Priority and emerging pollutants in the Moscow rain

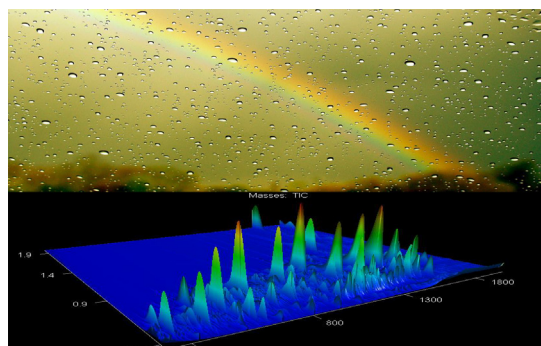Olga V. Polyakova [a], Viatcheslav B. Artaev [b], Albert T. Lebedev [a],*

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HIGHLIGHTS

- Over 700 organic compounds were identified in Moscow rainwater by GCxGC-HRMS.
- 160 priority pollutants and emerging contaminants were reliably quantified.
- PAH, PCB, phenols, phthalates, phosphates, and pyridines dominate in rainwater.
- The levels of phenol, dibutylphthalate, and benz[*a*]pyrene exceed the safe values.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Air quality is a worldwide problem. Nowadays, thousands of chemicals may be found in the atmosphere from biogenic and anthropogenic sources due to numerous atmospheric reactions. Unfortunately, throughout the world only a small group of organic compounds is monitored on a regular basis. Therefore, an important environmental task involves discovering the most important pollutants for particular cities and regions for regular monitoring in the future. Direct measurements of contaminants in the atmosphere are not always efficient as air represents an extremely dynamic medium. Thus indirect analysis by using precipitations becomes a more popular method of environmental analysis. Over 700 organic compounds belonging to the various classes of chemicals were identified in the Moscow rainwater samples collected in the spring of 2017 using GC/MS instruments including the most analytically powerful modern technique - GC × GC-HRMS. Here we report the nature and levels of 160 priority pollutants and emerging contaminants belonging to the most relevant classes from the environmental point of view: polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organophosphates, dialkylphthalates, phenols, and alkylpyridines. This is the first work dealing with GC–MS analysis of the rainwater in Moscow (Russia).

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1. Introduction

Organic compounds appear in the atmosphere from the natural and anthropogenic sources. They may be present in the form of gases (Volatile Organic Compounds (VOC)) or as aerosols (Primary Organic Aerosols (POA)). While in the atmosphere, all volatile organic compounds efficiently undergo transformation, mainly due to oxidation by sunlight, ozone, hydroxyl, or nitro radicals, leading to formation of the Secondary Organic Aerosols (SOA) by nucleation and condensation (Hallquist et al., 2009). Rainwater-dissolved organic matter plays an important role in the atmospheric carbon cycle with its global rainwater flux of 420×10^{12} gC/year (Willey et al., 2000). The diameter of the aerosol particles may be rather different varying from 1 nm to 100 μm.

The size of aerosol particles is important, as it defines the residence time of the particles in the air (Jaenicke, 1988). The composition of the aerosol is incredibly complex (Goldstein and Galbally, 2007), including any sort of chemicals from sea salt to micro organisms. All these issues are relevant to climate, biogeochemical cycles, and finally to the human health, which is well covered in a few comprehensive reviews (Fowler et al., 2009; Kanakidou et al., 2005; Poschl, 2005).

Analysis of organic compounds in the air may be carried out by using various techniques, depending on the targeted compounds. Mass spectrometry and related techniques such as selected ion flow tube (SIFT) (Smith and Spanel, 2005; Spaněl and Smith, 2011; Storer et al., 2013) or proton transfer reaction (PTR) (Blake et al., 2004; Blake et al., 2009) are rather efficient for the most various molecules, especially the simple gases. However, mass spectrometry is the most efficient tool when it deals with non-targeted analysis of the complex mixtures of organic compounds (Lebedev, 2013), while the most sophisticated systems (e.g. ion-cyclotron resonance or comprehensive two-dimensional gas chromatography coupled to high resolution mass spectrometry) are definitely highly efficient for the most complex samples (Cottrell et al., 2013; Lebedev et al., 2013; Mazur et al., 2016; Mead et al., 2015).

Air is a very dynamic medium, which makes it very difficult to obtain representative results. The most straightforward method involves direct measurement in the field (Diaz et al., 2010; Hinz, 2012). However, when it deals with the identification of hundreds of various organic compounds, sample collection and laboratory analysis with the use of GC or LC coupled to high resolution mass spectrometers becomes much more efficient in obtaining the most comprehensive results. Various traps, tubes with sorbent, vacuum canisters, etc. are used for sample collection in the field followed by the direct analysis or analysis after desorption trapped analytes. Thus the obtained results reflect pollution of a certain place at a certain time.

Another analytical approach involves the analysis of precipitates (snow, rain, fog). It is a non-direct method of analysis. However, it can be very efficient as both gas phase and aerosol particles are washed from the atmosphere with snow or rain. Moreover snow analysis allows estimating long-term air pollution in the countries with cold climate or in the mountains. Since snow works as a cold absorbing matrix it may store chemicals for a rather long time. As a result, researchers may obtain information about air contamination above some territories during several months (Lebedev et al., 2015).

A certain problem involves the fact that the safe levels for the contaminants are usually defined only for air, water, and soil. Thus, direct application of the obtained results of rainwater or snow pollution to derive conclusions regarding their effect on the population health or ecosystem safety should be done rather carefully. Anyway qualitative MS data is very reliable when making these decisions.

For the last several years we were using GC–MS to analyze snow samples collected in Russia and Finland (Polyakova et al., 2000; Lebedev et al., 2003; Polyakova et al., 2012; Lebedev et al., 2013; Mazur et al., 2016; Lebedev et al., 2018). The most recent research on Moscow snow contaminations resulted in the discovery of several hundred organic compounds, proposing a priority pollutants list for the city

(Polyakova et al., 2012; Mazur et al., 2016). Rather successful experiment with the analysis of cloud water (A.T. Lebedev et al., 2018a) made us consider working with rain. Encouraging results from a comparative study of the same organic pollutants found in the snow and rainwater samples have demonstrated that these levels were rather comparable, and in many cases, rain samples contained more organic matter than the snow ones (Regnery and Puttmann, 2009).

