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Long-Term Changes in the Water Chemistry of Arctic Lakes as a Response to Reduction of Air Pollution: Case Study in the Kola, Russia

Tatiana Ivanovna Moiseenko · Marina Ivanovna Dinu · Maria Mihailovna Bazova · Heleen A. de Wit

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Abstract Sixty years of air pollution from two Cu-Ni smelting plants ("Pechenganikel" and "Severonikel") in the Kola region in northwest Russia have posed a severe threat for water quality, specifically acidification, in subarctic lakes. In the last two decades, emissions of SO2, Cu and Ni from the smelters have declined with 33 %, 40 % and 36 %, respectively. The 75 lakes in Kola Peninsula were sampled with 5-year intervals for the period 1990 to 2010. In addition, were analysed for major anions and cations, DOC and heavy metals. The lakes were grouped according to geology and distance to emission sources into 6 subregions. The most acid-sensitive lakes are located on granites, quartz sands or in highlands. Since 1990, ANC has increased, which is connected to the reduction of the contents strong acids in water (sulphate, chloride) while base cations concentrations have been almost unchanged. Despite the reduction of sulphate, concentrations of alkalinity have not increased in lake water. We have found an increase in concentration of dissolved organic carbon (DOC) and nutrients in Kola lake waters over a 20-year period. We suggest this phenomenon can be explained by two mechanisms: a reduction in deposition of strong acids and warming climate. Concentrations of Ni and Cu have decreased 5-10-fold over the last 20 years. We conclude that reduced emissions from Cu-Ni smelting plants has led to improved water quality in the Kola region.

Keywords Water chemistry · Cu-Ni smelters · Acidification · Metal pollution · Recovery

1 Introduction

Air pollution can pose a threat to water quality because of deposition of pollutants and leaching of acidifying components and heavy metals from soils to surface waters. In North America and Europe, emissions of SO_2 and heavy metals began to decrease in the mid-1980s of the last century because of policy to reduce air pollution. Surface waters began to recover from acidification in many acid-sensitive areas in Europe and North America as response to reduced SO_2 emissions (Stoddard et al. 1999; Evans et al. 2001; Driscoll et al. 2003; Skjelkvåle et al. 2001a, 2005; Garmo et al. 2014). So far, few data on surface water quality from areas in Northwest Russia that were heavily impacted by pollution from copper and nickel smelters have been documented. However, water chemistry responses to air pollution may be slow and not directly proportionate to the reduction in deposition. There are three scenarios of water chemical changes: (i) Further water acidification is progressing, (ii) pH and alkalinity levels remain the same, and (iii) lake's water chemistry recovery. Differences in recovery of water quality to reduced sulfur deposition depend on catchment characteristics, especially base cation stores and buffering

T. I. Moiseenko (✉) · M. I. Dinu · M. M. Bazova
V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of RAS,
Moscow, Russia
e-mail: moiseenko.ti@gmail.com

H. A. de Wit
Norwegin Institute for Water Research (NIVA),
Oslo, Norway

capacities. These are in turn affected by geology and soil thickness. For example, Skjelkvåle et al. (2001a) documented trends in water chemistry from lakes and streams in Europe and North America, where water chemical recovery was most rapid in regions dominated by granite rocks and thin soils. Several studies have investigated the general trend in changing of other water chemical parameters (lakes and rivers of Europe and North America). In such studies was proved the increase in total organic carbon (TOC) (Evans et al. 2001; Stoddard et al. 1999; Skelkvale et al. 2005; Monteith et al. 2007).

In Northwest Russia, acidification and soil and water pollution have occurred in the Kola region, related to emissions from two large Cu-Ni smelting plants—"Pechenganikel" and "Severonikel." These production facilities are situated in the western part of the Kola region and have emitted SO_2 and heavy metals for more than 60 years. These atmospheric emissions have resulted in high concentrations of anthropogenic SO_4^{2-} and heavy metals in surface waters, and acidification of streams and lakes (Moiseenko 1994, 1999, 2001).

In the present study, we aim to investigate the trends water chemistry, including major cations and anions, dissolved organic matter, and nutrients, in lakes in the Kola region, affected by air pollution from the Cu-Ni smelters, for the period of 1990 to 2010. In addition, we aim to assess the recovery of water chemistry from acidification. The lakes are grouped into six subregions, which differ in distance to the smelters and in sensitivity to acidification. The trends will be presented against the background of changing emissions from the smelters and climate change.

1.1 Here We Present the Results of Solving the Following Problems

To assess the changes of water chemical composition over the last 20-year period, to identify the main tendencies of the water chemistry changes of subarctic lakes as response to decreasing emissions, and to assess the recovery of the lake water chemistry.

2 Materials and Methods

2.1 Study Area

The Russian part of the Euro-Arctic region (the Kola region) is situated above the Article Circle and is included in two geographical zones: tundra and taiga. In the north, it borders with the Barents Sea and in the south and east with the White Sea. The eastern part is called the Kola Peninsula (approximately two thirds of the territory), and the western part of the Kola region is represented by mainland Scandinavian Shield.

The Kola region is most densely populated and industrially developed among the Arctic regions. Considerable industrial expansion in the early 1930s resulted in building of large industrial enterprises in the region. Industrial development of copper-nickel deposits in the Kola region began in the 1940s. Large amounts of pollutants were polluted by airborne contaminants. The main pollutants were heavy metals (predominantly nickel and copper) and sulfates. The main pollution occurred in the northern-western part of region due to emissions of the plant Pechenganikel (on the border with Norway), and in central parts of the region. In the period of 1970–1990, annual emissions of dust from the smelters were up to 64,000 t/year, including up to 3000 t/year of Ni and 2000 t/year of Cu during the 1980s. In addition to the metal pollution, SO_2 emission was about 500,000 t/year in 1987–1990s (Moiseenko 1994). Deposition of anthropogenic sulfur in 1980–1990 was over 3 g S m^{-2} $year^{-1}$ in the areas of distribution of smoke emissions from smelter and less than 0.3 g S m^{-2} $year^{-1}$ in eastern part of Kola Peninsula (Moiseenko 1994).

The geology of the Kola Peninsula has a high variation, from basic to ultrabasic rocks to granites and gneisses, which strongly affects the sensitivity to acidification and thus the vulnerability of surface waters to acid deposition. We identified six subregions with differing sensitivity for acidification, grouped according to the distance from the smelters, geology, and landscape (Fig. 1).

