (PHE + CHR)	(PYR + BaP + BghiP)/ (PHE + CHR)	ANT/ (ANT + PHE)	FLT/ (FLT + PYR)	BaA/ (BaA + CHR)	HMW/LMW
1	0.2	0.2	0.0	0.6	0.1	0.26
2	0.8	0.9	0.1	0.7	0.1	0.46
3	0.4	0.4	0.0	0.6	0.2	0.32
4	4.9	5.0	0.1	0.2	0.2	2.12
5	0.4	0.4	0.0	0.6	0.2	0.49
6	0.4	0.4	0.0	0.5	0.1	0.40
7	0.3	0.3	0.0	0.5	0.1	0.30
8	0.5	0.6	0.0	0.6	0.1	0.39
9	0.4	0.4	0.0	0.6	0.2	0.38
10	0.6	0.7	0.0	0.6	0.1	0.58
11	0.2	0.2	0.1	0.6	0.0	0.93
12	0.7	0.8	0.1	0.6	0.2	0.43
13	0.1	0.1	0.0	0.6	0.2	0.20
14	0.0	0.0	0.0	0.6	0.2	0.07
15	0.7	0.8	0.0	0.6	0.2	0.70
16	0.6	0.6	0.0	0.6	0.0	0.40
17	0.8	0.8	0.0	0.6	0.2	0.55
18	1.1	1.2	0.1	0.5	0.1	0.74
19	0.5	0.5	0.0	0.6	0.2	0.38
20	0.5	0.5	0.0	0.6	0.1	0.37
21	0.6	0.7	0.0	0.5	0.3	0.65
22	0.5	0.5	0.1	0.6	0.0	0.39
23	1.1	1.2	0.1	0.5	0.3	0.65
24	0.5	0.5	0.0	0.6	0.3	0.45
25	0.4	0.4	0.0	0.6	0.0	0.33
26	0.8	0.8	0.1	0.6	0.0	0.53

Point N	(PYR + BaP)/ (PHE + CHR)	(PYR + BaP + BghiP)/ (PHE + CHR)	ANT/ (ANT + PHE)	FLT/ (FLT + PYR)	BaA/ (BaA + CHR)	HMW/LMW
27	0.5	0.5	0.0	0.6	0.4	0.64
28	0.6	0.6	0.1	0.6	0.4	0.44
29	0.2	0.2	0.0	0.6	0.0	0.18
30	0.2	0.2	0.0	0.6	0.0	0.22
31	0.8	0.9	0.0	0.6	0.2	0.61
32	0.3	0.3	0.0	0.6	0.2	0.32
33	0.8	0.8	0.0	0.5	0.2	0.28
34	0.3	0.3	0.0	0.7	0.2	0.30
35	0.5	0.5	0.0	0.6	0.2	0.41
36	0.2	0.2	0.0	0.6	0.2	0.25
37	0.5	0.6	0.0	0.6	0.0	0.39
38	0.4	0.4	0.1	0.6	0.0	0.36
39	0.9	1.0	0.1	0.6	0.2	0.74
40	1.3	1.4	0.1	0.5	0.2	0.84
41	0.9	0.9	0.0	0.5	0.3	0.55
42	0.7	0.7	0.0	0.6	0.2	0.48
43	0.5	0.5	0.0	0.5	0.2	0.42
44	1.1	1.2	0.1	0.6	0.5	0.94
45	0.6	0.6	0.1	0.6	0.1	0.47
46	0.3	0.3	0.1	0.6	0.5	2.93

Regression analysis was performed to find correlations between the presence of BaP and other PAHs in snow samples.

Discussion

We have determined the concentrations of 13 PAHs in the snow cover of Arkhangelsk. Average, maximum and minimum values of $\sum_{13} PAH$ were 167.7, respectively; 664.5 and 16.0 ng / kg of snow 17 times less than in Moscow Toxic equivalence to BaP for all sampling points and found that the average toxic equivalence is 3.6 ng / kg in BaP units, which is three times less than the established MPC.