The first publications dealing with organic compounds in rainwater appeared from 1970 to 1980 (Nojima et al., 1976; Kawamura and Kaplan, 1983). Nowadays there are quite a few publications dealing with certain classes of organic pollutants in rain samples, including PAHs (Grynkiewicz et al., 2002; Holoubek et al., 2007; Levsen et al., 1991; Li et al., 2011; Olivella, 2006; Švancarova et al., 2016; Wang et al., 2015), organochlorines (Laniewski et al., 1998; Holoubek et al., 2007; He and Balasubramanian, 2010), PCBs (He and Balasubramanian, 2010; Holoubek et al., 2007), organophosphates (Bacaloni et al., 2008; Fries and Puttmann, 2003; Laniewski et al., 1998; Regnery and Puttmann, 2009), and phenols (Levsen et al., 1990; Leuenberger et al., 1988; Schummer et al., 2009; Schussler and Nitschke, 2001).

The studies mentioned above deal with particular classes of organic compounds, i.e. only targeted analyses of the rain samples were conducted. Since we were not aware of any studies of Moscow rainwater to detect the most widespread organic contaminants, it was interesting to carry out a screening analysis, more or less similar to the comprehensive study of the organic constituents in the rainwater in Canada (Cottrell et al., 2013). Therefore, the main goal of the present study involved the screening of the rainwater samples for all types of semi-volatile organic compounds. It is worth mentioning that we were dealing with semi volatiles only, as highly volatile organic compounds (Mullaugh et al., 2015) were out of the scope of the present study. We were aiming for identification of as many organic contaminants as possible and quantification of all relevant from the environmental point-of-view pollutants. Thus, eight samples of rain water were collected in the spring of 2017 in two locations in Moscow (Table 1). The results of GC-HRMS and GCxGC-HRMS even at the first glance were very interesting as each chromatogram contained over 1000 peaks of organic semi-volatile compounds, about 700 of which were finally assigned with the various levels of reliability. Here we report only the most reliably identified compounds, which are on the list of US EPA water priority pollutants or emerging contaminants, and which standards we had in our laboratory. The resultant list appeared to be rather long. It includes phenols, phthalates, phosphates, PAHs, and their alkylated homologs, PCB, alkylpyridines, etc. The other identified contaminants, which are not part of US EPA priority pollutants list, will be the matter of future publication.

2. Materials and methods

2.1. Rain sampling

Samples of rain water were collected using a glass funnel and bottle installed on the roof of the Chemistry Department building of the Moscow State University in the south-west Moscow, and on the roof of an

Table 1
Rainwater samples analyzed in the present study.

#	Date	Water volume mL	Internal standards	Sampling site
1	07.04.17	400	1 µg	Volokolamskoe shosse
2	12.04.17	500	1 µg	Volokolamskoe shosse
3	13.04.17	800	1 µg	Volokolamskoe shosse
4	15.04.17	900	1 µg	Volokolamskoe shosse
5	25.04.17	400	1 µg	Volokolamskoe shosse
6	28.04.17	250	1 µg	Chemistry department
7	27.04.17	1000	1 µg	Volokolamskoe shosse
8	15.05.17	500	1 µg	Chemistry department
9	Dist.water	500	1 µg	Chemistry department
10	Dichloromethane	100	1 µg	Chemistry department

apartment building in the city's north. The samples were collected in the period between April 7 and May 15, 2017. Only wet depositions were collected and the sampling vessels were dismantled after the rain stopped. To prepare the Field Blank, the 0.5 l of ultrapure Milli-Q water was placed in the similar container as the samples and taken into the field where it was exposed to the atmosphere at the sampling site and then transferred into another container. Then this Field Blank sample was processed in the same manner as the rainwater samples. This blank sample was used to record the chemical "background" of the environment during sampling and to take into account contamination of the samples from the laboratory environment, as well as equipment and chemicals used in sample preparation and analysis.

The dates, sample numbers, and collected rainwater volumes are summarized in Table 1. The pH values were measured immediately after sampling. For all the samples, pH was in the range of 7.5–7.8, i.e. slightly basic, although some studies demonstrated very broad range of rainwater pH values from 3.83 to 8.90 in (Chon et al., 2015).

2.2. Sample preparation

Sample preparation was carried out according to the US EPA 8270D Method (Method 8270D, 2007) for semi volatile pollutants. Rain water samples were spiked with a surrogate solution (phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}) and filtered through a filter paper with a pore size of 23 μm. Triplicate extraction at pH 2 and 11 with dichloromethane (30 ml) was followed by drying over sodium sulphate and concentrating to 500 μl. Concentrated basic and acidic dichloromethane extracts were combined before the injection. Perdeuterated naphthalene and phenanthrene (SV Internal Standards, Restek, USA) were used as internal standards.

2.3. GC–MS analysis

All samples were analyzed with a Pegasus® GC-HRT$^+$ 4D high resolution mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) and Pegasus BT 4D GC × GC time-of-flight mass spectrometer (LECO Corporation, Saint Joseph, MI, USA).

2.3.1. GC-HRMS analysis

The Pegasus GC-HRT$^+$ 4D high resolution mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) was equipped with an Agilent 7890A gas chromatograph (Agilent Technologies, Palo Alto, CA, USA), and LECO quad-jet liquid nitrogen cooled thermal modulator with a secondary column oven. The system was controlled by ChromaTOF® software (Version 5.20, LECO Corporation), which was also for spectra collection and data processing. All 1D GC–MS experiments were performed as described in Mazur et al., 2017. Mass spectra for all GC × GC runs (2D mode) were acquired at the rate of 200 spectra per second in the mass range of m/z 15–800. The mass spectrometer was operated in high resolution mode with resolving power of 25,000 or more. The novel duty cycle enhancement data collection technique – Encoded Frequent Pushing™ – was applied during all modes of data acquisition.

