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Trace Elements in the Spring Waters of Moscow

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Abstract—Data on the levels of major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) and dissolved trace elements (Rb, Cs, Be, Sr, Ba, B, Si, P_{min}, V, Cr, Ge, As, Mo, W, Sb, Te, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ag, Sn, Pb, Al, Ga, Ti, Zr, and U) in the waters of 30 springs in Moscow during the winter low water period are presented. The geometric mean values and ranges of concentration of the studied components, as well as correlations between them were established. The presence of hydrochemical anomalies of dissolved iron and manganese in the northeast of Moscow with an excess of the maximum permissible concentration (MPC) for these elements was revealed, whereas in the rest of the city their concentrations corresponds to the natural background levels almost everywhere.

Keywords: spring waters, major ions, dissolved trace elements, hydrochemical anomalies, Moscow

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INTRODUCTION

Spring testing is an important element of environmental and geochemical monitoring, since the composition of constantly renewing spring waters reflects the current level of pollution of the geological environment (soil and ground strata). The springs of Moscow have repeatedly been the objects of hydrogeological and ecological geochemical studies (Khramenkov et al., 1997; Limantseva, 2004; Shvets et al., 2002); however, their trace element composition has been studied extremely poorly. Meanwhile, many trace elements, even in very small quantities, have very pronounced toxicity and also serve as sensitive indicators of various natural and anthropogenic processes that are involved in the formation of the ecological state of the environment. The goal of our study was to determine the level of concentrations of a wide range of dissolved trace elements in the spring waters of Moscow and to identify problem areas that require a more detailed examination

MATERIALS AND METHODS

Characterization of Research Objects

To obtain a representative sample, 30 springs that were evenly distributed in the city were tested (Fig. 1, Table 1). Samples of spring water were taken during the winter low water period, when they are least susceptible to short-term fluctuations in their chemical composition. All springs are runoff zones of the Quaternary and Mesozoic (Cretaceous and partially Jurassic) aquifers. Overflow from the underlying horizons occurs only in local areas (*Gidrogeologiya* ..., 1966; Shvets et al., 2002).

In the Northern and Northeastern Administrative Districts (ADs) the springs are located in the regions of Koptevo, Mitino, Sviblovo, and Otradnoe (points 1–7). The territory of these districts is located mainly within the valley of the Yauza River and only its eastern part is on the fluvioglacial plain of the Meshchera Upland. The upper part of the geological section is formed by deposits of the Carboniferous and Quaternary systems. Aquifers are present in Quaternary and Carboniferous sediments. Aquifers of alluvial, Oka-Dnieper fluvioglacial sands and Upper Carboniferous dolomites form a combined Paleozoic–Cenozoic aquifer complex. Moraine Dnieper loams and Kasimov clays serve as relative confining layers that separate Quaternary and Carboniferous aquifers. The springs are fed by the waters of the Mesozoic–Cenozoic aquifer complex with the participation of the waters of the Paleozoic aquifer complex due to overflow from Carboniferous deposits.

In the territory of the Eastern AD, spring rises were found in the Izmailovsky Park and Kuskovsky Forest Park (Veshnyaki) within the limits of a wavy moraine-outwash landscape (points 8–10). The geological sec-

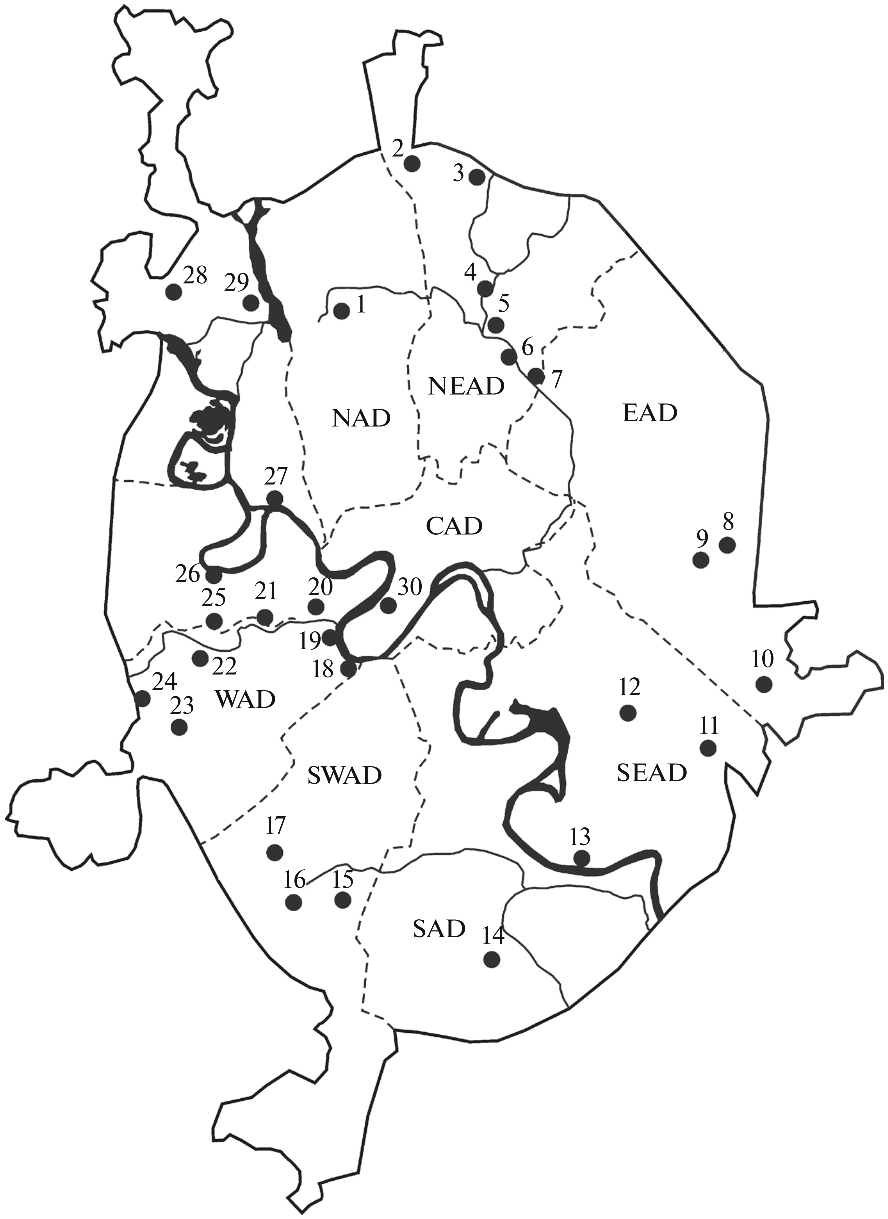

Fig. 1. The location of the water sampling points of the springs of Moscow.

tion in the area to a depth of 20 m consists of Quaternary sediments of different ages and geneses. The groundwater level is at a depth of 9.5 m in fluvial sands.