Region I is located around the smelting of copper-nickel production within a radius of 30 km in the northwest around "Pechenganikel," near the Norwegian border and in the central part of the region, Severonikel, near Khibiny mountain. The geological structure is mainly represented by complex metamorphic rocks and ultrametamorphic: biotite gneisses, amphibole-pyroxene gneisses, and granodiorite gneisses in the northwestern part of the region in the zone of influence of the smelter Pechenganikel (Pogilenko et al. 2002). Soils are generally thin, including peat-gley soils with sphagnum and illuvial humus podzol soils. In the area of the plant Pechenganikel are concentrated three large

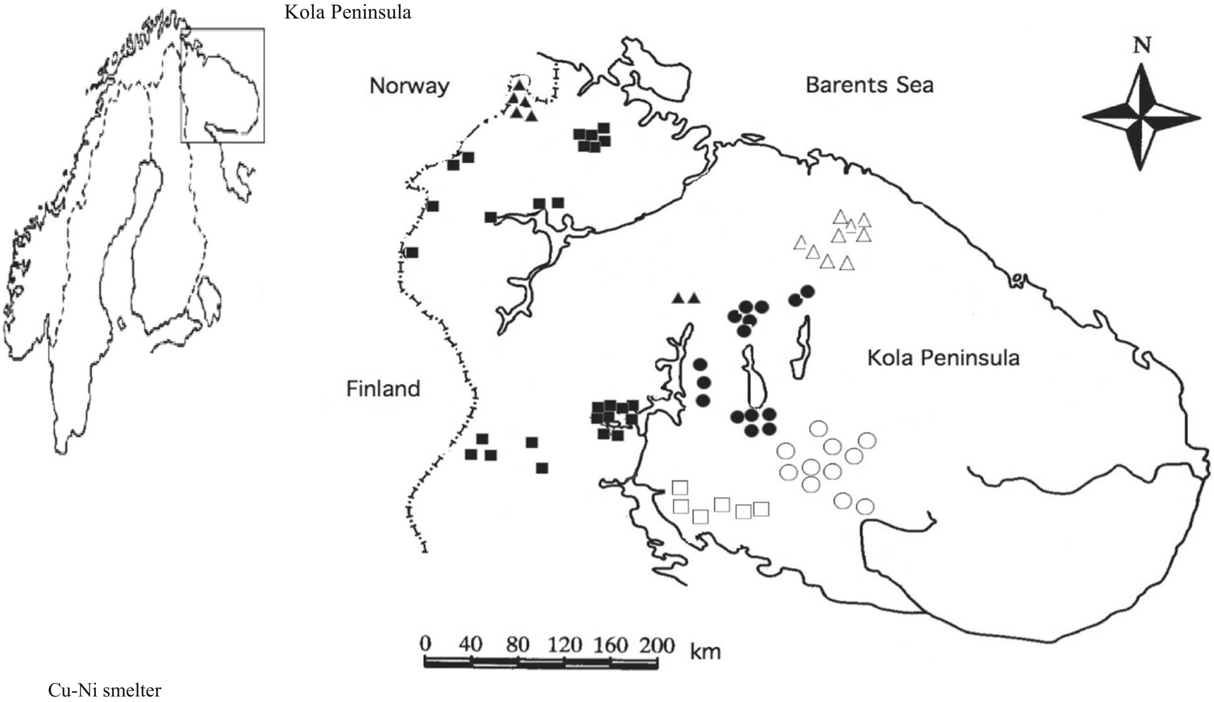


Fig. 1 The scheme of the investigation of small lakes in the Kola Region

copper-nickel deposits. In the central part of region I (where the smelter Severonikel is located), the geological structure is mainly represented by gneisses, amphibolites, and ferruginous quartzites. The Monchegorsk deposits (Cu-Ni ores) are located in the central part of region I (Pogilenko et al. 2002).

Region II is located 30 to 100 km from the smelter and covers the northern taiga and tundra. The geological structure is represented by complex rocks of acid and intermediate composition. The northern part of the territory is composed of acid granulites, basic granulites, and intermediate granulites. The southwestern part of this area is represented the rocks of the Upper Archean formations: biotite gneisses, amphibole-pyroxene gneiss, and garnet-micaceous gneiss. Sixty percent of region II is forested. Fifteen percent of region II is covered by illuvial humus shallow soils (Pogilenko et al. 2002).

Region III covers the taiga zone and located on the territory of the alkaline massifs of the Khibiny and Lovozero mountain tundra. This area is characterized by a series of lithological features, a variety of rocks, and large fragmentation of the topography. The predominant rock types are gabbro-amphibolites, alkaline granites, and syenites. The soils include peat-gley with sphagnum peat soils and herbal peat, and shallow illuvial humus (ferrous) podzols. The main minerals in the Khibina area are complex phosphorus apatite-nepheline ores (Pogilenko et al. 2002).

Northeastern tundra (region IV) is located at a distance of over 100 km from the smelters. The geological structure is acid rock outcrops of granites, diorite, leucogranites. Here there are peaty-gley with sphagnum peat soils and herbal peat, and tundra illuvial humus podzol soil and indigenous crystalline rocks, which often come to the surface.

Taiga zone (region V) is located at a distance of over 100 km from the smelters. The geology is mainly confined to quartzites and sandstone.

Region VI consists of forests and wetlands located more than 100 km from the smelter. The predominant types of geological structure of the region are granites, plagiogranites, tonalite, and acid and basic granulites. The southern part of the territory is composed of basic, average, and acid metavulkanites. The presence of peaty-gley with sphagnum peat soil and herbal peat are responsible for the enrichment of water humus substances.

Winter conditions in subarctic Kola region have an impact on water quality: atmospheric deposition accumulates in the snowpack during the long polar winter (6–7 months) and acidified snowmelt water is released into the drainage basins during the short spring-flood period. The water supply to lakes and rivers is mainly controlled by precipitation, and not by groundwater, because of thin soil cover.

2.2 Water Sampling and Analytical Analyses

The 75 lakes are a subset of a lake survey in the Kola region, conducted in 1990 (Moiseenko 1994). In 1995, the 75 lakes were resampled as part of the Northern European Lake Survey (Henriksen et al. 1998). From 2000, the lakes were investigated at 5-year intervals (2000, 2005, and 2010), using the same methods as those applied in 1990 and 1995. The map of the region, location of the smelters, and sample points are shown in Fig. 1.

The selected lakes range from 0.4 to 20 km^2 in surface area and do not have direct sources of anthropogenic pollution in their catchments. Water samples were transported to the laboratory as soon as possible (within 2–5 days). To minimize the effect of interannual and seasonal variations, sampling was carried out after autumn turnover (from September for tundra lakes to late October for taiga lakes).