2.3.1.1. Chromatographic separation. 1D chromatographic separations of the snow samples were performed as described in Mazur et al., 2017 while 2D gas chromatography (GC × GC) separations were carried out with an Rxi-5SilMS 30 m × 0.25 mm (id) × 0.25 μm (df) (Restek, Bellefonte, PA) as the first dimension column and an Rxi-17SilMS column 1 m × 0.25 mm (id) × 0.25 μm (df) (Restek, Bellefonte, PA) as the second dimension column. The GC oven program was as follows: a 2 min isothermal hold at 40 °C, then ramping at 20 °C min^{-1} to 280 °C followed by a 10 min isothermal hold at 280 °C. The secondary oven temperature was set to a 20 °C higher than the primary oven. The modulator temperature was offset by 15 °C above the secondary oven

temperature and the modulation period was set to 2 s. The remaining GC conditions (flow rates, etc.) are described in Mazur et al., 2017.

2.3.1.2. Data processing. In case of coeluting peaks in 1D chromatograms, the comprehensive GC × GC separation provides better results by minimizing or even excluding coelutions, thus generating purer Peak True (deconvoluted) mass spectra (Tranchida et al., 2016). When coupled with high resolution mass spectrometry, GC × GC provides better chances for the correct assignment of the analytes detected in the sample. The efficiency of the ChromaTOF software's data processing and compound identification was demonstrated in detail in our previous paper (Mazur et al., 2017).

2.3.2

The Pegasus® BT 4D time-of-flight mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) was equipped with an Agilent 7890B gas chromatograph (Agilent Technologies, Palo Alto, CA, USA), a LECO quad-jet, liquid nitrogen cooled thermal modulator and secondary column oven. The system was controlled by ChromaTOF® software (Version 5.31, LECO Corporation), which was also used for spectra collection and data processing. The EI source temperature was kept at 250 °C, and the transfer line temperature was at 320 °C. Mass spectra for all GC × GC runs (2D mode) were acquired at a rate of 200 spectra per second and the GC-only (1D mode) data were acquired at a rate of 10 spectra per second. The acquired mass range was m/z 30–635 with resolving power 1200 (FWHH at m/z 219) in both 1D and 2D modes.

2.3.2.1. Chromatographic separation. One-dimensional chromatographic separations of the rain samples were performed with an Rxi-5SilMS 30 m × 0.25 mm (id) × 0.25 μm (df) (Restek Corporation, Bellefonte, PA) column. The GC oven program was as follows: a 3 min isothermal hold at 40 °C, then ramping at 20 °C min^{-1} to 280 °C followed by a 10 min isothermal hold at 280 °C. The two-dimensional gas chromatography (GC × GC) separation was carried out with an Rxi-5SilMS 30 m × 0.25 mm (id) × 0.25 μm (df) (Restek Corporation, Bellefonte, PA) column for first dimension separation and an Rxi-17SilMS column 1 m × 0.25 mm (id) × 0.25 μm (df) (Restek Corporation, Bellefonte, PA) for the second dimension separation. The GC oven program was as follows: a 3 min isothermal hold at 40 °C, then ramping at 20 °C min^{-1} to 280 °C followed by a 15 min isothermal hold at 280 °C. The secondary oven temperature was set to an offset 5 °C higher than the primary oven. The modulator temperature was offset 15 °C above the secondary oven and the modulation period was set to 3 s. The injector was a split/splitless type set at 10:1 split.

2.4. Quantification procedure

Quantification of the target compounds was performed using the internal standard method. The standard solutions at different concentrations of all compounds mentioned in Tables 2–7 containing internal standards (perdeuterated PAH) were used for obtaining the retention times and for calculating the response factors (RF) as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

A_s – peak area of the analyte A_{is} – peak area of the internal standard C_s – concentration of the analyte, in ng/l C_{is} – concentration of the internal standard, in ng/l.

The obtained RFs were subsequently used for the quantification of each identified target compound. The described procedure was validated using surrogates recommended by US EPA method 8270 D (Method 8270D, 2007): phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. The recoveries were 85% or higher. The limit of quantification (LOQ) obtained for the applied method was based on a S/N ratio 3:1.

Table 2
The levels of PAH (ng/l) in the rain samples.

#	Name	R.T. (s)	1	2	3	4	5	6	7	8
1	Naphthalene	526.46	53	23	32	33	24	77	38	36
2	2-Methylnaphthalene	577.122	9.7	5.2	9.5	7.8	4.6	23	11	10
3	1-Methylnaphthalene	585.028	7.5	4.6	8.5	8.1	4.7	19	8.4	12
4	Acenaphthylene	643.347	4.2	6.1	8.4	4.9	5.4	17	14	4.5
5	Acenaphthene	659	14	20	18	23	11	40	22	9.8
6	Fluorene	693.689	5.8	8.1	12	8.2	5.8	25	14	6.3
7	Phenanthrene	763.52	50	84	97	70	83	181	102	2.0
8	Anthracene	766	0.92	6.6	4.7	2.9	5.5	9.5	8.9	1.5
9	Fluoranthene	851.158	30	100	111	57	86	165	110	37.5
10	Pyrene	867.466	15	7.0	83	41	62	124	85	25.5
11	Benz[a]anthracene	963.224	0.87	13	18	6.0	18	21	16	2.8
12	Chrysene	966.765	5.5	100	133	55	118	148	100	23.9
13	Benzo[b]fluoranthene	1091.8	10	105	52	24	110	81	100	13.3
14	Benzo[k]fluoranthene	1094.52	4.4	40	22	13	49	44	40	5.8
15	Benzo[a]pyrene	1142.14	0.57	27	27	5.9	28	23	30	3.4
16	Indeno[1,2,3-cd]pyrene	1384.64	13	55	58	58	72	63	57	27.3
17	Dibenz[a,h]anthracene	1394.38	0.42	7.9	6.5	3.1	9.1	11	0.41	0.83
18	Benzo[ghi]perylene	1452.33	0.22	46	54	14	61	54	48	8.9

Table 3
The levels of alkylated PAH (ng/l) in the rain samples.