In the territory of the Southeastern AD, the springs are located in the regions of Kuzminki and Maryino (points 11–13). The Kuzminki region is located within the Meshchera outwash lowland with a wavy moraine-outwash landscape. The geological section of the territory to a depth of 30 m consists of Quaternary sediments of different ages and genesis and Upper Jurassic rocks. The groundwater level is at a depth of 6.0 m in alluvial sands.

The Southern AD is represented by a spring in the Tsaritsyno region (point 14). The region is located on the third floodplain terrace of the Moskva River and its tributaries, as well as in the fluvioglacial plain of the Teplostanskaya upland at the western boundary. The upper part of the geological section in Tsaritsyno is formed by Carboniferous, Jurassic, Cretaceous, and Quaternary deposits. Aquifers in the modern alluvial, Oka-Dnieper fluvioglacial and Lower Cretaceous sands form a combined Mesozoic–Cenozoic aquifer complex, the groundwater of which serves as the main source of spring runoff in this region. The clay stratum of the Callovian Middle Jurassic layer, as well as the Oxfordian and Volga Upper Jurassic layers with a thickness of 14 m, create a regional confining layer that separates the overlying Mesozoic–Cenozoic

Table 1. A description of the water sampling points at the springs of Moscow

# Points	Coordinates	Description of sampling points
1	55°49′28″ N 37°32′17″ E	Koptevo region, near the Bolshaya Akademicheskaya Street. A non-captured spring
2	55°54′21″ N 37°35′47″ E	Northern outskirts of the Lianozovo Forest Nursery. A descending, captured spring
3	55°54′15″ N 37°36′20″ E	700 m to the east of the Altufevsky Pond, the left bank of the Samoteka River, at a distance of 50 m from the MKAD, at the base of a low slope of the left river bank. A non-captured spring
4	55°51′9″ N 37°37′40″ E	Near the Sviblovo Estate, on the right bank of the Yauza River, in the back part of the floodplain, at a distance of 5 m from the water edge. A non-captured spring
5	55°50′27″ N 37°38′35″ E	The territory of the Sad Budushchego Park, at a distance of 15 m from the northeastern shore of the Leonovsky Pond. A non-captured spring
6	55°49′39″ N 37°39′45″ E	At a distance of 8 m from the left bank of the Yauza River. An ascending weak spring captured by a vertical pipe with a diameter of 20 cm; water gives a bright ferriferous precipitate
7	55°49′59″ N 37°40′16″ E	At a distance of 15 m from the right bank of the Budaika River, 400 m to the north of the Yauza railway platform. A descending non-captured spring; water accumulates in a ground niche
8	55°46′57″ N 37°48′2″ E	Izmailovsky Park. A non-captured spring
9	55°46′50″ N 37°46′7″ E	The same park, on a dirt road from the Glavnaya Alleya to the Sovkhoznyi Pond. A descending, non-captured spring
10	55°44′3″ N 37°48′20″ E	Kuskovsky Forest Park, near the Bolshoi Pond. A non-captured spring
11	55°41′30″ N 37°46′22″ E	Kuzminsky Forest Park, near the Shibaevsky Pond, at a distance of 10 m from the water edge of the Ponomarka River. A non-captured spring
12	55°41′27″ N 37°45′51″ E	The same park, at a distance of 30 m from the water edge of the Ponomarka River, in the back part of the floodplain. A descending spring captured by a supporting wall, from which two zinc-plated pipes with a diameter of 3 cm come out
13	55°38′32″ N 37°43′31″ E	Maryinsky Park. A non-captured spring
14	55°36′49″ N 37°40′45″ E	Tsaritsyno Park, the right bank of the Upper Tsaritsyno Pond, at a distance of 10 m from the water edge. A descending spring captured by a zinc-plated tube
15	55°37′56″ N 37°33′24″ E	900 m to the east of the overpass on the Sevastopol Avenue over the Chertanovka River. A descending, non-captured spring
16	55°36′50″ N 37°32′44″ E	Yasenevo region, Solovyinyi passage. A descending, captured spring
17	55°37′12″ N 37°32′20″ E	Bitsevsky Forest Park, Uzkoe Estate. A descending, captured spring
18	55°42′49″ N 37°32′19″ E	The edge of a landslide terrace at a distance of 330 m to the northwest of the Church of the Saint Life-giving Trinity on the Vorobyovy Gory Hills. An ascending spring captured by a pipe with a diameter of 40 cm, which was vertically depended in the ground
19	55°42′29″ N 37°32′54″ E	Vorobyovy Gory Nature Reserve, 40 m down the slope from the monument to Herzen and Ogarev, in the back part of the terrace of a landslide bench. A descending, captured spring
20	55°43′7″ N 37°29′10″ E	Volynsky forest, at a distance of 100 m from the water edge of the Setun River. A descending, non-captured spring
21	55°42′49″ N 37°28′13″ E	Setun River Valley Nature Reserve (Ramenki), opposite to the Veernaya Street, at a distance of 25 m from the water edge of the river, in the floodplain. A non-captured spring
22	The same coordinates	The same nature reserve, above point 21. A non-captured spring

Table 1. (Contd.)

# Points	Coordinates	Description of sampling points
23	55°42′57″ N 37°26′47″ E	The same nature reserve, 70–80 m to the northeast from the floodplain Pyatachok Pond, in the back part of the first floodplain terrace, at a distance of 50 m from the river water edge. A non-captured spring
24	55°43′5″ N 37°29′3″ E	Volynsky forest, at a distance of 90 m from the water edge of the Setun River on its right bank. A non-captured spring
25	55°43′20″ N 37°30′16″ E	Setun River Valley Nature Reserve, 20 m upstream from the Staryi Rublevsky Bridge, on the right bank, at a distance of 1.5 m from the water edge. A non-captured spring
26	55°44′45″ N 37°26′9″ E	Moskvoretsky Natural Historical Park, 450 m downstream of the Moskva River from the Krylatsky Bridge, at a distance of 100 m from the water edge, at the foot of a landslide slope. A descending, captured spring
27	55°46′5″ N 37°28′44″ E	The same park, 200 m downstream of the Moskva River from the Karamyshevsky Bridge, in the second floodplain terrace, at a distance of 50 m from the water edge. A descending, captured spring
28	55°51′18″ N 37°24′1″ E	Khoroshevo-Mnevniki region, the floodplain the Bratovka River. A non-captured spring
29	55°52′30″ N 37°26′13″ E	The same region, near the Svobody Street, near the “Butakovsky Bay” stop, in the upper part of a ravine. A non-captured spring
30	55°42′51″ N 37°34′59″ E	Yakimanka region, Neskuchny Sad, at a distance of 5 m from the water edge of the Andreevsky Pond. An ascending, non-captured spring

aquifer complex from the underlying Middle Carboniferous aquifer complex in Podolsk–Mayachkovsk limestones.

In the territory of the Southwestern AD, springs are located in the Yasenevo region and in the Bitsevsky forest park (points 15–17). The territory of the Yasenevo region is located in the moraine plain of the Teplostanskaya upland. The river network is that of the Chertanovka River. The hydrogeological structure of the region is formed by aquifers in Quaternary, Cretaceous, Jurassic, and Carboniferous deposits. Aquifers in fluvioglacial sands and sandy loams of the Oka-Dnieper and Dnieper-Moskva ages form a single Cenozoic aquifer complex with a total thickness of 26 m. Lower Cretaceous Albian clays serve as a relative confining layer that separates the Cenozoic and Mesozoic aquifer complexes. All springs in the territory of this district are fed by the waters of the Mesozoic–Cenozoic aquifer complex.

