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Physicochemical Modelling of Element Speciation as an Addition to a Biotesting Method of Melted Snow Water

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Abstract

Assessment of the chemical composition of snow melt water was carried out in the zone of influence of the aerial technogenic load from the largest source of emissions in the territory of the Murmansk Region that is a copper-nickel combine (Monchegorsk area) of the Kola Mining and Metallurgical Company (Kola MMC). The results of direct analytical determination in the framework of annual monitoring were complemented by the results of retrospective analysis by means of physicochemical modelling (Selektor program complex). The obtained results testify a change in the deportments of elements in snow melt water when decreasing the level of the multicomponent aerial technogenic load after production modernization. The minimisation of dust emissions and an increase in the efficiency of purification of fume gases from sulphurous anhydride contributed to a shift of the redox potential of snow melt water from the negative to positive region and a transfer of some pollutants elements with a variable valence into the oxidized form. A decrease in dust emissions that exerted the alkalinizing effect contributed to an increase in water acidity and consequently, an increase of the proportion in them of the aluminium ionic form recognized most toxic for biota. The sulphates concentration in the atmospheric deposition of the winter season currently does not go beyond All-Russian weighted average concentrations even in the local area of model objects. Increasing the proportion of copper chloride complexes was noted in snow melt water, a basic pollutant, which testifies a possible increase in its migratory activity that is driven by an increasing effect of sea aerosols when softening the regional climate. The practical significance of the work is expressed in an opportunity to reconstruct element speciation in melt water both during retrospective analyses and planning the procedure of biotesting in engineering and environmental survey and monitoring studies.

Key words: aerial technogenic load, Selektor program complex, element speciation

INTRODUCTION

Biotesting of surface water (ponds and water flows) in the area of the planned construction is included in the list of engineering and environmental survey for construction (SP 11-102–97) accepted in the practice of environmental expertise of the RF. Herewith, biotesting of snow melt water is very rarely used. However, their increasing toxicity in industrial and urbanized areas of the RF increases the importance of expanding research methods of winter precipitation [1–4]. The leading enterprises of oil and gas complex of the RF even include this type of analysis into the corporate environmental management system [5]. Laboratory experiments demonstrated that 50–80 % of mass of pollutants accumulated in the snowpack moved to the mass flow of the first 30 % of snow water, which exerts intensive effects on biota [6]. Thus, episodic acidification of small watercourses was noted during spring tide even at the territories poorly prone to aerial technogenic influence. This fact is widely known in Europe, Canada and the USA [7], the problem is also relevant in the Kola North [8], and the fact itself is called sometimes acid shock [9]. The areas, where snow nutrition of surface water is dominating, could become some sort of model areas of the RF, where large-scale biotesting of melted snow water is advisable to conduct. The Murmansk Region could be proposed as one of such regions of the RF. Extraction and processing of copper-nickel, iron, apatite nepheline ores, as well as ores of rare and scattered elements are carried out in its territory. The maximum number of days with adverse weather conditions (AWC) at the territory of the Murmansk Region falls on the cold season: January, February, March, November, and December [10], when the role of snowpack as deposit environment is large. Periods of AWC (surface inversion, calm and fog, stagnant air combined with unfavourable winds directions) contribute to accumulation and an increase in the content of pollutants in the atmospheric air.

Enterprises of the Kola Mining Metallurgical Company (Kola MMC or KMMC) of the MMC Norilsk Nickel JSC are the major source of air industrial pollution in the Murmansk region. Modernization of manufacture at Severonikel Combine (Monchegorsk area now) allowed minimizing dust emissions. The closure in 1998 of a workshop of smelting copper-nickel ore contributed to the reduction in emissions of the main pollutants in the indicated area in the period from 1990 to 2009: SO_2 (kt) – from 232.5 to 33.5 (6.9 %); Cu (t/year) – from 1813 to 439.3 (4 times); Ni (t/year) – from 2712 to 387 (7 times) [11]. It is known that the major mass of metals is contained in emissions of metallurgical productions in so called sublimates formed during condensation of powder-gas emission on particles of submicron dimensions [12]. From here, the major part of pollutants continues to be in the composition of a water-soluble fraction of melted snow water (Table 1) and assessment of its potential toxicity is a relevant issue until presently.