Name	1	2	3	4	5	6	7	8
Diisopropylnaphthalene 7 isomers	–	–	–	–	–	1803	–	357
Phenanthrene, -methyl- 4 isomers	57	23	29	30	13	62	20	11
Phenanthrene, C2 7 isomers	4.2	1.1	13	8.1	12.2	8.8	5.1	2.0
Methyl-pyrene(fluoranthene), 6 isomers	4.5	5.8	8.0	2.8	7.7	8.4	20	3.8
Phenanthrene, C3 2 isomers	1.5	4.7	3.5	2.7	3.1	6.2	2.6	1.2
Retene	1.3	5.0	4.9	2.6	4.0	5.9	3.8	0.97

Table 4
The levels of PCB (ng/l) in the rain samples.

Name	1	2	3	4	5	6	7	8
∑ Biphenyl,-tetrachloro- (9)	3.7	3.2	0.87	1.0	1.3	4.6	0.25	2.6
∑ Biphenyl,-pentachloro- (13)	14	11	7.3	8.1	7.8	15	6.5	11
∑ Biphenyl,-hexachloro- (16)	4.3	0.74	0.69	0.90	0.48	3.83	0.51	6.1
∑ Biphenyl,-heptachloro- (2)	–	–	–	–	–	–	–	0.3
∑	22	15	8.9	10	9.6	19	7.3	20

3. Results and discussion

Over 700 chromatographic peaks were detected in each rain sample with one-dimensional GC–MS (Fig. 1), while the application of comprehensive GC × GC (Fig. 2) significantly increased this number over 1000. Over 700 organic compounds were identified with different levels of reliability. In the present paper we report only priority and emerging contaminants (160 compounds). These chemicals belonging to the classes of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), phenols, dialkylphthalates, alkylpyridines, and organophosphates were identified with the highest reliability and quantified using Internal Standards approach. It should be mentioned that all

compounds detected in the blank samples were excluded from consideration with a few exceptions when the quantity of an analyte in the sample was 100 or more times higher than in the blank. Then the analytes were included in the finding.

3.1. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are the most studied class of environmental pollutants by ecologists. Although the rain samples are not studied often, there are still a number of publications on PAH levels in rain in Italy (Olivella, 2006), China (Li et al., 2011; Wang et al., 2015), Poland (Grynkiewicz et al., 2002), Singapore (He and Balasubramanian, 2010), Germany (Levsen et al., 1991), and Czech Republic (Holoubek et al., 2007). Low molecular weight PAHs demonstrate acute toxicity, while high molecular weight PAH are carcinogenic and mutagenic (Perugini et al., 2007). The former exist mainly in the gas phase, while the latter are mainly attached to the aerosol particles due to their higher hydrophobicity (Tsapakis and Stephanou, 2005).

Table 2 presents the results of the measured concentrations of the priority PAHs in the collected Moscow rain samples. As one can see, the compound's concentration vary significantly depending on the date and place the samples were collected. It is worth mentioning that phenanthrene, fluoranthene, and chrysene were present at the highest levels among all PAHs. These results are similar to the data published on the tropical rain studies (He and Balasubramanian, 2010), and similar to Arctic snow analysis results (Lebedev et al., 2018). The similar results were also observed in the Moscow snow studies (Polyakova et al., 2012), although the PAH levels were higher there as the snow samples were collected in March before the period of active snow melting, and deposits of organic compounds were accumulated in those samples due to snowfalls at least during 3 months.

Speaking about environmental and human health concerns, one should mention that in Russia there are standard safe values established
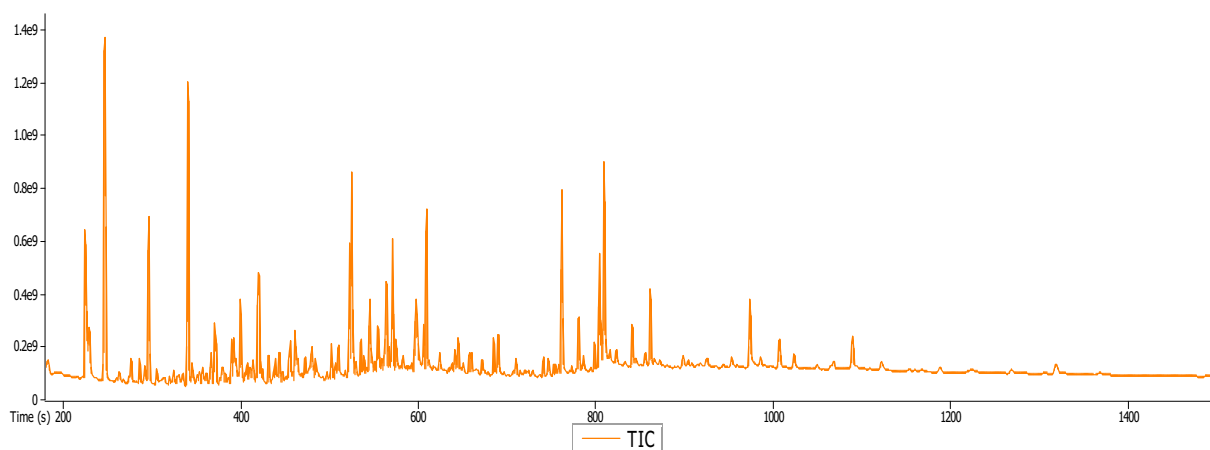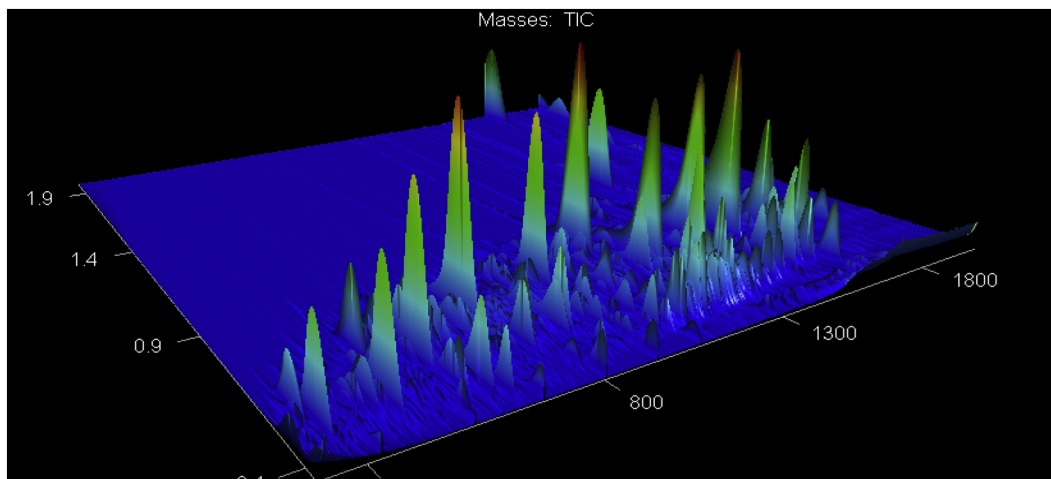
Table 5
The levels of phthalates (ng/l) in the rainwater samples.