In the territory of the Western AD, springs were examined in the regions of Krylatskoye (point 25), Fili-Kuntsevo (point 26), Mozhaisky (points 20, 24), and in Vorobyovy Gory (points 18, 19, 21–23).

The greater part of the Krylatskoye region is located in the floodplain of the Moskva River. The main role in the formation of spring runoff in the Krylatskoye region is played by Mesozoic–Cenozoic deposits. The hydrogeological section includes aquifers in the alluvial sands of the floodplain and third floodplain terrace, as well as in the Lower Cretaceous sands, which make up the combined Mesozoic–Cenozoic aquifer complex. The clays of the Oxfordian and Volga Upper Jurassic layers form a regional confining complex that separates this aquifer complex and aquifer complex in Middle Carboniferous limestones, whose groundwater has a pressure character.

The hydrogeological section of the Fili-Kuntsevo region is presented by aquifers in the Jurassic, Cretaceous, and Quaternary sands, which do not have clearly formed separating low-permeability layers and are fed by the infiltration of atmospheric precipitation and surface watercourses. This makes it possible to distinguish a single Mesozoic–Cenozoic complex, which forms spring runoff in the forest park. Middle Jurassic and Upper Jurassic clay deposits of Callovian and Oxfordian age serve as a regional confining layer and separate the Mesozoic–Cenozoic aquifer complex from the combined aquifer complex in the Callovian-Bathonian Middle Jurassic sands and in the Upper Carboniferous and Middle Carboniferous limestones.

The territory of the Mozhaisky region is located in the Moskva-Oka moraine-erosion plain within the southern bumpy erosion Teplostanskaya upland with the ancient valley of the Setun River.

In Vorobyovy Gory, Upper Carboniferous and Middle Carboniferous limestones are overlain by the strata of the Jurassic, Cretaceous, and Quaternary systems. Aquifers in the sandy deposits of the Upper Jurassic Volga layer, Aptian Lower Cretaceous layer, and in the Quaternary landslide sand–clay deposits form a combined Mesozoic–Cenozoic aquifer complex. The Callovian, Oxfordian, and Volga clays create a regional confining layer with a thickness of up to 40 m. The aquifer in the Upper Carboniferous and Middle Carboniferous limestones does not affect the formation of spring runoff.

In the Northwestern AD, springs are located in the Khoroshevo-Mnevniki region (points 27–29). Here, Upper Jurassic Volga sands, fluvioglacial Oka-Dnieper sands, alluvial and sometimes Cretaceous sands form a combined Mesozoic–Cenozoic aquifer complex, which plays the main role in the formation of spring runoff. The clay deposits of the Volga and Oxfordian Upper Jurassic layers are a regional confining layer that separates this aquifer complex and the combined aquifer complex in Middle Carboniferous limestones and in Bathonian Middle Jurassic sand deposits.

In the territory of the Central AD, springs (point 30) are located in the Yakimanka region (Neskuchny Sad). Upper Carboniferous deposits are represented by marls with clay interlayers of the Kasimov stratum. Jurassic deposits lie above (Callovian and Oxfordian clays, Volga sands). Quaternary fluvioglacial and alluvial deposits lie in the upper part of the section on Volga sands.

The total alkalinity (Alk ≈ HCO_3^-), the contents of other major ions (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+}) and fluorine were determined in samples filtered through a thick paper filter by the volumetric acidimetric method (Lur'e, 1971), by capillary electrophoresis (Komarova and Kamentsev, 2006), and by direct ionometry (Savenko, 1986), respectively. The concentrations of dissolved trace elements were measured by inductively coupled plasma mass spectrometry on an Agilent 7500ce instrument in samples that were filtered immediately after collection through a 0.45 μm membrane filter into polypropylene bottles with aliquots of 5 N nitric acid (0.2 mL per 8 mL sample). The error of individual measurements did not exceed ±3%. The discrepancy in the equivalent concentrations of cations and anions of the basic salt composition did not exceed 5%.

RESULTS AND DISCUSSION

Mineralization and Components of the Basic Salt Composition (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-)

The results of determining the contents of major ions in the spring waters of Moscow and their mineralization are given in Table 2. Mineralization of the spring waters varies over a wide range: from 188 to 1080 mg/L; however, an excess of the maximum permissible concentration (MPC) for the total level of salts (1000 mg/L (SanPiN ..., 2002)) was found only at two points (2 and 4) located on the northern outskirts of the city and is due to an abnormally high contents of chlorides and sodium. In a number of samples (points 8, 9, 16, and 17), the increased mineralization (700–750 mg/L) is also caused by the presence of chlorides and sodium, whose genesis is not entirely clear. Some of these are probably of anthropogenic origin. In three springs (points 5, 7, and 22), the increased mineralization (750–875 mg/L) is due to high contents of calcium and sulfates. Pronounced dependences are observed between the concentrations of sodium and chlorides, as well as calcium, magnesium, and sulfates (Fig. 2), which is reflected in the values of the correlation coefficient (Table 3). This indicates the relationship between the increased concentration of these components in the spring waters and the presence of a gypsum–halite impurity in the composition of rocks, which in some way interacts with groundwater. Mineralization was found to have the closest correlations with magnesium, calcium, and sodium, as well as with chlorides and, to a lesser extent, with sulfates.

Rare Alkaline and Alkaline Earth Elements (Rb, Cs, Be, Sr, and Ba)

With the exception of beryllium, the concentrations of rare alkaline and alkaline earth elements in the spring waters of Moscow do not differ much from their average contents in the underground waters of the leaching zone and rivers of the world (Table 4). A close correlation is observed between the concentrations of rubidium and potassium (r = 0.86), which have very similar chemical and geochemical properties. Cesium was noted to have significant correlations[1] with chlorides (r = 0.76), sodium (r = 0.71), and barium (r = 0.75). An important role in the hypergene geochemistry of cesium and barium is played by sorption–desorption processes with the participation of clay minerals, which probably causes a correlation between these elements. The barium concentration is closely correlated with salinity (r = 0.76) and, similarly to cesium, with the concentration of chlorides (r = 0.94) and sodium (r = 0.89). Strontium was found to have only one significant correlation with germanium (r = 0.90), whose origin is not clear.

Beryllium concentration in the spring waters varies from 0.7 to 10.7 ng/L with an average level of 2.5 ng/L. The latter value is close to the average beryllium concentration in the waters of the world's rivers (8.9 ng/L), but is much lower than the average level of this element in the underground waters of the moderate climate leaching zone (240 ng/L). Beryllium does not display significant correlations with any of the studied elements. Until recently, the determination of a low beryllium concentration in natural waters was a very difficult task; therefore, it is possible that the estimate of its average level in underground waters that was made by S.L. Shvartsev (1998) is overstated. Mean-

[1] Here and below, correlations with $r \geq 0.7$ are considered.