We have compared the PAHs concentrations in the snow cover of Moscow [12] and Arkhangelsk. in Arkhangelsk PAHs is 17 times less than in Moscow. However, more important is not the total concentration of PAHs, but the concentration expressed in toxic equivalents in BaP. Typically, structurally related compounds are indexed to a well-studied reference agent to generate TEFs on the basis of shared characteristics. In Russia, the PAH content in water is standardized only for naphthalene and benzo (a) pyrene. For Benz (a) pyrene, as a very persistent carcinogen among PAHs, MACs in water are set at 10 ng / kg. We calculated the toxic equivalence to BaP for all sampling points and found that the average toxic equivalence is 3.6 ng / kg in terms of BaP, which is three times less than the established maximum permissible concentration. The maximum permissible concentration was exceeded only at two points: in the city center (Fig. 1 is marked in red), and in one of the places, this value exceeded the MPC by only 10%, thus it can be concluded that the atmosphere of the urban agglomeration of Arkhangelsk is slightly polluted PAHs.

The ratio (PYR + BaP) / (PHE + CHR) was used as markers to establish the relationship between technogenic and natural PAHs. Ratio values > 1 indicate anthropogenic sources of PAH inputs [13]. Analyzing the data obtained, one can see that only at four points there is an excess of this parameter, in two of them, by only 10%. The average value of this ratio was 0.5 units, which indicates that the urban agglomeration of Arkhangelsk is not contaminated with PAHs of anthropogenic origin. This parameter significantly exceeds 1 only at one point 4 where there is also a very large traffic of vehicles.

The values of the ratio (PYR + BaP + BghiP) / (PHE + CHR). These values also showed an excess of 1 only at the aforementioned points, on average this parameter was 0.5 units.

Also we calculated the ratio ANT / ANT/(ANT + PHE). We calculated this like observed in [13]. Using the PAHs molecular mass 178 we can to distinguish between petroleum and combustion Sources. If the ratio ANT/(ANT + PHE) or (An/ 178) < 0.10 then the sourse is petrolium. If this ratio > 0.1 then the sourse is combastion. Carbonization of coal to form creosote takes place at a high temperature and this process has the same PAH ratio as burning coal tar or coal and is usually indistinguishable from burning. The boundary value of the ratio An / 178, equal to 0.10, refers to such sources as combustion of diesel fuel, shale oil, coal and some crude oil samples, and the ratio < 0.10 is typical for combustion of lignite, diesel fuel and fuel oil.On average, this ratio was 0.05 at 11 points, the value reached 0.1. Analyzing this ratio, it can be concluded that the observed PAHs are of mixed oil origin and origin from combustion, however, this ratio is applied with sufficient restrictions and using this parameter alone it is impossible to reliably assert the origin of PAHs.

The ratio was also obtained FLT / (FLT + PYR) [13]. This value less than 0.4 is indicative of oil production as a source; values of 0.4–0.5 are indicators of combustion of liquid fossil fuels and a value greater than 0.5 is an indicator of combustion of coal / grass / forest (wood). In our case, this ratio averaged 0.6, and was not observed anywhere below 0.5, which indicates that PAHs originate from combustion. Combustion of wood, pallets and lignin for the purpose of generating heat and electricity is traditional for the economic activity of the agglomeration of Arkhangelsk.

The BaA / (BaA + Chr) ratio is another marker, its values 0.2, 0.20–0.35 and > 0.35 suggest the presence of PAHs mainly from oil, mixed oil / combustion and coal / wood combustion, respectively. In our case, this ratio varied from 0 to 0.5 on average = 0.2. Evidence suggests that PAHs come from the combustion of wood and coal.

High molecular weight (HMW) / and low molecular weight (LMW) PAHs did not exceed 0.5, which is well below 1 and indicating pyrolytic origin pollution [14]. Only at 2 points (4, 46) this ratio was more than one. This also indicates the origin of PAHs from combustion

An identification assessment of the origin of PAHs has shown that PAHs originate predominantly from combustion processes. PAHs: ANT, FLT, PyR, BaA, CHR, BbF, BkF, BghiP are of anthropogenic origin. In general, the agglomeration of Arkhangelsk is slightly polluted with PAHs.