Mention should be made that water toxicity detected by biotesting methods is an integrated index, and consequently, cannot qualify for

TABLE 1

Characteristics of monitoring sites

Characteristics	Site number					
	1	2	3	4	5	6
Coordinates	67°51.08′N 32°47.49′E	67°49.72′N 32°46.03′E	67°39.92′N 32°47.29′E	67°38.21′N 32°42.19′E	67°22.84′N 32°26.02′E	66°57.17′N 29°36.65′E
Height above sea level, m	240	215	298	162	170	242
Distance from a source of emission, km	7	10	28	31	100	260 (Background)
Amount of precipitation in winter*, mm	154/182	225/213	260/243	235/196	181/164	N. D./170
Chemical composition of snow melt water, μg/L:						
Cu	116±119 52±70	97±106 33±34	37±48 8±9	7±6 3±4	7±6 2±2	2±1 1±1
Ni	98±68 141±153	70±52 88±70	16±10 11±9	9±8 8±15	2±2 2±3	0.5±0.3 0.5±1.0
Fe	36±17 14±13	303±876 10±10	24±16 5±4	25±9 3±3	25±14 5±4	14±9 3±2
Al	16±13 14±12	33±36 10±8	12±8 12±8	22±19 8±9	38±21 34±40	24±24 5±5
SO_4^{2-}	1856±349 1410±754	1603±531 1240±391	1537±534 912±331	1012±315 677±219	1208±599 734±628	605±110 455±389
Cl^-	867±369 951±637	979±483 1240±676	922±575 706±418	807±681 636±332	822±533 576±263	490±20 321±120

Note. 1. In the numerator – annual snow sampling results, 1995–1999, in the denominator – 2000–2013. 2. N. D. – not determined.

* The first value – the data of 1995, second – 2013.

universality and commonality. Firstly, stimulation that is a positive reaction of a test object for the water sample tested containing toxicants may be noted. This is especially relevant, if high contents of biogenic elements characterize the sample. Secondly, a solution of a model toxicant (as a rule, a certain heavy metal sulphate) is usually used when determining sensitivity and response range of a test object. This does not guarantee an adequate response of organisms for other toxicants, much less, for their mixtures present in the sample, what is met more often in practice. Thirdly, a change in climatic factors marked in many regions of the RF may prove a trigger mechanism of an increase in bioavailability of pollutants even under conditions of aerial technogenic load reduction. It is desirable to add biotesting results by other methods for conduction of environmental assessment in such situations, for example, retrospective and prognosis assessment of element speciation by physicochemical modelling (PCM).

The purpose of this study is assessment of element speciation in melted snow water with different levels of multicomponent aerial technogenic loads from a selected model object (Monchegorsk area) for further planning of an in-depth assessment procedure of water toxicity.

EXPERIMENTAL

A network of monitoring sites, located at different distances from the Monchegorsk area along the southwest gradient has existed at the Institute of the Industrial Ecology Problems of the North of Kola Science Center RAS since the early 1990s. The location of monitoring sites relatively to a source of emissions is given in Fig. 1, and main characteristics of the sited –