Name	1	2	3	4	5	6	7	8
Dimethyl phthalate	48	34	29	64	29	177	54	43
Diethyl phthalate	237	435	212	268	235	1180	232	190
Di-iso-butyl phthalate	724	951	16	845	261	2320	484	416
Di-sec-butyl phthalate	30	24	49	18	8.1	101	26	17
Dibutyl phthalate	3970	4460	29	3830	566	7600	1375	131
Benzyl butyl phthalate	3.2	7.3	17	25	1.5	6.6	3.1	1.5
Bis(2-ethylhexyl) phthalate	673	789	48	1200	723	683	400	185
∑	5685	6700	400	6250	1824	12,068	2574	984

Table 6
The levels of phenols (ng/l) in the rain samples.

Name	1	2	3	4	5	6	7	8
Phenol	204	316	184	222	100	1290	345	308
2-Methylphenol,	34	40	50	38	40	202	96	69
4-Methylphenol,	102	137	120	114	75	532	223	155
3-Methylphenol,	5.6	5.2	10	13	5.4	23	17	6.0
4-Nitrophenol	4.8	7.4	9.2	11	2.6	11	11	2.4
2,4-Dimethylphenol	51	14	38	53	34	194	40	59
2-Nitrophenol	23	456	38	57	71	947	228	35
2,4-Dinitrophenol	3.3	41	10	12	4.3	61	27	2.3
2-Methyl-3,5-dinitrophenol	2.4	11	3.4	7.0	1.1	17	8.0	1.2

Table 7
The levels of organophosphates (ng/l) in the rain samples.

Alkyl phosphates	1	2	3	4	5	6	7	8
Triethyl phosphate	5.2	6.1	5.7	19	7.9	20	5.0	17
Tributyl phosphate	10	142	78	52	40	71	58	33
Tributylphosphate isomer	28	15	0.10	49	7.6	48	19	15
Chloroalkyl phosphates								
Tri(2-chloroethyl) phosphate	40	31	665	30	19	130	17	23
Tris(chloropropyl) phosphate	6.7	42	124	43	6.8	33	31	14
Tris(chloropropyl) phosphate isomer	–	68	–	12	–	–	8.9	–
Tris(chloropropyl) phosphate isomer	0.36	–	0.41	13	–	1.3	–	0.23
Tris(1,3-dichloroisopropyl)-phosphate	–	–	–	175	0.82	0.66	0.51	–
Phenylphosphates								
Dibutyl phenyl phosphate	1.6	13	1.7	9.0	–	12	–	1.2
Triphenyl phosphate	5.8	5.5	150	20	4.2	17	6.0	5.6
2-Methylphenyl diphenyl phosphate	3.8	3.0	16	13	2.3	5.9	2.9	3.8
4-Methylphenyl diphenyl phosphate	1.61	1.0	0.61	8.8	1.1	2.3	0.67	1.9
Bis(methylphenyl) phenyl phosphate	0.51	0.89	0	1.6	–	0.46	0.13	0.32
Bis(methylphenyl) phenyl phosphate - isomer	0.73	0.67	1.4	8.5	0.97	1.5	1.4	1.7
Bis(methylphenyl) phenyl phosphate - isomer	0.95	2.4	1.5	5.4	1.9	2.1	0.60	1.7
Bis(methylphenyl) phenyl phosphate - isomer	0.49	1.0	0.83	1.5	0.43	0.37	0.17	0.55
Tris(methylphenyl) phosphate	0.64	0.61	1.2	2.4	0.98	0.86	0.40	0.62
Tris(methylphenyl) phosphate - isomer	0.55	1.9	2.0	2.3	0.69	0.88	0.35	0.49
Tris(methylphenyl) phosphate - isomer	0.58	1.3	0.81	1.1	0.52	0.69	0.27	0.22

Fig. 1. 1D GC–MS total ion current chromatogram of the rain sample 1.

Fig. 2. 2D GC × GC total ion current chromatogram of the rain sample 46.

only for naphthalene - 4 μg/l (List of Fishery Farming Regulations, 1999) and the most dangerous carcinogen benz[*a*]pyrene - 5 ng/l (Maximum Permissible Concentrations, 1998). The levels of benz[*a*]pyrene have exceeded the safe level in 6 out of 8 samples.

Using the diagnostic ratios of PAH (Larsen and Baker, 2003) it is possible to estimate the sources of their origin. The ratio of anthracene to the sum of anthracene + phenanthrene is below 0.1 for all the samples, suggesting the fuel origin of these compounds in the atmosphere. On the contrary, the levels of fluoranthene are always higher than what the isomeric pyrene is, suggesting that the source of higher PAHs involves wood or coal burning.

Besides the classic PAHs, a number of alkylated PAH were detected. Table 3 contains the results on concentration of some homologs of naphthalene, phenanthrene, and pyrene found in our rain samples. Unfortunately there is no detailed information on their toxicities. Retene is known as a biomarker of wood burning. Its detection proves the conclusion done in the previous paragraph concerning the origin of the heavy PAHs.