We found that BaP has a very high degree of correlation at a level of 0.01 with PAHs with high molecular weights ANT, FLT, PyR, BaA, CHR, BbF, BkF, BghiP. And has no correlation with PAHs of low molecular weight N, ACE, PHE. This suggests a different origin for PAHs. PAHs: ANT, FLT, PyR, BaA, CHR, BbF, BkF, BghiP are of anthropogenic origin.

Material And Methods

We have determined the concentrations of 13 polyaromatic PAHs in the snow. To determine all PAHs, we used the analytical standard, Aldrich, Germany. In what follows, we will use the following abbreviations for the names of PAHs: naphthalene (N), acenaphthene (ACE), fluorene (F), phenanthrene (PHE), anthracene (ANT), fluoranthrene (FLT), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(g,h,i)perylene (BghiP).

PAHs were detected by chromatographic method. As a mobile phase, we used acetonitrile HPLC-hypergradient ("Cryochrome", Russia), as well as high purity water "type I" Milli-Q. We used acetonitrile for the preparation of analyte solutions and sample preparation. We used for sample preparation HPLC-hypergradient grade hexane (Cryochrom, Russia).

Sample preparation. We took snow samples near the city's main thoroughfares. The sampling locations are shown in Fig. 1. The snow samples (46 samples) were taken from the most and least loaded intersections of the city. Sampling was carried out using a special core with a diameter of 10 cm. In this case, the surface layer of snow was not sampled. The collected snow was placed in 1 liter dark glass bottles. Then, without opening the bottles, the snow was melted at room temperature. Extraction of PAHs from melt water was carried out with 5 ml of hexane for 30 minutes with vigorous stirring. The hexane extract was separated from water and kept for at least 2 hours in a freezer at a temperature of minus 25 ° C. The extract was poured into a separate flask and evaporated in a sand bath at a temperature of 60 ° C in an air flow to a volume of 0.5-1 ml. The remainder of the extract was poured quantitatively into a 1.5 ml vial and left until the hexane was completely volatilized. At the end of the evaporation, 0.5 ml of

acetonitrile was added to the vial. Thus, the concentration factor was 2000. The prepared extracts were subjected to chromatographic analysis on the same day.

Determination of PAHs using high performance liquid chromatography with fluorescence detection (HPLC-FLD). An Agilent 1260 HPLC system (Agilent, USA) was used to determine PAHs. Separation was performed on a LiChrospher PAH chromatographic column (Agilent, United States), 250 × 3 mm, 5 μm. The column oven temperature was 20 ° C. The mobile phase flow rate was 0.56 ml / min. The volume of the injected sample was 20 μL. A mixture of water (solution A) with acetonitrile (solution B) was used as a mobile phase. A gradient elution was used with the following program: 0–3 min: 50% B, 10 min – 100% B. The total analysis time was 28 minutes. The registration of fluorescence was carried out with programming of the excitation (λex) and radiation (λem) wavelengths in time according to the program: 0–12 min: λex = 280 nm, λem = 340 nm; 12.0-12.8 min: λex = 292 nm, λem = 336 nm; 12.8–13.2 min: λex = 253 nm, λem = 402 nm; 13.2–13.8 min: λex = 360 nm, λex = 460 nm; 13.8–16.1 min: λex = 305 nm, λex = 430 nm; 16.1–17.0 min: λex = 268 nm, λex = 383 nm; 17–28 min: λex = 305 nm, λem = 430 nm. The identification of the compounds was confirmed by a spectrophotometric detector at a wavelength of 254 nm. Filtration of samples before entering the chromatographic system was carried out on syringe nylon membrane filters (Supelco, USA) with a diameter of 13 mm and a pore size of 0.2 μm.

The quantitative determination of PAHs was carried out in accordance with the constructed calibration dependences of the analytes. Calibration solutions with the concentration of each compound in the range of 0.5–0.001 mg / L were prepared by sequential dilution and mixing of the stock solutions with acetonitrile (10 mg / L each) immediately before the experiment. All calibration dependences in the studied range were linear and the correlation coefficient was more than 0.999. An example of a chromatogram of one of the investigated snow samples is shown in Fig. 2. This chromatogram shows that all analytes are well separated and the matrix has no interfering effects.