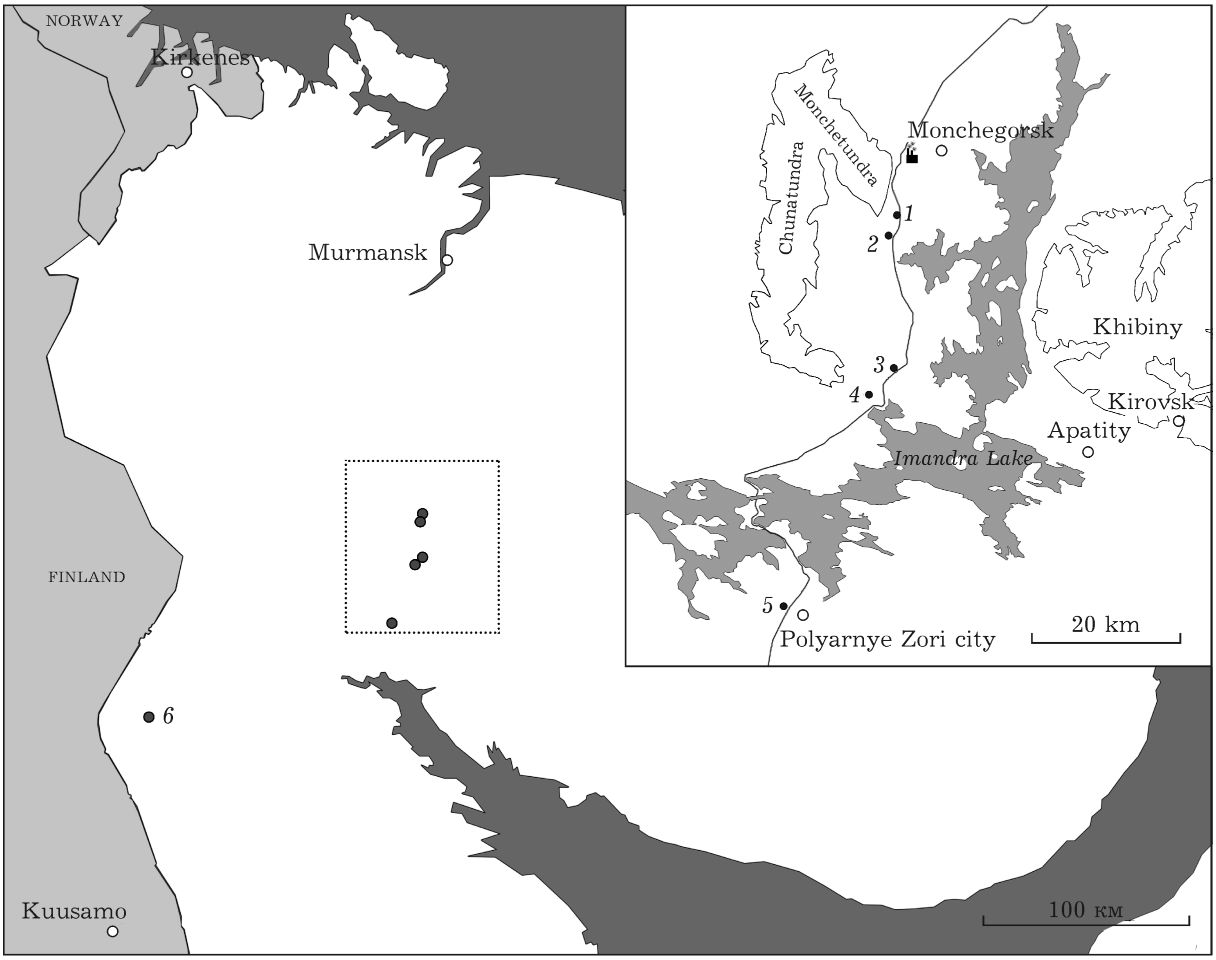

Fig. 1. Location of monitoring sites on the territory of the Murmansk Region.

in Table 1. The obtained results of monitoring studies are divided by us into two periods: 1995–1999 and 2000–2013 (before and after a sharp decline in emissions of major pollutants at the industrial site).

Snow survey (snow core sampling) was carried out annually during maximum snow accumulation (early in April) in three repeats. A sampler represents a tube of plexiglass with a diameter of 11 cm. Right after unfreezing of samples and bringing the tube temperature to that of the laboratory room, pH of water was determined by the potentiometric method without preliminary filtration. Afterwards, each sample was filtered off through a paper blue ribbon filter (pore diameter of 1–2.5 μm). Analysis of the filtrate was performed by the methods of atomic emission (K, Na) and atomic adsorption (Ca, Mg, Zn, Mn, Cu, Ni, Al, Fe) spectrometry of total P, P of phosphates, Si and NH_4^+ – by a photocolorimetric method of total carbon, total carbon - by the dichromate or permanganate method, the determination of the anionic composition of water including NO_3^-, SO_4^{2-} and Cl^- – by an ion exchange chromatographic method. The spatial and temporal variability of hydrochemical characteristics of melt waters most significant for description of the results of PCM are given in Table 1.