Table 2. The mineralization (*M*) and contents of major ions in the spring waters of Moscow

# Point (parameter)	M	Cl^-		SO_4^{2-}		HCO_3^-		Na^+		K^+		Mg^{2+}		Ca^{2+}	
	mg/L	mg/L	%-eqv.	mg/L	%-eqv.	mg/L	%-eqv.	mg/L	%- eqv.	mg/L	%-eqv.	mg/L	%-eqv.	mg/L	%-eqv.
1	412	46.3	11.1	87.3	15.5	173	24.1	21.3	7.9	0.98	0.2	20.4	14.3	63.3	26.9
2	1080	500	38.5	102	5.8	101	4.5	196	23.3	2.49	0.2	38.3	8.6	141	19.2
3	344	89.9	24.1	53.2	10.5	108	16.8	5.51	2.3	2.96	0.7	17.8	13.9	66.9	31.7
4	1026	467	37.9	94.3	5.6	110	5.2	170	21.3	2.53	0.2	38.8	9.2	144	20.6
5	859	80.0	8.8	375	30.3	172	10.9	27.4	4.6	1.84	0.2	47.4	15.1	155	30.1
6	332	65.0	18.6	75.7	16.0	107	17.8	5.52	2.4	2.89	0.7	17.8	14.9	58.4	29.6
7	875	67.2	7.2	414	32.9	159	9.9	28.0	4.6	1.53	0.1	47.9	15.0	159	30.2
8	717	272	33.2	129	11.6	93.9	6.7	115	21.6	3.60	0.4	30.6	10.9	72.9	15.7
9	698	285	35.2	92.5	8.4	101	7.2	110	21.0	3.74	0.4	31.6	11.4	74.9	16.4
10	325	42.0	12.6	68.9	15.3	123	21.5	29.8	13.8	0.90	0.2	13.2	11.6	46.7	24.9
11	354	41.3	11.2	80.6	16.1	130	20.5	26.7	11.2	0.82	0.2	16.7	13.2	57.6	27.6
12	428	43.0	10.3	85.1	15.0	193	26.8	26.8	9.9	1.37	0.3	16.1	11.2	62.6	26.5
13	419	40.1	9.7	75.3	13.5	196	27.7	25.0	9.3	0.81	0.2	17.5	12.4	63.6	27.3
14	415	43.8	10.8	86.1	15.6	182	25.9	25.6	9.7	0.74	0.2	15.8	11.3	61.0	26.5
15	235	5.48	2.4	34.6	11.2	135	34.6	6.22	4.2	0.89	0.4	12.7	16.2	39.9	31.0
16	714	306	36.6	99.9	8.8	81.1	5.6	118	21.8	3.33	0.4	31.8	11.1	73.9	15.7
17	752	317	36.5	101	8.6	100	6.7	127	22.6	3.49	0.4	30.8	10.4	72.9	14.9
18	419	28.5	6.8	44.1	7.8	237	33.0	9.38	3.5	1.64	0.4	25.2	17.6	72.9	30.9
19	513	61.8	11.5	104	14.3	208	22.5	12.3	3.5	1.25	0.2	30.6	16.6	94.9	31.3
20	503	86.8	16.0	114	15.5	156	16.7	32.6	9.2	1.91	0.3	28.7	15.4	82.6	26.9
21	636	127	18.0	186	19.5	142	11.7	18.4	4.0	1.25	0.2	37.7	15.6	124	31.1
22	746	141	16.9	219	19.4	162	11.3	32.5	6.0	1.62	0.2	44.6	15.6	145	30.7
23	350	37.2	10.4	78.4	16.1	143	23.1	8.49	3.6	0.96	0.2	19.5	15.9	62.5	30.7
24	585	113	17.7	105	12.1	195	17.7	23.2	5.6	1.82	0.3	35.3	16.1	111	30.6
25	582	77.4	13.2	127	15.9	232	22.9	32.8	8.6	2.00	0.3	28.8	14.3	82.3	24.8
26	407	54.0	12.9	96.6	17.0	149	20.7	22.1	8.1	0.94	0.2	19.2	13.4	65.5	27.7
27	265	23.1	9.0	49.0	14.1	121	27.3	36.2	21.7	1.03	0.4	7.83	8.9	27.1	18.6
28	345	43.9	12.1	77.4	15.8	125	20.0	25.2	10.7	1.11	0.3	18.0	14.5	54.5	26.6
29	188	5.20	3.1	19.3	8.6	113	39.6	43.8	40.7	1.20	0.7	2.23	3.9	3.13	3.3
30	538	144	24.7	109	13.7	123	12.3	60.3	15.9	8.44	1.3	19.1	9.6	74.6	22.6
SW_{GM}	489	72.6	–	93.0	–	140	–	30.0	–	1.66	–	22.1	–	68.6	–
SW_{min}	188	5.20	–	19.3	–	81.1	–	5.51	–	0.74	–	2.23	–	3.13	–
SW_{max}	1080	500	–	414	–	237	–	196	–	8.44	–	47.9	–	159	–
UWLZ according to (Shvartsev, 1998)	354	15.9	–	18.2	–	222	–	23.8	–	2.74	–	16.5	–	38.3	–
WR according to (Meybeck, 2004)	85.1	5.92	–	8.40	–	48.6	–	5.52	–	1.72	–	2.98	–	11.9	–

Here and in Tables 4–7: SW_{GM}, SW_{min}, and SW_{max} are the geometric mean, minimum, and maximum contents in the spring waters of Moscow; UWLZ and WR are the average (weighted) contents in the underground waters of the moderate climate leaching zone and in the rivers of the world, respectively.