The toxic equivalence at each sampling point was calculated using the formula:

$$TEQ = \sum (C_i * TEF_i)$$

This formula takes into account the contribution of each PAH to the total toxicity of the most dangerous compound Bap. The contribution of other PAHs (C_i) was calculated according to the coefficients: PHE (0.001), ANT (0.01), BaA (0.1), FLT (0.001), PYR (0.001), CHR (0.01), BbF (0.1), BkF (0.1), BaP (1), BghiP (0.01) [2, 11].

Statistical calculations were performed using software package IBM SPSS STATISTICS Version 23. Regression statistics (calculation of equation of dependence between two values); coupled correlation coefficients (r) at specific significance level ($p \leq 0.05$).

Declarations

Author contributions

A.Yu. Kozhevnikov - Designed and performed experiments, analyzed data and co-wrote the paper.

D.S. Kosyakov - Designed and performed experiments, analyzed data and co-wrote the paper.

1. I. Falev - Performed chemistry analyses

S.A. Sypalov - carried out mathematical processing of the results

I.S. Kozhevnikova - Performed chemistry analyses and the results were formalized

Acknowledgements.

This research was performed using instrumentation at the Core Facility Center “Arktika” of Northern (Arctic) Federal University and was supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment project No. 0793-2020-0007)

References

1. Aleksandr Khaustov & Margarita Redina (2019): Polycyclic Aromatic Hydrocarbons in the Snow Cover of Moscow (Case Study of the RUDN University Campus), Polycyclic Aromatic Compounds, DOI: 10.1080/10406638.2019.1645707
2. Svetlana Levshina. Distribution and Characteristic of PAHs in snow of the Urban and Reserve Areas of Southern Far East Russia. Bulletin of Environmental Contamination and Toxicology (2019) 102:160–167 https://doi.org/10.1007/s00128-018-02533-6
3. Izvekova, T.V., Kobeleva, N.A., Gushchin, A.A., Grinevich, V.I., Rybkin, V.V. Distribution of Policyclic aromatic hydrocarbons in a snow cover in the territory of Ivanovo city, Russia. 2020. Chemosphere 242,125150
4. Cao, X., Li, J., Cheng, L., Deng, Y., Li, Y., Yan, Z., Duan, L., Yang, J., Niu, Q., Perera, F. Nie, J., Tang, D. The associations between prenatal exposure to polycyclic aromatic hydrocarbon metabolites, umbilical cord blood mitochondrial DNA copy number, and children's neurobehavioral development. Environmental Pollution.Volume 265, October 2020, N 114594
5. EPA 40 CFR, Part 136, Method 610 - Polynuclear Aromatic Hydrocarbons, Fed. Regist. 49, Washington, DC, 1984.
6. US EPA, EPA Method 550.1 Determination of Polycyclic Aromatic Hydrocarbons in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection. Washington, DC, 1990.
7. Arellano, L., Fernández, P., Van Drooge, B.L., Rose, N.L., Nickus, U., Thies, H., Stuchlík, E., Camarero, L., Catalan, J., Grimalt, J.O. Drivers of atmospheric deposition of polycyclic aromatic hydrocarbons at

European high-altitude sites. Atmos. Chem. Phys., 18, 16081–16097, 2018. https://doi.org/10.5194/acp-18-16081-2018