All samples were analyzed using the techniques outlined in the Standard Methods for the Examination of Water and Wastewater (Eaton et al. 1992). Parameters determined included pH, cations, anions, conductivity, alkalinity, NH_4^+, PO_4^{3-}, Si, total N (Ntot), total P (Ptot), and dissolved organic carbon (DOC). pH and conductivity (20 °C) were measured using a Metrohm pH meter, alkalinity using the Gran titration method, and DOC using the Mn oxidation method. Cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) were measured using flame atomic absorption spectroscopy (FAAS), and anions (SO_4^{2-}, Cl^-, NO_3^-) were measured using ion chromatography. Si, total N, PO_4^{2-}, and total P were analyzed using spectrophotometric methods.

Al, Cu, Ni, Zn, Cd, and Pb were determined using atomic absorption spectroscopy (GFAAS, model PerkinElmer 5000, Corp., Norwalk, USA) equipped with a graphite furnace HGA-400 and a hydride system MHS-10. The quality of the analytical results was repeatedly tested by annual intercomparison within the framework of the "International Cooperative Program on Assessment and Monitoring of Acidification of Rivers and Lakes" (Intercomparison 2010). Base cation concentrations are expressed in μeq L^{-1}. Water acid neutralizing capacity (ANC) was calculated without correction for sea salts, using the following system:

$$\mathrm{ANC} = \left[\mathrm{Ca}^{2+}\right] + \left[\mathrm{Mg}^{2+}\right] + \left[\mathrm{Na}^{+}\right] + \left[\mathrm{K}^{+}\right] + \left[\mathrm{NH_4}^{+}\right] - \left[\mathrm{SO_4}^{2-}\right] - \left[\mathrm{NO_3}^{-}\right] - \left[Cl^{-}\right]$$

To assess the anthropogenic sulfur (SO4*) concentrations, total lake SO_4^{2-} concentration was corrected by deducting sulfates of sea salt. Mathematical data processing was accomplished using the computer program "Statistika 6." The trends in water chemistry parameters for each region were evaluated based on the calculations of reliability differences by Fisher between 2010 and 1990. The significant change between 1990 and 2010 was estimated by significant differences, where significant differences accepted in the parameter were $p \leq 0.01$ and $n = 75$.

3 Results

Since 1990, the anthropogenic impact on the lakes has decreased due to technological modernization and stricter controls of pollutant emissions into the atmosphere. Over the last 30 years, S-emissions have decreased substantially (by 2000 t). Figure 2 shows the reducing emissions from smelters in last periods. Deposition of technogenic sulfur in 2010 was estimated as 0.2–0.4 g S/m^2/year according to the station on the border with Finland (station Rayakosski) (Over review.., 2010). Precipitation of nickel decreased by 40 % and copper by 35 % compared with 1990, and in the period of 1990–2000, emissions decreased by more than two times; then, in 2000–2010, by another 10–15 % (see Fig. 2).

The dominant ions in tundra and forest tundra lakes are Cl^- and Na^+ due to the influence of sea salt aerosols from the Barents Sea. Marine influence drives the natural SO_4^{2-} and Cl^- content of these lakes. SO_4^{2-} of anthropogenic origin from the atmospheric deposition also plays an important role due to Pechenganikel and Severonikel.

The majority of the lakes in the Kola regions are oligotrophic, with low concentrations of nutrients (P and N species). The concentrations of nutrients in mineral forms were relatively low: Concentrations of PO_4^{3-} were from 0 to 6 μg L^{-1} P, NO3$^-$, and NH_4^+—within the range of 0–3 μg L^{-1} N. Mineral phosphorus concentrations were equal to zero in most of the lakes (Moiseenko

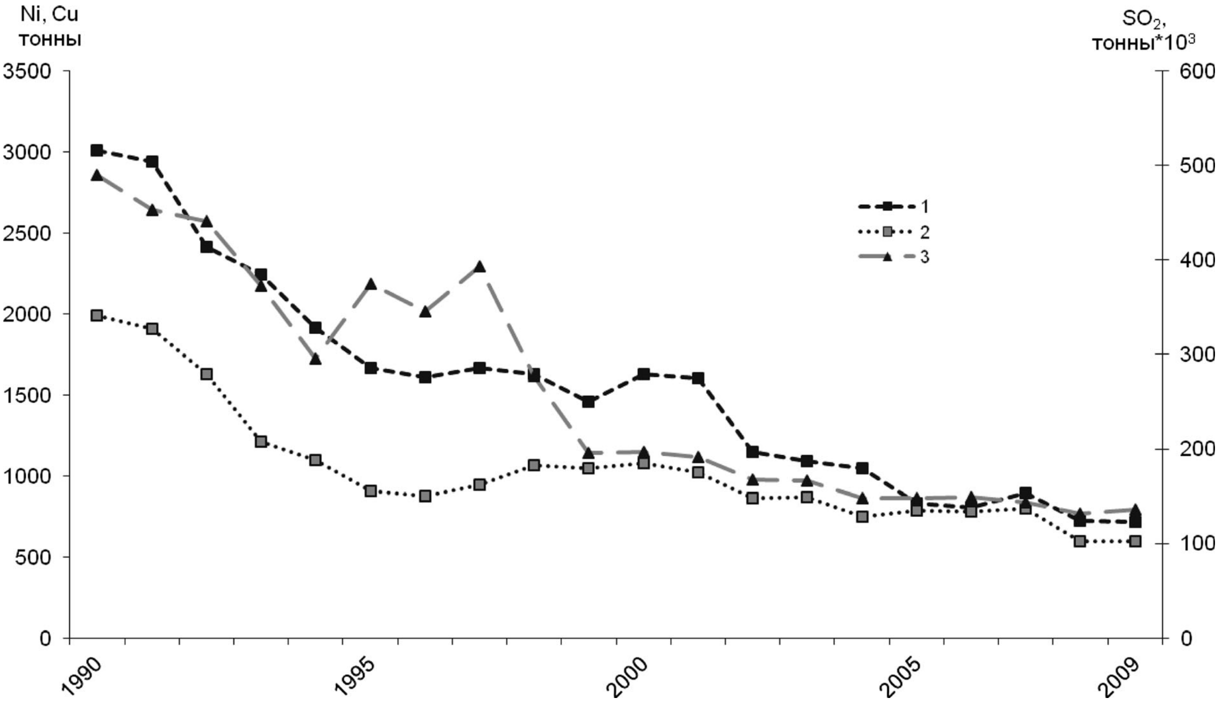


Fig. 2 Emissions from Ni-Cu smelter in the Kola Region: *1*=Ni and *2*=Cu (tons per year), and *3*=SO_2 (thousand tons per year)

et al. 2013). Ni and Cu are primarily airborne contaminants from Kola Cu-Ni smelters.

The distribution of the general water chemistry parameters in investigation period is shown in Fig. 3. The following significant trends in water chemistry were found for the period of 1990 to 2010: a decrease of anthropogenic SO4*, Ni, and Cu (*p=0.001)* and an increase of DOC (*p= 0.01*), P_{tot}, and N_{tot} ($P \leq 0.01$). In 34 % of the lakes, SO_4^{2-} dominated among anions in the 1990s. By 2010, its number dropped to 25 %.