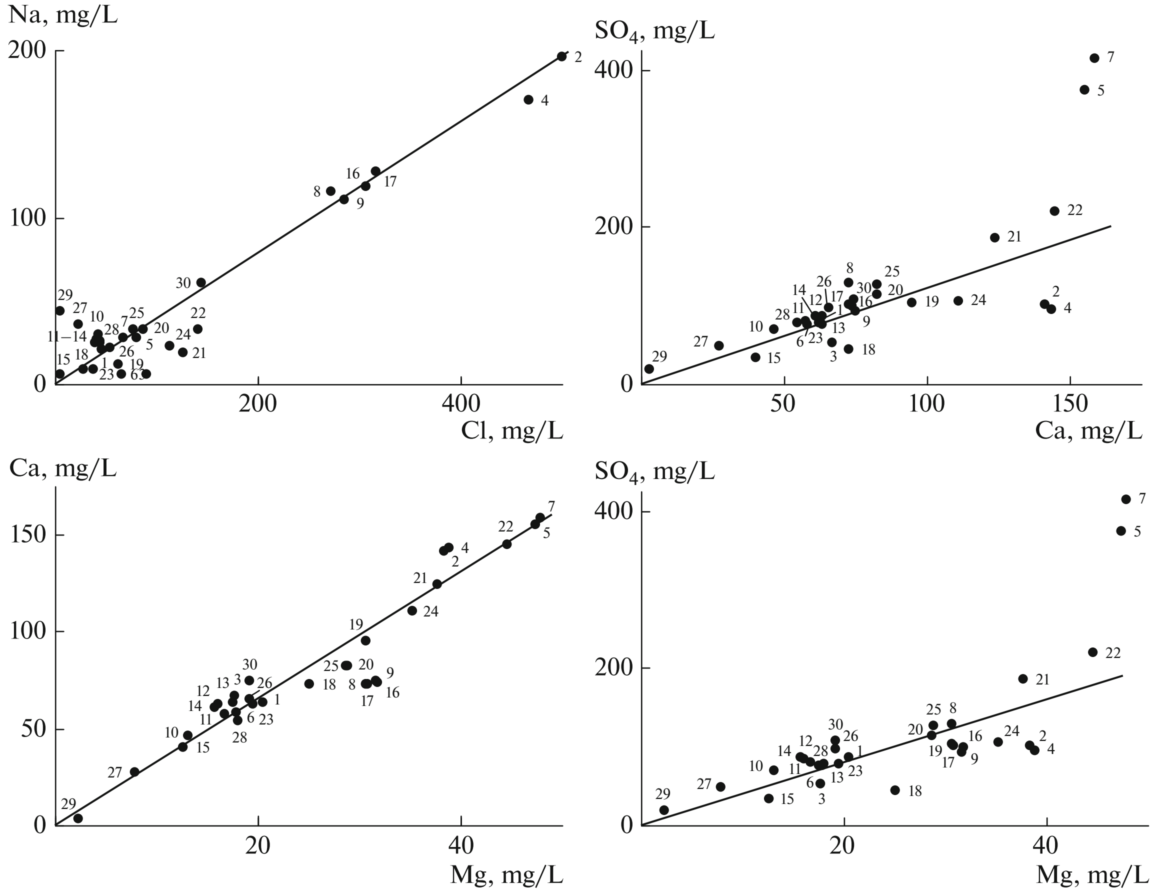

Fig. 2. Correlation of the concentrations of sodium and chlorides, calcium, and manganese, as well as sulfates with the levels of calcium and manganese in the spring waters of Moscow. The inscriptions near the icons mark the numbers of sampling points.

while, the concentrations of dissolved trace elements in underground waters in most cases exceed their contents in river waters; it is possible that the low beryllium level in the springs of Moscow is a regional feature. Beryllium is an extremely toxic element. The MPC value in drinking water for this element is 0.2 μg/L; however, this value is approximately 80 and 20 times higher than the average and maximum spring water levels, respectively.

Table 3. The values of the coefficient of correlation between mineralization and the contents of major ions in the spring waters of Moscow*

Component	*M*	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
M	1							
Cl^-	**0.81**	1						
SO_4^{2-}	0.59	0.05	1					
HCO_3^-	–0.15	–0.51	0.15	1				
Na^+	*0.72*	**0.95**	–0.02	–0.55	1			
K^+	0.32	0.45	0.02	–0.38	0.42	1		
Mg^{2+}	**0.89**	0.53	*0.76*	0.09	0.36	0.16	1	
Ca^{2+}	**0.86**	0.47	*0.77*	0.15	0.30	0.11	**0.95**	1

* Level of statistical significance $p < 0.01$.

Table 4. The contents of the dissolved forms of rare alkaline and alkaline earth elements in the spring waters of Moscow

# Point (parameter)	Rb	Cs	Be	Sr	Ba
	μg/L	ng/L		μg/L	
1	0.46	6.1	2.8	246	39.8
2	0.99	43.0	0.8	327	161
3	1.68	1.0	3.4	848	40.6
4	1.00	46.3	0.7	329	161
5	0.53	8.7	1.1	328	40.7
6	1.64	1.6	3.4	858	41.7
7	0.41	6.4	1.5	331	38.8
8	1.61	45.2	6.9	336	159
9	1.69	49.4	6.3	343	159
10	0.37	6.8	10.7	137	23.0
11	0.32	8.3	1.8	154	28.9
12	0.79	8.1	1.9	148	28.3
13	0.31	7.4	3.3	175	31.0
14	0.26	7.4	3.1	147	27.1
15	2.08	2.9	1.0	125	4.0
16	1.60	40.7	6.3	339	160
17	1.51	45.5	10.7	335	158
18	1.28	33.0	2.7	311	17.6
19	0.69	29.6	2.2	387	59.1
20	0.37	16.5	2.5	291	52.9
21	0.38	25.9	1.9	335	76.8
22	0.89	30.9	2.4	367	72.6
23	1.38	3.9	–	234	29.4
24	0.97	54.2	–	387	29.7
25	0.46	15.2	1.6	289	53.2
26	0.43	8.5	2.6	207	35.5
27	0.42	10.8	3.1	117	15.9
28	0.54	9.4	1.5	229	37.0
29	0.51	15.2	2.8	90	7.9
30	4.24	34.7	1.9	320	47.8
SW_{GM}	0.77	13.4	2.5	265	43.3
SW_{min}	0.26	1.0	0.7	90	4.0
SW_{max}	4.24	54.2	10.7	858	161
MPC, according to (*SanPiN 2.1.4.1074-01...*, 2002)	100	–	200	7000	100
UWLZ according to (Shvartsev, 1998)	2.55	–	240	185	25.3
WR, according to (Gaillardet et al., 2004)	1.63	11	8.9	60	23

Trace Elements that Form Oxyanions (B, Si, P_{min}, V, Cr, Ge, As, Mo, W, Sb, and Te)

Many chemical elements are present in natural waters in the form of hydroxy acids and the products of their dissociation, that is, oxyanions. The most common elements of this group include silicon and phosphorus, whose concentrations in surface and underground waters are at the levels of *n* and 0.*n* mg/L, respectively, while the concentrations of other elements is 3–4 orders of magnitude lower and equal *n*–0.0*n* μg/L.

The silicon level in the spring waters is close to that in the underground waters of the leaching zone and in the rivers of the world (Table 5), which is due to its influx from rocks, in which silicates predominate. The concentrations of other oxyanions are also comparable to their contents in the underground waters of the moderate climate leaching zone and in the rivers of the world. Antimony is an exception, since its average level in underground waters in the leaching zone is almost 10 times higher than the average concentration in the spring waters, which is only 20% lower than the level in the global river flow. The waters of all the Moscow springs contain anionic trace elements at a significantly smaller level compared to the MPC for drinking water.

The spring waters are observed to have a fairly close correlation between the concentrations of silicon and titanium ($r = 0.89$), whose appearance is due to the fact that titanium, like silicon, belongs to the major petrogenic elements and is leached from silicate rocks together with it. The contents of molybdenum, tungsten and antimony significantly correlate with that of iron: $r_{Mo-Fe} = 0.75$, $r_{W-Fe} = 0.81$, $r_{Sb-Fe} = 0.76$. These oxyanions are actively adsorbed by iron (III) hydroxides and pass into solution together with iron under conditions of hypoxia, when iron (III) is reduced to a divalent state and forms more soluble compounds.