8. Wei & ShaSha Liu & Zhongqiang Wang &Zucheng Wang & Shengzhong Wang. The Distribution Variation of Polycyclic Aromatic Hydrocarbons Between Fresh Snow and Seasonal Snowpack in Campus in Changchun City, Northeast China Yan. Water Air Soil Pollut (2017) 228: 233.DOI 10.1007/s11270-017-3409-2
9. Boom, A. Accumulation of polycyclic aromatic hydrocarbons (PAHs) in an urban snowpack [Text] / A. Boom ; J. Marsalek. - Sci. Total Environ, 1988. –148 p.
10. Snow samples as markers of air pollution in mass spectrometry analysis. Book Chapter/Lebedev, A.T., Mazur, D.M., Polyakova, O.V., Hänninen, O. Environmental Indicators.1 January 2015, Pages 515-541.
11. Damon Delistraty Ph.D., D.A.B.T. (1997) Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons, Toxicological & Environmental Chemistry, 64:1-4, 81-108, DOI: 10.1080/02772249709358542,
12. T. Lebedev, O. V. Polyakova, D. M. Mazur, M. A. Bol'shov, and I. F. Seregina. Estimation of Contamination of Atmosphere of Moscow in Winter. Journal of Analytical Chemistry, 2012, Vol. 67, No. 14, pp. 1039–1049.
13. Yunker MB, Macdonald RW, Vingarzan R et al (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33:489–515
14. Soclo HH, Garrigues PH, Ewald M. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Marine Pollution Bulletin Vol. 40, No. 5, pp. 387±396, 2000