To assess the sensitivity of the lakes to chemical recovery, the 75 lakes were divided into six subregions which contrasted in geology and distance to the emission sources. Table 1 shows median values of water chemistry for the specific years of investigation in the six subregions. Significant differences between 1990 and 2010 are shown in Table 2.

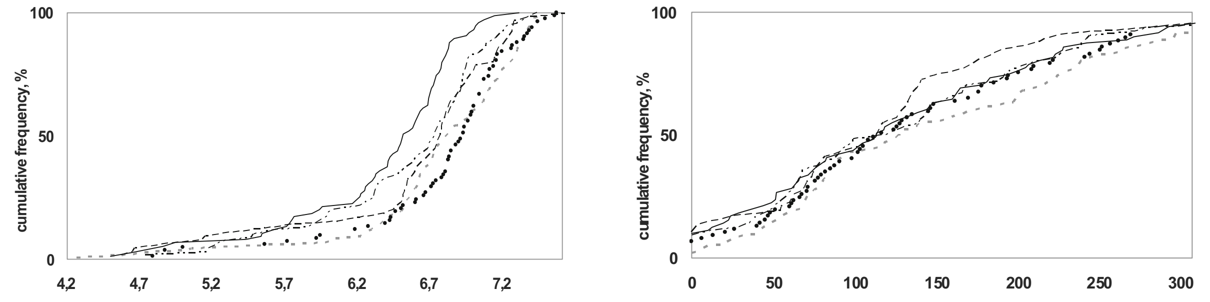
In region I, deposition and main bedrock controlled the concentrations of the cations. Sulfate concentrations were high and decreased only by 15–20 % between 1990 and 2010. The alkalinity and ANC levels increased. Water concentrations of Cu and Ni have decreased (Table 1).

Water chemistry of lakes in this region is strongly influenced by emissions from the smelter, including dust emissions. The lakes in this area are characterized by a high variability of the parameters. Water quality improves between 1990 and 2010, as demonstrated by higher ANC, lower Al, and lower Cu and Ni concentrations. This is consistent with the reduced emissions of acidifying components and metals from the smelters.

The lakes in region II have shown a good buffering capacity capable of neutralizing acidic deposition. SO_4^{2-} and Al decreased while alkalinity and ANC level increased between 1990 and 2010. The DOC and N_{tot} increased. Concentrations of Ni and Cu did not change and vary by up to 1 to 2 μg L^{-1} which is close to the background values.

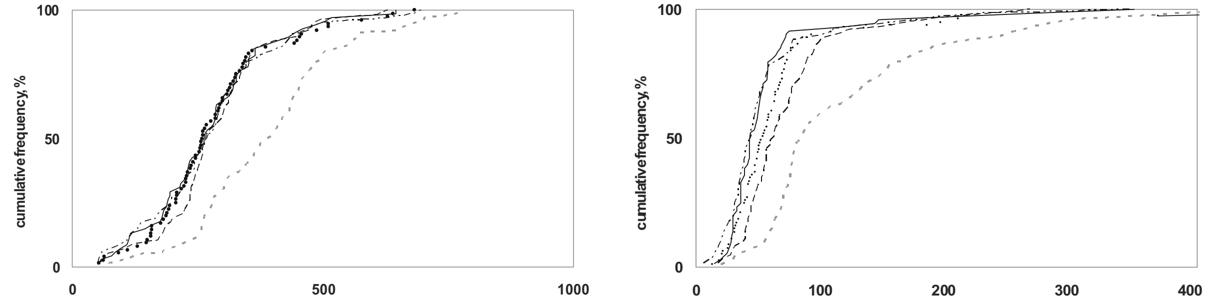
In region III, the lakes have high concentrations of basic cations with predominance of Na^+. Between 1990 and 2010, SO_4^{2-} concentrations decreased to a lesser extent than in subimpact II, whereby it is caused by relative proximity of the Khibiny mountains to the smelter Severonikel. An increase in DOC, P_{tot}, and N_{tot} concentrations was observed. Al concentrations increased, whereas in the water of Ni and Cu they vary from year to year within a small range. This is due to the apatite-nepheline syenites containing sodium, which in these lakes dominate among cations.

The lakes located in region IV are characterized by a high drainage regime. SO_4^{2-} concentrations in lakes of this subregion dropped sharply between 1990 and 1995



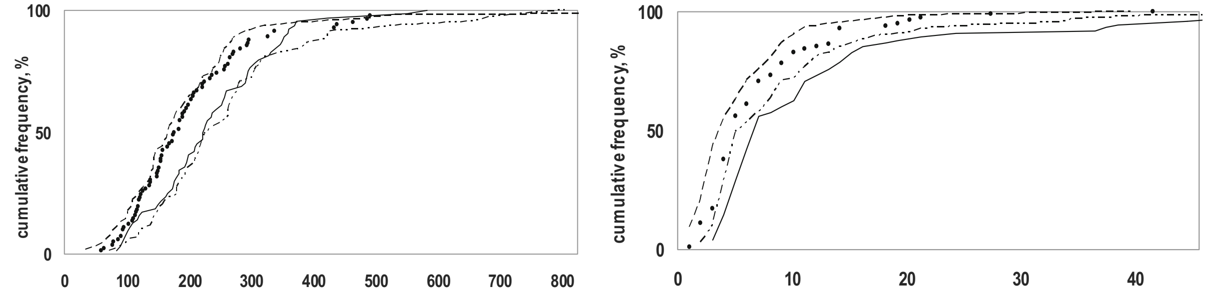
a) pH

b) Alk, μeq L



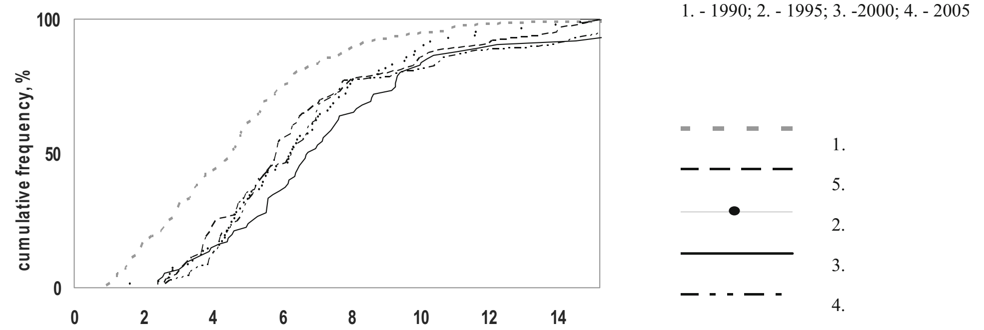
c) (Ca + Mg + Na+ K), μeqL^{-1}

d) SO_4^*, μeq L^{-1}



e) N_{tot}, μeq L^{-1}

f) P_{tot}, μeq L^{-1}



g) DOC, mg C L^{-1}

Fig. 3 Cumulative frequency diagrams for **a** pH, **b** alkalinity (*Alk*), **c** base cations (Ca+Mg+Na+K), **d** non-marine sulfate (SO_4*), **e** dissolve organic carbon (*DOC*), **f** total phosphorus (P_{tot}), and **g** total nitrogen (N_{tot})