3.2. Polychlorinated biphenyls

Since their first synthesis in 1929, the polychlorinated biphenyls (PCB) have been traditionally used as dielectric liquids in transformers and capacitors, in glues and mastics, as the stabilizing additives in polyvinylchloride (PVC) coatings, as lubricants, flame retardants, hydraulic liquids, etc. The PCBs' production was banned in 1986 after discovering their high toxicity (including endocrine system breakdown and neurotoxicity). However, by that time about 2 million tons of PCB were produced. Due to their high chemical stability these pollutants are still found in most environmental samples. Their sources may be far away from the detection site, as trans-boundary transfer of these persistent pollutants may be very efficient. PCBs were detected in the rain water samples collected in Switzerland (Rossi et al., 2004), the USA (Poster and Baker, 1995), and in Czech Republic (Holoubek et al., 2007).

Moscow is not an exception in this unfortunate trend. We regularly detect PCBs in Moscow snow (Polyakova et al., 2012). Table 4 illustrates the levels of identified PCBs in the Moscow rain samples. Forty PCB congeners were detected. Fig. 3 illustrates mass chromatogram based on the characteristic ions of the PCBs with different number of chlorine atoms.

As one can see in Table 4 the levels are quite high (7.3–22 ng/l), although there are no known sources of PCBs around Moscow.

Considering that the safe value in Russia (List of Fishery Farming Regulations, 1999) for this class implies "absence", we propose that this group of compounds should be included into the list of priority pollutants for Moscow air. Since we did not have the standards of all PCB congeners the RF values were calculated based on that value for the available representative with 1 to 7 chlorine atoms in the molecule.

3.3. Dialkylphthalates

Phthalates are the most widespread class of anthropogenic pollutants in Russia as well as in many other countries. Their high stability and wide use as plasticizers in polymers created situations where it is hardly possible to find an environmental sample from anywhere in the world without phthalates in them.

Traces of nearly all phthalates were detected in the Field Blank sample. However the levels of phthalates in the rainwater were much higher. Fig.4 demonstrates the example of the difference in the levels of phthalates in the blank and sample No 8. The data summarized in Table 5 contains the corrected values of the phthalates' concentration. As one can see, the levels of individual phthalates vary in a range over 2 orders of magnitude.

Dimethylphthalate is used as a plasticizer for polymer coatings, pesticide formulations component, and a repellent (popular in Russia). The presence of dimethylphthalate may be rationalized by its higher volatility in comparison with other phthalates (vapor pressure 0.01 mmHg at 20 °C (NIOSH)). The levels of dimethylphthalate, although being different from sample to sample, were way below its safe level limits (300 μg/l). Teil et al. (2006) reported quite similar levels of dimethylphthalate in Paris rainwater (116 ng/l).

Diethylphthalate is used in aerosol sprays (Ghorpade et al., 2002) and cosmetic preparations (Api, 2001). There is some data on the negative influence of diethylphthalate on neural system and feminine and masculine reproductive organs (Colon et al., 2000; Miodovnik et al., 2011). The levels of this compound are generally in the range of hundreds of nanograms per liter, exceeding 1 μg/l in sample 6. Again, it is rather close to the value (333 ng/l) reported (Teil et al., 2006) for Paris rainwater. However, it is two orders of magnitude lower than in the snow samples collected in Moscow in March 2012 (Polyakova et al., 2012).

Dibutylphthalate is the most widespread plasticizer. However, in 1976 it was banned as a cosmetic component by directive of the European Union 76/768/EEC. In 1999 it was prohibited to be used in toys. In 2006 dibutylphthalate was included into the list of potential
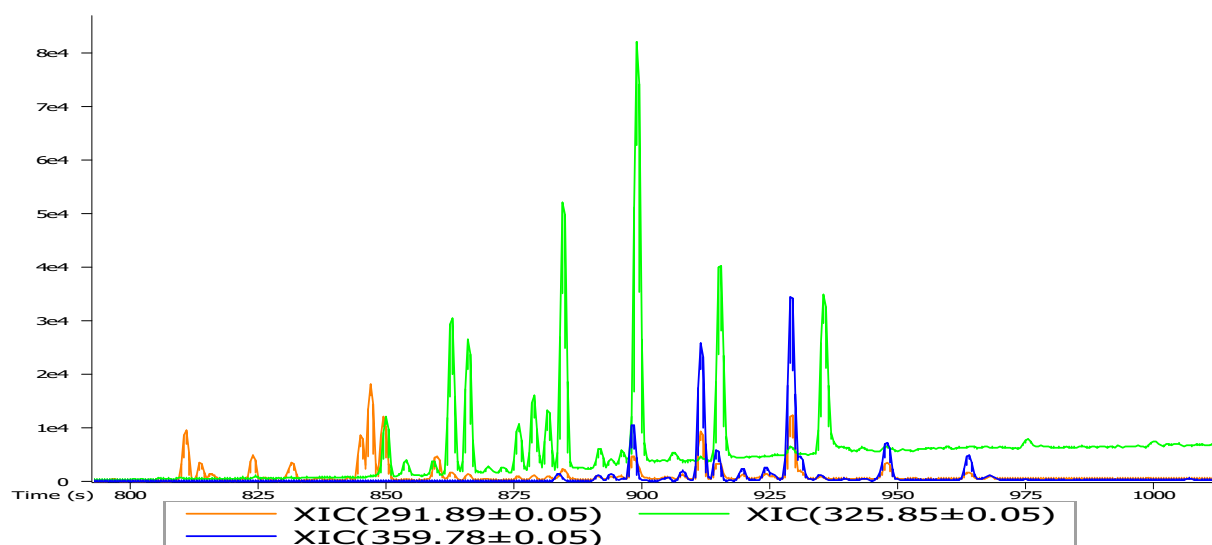