Heavy Metals (Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd, Ag, and Sn)

Chemical elements that are classified as heavy metals have strong biological activities and they become highly toxic substances when the MPC is exceeded. All heavy metals, except iron and manganese, are contained in the spring waters of Moscow at levels that are significantly lower than the MPC (Table 6). The concentration of iron and manganese in some samples (points 2–7 and 18) exceeds the MPC for drinking water up to 36 and 3.6 times, respectively. A previous examination of seven springs (Shvets et al., 2002) showed a lower contents of iron and manganese in the range of 10–330 and ~0–30 μg/L, respectively, which may be due to the small number and unevenness of the samples. According to our data, the region of the maximum iron and manganese concentration forms a pronounced hydrochemical anomaly in the northeast of

Table 5. The contents of the dissolved forms of anionic trace elements in the spring waters of Moscow

# Point (parameter)	Si	B	P_{min}	V	Cr	Ge	As	Mo	W	Sb	Te
	mg/L	μg/L							ng/L		
1	5.58	26.5	108	0.83	1.69	0.014	0.45	0.43	86.9	46.9	17.9
2	6.27	15.1	78.8	0.30	0.86	0.020	0.32	0.31	14.7	35.9	13.8
3	6.09	23.9	380	0.10	0.08	0.144	1.91	0.35	57.3	13.3	7.0
4	6.30	15.8	82.0	0.30	0.86	0.018	0.32	0.40	12.3	55.2	9.6
5	5.19	10.6	152	0.16	0.15	0.014	0.52	0.89	118	208	13.2
6	6.02	27.0	413	0.10	0.08	0.145	1.99	0.34	72.2	19.1	9.1
7	4.89	9.9	62.7	0.13	0.12	0.018	0.64	1.18	152	259	12.1
8	6.56	22.7	21.3	0.19	0.67	0.016	0.21	0.03	10.9	36.3	6.3
9	6.64	26.2	24.1	0.22	0.75	0.016	0.22	0.04	18.0	41.4	11.7
10	3.68	35.3	156	0.74	1.03	0.009	0.39	0.43	45.4	49.6	8.2
11	4.04	23.5	208	0.99	2.07	0.006	0.49	0.40	6.7	39.4	10.6
12	4.00	23.5	250	1.00	11.3	0.006	0.45	0.37	6.2	61.1	9.5
13	4.41	24.6	172	0.91	1.40	0.008	0.45	0.41	27.6	39.4	3.9
14	4.00	24.1	194	0.92	1.34	0.005	0.46	0.37	18.8	36.8	8.5
15	8.76	11.2	7.4	0.25	0.23	0.012	0.23	0.39	19.9	118	2.9
16	6.50	23.3	26.0	0.18	1.22	0.018	0.23	0.04	35.1	42.0	15.8
17	6.60	21.5	19.5	0.20	0.74	0.017	0.21	0.03	23.5	34.5	11.6
18	8.93	19.5	117	0.21	4.10	0.017	5.00	0.81	32.6	51.5	7.1
19	7.85	20.6	93.8	0.97	2.78	0.022	0.56	0.44	7.2	48.1	9.9
20	7.40	21.6	470	0.25	1.10	0.016	0.81	0.35	45.1	54.4	9.9
21	7.35	13.6	109	0.95	1.74	0.012	0.31	0.17	2.9	44.8	8.9
22	8.09	11.0	162	0.77	2.13	0.016	0.46	0.19	8.5	30.4	6.6
23	8.22	13.6	39.9	0.49	1.17	0.013	0.34	0.35	9.9	20.6	4.6
24	8.83	22.1	73.1	0.54	0.72	0.014	0.24	0.42	35.9	95.3	7.9
25	7.34	22.4	479	0.26	1.14	0.015	0.83	0.34	82.7	104	19.0
26	4.93	22.0	162	0.94	1.68	0.008	0.45	0.39	1.9	34.8	4.7
27	3.13	55.0	79.9	0.39	0.59	0.012	0.24	0.48	1.0	61.5	2.3
28	5.30	34.9	93.2	0.71	1.52	0.013	0.39	0.46	0.7	42.0	11.5
29	2.49	76.0	11.0	0.02	0.28	0.018	0.09	0.55	2.9	73.0	3.7
30	7.34	62.1	233	5.82	1.17	0.029	2.86	0.23	17.2	122	9.6
SW_{GM}	5.82	22.3	94.9	0.38	0.87	0.016	0.47	0.29	16.1	51.0	8.3
SW_{min}	2.49	9.9	7.4	0.02	0.08	0.005	0.09	0.03	0.7	13.3	2.3
SW_{max}	8.93	76.0	479	5.82	11.3	0.145	5.00	1.18	152	259	19.0
MPC, according to (*SanPiN 2.1.4.1074-01...*, 2002)	10	500	–	100	50	–	50	250	50 000	50 000	–
UWLZ according to (Shvartsev, 1998)	6.2	55.9	98.2	1.28	2.83	–	1.64	0.89	–	550	–
WR*	4.07	10.2	38	0.71	0.70	0.0068	0.62	0.42	100	70	–

* Si, according to (Meybeck, 2004); P_{min}, according to (Savenko V.S. and Savenko A.V., 2007), other elements according to (Gaillardet et al., 2004).

Table 6. The contents of the dissolved forms of heavy metals in the spring waters of Moscow