Table 1 The 50th percentile values (weighted) for selected variables and trace elements (μg L^{-1}) of the lake water chemistry in a 20-year period (1990–2010) in different subregions in the Kola North

Year	pH	BC μeq L^{-1}	ALK μeq L^{-1}	SO4 μeq L^{-1}	Cl μeq L^{-1}	TOC mg C L^{-1}	Tot-N μg N L^{-1}	Tot-P μg L^{-1}	ANC μeq L^{-1}	Al μg L^{-1}	Cu μg L^{-1}	Ni μg L^{-1}	Pb μg L^{-1}	Cd μg L^{-1}
I - Around the smelters, Kola, *n*=7														
1990	6.76	381.00	124.00	124.00	116.00	3.50	–	–	89.00	76.00	9.50	24.50	–	–
1995	6.74	328.00	112.00	100.00	90.00	3.70	–	–	128.00	27.00	1.50	8.30	–	–
2000	6.92	282.00	113.00	105.00	66.00	3.80	103.00	5.00	140.00	30.00	2.50	7.50	0.50	0.10
2005	6.50	274.00	121.00	70.00	71.00	3.60	106.00	6.00	128.00	27.00	5.00	5.60	0.20	0.10
2010	6.79	361.00	146.00	102.00	105.00	5.00	159.00	3.00	143.00	22.00	6.20	8.40	0.30	0.50
II - Forest tundra and northern taiga (basic rocks) *n*=27														
1990	6.63	257.00	93.00	77.00	63.00	3.20	–	–	129.00	64.00	1.30	1.00	–	–
1995	6.70	261.00	125.00	62.00	40.00	5.90	168.50	4.50	189.00	33.00	0.70	0.70	–	–
2000	6.84	261.00	106.00	52.00	37.00	6.70	179.50	3.50	178.00	45.00	0.70	0.90	0.20	0.10
2005	6.60	263.00	124.00	52.00	39.00	6.50	217.00	6.00	187.00	52.00	0.60	0.90	0.30	0.10
2010	6.67	264.00	140.00	48.00	30.00	6.30	207.00	5.00	213.00	29.00	1.50	3.50	0.40	0.10
III - Taiga (alkaline mountain ranges) *n*=15														
1990	7.16	435.00	328.00	54.00	45.00	5.20	–	–	334.00	–	–	–	–	–
1995	7.08	399.00	295.00	55.00	32.00	7.00	203.00	7.00	326.00	28.00	0.60	0.40	–	–
2000	7.18	411.00	318.00	52.00	34.00	6.30	228.00	5.00	355.00	55.00	0.70	0.60	0.50	0.10
2005	6.74	410.00	286.00	43.00	33.00	8.20	319.00	11.00	312.00	55.00	0.60	0.70	0.20	0.20
2010	6.98	473.00	330.00	45.00	33.00	8.50	261.00	14.00	402.00	56.00	0.80	0.60	0.40	0.10
IV - Tundra (granite rock) *n*=9														
1990	6.31	269.00	83.00	127.00	150.00	3.10	–	0.00	−9.00	18.00	2.00	0.00	–	–
1995	6.46	244.00	69.00	45.00	139.00	3.80	148.00	6.00	65.00	27.00	0.50	0.20	–	–
2000	6.64	253.00	74.00	42.00	121.00	4.20	161.00	5.00	88.00	34.00	0.40	0.20	0.50	0.10
2005	6.15	277.00	48.00	39.00	144.00	5.20	246.00	11.00	72.00	41.00	0.50	0.70	0.30	0.30
2010	6.29	263.00	50.00	35.00	142.00	4.10	244.00	6.00	69.00	68.00	0.60	0.80	0.40	0.10
V - Taiga (silica sands) *n*=6														
1990	4.55	137.00	0.00	79.00	39.00	8.70	–	–	−14.00	–	–	–	–	–
1995	5.29	97.00	0.00	42.00	21.00	4.90	230.00	6.00	21.00	18.00	0.90	0.70	–	–
2000	5.67	93.00	0.00	40.00	17.00	6.80	259.00	3.00	18.00	70.00	0.70	0.70	0.50	0.08
2005	5.50	86.00	0.00	43.00	23.00	2.60	–	7.00	10.00	35.00	0.70	0.80	0.20	0.10
2010	5.44	63.00	0.00	26.00	22.00	4.80	257.00	11.00	13.00	38.00	0.60	0.70	0.30	0.11

Table 1 (continued)

Year	pH	BC µeq L^{-1}	ALK µeq L^{-1}	SO4 µeq L^{-1}	Cl µeq L^{-1}	TOC mg C L^{-1}	Tot-N µg N L^{-1}	Tot-P µg L^{-1}	ANC µeq L^{-1}	Al µg L^{-1}	Cu µg L^{-1}	Ni µg L^{-1}	Pb µg L^{-1}	Cd µg L^{-1}
VI - Forest and wetland landscapes, *n*=11														
1990	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1995	5.54	179.00	40.00	40.00	30.00	11.30	135.50	29.90	83.00	42.00	1.60	1.90	–	–
2000	5.49	153.00	33.00	24.00	27.00	12.20	269.50	12.15	82.00	173.00	1.50	1.50	0.50	0.10
2005	5.12	168.00	11.00	27.00	28.00	14.70	238.50	14.56	21.00	277.00	1.20	2.10	0.30	0.10
2010	5.54	136.00	29.00	20.00	25.00	14.60	341.50	14.72	80.00	174.00	1.30	1.90	0.30	0.10

(almost three times) and continued to decrease to 2010. ANC increased between 1990 and 1995 (from −9 to 65). Base cation concentrations did not have significant differences in the investigated period. Gradually, alkalinity decreased and DOC increase was observed in these lakes between 1990 and 2010. ANC increased due to a significant decrease in the concentration of sulfates (especially compared to 1990). We have found that the concentrations of aluminum increased and Ni and Cu ranged between regional background values.