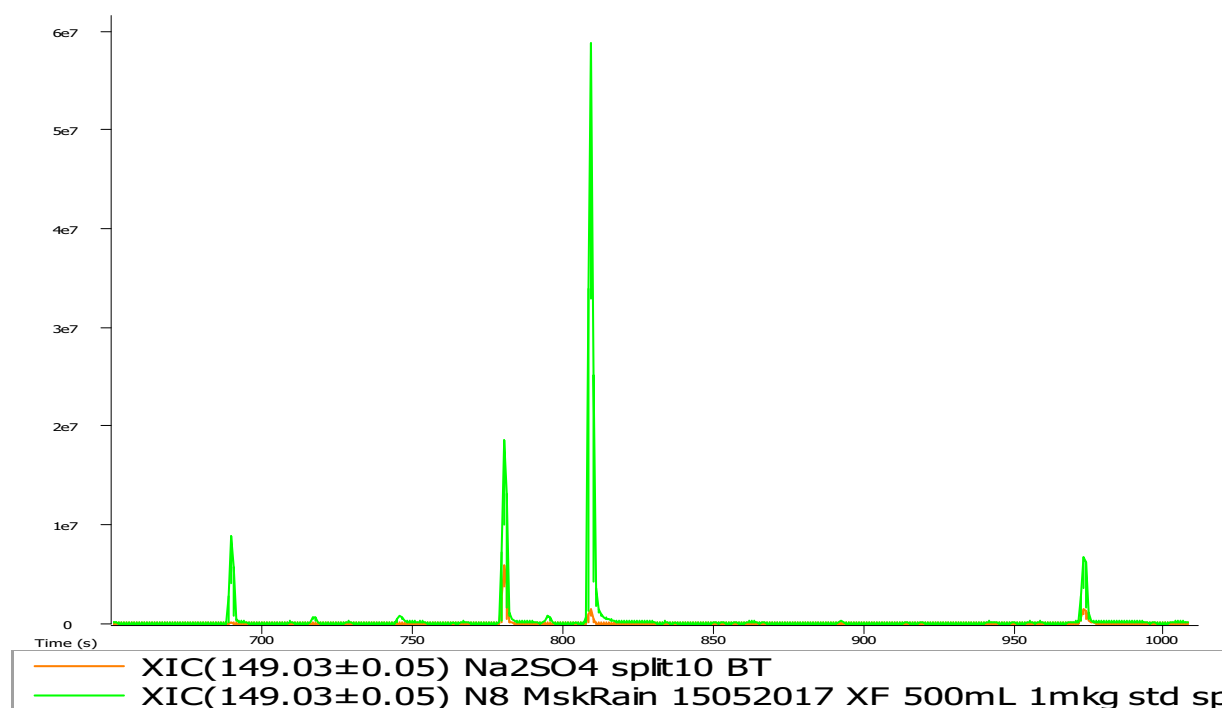Fig. 3. Mass chromatogram based on the characteristic ions for tetra-, penta-, and hexachlorobiphenyls.

Fig. 4. Extracted ION Current plots for the dialkylphthalates characteristic ion of m/z 149 in the blank (red) and № 8 rain samples (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

teratogens in the USA. The maximal level of this compound (7600 ng/l) was detected in sample 6, while the minimal (29 ng/l) in sample 3. Teil et al. (2006) has reported quite similar levels of dibutylphthalate in Paris rainwater (592 ng/l). Again these values were two orders of magnitude lower than in the Moscow snow. However taking into account the accumulation of dibutylphthalate in the snow that was going on during 3–4 months or about 100 days we came to the same figures. The dibutylphthalate-safe value for fishery reservoirs in Russia is set to 1 μg/l. Therefore, it is obvious, that this compound is evidently a priority eco-toxicant for the Moscow region.

Bis(2-ethylhexyl)phthalate is very often detected in the environmental samples collected in Russia. Due to its low cost, it is still used as a plasticizer and as a component in hydraulic liquids in capacitors. Polyvinylchloride (PVC) products may contain up to 40% of this phthalate. Its levels in the analyzed rain samples were quite high (up to 1200 ng/l in sample 4). However, it is still 10 times lower than its safe level (List of Fishery Farming Regulations, 1999). Teil also reported similar level of bis(2-ethylhexyl)phthalate in Paris rainwater (592 ng/l) (Teil et al., 2006).

Although the benzylbutylphthalate was included in the list of priority pollutants in the USA back in 1979, until recently it has appeared in the environmental samples collected in Russia quite rarely. Nowadays it is a common representative of the phthalate family of pollutants in the Russian environment, though its reported levels are still lower than in the European samples. For example, Teil reported benzylbutylphthalate level in Paris rainwater as 81 ng/l (Teil et al., 2006). It is an important component in PVC building foams, which are more and more widely used in housing construction in Russia. The maximal benzylbutylphthalate concentration (25 ng/l) is found in sample 4, with very little variation of concentration between the samples.

3.4. Phenols

Phenols are considered as priority eco-toxicants all over the world. These compounds may appear in the atmosphere due to primary emissions from industrial or biogenic sources (Furuta et al., 2008; Tremp et al., 1993). On the other hand, they may represent the secondary

products due to their active transformations in the gas phase, considering that nitrate and hydroxyl radicals are the most reactive species in the atmosphere. Thus, Volkamer et al. (2002) demonstrated that phenol could be a product of photo transformation of benzene in the gas phase. Similarly, 4-methylphenol can result from the photo transformation of alkylbenzene (Herrmann et al., 2015; Rayne et al., 2009) and 4-nitrophenol can come from nitration of phenol (Harrison et al., 2005).

Thirty-two phenols were identified in the Moscow rain samples. Here we report only the reliably measured levels of nine phenols, which are included into the US EPA list of priority pollutants (Table 6). Their levels are in the range from nanograms to over one microgram per liter, with definite domination of the unsubstituted phenol, 4-methylphenol, and 2-nitrophenol. Actually, it is worth mentioning that these levels are lower than those reported earlier in rain samples collected in France (Schummer et al., 2009), Switzerland (Leuenberger et al., 1988), or Germany (Levsen et al., 1990; Schussler and Nitschke, 2001). Our data shows that 2,4-dinitrophenol concentrations in Moscow samples were an order of magnitude lower than in the mentioned above European countries. Among the compounds regulated in Russia in that group, phenol is the most dangerous with the safe level set as 1 μg/l (List of Fishery Farming Regulations, 1999). This level was exceeded in sample 6, and our results may suggest including phenol into the list of priority pollutants for the Moscow air. It is also worthwhile to mention that the assortment and levels of phenols in the Moscow snow were lower (Polyakova et al., 2012). This can be due to degradation of unstable compounds deposited in the snow for a couple of months.