# Point (parameter)	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd	Ag	Sn
	μg/L							ng/L		
1	0.38	30.9	0.16	0.51	0.66	5.4	0.41	17.7	2.40	57.1
2	272	361	0.09	0.55	1.28	50.6	0.15	14.3	1.40	10.9
3	90.2	3090	0.03	0.11	1.42	32.8	0.35	7.4	1.76	27.2
4	260	338	0.08	0.68	1.52	36.1	0.20	19.8	4.61	21.4
5	357	8640	0.66	1.89	1.05	89.6	0.29	14.3	1.20	15.7
6	91.0	3290	0.03	0.05	0.25	56.7	0.31	4.6	1.28	22.4
7	326	10 900	0.63	3.01	0.95	76.1	0.32	12.9	1.06	24.8
8	4.19	44.0	0.09	7.14	2.28	60.5	0.20	47.3	3.36	12.9
9	4.29	44.6	0.09	7.34	2.82	55.6	0.21	35.5	5.37	31.5
10	0.59	24.1	0.24	0.63	0.84	9.9	0.44	–	1.75	33.1
11	1.52	32.9	0.28	1.04	2.45	15.1	0.53	274	0.33	13.6
12	2.68	35.4	0.36	2.40	8.60	27.7	0.60	–	1.74	61.2
13	0.54	29.4	0.24	0.71	0.71	6.8	0.40	168	1.04	28.7
14	0.68	28.1	0.26	0.76	0.74	8.4	0.40	87.1	0.57	24.5
15	0.66	28.2	0.06	0.26	0.94	130	0.23	10.2	0.40	9.0
16	3.21	45.0	1.04	7.56	3.09	63.1	0.37	42.8	11.1	63.3
17	4.14	39.7	0.07	7.19	1.45	126	0.15	30.7	3.45	19.5
18	230	2140	0.29	0.77	1.83	8.8	0.37	20.9	1.47	25.2
19	4.04	60.1	0.05	0.66	1.15	8.2	0.30	10.9	0.71	15.3
20	0.15	38.4	0.08	0.51	0.70	29.7	0.28	9.9	2.01	32.8
21	13.6	61.1	0.05	0.88	2.35	11.3	0.56	37.0	5.92	18.5
22	4.96	120	0.06	1.08	3.44	14.4	0.38	28.6	7.93	18.2
23	0.23	32.5	0.05	0.26	0.51	42.0	0.35	10.0	2.26	2.3
24	3.86	94.7	0.06	1.13	5.08	18.4	0.72	93.6	7.43	59.9
25	0.25	41.5	0.10	1.87	4.69	57.8	0.51	23.1	4.31	106
26	0.78	31.1	0.20	0.90	1.52	8.7	0.41	123	0.34	14.1
27	0.50	13.8	0.18	0.38	0.62	5.7	0.36	26.5	0.12	0.9
28	0.41	25.6	0.13	0.52	1.14	15.5	0.44	32.4	1.06	23.3
29	0.54	3.3	0.10	0.17	0.51	4.5	0.22	21.6	0.42	2.3
30	2.52	44.0	0.76	6.98	1.35	10.7	0.33	74.4	2.92	41.6
SW_{GM}	4.05	91.1	0.14	0.93	1.37	22.9	0.34	27.7	1.64	19.5
SW_{min}	0.15	3.3	0.03	0.05	0.25	4.5	0.15	4.6	0.12	0.9
SW_{max}	357	10 900	1.04	7.56	8.60	130	0.72	274	11.1	106
MPC, according to (*SanPiN 2.1.4.1074-01...*, 2002)	100	300	100	100	1000	5000	30	1000	50 000	–
UWLZ according to (Shvartsev, 1998)	59.2	689	0.34	3.45	4.85	42.8	3.10	150	240	440
WR, according to (Gaillardet et al., 2004)	34	66	0.15	0.80	1.48	0.60	0.079	80	4	–

the city, while the contents of these elements in the rest of its territory correspond to the natural background almost everywhere (Fig. 3). The fact that the noted anomalies are not the result of anthropogenic pollution confirms the absence of anomalies of other heavy metals in this region.

The concentration values of the dissolved forms of iron and manganese are closely correlated with each

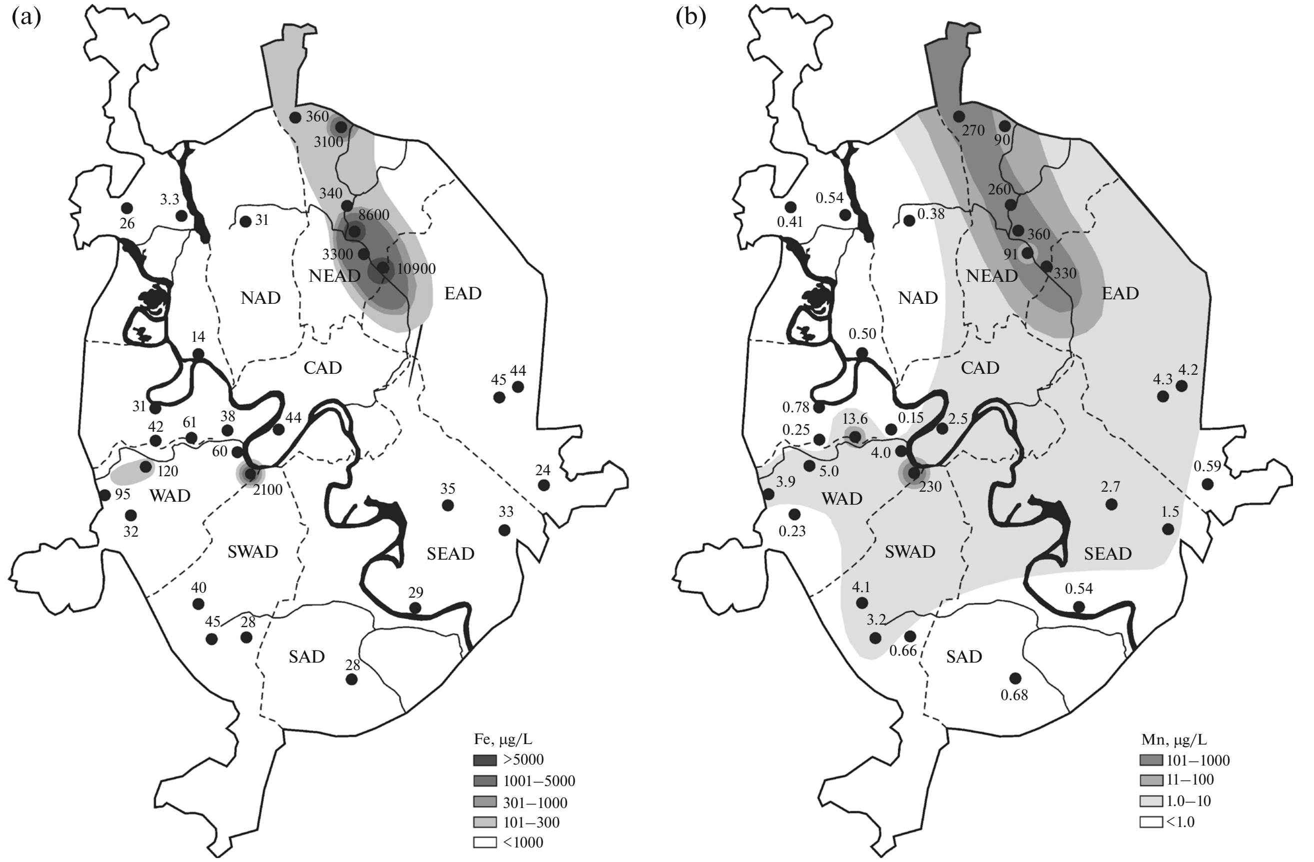

Fig 3. The spatial distribution of the dissolved forms of iron (a) and manganese (b) in the spring waters of Moscow.

other ($r = 0.77$). In addition to the above-described correlations with molybdenum, tungsten, and antimony, the level of iron also correlates with those of sulfates ($r = 0.80$) and uranium ($r = 0.84$), while the manganese level correlates only with the uranium level, moreover, to a lesser extent ($r = 0.72$). The correlation of the iron level with the sulfate level is most likely due to the fact that both components enter underground waters as a result of oxidation of the pyrite in the host rocks, during which sulfates are formed and the acidity of the aqueous medium increases, which contributes to the transition of iron into a dissolved state. For other heavy metals, significant correlations have not been established.