In region V, a threefold reduction in SO_4^{2-} concentrations was observed, while pH not significant (from 4.55 to 5.44). The content of base cations continued to decrease by 2010 and alkalinity has not recovered (values around 0). ANC has increased as a consequence of reduction of sulfates in water, but there was no recovery in alkalinity. Al concentrations in water of lakes have increased considerably in three lakes out of six in this zone. These lakes are very sensitive to acidification.

In the region VI, the watersheds are characterized by large areas of wetlands and forests. Here, SO_4 was reduced to twofold between 1990 and 2010. Along with the reduction of sulfate were decreases of cations. However, no increase in alkalinity and ANC occurred. Within this region, the concentrations of DOC and Al in lakes increased significantly, as well as P_{tot} and N_{tot}.

4 Discussion

4.1 Basic Cations, Alkalinity, and ANC Responses to Reduction in Acid Deposition

Water chemistry records in the lakes located in the Kola region from 1990 to 2010 show a strong reduction in SO_4^{2-} concentrations, caused by decreased SO_2 emissions from local smelters. An earlier study shows that emissions of sulfate and metal from these smelters were highest during the years 1980 to 1990 (Moiseenko 1999). It should be noted that beyond the boundaries of the 100-km area from smelters, the water chemistry might be also be significantly affected by long-range transboundary transport of contaminants from Europe. Large reductions in anthropogenic sulfur emission reductions in Europe occurred between 1980 and 2000 (Skelkvale et al. 2005; Garmo et al. 2014), which could also influence on acid deposition in the Kola region. In the 1990s, SO_4^{2-} was the dominating anion in 34 % of

Table 2 Comparison of trends in surface water chemistry

Subregion	SO_4	BC	ALK	ANC	H^+	DOC	N_{tot}	P_{tot}
I		(+)*	(+)*		(+)*	(+)*	(+)*	(+)**
II	(-)*		(+)*	(+)*			(+)*	
III	(-)**	(+)*	(+)*	(+)*			(+)*	(+)*
IV	(-)**	(+)**	(-)**		(-)*	(+)*	(+)*	
V	(-)**	(-)*			(-)**		(+)*	(+)**
VI	(-)**	(-)*	(-)**	(-)**	(+)**	(+)*	(+)*	(+)*

*$p<0.001$ significant

**$p<0.01$ near significant

lakes. By 2010, this number had dropped to 25 %, related to strong declining trends in concentrations of strong acids. Alkalinity showed a strong interannual variation, and no significant changes were found in the period of 1990–2010 when all lakes were considered. In the acid-sensitive regions (in the east: regions IV, V, and VI), we found that alkalinity of lakes remains low or falls (see Fig. 3).

We found that the reduction of anthropogenic sulfate in lakes was accompanied by a decrease base cation concentrations. The significant positive relation between changes in SO4-2 and changes in base cations (Fig. 4) supports this. Due to the principle of electroneutrality, reduced concentrations of strong acid ions also leads to reduced concentrations in base cations. This phenomenon is in agreement with earlier trend reports of chemical recovery of lakes (Stoddard et al. 1999; Skjelkvåle et al. b). Probably, the long-period acid deposition in the Kola region resulted in strong soil base cation depletion, which again leads to delayed recovery of the cations and alkalinity in the most sensitive lakes.

The second important characteristic of the water chemistry changes over 20 years is the increase in ANC. As noted, calculation was made based on the difference between all the cations and anions of strong acids without correction by sea salt (Table 1). The increase of ANC was primarily due to a decrease in

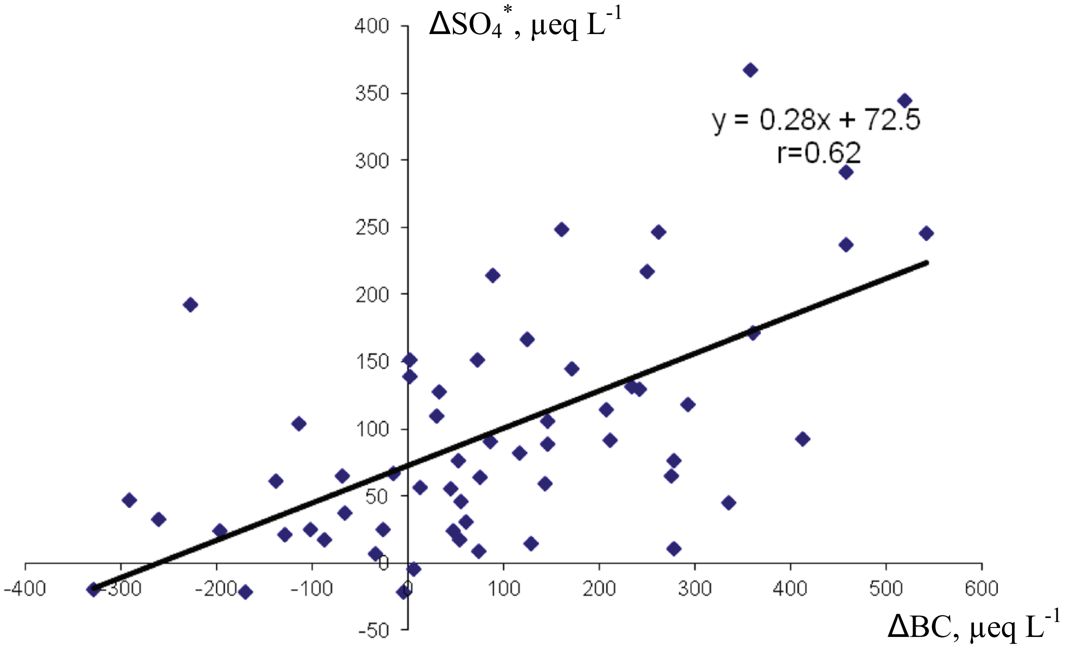


Fig. 4 The correlation between the change of sulfate ions (ΔSO_4^*) and major cations (ΔBC)

contents of strong acids, such as sulfate and chloride. The controls of acidification or recovery of lake waters in the Kola region are bedrock geology and landscape characteristics, and extent of acid deposition. Basic rocks (basalts, gabbros, etc.), as well as alkaline massifs of the Khibiny and Lovozero Mountains (nepheline syenites), determine buffering properties of the lakes in regions I, II, and III, located at a distance <100 km from the smelters. Most of the lakes in these regions have good buffering properties with alkalinity greater than 100 μeq L^{-1}. The exceptions are the lakes located on the hills Chuna, Volchie, and Salnie tundra, which are sensitive to acidification.

4.2 Assessing the Role of Chloride Ions

Chloride anions play in important role in the lake chemistry and acidification in the Kola regions, especially in the 1990s, similar to what has been shown for the UK (Evans et al. 2011).The main source of Cl in the lakes is sea salt deposition. There was a tendency toward reduced Cl^- concentrations in the lake water.