3.5. Organic esters of phosphoric acid

Unexpectedly, a notable number of esters of phosphoric acid were detected in the rainwater samples (Table 7). Their levels are in the range between hundreds of picograms and hundreds of nanograms per liter, which is quite similar to the results obtained earlier for the urban locations in Germany (Fries and Puttmann, 2003; Regnery and Puttmann, 2009) and Italy (Bacaloni et al., 2008). These compounds do not occur in nature and are exclusively anthropogenic. Organophosphates are non-flammable, non-explosive, temperature and light

Table 8
The levels of pyridines (ng/l) in the rain samples.

Name	1	2	3	4	5	6	7	8
Pyridine	3500	27	6.7	32	23	114	43	40
Pyridine, 2-methyl-	261	69	–	13	36	91	47	47
Pyridine, 3-methyl-	253	45	–	28	44	42	96	36
Pyridine, 2,6-dimethyl-	57	25	7.1	10	25	40	26	14
Pyridine, 2-ethyl-	46	22	–	8.0	7.0	17	17	15
Pyridine, 2,5-dimethyl-	88	97	15	22	42	86	69	23
Pyridine, 2,3-dimethyl-	31	41	–	7.8	13	32	24	7.8
Pyridine, 3-ethyl-	20	9.2	–	–	–	–	7.3	–
Pyridine, 3-propyl-	6.4	6.6	–	3.2	6.5	8.8	4.2	3.1
Pyridine, 2-ethenyl-	–	–	–	10	4.8	30	13	28
Pyridine, 2,3-dimethyl-	6.8	18	–	–	–	–	8.9	–
Pyridine, 2,5-dimethyl-	5.5	22	–	–	–	–	13	–
Pyridine, C3	7.1	7.6	2.2	3.0	4.4	9.4	5.6	1.5
Pyridine, C3	3.0	30	3.2	4.4	11	18	14	2.8
Pyridine, C3	23	17	1.6	2.6	5.0	6.6	11	2.9
Pyridine, 4-propyl-	2.4	8.6	1.2	2.1	3.6	10	7.4	2.1
Pyridine, C3	3.2	6.5	2.2	2.6	1.7	14	4.1	0.54
Pyridine, 3-methoxy-	22	37	7.7	14	15	25	22	3.0

resistant, colorless, and odorless. Thus, they are actively used as anti-foaming agents, additives, and plasticizers, substituting more hazardous phthalates. Organophosphates containing chlorine are widely used as antipyrenes (Svara et al., 2006). Since organophosphates are not chemically bound to the polymers they can easily volatilize. Urban areas and traffic are considered the main sources of organophosphates (Bacaloni et al., 2008; Regnery and Puttmann, 2009) in the air.

All compounds listed in Table 6 do not have any established safe level values in Russia, therefore it is rather difficult to estimate their effect on the ecosystem and human health. Nevertheless, it was noticed that they became more widespread in the environment, being the only class of organic contaminants with their levels in the snow increasing every year since we have started our studies in 2012.

3.6. Alkylpyridines

Another representative group of emerging contaminants found in the rain samples are alkylpyridines (Table 8). Eighteen compounds were identified at the concentrations range 0.5–3500 ng/l, with pyridine itself being an undisputable leader in concentration. The sources of these compounds may involve industry or transport as well as coal and fuel production processes (Brody and Ruby, 1960) or biomass combustion (Stockwell et al., 2015). Being more soluble in water than the corresponding alkylbenzenes, they constitute a notable amount of organic matter in the rain water. Earlier we have detected alkylpyridines in Moscow (Polyakova et al., 2012) and Arctic (Lebedev et al., 2018) snow, as well as in cloud water in France (Lebedev et al., 2018a).

3.7. Dichloronitromethane

In our earlier article (Lebedev et al., 2013) we have already reported the detection of a very simple analyte, dichlornitromethane, which to the author's knowledge had been reported in the past environmental studies only once by (Laniewski et al., 1998) in the rainwater from Sweden, Poland and Ireland, but it was persistently occurring in Russian samples collected in 2011–2018. It was also mentioned as a disinfection by-product in drinking water (Krasner et al., 2006; Plewa et al., 2004), however in our opinion the waste incinerators are the most probable source of dichloronitromethane in the atmosphere. Its levels in the rain samples appeared to be quite high (Table 9). Moreover, since this

Table 9
The levels of dichloronitromethane (ng/l) in the rain samples.

ng/l	1	2	3	4	5	6	7	8
Methane, dichloronitro-	876	1241	918	1450	605	2555	770	1300

compound belongs to the group of volatiles while all sample preparation was carried out according to the US EPA 8270 Method for semi volatile compounds, the major portion of that chemical was lost. It means that the levels of dichloronitromethane may reach hundreds of micrograms per liter of rain water. Since toxicological characteristics of this compound remain unknown, it requires more attention in future studies.

4. Conclusions

Rain is a very convenient matrix to study atmospheric pollution allowing for identification in the present study of over 700 semi-volatile compounds in each of eight samples of Moscow rainwater using comprehensive 2D gas chromatography coupled to high resolution and low resolution mass spectrometry. Oxygenated compounds constitute the vast majority of the identified pollutants. While all classes of priority pollutants were also well represented, the levels of phenol, dibutylphthalate, and benz[a]pyrene exceed the country safe level, making them atmospheric priority pollutants for Moscow. Pyridines, organophosphates, and dichloronitromethane may be considered as emerging contaminants. An unknown source of PCBs should be specially mentioned, while other persistent organochlorines of the major concern were not detected in the samples.

Acknowledgments

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