To determine element speciation in this work a Selektor 2007 program complex (SC) was used [13, 14]. The incorporation of developed long-term experiences on using this SC in environmental research, as well as intricacies of building a model for melted snow water were given by us in work [15]. This work selected for PCM the results of analytical determination of water according to two key periods: 1995 and 2013. Retrospective analysis results of element speciation carried out by PCM are given in Table 2.

RESULTS AND DISCUSSION

Acidity of melted snow water

Despite a high level of aerial technogenic loads in 1990th during the indicated period was not an expressed trend of relevant acidity (pH increase) of melted water when removing from a source of emission of sulphurous acid anhydride that is a major acid-forming component in the composition of emission. A weak transition (oxidation) of SO_2 into H_2SO_4 is recognized as the main cause in winter [16]. After a significant decrease of SO_2 emission, acidity of snow water remained in the framework of the interannual variability in all areas, except for the local zone (7 km from a source of emission, see Table 1). A possible cause of the reduction in the water pH in this area may be weakening of the alkalizing action of dust emission occurred after manufacture modernization. The impact was mainly driven by the presence of oxides of alkaline earth elements in emission as impurities.

Aluminium speciation

The content of water-soluble fractions of aluminum in melted water in all monitoring sites did not exceed 40 μg/L that is its concentration in water is quite far from the toxic level. For example, aluminum toxicity in respect to phytoplankton in work [17] was detected only with a concentration of this element of 300 μg/L and the pH of water of 8.5. However, aluminium speciation in melt waters receives our attention, since this element has capacity for forming anion complexes with heavy metals. This may contribute to an increase in the migratory activity of the latter, and consequently, to the enhancement of the toxic action of water on biota.

When analysing Al forms in the composition of natural water high priority is focused on its presence as Al^{3+}, since this form is most toxic for biota. When analysing on plant tests yet $Al(OH)^{2+}$ is added to the most toxic forms [18]. Our modelling results demonstrated the significant spatial and temporal variability of the proportion of this Al form in the zone of influence of aerial technogenic load; moreover, forms redistribution depended to a large extent on acidity of heavy water, because of the amphoterism of aluminum. The content of ionic aluminium forms in the background territory with the lowest acidity of melt waters was minimum (no more than 20 %). The acidity of melt waters in the local zone of influence increased after load reduction (a decrease of pH from 4.68 in 1995 to 4.60 in 2013 was marked). Herewith, the proportion of ionic aluminium forms increased from

TABLE 2

Fractional distribution of heavy metals and Al in melt water on the main chemical forms