The main flow of chloride is associated with marine aerosols. The lakes in the northern part of the Kola regions showed significant decrease of chloride content between 1990 and 2010 ($p \leq 0.001$, $n=75$). However, the source of chloride can be also be anthropogenic, for instance, coal power stations. In recent years, the emissions of chloride in some countries decreased due to use of more effective emission purification systems (in UK by 70 % by 2007). It is possible that that implementation of similar systems in the Kola smelters has occurred, leading to lower Cl emissions from the smelters. We do not have data on chloride emissions in the Kola region, but we assume that these were considerable because coal power generation was common in many power plants and local boiler houses in the Kola region the middle of the last century. A synchronous decrease in SO_4^{2-} and Cl^- concentrations in the lakes is shown by a correlation calculated according to median values for all subregions involved on a year-by-year basis ($r=0.90$, $n=29$).

There was a period of high sea salt deposition in northwestern Europe around the 1990s because of strong storms (Evans et al. 2011). Whether these meteorological phenomenons also caused high Cl deposition in the Kola regions is not known. It is possible that the reduced sea salt deposition, related to climate change, has reduced the deposition of chloride of marine origin in Kola region. Therefore, in calculating ANC levels, as shown above, the cations and SO_4^{2-} have not been corrected by marine salts. Since the anthropogenic emissions of chlorides may also influence on the acidification and on the recovery. Moiseenko et al. (2001) also showed the phenomenon of combined influence of Cl^- and SO_4^{2-} over short-time brook acidification. Due to its high mobility, Cl^- is capable of both contributing to acidification and exerting influence on recovery process by either accelerating or slowing it down (Evans et al. 2011).

4.3 Dissolved Organic Carbon

The phenomenon of increasing DOC levels in water systems over the last decades has been shown by numerous studies (Driscoll et al. 2003; Stoddard et al. 1999; Skjelkvåle et al. 2001a; Monteith et al. 2007; Evans et al. 2008; Clark et al. 2013). The increasing of organic matter concentrations in lake waters was also observed for the lakes in the Kola region, more markedly in forest and waterlogged subregions. Monteith et al. (2007) explain the increased DOC levels by reduction of acid deposition, and return of water chemistry to its natural condition. DOC has an important influence on water quality, influencing acidity, light penetration, and the form and solubility of nutrients and some pollutants. For organic acids, the strong organic acid concentration represents that part of the total humic acid that remains dissociated at the equivalence point of the Gran titration. Weak organic acids are incorporated within the measurement of alkalinity (Evans et al. 2008). Clark et al. (2013) demonstrated that natural humus substances are capable of producing strong organic acids and increase water acidity. Perhaps this explains the lacking recovery of ANC in the tundra and wetland watershed lakes (regions V and VI). At the same time, the above studies do not exclude the possibility of the role of climate warming on the increase in the content of organic matter.

4.4 Nutrients and Climate Warming Effects

Nature surface waters in the Kola region are characterized by low concentrations of nutrients because of low temperatures, predominantly atmospheric precipitations and a thin soil layer. Extremely low concentrations of NO_3^- and PO_4^{3-} are explained by their rapid recycling in production processes. Ammonium concentration is also insignificant, and in the 1990s, when concentrations varied within the range from 0 to 7 μg L^{-1}, nitrate concentration varied from 0 to 8 μg L^{-1} (Moiseenko et al. 2013). A marked increase in nutrient content (N_{tot} and P_{tot}) through their organic forms was observed (Fig. 3). Overall, we can see from Table 1 and the cumulative curves the total concentrations of nitrogen and phosphorus, for example (zone 1) from 86 to an increase to 159 μg L^{-1} of total nitrogen.

In order to estimate a possible change in total phosphorus due to increased temperature, we used a regression model based on data for 280 lakes along the climatic gradient where the dependent variable (Moiseenko et al., 2013). Based on a regression model for Russian lakes, we have assessed that with a mean increase in daily temperature of 0.5 °C, there would be an increase in total P content in 25–30 % in lake waters of tundra and taiga ecoregions. According to Grouza and Ya Rankova (2012), between 1970 and 2010, in Northwest Russia, air surface layer temperature increased every 10 years with 0.53 °C, i.e., it has risen by 1.06 °C over the period of investigations. This can promote eutrophication of lakes by increased transport of P and N from the catchments (Feuchtmayr et al. 2009). It is possible that the increase in concentrations of organic forms of N and P is related to climate warming, although it is also possible that it is related to the increase in DOC. Possibly, the increases demonstrate an acceleration of production processes and raise of lake trophic status due to climate warming. The ratio of P to DOC was 2.2 times higher in 2010 in regions II and III (42 lakes) than in 1990. Such a ratio might be indicative of the role of autochthonous processes in a number of lakes as a result of climate warming. It should be noted that in the Kola region, distributed apatite minerals contain phosphorus that may influence on concentration of phosphorus in water. Although phosphorus in these minerals is strongly associated in the crystal grating, in a warming climate, it might be mobilized at increasing rates under the influence of microbial activity.

4.5 Trace Elements

Ni and Cu emissions from the smelters operating in the Kola region have declined strongly (see Fig. 2). The highest concentrations of these elements were found in water of lakes located within the range of 30 km from smelters (see Table 1). Within this area, a significant reduction in their concentrations has been observed over a 20-year period of investigations. In other subregions of Kola regions, concentrations of these elements were close to the regional reference values (Moiseenko 1999; Skjelkvåle et al. 2001b).

Pb, Cd, and Hg concentrations in the lakes of the Kola Peninsula have been measured since 2000. Hg concentrations in water were below an analytical threshold of measurement (<0.05 μg L^{-1}). Pb concentrations were from 0.1 to 0.5 μg L^{-1}, whereas Cd concentrations were within the range of 0.1–0.8 μg L^{-1}. Pb and Cd concentrations in waters of the lakes vary slightly with a tendency to increase. This may be associated with the global processes of increase in contents of these elements in the environment of the northern regions. Norton et al. (1990) has presented data of Cd, Pb, and Hg enrichment of northern areas. In the lakes located over granite and quartz rocks (regions IV and V), Al concentrations increased. Acid leaching is the main mechanism of determining the increase in concentrations of these elements in these regions. The largest Al concentrations are present in wetland catchment (region VI). It is possible that Al concentrations have increased because Al is strongly bound to DOC, and DOC has increased significantly.

5 Conclusion

A trend analysis of the change in chemical composition of waters in 75 lakes in the Kola regions showed that sulfate and metal (Ni and Cu) concentrations in lake waters have decreased over the last two decades. Concentrations of basic cations in water did not recover, probably due to soil depletion of base cations for the 60-year period of smelter functioning. ANC increased due to a significant decrease in the content of strong acids. In acid-sensitive lakes, alkalinity decreased or remained unchanged. DOC concentration in lake waters has increased, which is consistent with other records of lake water browning from Europe and North America.