Figures

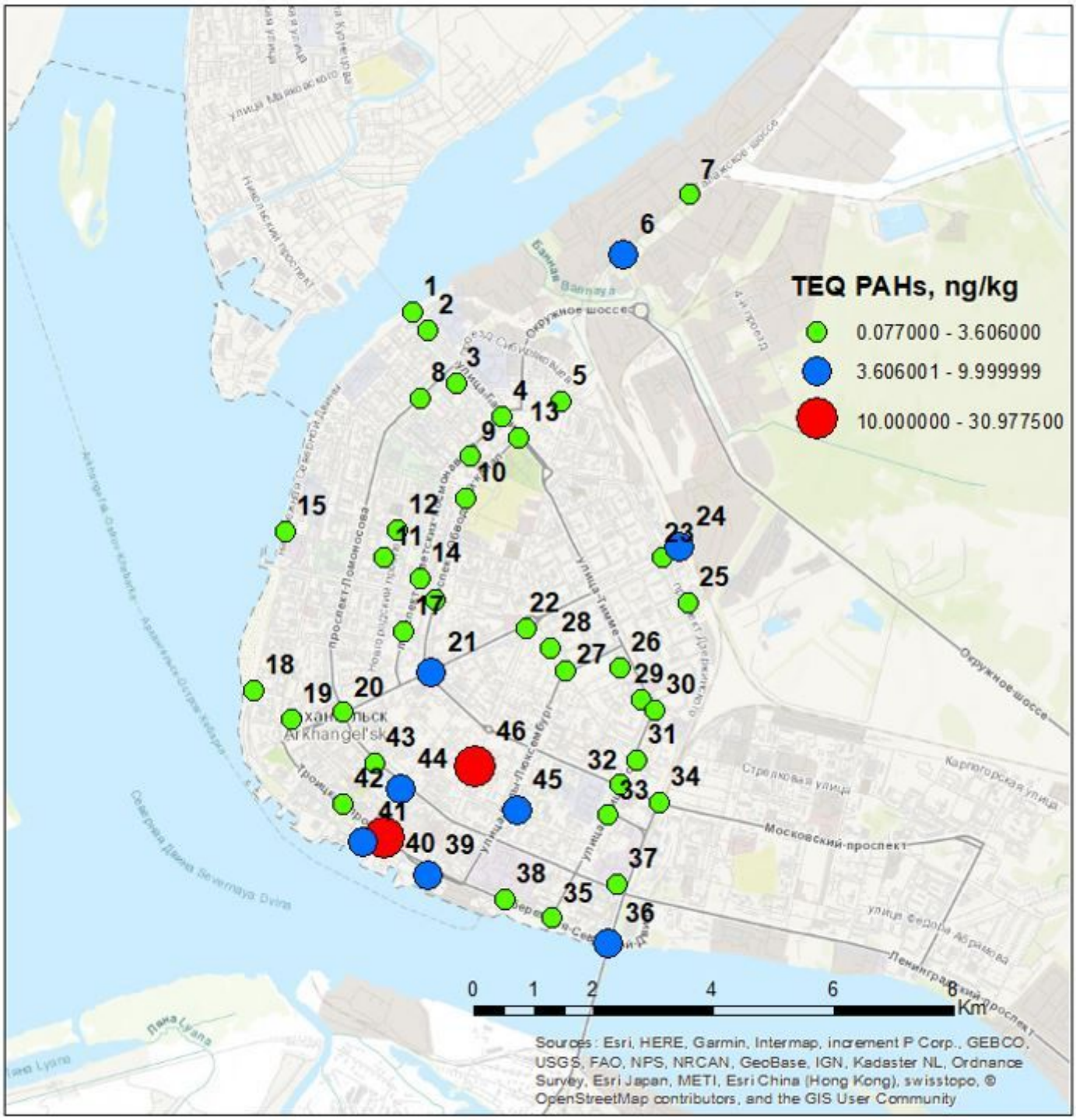

Figure 1

snow sampling points and the toxic equivalency value

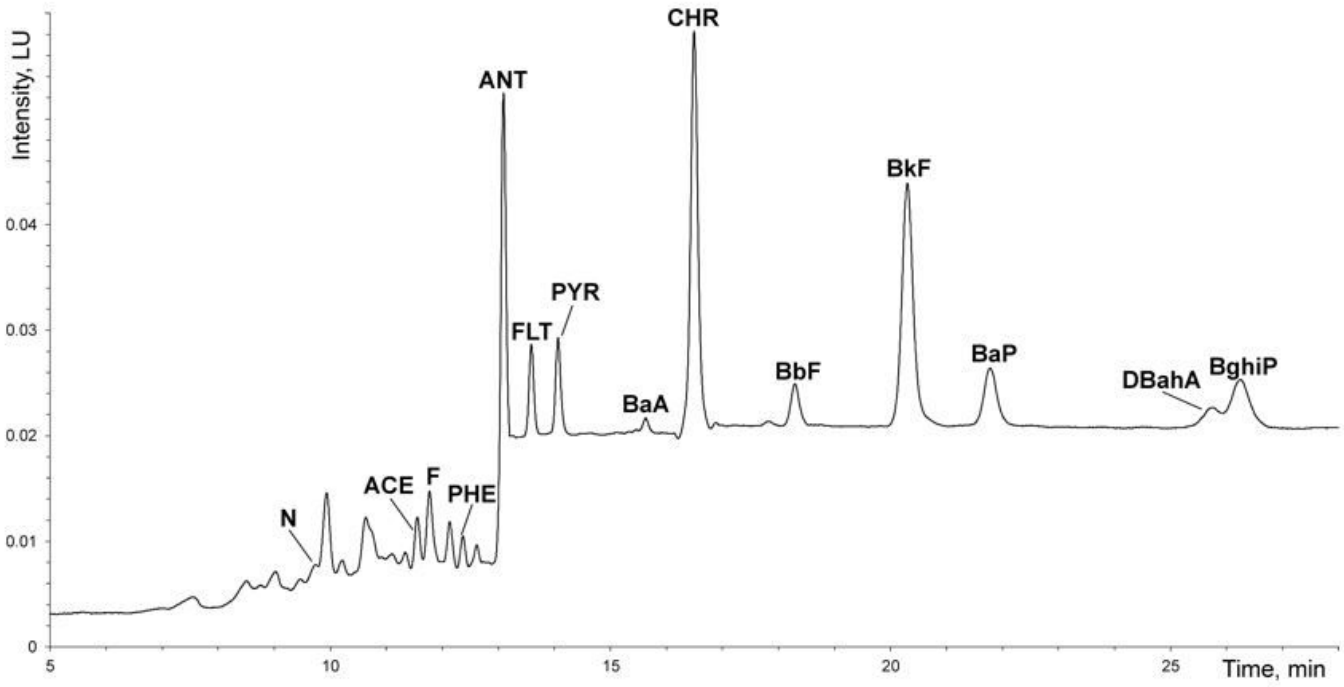

Figure 2

HPLC-FLD chromatogram of snow

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Abstract.jpg