Parameters	Site number, distance from a source of emission			
	No. 6 (260 km)	No. 5 (100 km)	No. 4 (31 km)	No. 1 (7 km)
pH	5.32	4.82/5.23	4.79/4.90	4.68/4.60
E_h, V	−0.06	0.93/0.89	0.93/0.92	−0.01/0.93
Fraction, %:				
Al				
AlO_2^-	0.5	0.01/0.3	0.01/0.03	0.01/*
$HAlO_2^0$	6.6	0.6/4.9	0.5/0. 9	0.5/0.2
$Al(OH)^{2+}$	45.9	39.1/47.3	37.7/42.0	37.8/29.7
$Al(OH)_2^+$	22.3	6.0/19.2	5.4/7.7	5.3/2.8
$Al(OH)_3^0$	4.7	0.4/3.4	0.3/0.6	0.3/0.1
$Al(OH)_4^-$	0.4	0.01/0.2	0.01/0.02	0.01/*
$AlSO_4^+$	*	0.03/0.02	0.02/0.02	0.1/0.1
$Al(SO_4)_2^-$	*	*/*	*/*	*/*
Al^{3+}	19.9	53.9/24.7	56.1/48.7	56.1/67.2
Cu				
Cu^+	99.8	*/*	*/*	99.60/*
Cu^{2+}	0.02	99.9/99.8	99.9/99.9	0.1/99.9
$CuOH^+$	*	0.1/0.2	0.1/0.1	*/0.1
$HCuO_2^-$	–	*/*	*/*	–/*
$CuCl^+$	*	*/0.01	*/*	*/*
$CuCl_2^0$	–	*/*	*/*	*/*
$CuCl^0$	0.2	–	–	0.3/*
$CuCl_2^-$	*	–	–	*/*
$CuCl_3^{2-}$	*	–	–	*/*
Ni				
Ni^{2+}	99.97	~100.00/~100.00	~100.00/97.10	~100.00/~100.00
$NiOH^+$	*	*/*	*/*	*/*
NiO^0	*	*/*	*/*	*/*
$HNiO_2^-$	–	–	–	–/*
Fe				
Fe^{2+}	99.95	*/*	*/*	99.9/*
$FeSO_4^0$	0.04	*/*	*/*	0.1/*
$Fe(OH)_3^0$	*	0.3/0.6	0.2/0.3	*/0.2
$FeSO_4^+$	–	*/*	*/*	*/*
$Fe(OH)_4^-$	–	*/*	*/*	*/*
Fe^{3+}	–	0.01/*	0.01/0.01	*/0.03
$FeOH^{2+}$	*	4.0/1.5	4.2/3.2	*/6.4
$FeOH^+$	0.01	*/*	*/*	*/*
FeO^+	*	93.1/90.9	93.0/93.2	*/91.8
$HFeO_2^0$	*	2.7/6.9	2.5/3.3	*/1.6
FeO^0	*	–	–	*/*
FeO_2^-	–	*/*	*/*	*/*
$FeCl^+$	*	*/*	*/*	*/*
$FeCl^{2+}$	–	*/*	*/*	*/*
$FeCHO_2^+$	*	–	–	*/*

Notes. 1. The first value – the data of 1995, second – 2013. 2. Dash – not detected.

* Less than 0.01 %.

56 to 67 %. It may be assumed that such a high proportion of aluminum cations with $pH < 5$ is driven by limited complexation with functional groups of weak acids. When increasing solution acidity, the dissociation degree of such groups decreases.

When increasing a pH of water the binding degree of metals into complexes increases, however, herewith, a competing action of hydrolysis processes could become apparent, especially, in case of polyvalent cations. Our modelling results confirm such an opportunity: there is redistribution of the forms to the side of increasing the fraction of Al in the molecular form ($Al(OH)_3$, $HAlO_2$) and in the form of hydroxyl complexes of $Al(OH)_2^+$ and $Al(OH)^{2+}$ at sites where a reduction in acidity happened after a decrease in load. Since pH values did not cross to the alkaline region (remained lower than 6), the proportion of aluminium anionic forms Al (AlO_2^- , $Al(OH)_4^-$) remained an insignificant value.

Redox potential (E_h)

The hydrochemical composition of snow cores is determined after bringing the selected sample to the liquid condition under laboratory conditions. Herewith, water aeration conditions are unambiguously changed; therefore, analytical determination E_h of snow melt water does not make sense. To reconstruct true values of E_h and the effect on element speciation PCM were also successfully applied by us, modelling results are given in Table 2. The obtained modelling results of E_h for samples of selection of 2013 under background under conditions particularly noticeable and of 1995 in the local zone of a model objects, precisely, negative values of this indicator. It is our belief that the compounds determining the formation of reductive conditions at these sites significantly spaced-apart in the spatial respect are also different. Monoterpenes that are recognized some of major organic compounds emitted into the atmosphere by boreal forests may be offered as compounds with a reductive function under baseline conditions. These compounds are reliably identified in the composition of the snowpack at the adjacent territory of Finland [19]. As for the local zone (7 km from a source of emissions) intensive emission of sulphur dioxide were a more probable cause of the formation of the reducing medium in the snow thickness during the active industrial development. The effect of its frosty condensation under Arctics conditions and accumulation even in background areas in volumes comparable with technogenic emission was described in [20]. Reduction of SO_2 emission after manufacture modernization and probably softening of climatic conditions in winter at the territory of the region contributed to the formation of the oxidizing medium in the snowpack in all sites removed more than on 30 km from a source of emission.