An increase in nutrient concentrations (N_{tot} and P_{tot}) was shown for 35 lakes. This phenomenon could lead to a change in the trophic status of the lakes, perhaps as a response to a climate warming in the region (i.e., approximately 1 °C in 20 years in the study region). This is also confirmed by the increase of eutrophication and an increase in phosphorus of autochthonous origin, as indicated by the increase in ratio of P_{tot} to DOC in a number of lakes. Possibly, weathering of phosphorus-containing minerals (apatite), which are common in the region, may have increased related to climate warming. Simultaneously, with the decrease in sulfate concentrations, concentrations of nickel and copper decreased, related to reduced emissions from the smelters.

In addition, all lakes show reduced SO_4 and most increased DOC; ANC increased in all regions by reducing anthropogenic deposition of strong acids, particular in acid-sensitive lakes.

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References

Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R., Rose, R., Newton, R. J., & Chapman, P. J. (2013). The importance of the relationship between scale and process in understanding long-term DOC dynamics. *AMBIO, 13*, 2768–2775. doi:10.1016/j.scitotenv.2010.02.046.

Driscoll, C. T., Driscoll, K. M., Roy, K. M., & Mitchell, M. J. (2003). Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. *Environmental Science and Technology, 37*(10), 2036–2042. doi:10.1021/es020924h.

Eaton, A., Arnold, E., Archie, A. E., Rice, E. W., & Clesceri, L. S. (1992). *Standard Methods for the Examination of Water and Wastewater.* (17th ed.). Washington: Public Health Association (APHA).

Evans, C. D., Cullen, J. M., Alewell, C., Kopacek, J., Marchetto, A., Moldan, F., Prechtel, A., & Rogora, M. (2001). Recovery from acidification in European surface waters. *Hydrology and Earth System Sciences, 5*(3), 283–298. doi:10.5194/hess-5-283-2001.

Evans, C. D., Monteith, D. T., Reynolds, B., & Clark, J. M. (2008). Buffering of recovery from acidification by organic acids. *Science of the Total Environment, 404*, 316–325. doi:10.1016./j.scitotenv.2007.11.003.

Evans, C. D., Monteith, D. T., Fowler, D., Cape, J. N., & Brayshaw, S. (2011). Hydrochloric Acid: An Overlooked Driver of Environmental Change. *Environmental Science & Technology, 45*, 1887–1894. doi:10.1021/es103574u.

Feuchtmayr, H., Moran, R., Hatton, K., Cannor, L., Yeyes, T., Harley, J., & Arkinson, D. (2009). Global warming and eutrophication: effects on water chemistry and autotrophic communities in experimental hypertrophic shallow lake mesocosms. *J. Appl. Ecol., 46*, 713–723. doi:10.1111/j.1365-2664.2009.01644.x.

Garmo, A., Skjelkvele, B., de Wit, A., Colombo, L., Curtis, C., Folster, J., Hoffmann, A., Hruska, J., et al. (2014). Trends in surface water chemistry in acidified areas in Europe and North America from 1990 to 2008. *Water Air Soil Pollut, 225*, 1880.

Grouza, G. V., & Ya Rankova, E. (2012). *The observed and expected climate change of Russia: air temperature.* Russian Academy of Sciences: Obninsk Institute of Global Climate and Ecology. 194p.

Henriksen, A., Skjelvåle, B. L., Mannio, J., Wilander, A., Harriman, R., Curtis, C., Jensen, J. P., Moiseenko, T., et al. (1998). Northern European Lake Survey, 1995. Finland, Norway, Sweden, Denmark, Russian Kola, Russian Karelia, Scotland and Wales. *AMBIO, 27*(2), 80–91.

Intercomparison. 2010. 1024: pH, Cond, HCO3 NO3 + NO2, C1, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. 2010. International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Reports of Norwegian Institute of Water Research 6029, Oslo. 75p.

Moiseenko, T. I. (1994). Acidification and critical loads in surface waters: Kola. *Northern Russia AMBIO, 23*, 418–424.

Moiseenko, T. I. (1999). The fate of metals in Arctic surface waters. Method for defining critical levels. *Science of the Total Environment, 236*, 19–39.

Moiseenko, T., Kudrjavzeva, L., & Rodyshkin, I. (2001). The episodic acidification of small streams in the spring flood period of industrial polar region, Russia. *Chemosphere, 362*, 45–50.

Moiseenko, T. I., Skjelkvale, B. L., Gashkina, N. A., Salabodov, A. D., & Khoroshavin, V. Y. (2013). Water chemistry in small lakes along a transect from boreal to arid ecoregions in European Russia: Effects of air pollution and climate change. *Applied Geochemistry, 28*, 69–79. doi:10.1016/j.apgeochem.2012.10.019.

Monteith, D. T., Stoddard, J. L., Evans, C. D., DeWit, H. A., Forsius, V., Hogasen, T., Wilander, A., & Skjelvåle, B. L. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature, 450*(7169), 537–539. doi:10.1038/nature06316.

Norton, S. A., Dillon, P. J., Evans, R. D., et al. (1990). The history of atmospheric deposition of Cd, Hg and Pb in North America: Evidence from lake and peat bog sediments. In S. E. Lindberg et al. (Eds.), *Sources, Deposition and Capony Interactions* (Vol. 111). New York: Springer-Verlag.

Pogilenko, V. I., Gavrilenko, B. V., Girov, D. V., & Gabin, S. V. (2002). *The geology of ore districts of the Murmansk region*. Apatity: Kola Scientific Center, Russian Academy of Sciences. 359 p.

Skelkvale, B. L., Stoddard, J. L., Jeffries, D. S., Torseth, K., Hogasen, T., Bowman, J., Mannio, L., Monteith, D. T., et al. (2005). Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution, 137*(1), 165–176.

Skjelkvåle, B. L., Stoddard, J. L., & Andersen, T. (2001a). Trends in surface water acidification in Europe and North America (1989–1998). *Water, Air, & Soil Pollution, 130*, 787–792. doi:10.1023/A: 1013806223310.

Skjelkvåle, B. L., Andersen, T., Fjeld, E., Mannio, J., Wilander, A., Johansson, K., Jensen, J. P., & Moiseenko, T. (2001b). Heavy metal surveys in Nordic Lakes; Concentrations, geographic patterns and relation to critical limits. *AMBIO, 30*, 2–10. doi:10.1579/0044-7447-30.1.2.

Stoddard, J. L., Jeffries, D. S., Lukewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., et al. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature, 401*, 575–578. doi:10.1038/44114.