Hydrolyzate Elements (Al, Ga, Ti, Zr, and U)

With the exception of uranium, the contents of hydrolyzate elements in the spring waters are significantly lower compared to their concentrations in the underground waters of the moderate climate leaching zone and in the world river flow (Table 7). The average aluminum and gallium concentrations in the spring waters are 8.7 and 5.6 times lower than in the rivers of the world and almost 2 orders of magnitude (45 and 96 times, respectively) lower than those in the underground waters of the leaching zone. Meanwhile, the Al/Ga ratios do not differ much, and are 680, 320, and 1070 for the spring waters, underground waters of the leaching zone, and river runoff, respectively. Given that the chemical and geochemical characteristics of aluminum and gallium are similar, the latter circumstance can be considered, on the one hand, as an indirect confirmation of the reliability of the analytical data on these elements that are presented in the article, and on the other hand, as evidence of the action of natural factors that determine their low concentration in the spring waters. One such factor may be the contact of the spring waters with carbonate rocks and carbonate-containing sands and clays. The dissolved forms of aluminum and gallium can be effectively sorbed on calcium and magnesium carbonates, while the aluminum and gallium contents in these rocks are known to be sharply reduced compared to other main types of sedimentary rocks.

The titanium and zirconium concentrations in the spring waters compared to their contents in the underground waters of the leaching zone are lower by factors of 7.5 and 70, respectively, while this is close to the average estimates for the rivers of the world, that is, 2.4 times larger for titanium and 1.8 times lower for zirconium. The average uranium level in the spring

Table 7. The contents of the dissolved forms of hydrolyzate trace elements in the spring waters of Moscow

# Point (parameter)	Al	Ga	Ti	Zr	U
	μg/L	ng/L	μg/L	ng/L	μg/L
1	2.35	5.5	1.05	70.4	1.91
2	1.79	11.4	1.26	17.0	4.16
3	2.19	6.2	1.47	16.5	0.01
4	3.63	11.4	1.28	14.7	4.20
5	3.64	9.8	1.15	54.1	17.3
6	1.80	6.7	1.52	25.8	0.01
7	3.63	10.4	0.96	66.8	17.6
8	3.90	13.4	1.13	6.3	0.04
9	5.04	13.9	1.20	13.1	0.07
10	2.72	5.3	0.76	26.2	1.04
11	3.04	5.8	0.92	22.2	1.34
12	5.76	5.4	0.99	33.3	1.29
13	3.02	4.8	0.91	28.7	1.47
14	2.80	4.8	0.83	17.3	1.29
15	4.00	1.6	1.48	6.8	0.45
16	6.12	15.7	1.17	41.3	0.04
17	4.31	13.9	1.11	7.1	0.04
18	4.91	7.3	1.64	42.8	0.34
19	3.02	2.9	1.38	54.3	3.01
20	2.74	2.1	1.71	23.9	2.94
21	5.44	3.5	1.41	13.2	2.86
22	12.3	7.0	1.95	12.3	6.39
23	3.58	2.0	1.37	8.1	1.65
24	24.1	8.7	2.03	28.1	1.25
25	3.62	4.5	1.75	46.4	2.93
26	2.32	3.7	0.98	23.9	1.69
27	2.24	2.5	0.62	10.1	0.54
28	3.00	4.1	0.97	41.4	1.64
29	1.76	0.8	0.41	11.9	0.02
30	5.04	4.1	1.54	19.9	1.76
SW_{GM}	3.66	5.4	1.17	21.5	0.74
SW_{min}	1.76	0.8	0.41	6.3	0.01
SW_{max}	24.1	15.7	2.03	70.4	17.6
UWLZ according to (Shvartsev, 1998)	165	520	8.82	1510	0.51
WR, according to (Gaillardet et al., 2004)	32	30	0.49	39	0.37

waters (0.74 μg/L with an alternation range from 0.01 to 17.6 μg/L) does not significantly differ from the average values for the underground waters of the leaching zone (0.51 μg/L) and rivers of the world (0.37 μg/L).

Similarly to iron, the uranium level is closely correlated with the levels of sulfates ($r = 0.94$) and antimony ($r = 0.81$), which is probably due to the release of these elements from iron oxyhydroxides during dissolution with sulfuric acid that is formed during oxidation of pyrite. There are no significant correlations with the proportions of other hydrolyzate elements.

The MPC for aluminum is 500 μg/L (*SanPiN 2.1.4.1074-01* ..., 2002). The maximum aluminum concentration in the springs of Moscow reaches 24 μg/L, which is 20 times lower than the current MPC.

CONCLUSIONS

The levels of macroelements and trace elements in 30 springs of Moscow during the winter low water period were determined. The geometric mean concentration values and ranges of values for the components of the basic salt composition and silicon are as follows (mg/L): Na^+, 30.0 (5.5–196); K^+, 1.66 (0.74–8.44); Mg^{2+}, 22.1 (2.2–47.9); Ca^{2+}, 68.6 (3.1–159); Cl^-, 72.6 (5.2–500); SO_4^{2-}, 93.0 (19.3–414); HCO_3^-, 140 (81.1–237); and Si, 5.82 (2.49–8.93). The corresponding values for trace elements are as follows (μg/L): Rb, 0.77 (0.26–4.24); Cs, 0.013 (0.001–0.054); Be, 0.0025 (0.0007–0.0107); Sr, 265 (90–858); Ba, 43.3 (4.0–161); B, 22.3 (9.9–76.0); P_{min}, 94.9 (7.4–479); V, 0.38 (0.02–5.82); Cr, 0.87 (0.08–11.3); Ge, 0.016 (0.005–0.145); As, 0.47 (0.09–5.00); Mo, 0.29 (0.03–1.18); W, 0.016 (0.001–0.152); Sb, 0.051 (0.013–0.259); Te, 0.0083 (0.0023–0.019); Mn, 4.05 (0.15–357); Fe, 91.1 (3.3–10 900); Co, 0.14 (0.03–1.04); Ni, 0.93 (0.05–7.56); Cu, 1.37 (0.25–8.60); Zn, 22.9 (4.5–130); Pb, 0.34 (0.15–0.72); Cd, 0.028 (0.005–0.274); Ag, 0.0016 (0.0001–0.011); Sn, 0.020 (0.0009–0.106); Al, 3.66 (1.76–24.1); Ga, 0.0054 (0.0008–0.016); Ti, 1.17 (0.41–2.03); Zr, 0.022 (0.006–0.070); U, 0.74 (0.01–17.6). The measured concentration values are consistent within an order of magnitude with the average levels of the studied elements in the rivers of the world and in the underground waters of the moderate climate leaching zone (for the latter, the estimates for Be, Ag, Sn, and Sb that were obtained earlier using less accurate and sensitive analysis methods are likely to be overstated).

Mineralization of groundwater in Moscow varies over a wide range: from 188 to 1080 mg/L. However, an excess of the MPC for the total amount of salts (1000 mg/L) was found only at two points on the northern outskirts of the city. Mineralization was found to have the closest correlations with magnesium, calcium, and sodium, as well as with chlorides and to a lesser extent with sulfates. In addition, there is a relationship between the concentration of individual macrocomponents: there are correlations of sodium with chlorine, magnesium with calcium, sulfates with magnesium and calcium.

A hydrochemical anomaly of dissolved iron and manganese was shown to exist in the northeast of Moscow; within the area of this anomaly, the excess of the MPC for these elements reaches 36 and 3.6 times, respectively, while the measured concentrations in the rest of the city are at the level of the natural background almost everywhere.

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