Sulphates

The sulphate load onto the region territory was and remains quite high, but it does not testify the increased regional background during winter. After comparison with background monitoring data of atmospheric emission in the RF [21], it could be argued that the concentrations of sulphate in the atmospheric fallout of the winter period do not go beyond the All-Russian weighted average concentrations (1.19–3.25 mg/L) even in the local zone of a model object. This is driven by both weak transformation of sulphur dioxide into sulphuric acid and its transfer over considerable distances from a source of emissions. The significance of sulphate complexes in the composition of snow melt water is almost not expressed: no more than 1 % of Al and Fe is bound with them, their proportions by other elements go beyond the significance (see Table 2).

Speciation of iron, copper and aluminium

It is known that Cu and Ni are characterized by high complexation ability, but other complexing agents, such as Al and Fe exert the competing effect for the availability of complexes. Perhaps, the formation of Cu and Ni complexes in water studied by us was not noted precisely on this reason. A change in E_h of the solution changes speciation of elements with variable valency, such as Fe, Cu, Ni. The dominant form of copper migration at those monitoring sites, where reductive conditions are formed, is Cu^+ (>99 %). When forming oxidizing conditions this basic pollutant is present in water as divalent ions (in the highest oxidation degree). A change in E_h or pH exerts weak effects for nickel speciation: this element dominates in the solution as ions in the highest oxidation degree of the metal during all periods in melt waters. Thus, it was demonstrated in work [22] that a steady state zone of Ni^{2+} in natural water spread up to pH ~ 9.

A particular attention was paid by us to migration forms of iron, since this element plays one of the key parts in geochemical cycles of many elements. A wide variety of speciation (ionic and molecular) was marked in our studies for it, as well as for Al in melt waters, however, FeO^+ и $HFeO_2^0$ were the dominating forms. As and in respect of Cu, redistribution of Fe (III) speciation is assumed to the side of the predominance of the reduced form (Fe^{2+}) after E_h decrease (see Table 2). A part of iron is presented as hydroxy complexes, as well as sulphate and chloride complexes, however, their proportion is negligibly low. Iron (III) hydroxide forms ($Fe(OH)_3$, $HFeO_2$) are poorly soluble in water but easily form colloidal solutions, which means have high adsorptive capacities in respect to pollutants. An increase in the proportion of these forms in melt waters most noticeable in the zone of weak aerial technogenic load (100 km from a source of emission) was marked by us in 2013. This may contribute to the enhancement of the technogenic effect of snow water for reservoirs and watercourses even after emission reduction.

Overlapping effects of climatic factors on ion composition (on example Na^+ и Cl^- ions)

Our results of PCM demonstrated that Na as an alkaline element is present in melt water mainly as free (hydrated) ions (over 99 % along all the studied sites). Domination of an ionic bond of s-elements and weak complexation drive this. It is noteworthy that an increase in the sodium concentration in snow melt water is obvious during 2000–2013 with a significant interannual variability of the content of chloride ions. Perhaps, this is due to an increase in cases of storms and a transfer of NaCl in the composition of sea aerosols from the surface of the Barents and White Seas. The area of ice cover of the White Sea and its duration invariably decrease beginning with 1987 with a linear trend of 209 km^2 and 2.2 days a year, respectively [23]. Ice cover after 2007 became seasonal in much of the Arctic Ocean, *i.e.* the area annually purified from ice steadily exceeded 50 % [24]. A proportion of chloride complexes of the major pollutant (Cu) became to increase in snow melt water, which testifies a possible strengthening of its migratory activity when increased influencing of sea aerosols (see Table 2). The marked trend is an example of the combined effect of climatic changes and anthropogenic load; however, the issue requires more detailed research.

CONCLUSION

The feasibility of including studies by the PCM method into the plan of monitoring the effect of operating manufactures for the environment was confirmed on the selected model object under the conditions of changing aerial technogenic load and climatic factors. The PCM method can be proposed as a complementary method when planning the in-depth biotesting procedure for toxicity of surface water when carrying out engineering and environmental survey in the areas scheduled for the construction.

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