Winter atmospheric nutrients and pollutants deposition on West Sayan mountain lakes (Siberia)

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Abstract. The world map of anthropogenic atmospheric nitrogen deposition and its effects on natural ecosystems is not described with equal precision everywhere. In this paper, we report atmospheric nutrient, sulphate and spheroidal carbonaceous particles (SCPs) deposition rates, based on snowpack analyses, of a formerly unexplored Siberian mountain region. Then, we discuss their potential effects on lake phytoplankton biomass limitation.

We estimate that the nutrient depositions observed in the late season snowpack (40±16 mg NO_3-N·m^{-2} and 0.58±0.13 mg TP-P·m^{-2}) would correspond to yearly depositions lower than 119±71 mg NO_3-N·m^{-2}·y^{-1} and higher than 1.71±0.91 mg TP-P·m^{-2}·y^{-1}. These yearly deposition estimates would approximately fit the predictions of global deposition models and correspond to the very low nutrient deposition range although they are still higher than world background values.

In spite of the fact that such low atmospheric nitrogen deposition rate would be enough to induce nitrogen limitation in unproductive mountain lakes, phosphorus deposition was also extremely low and the lake water N:P ratio resulted to be unaffected by atmospheric nutrient deposition. In the end, the studied lakes phytoplankton appeared to be hanging on the fence between phosphorus and nitrogen limitation. We conclude that these pristine lakes are fragile sensitive systems exposed to the predicted climate warming, increased winter precipitation, enhanced forest fires and shifts in anthropogenic nitrogen emissions that could finally couple their water chemistry to that of atmospheric nutrient deposition and unlock temperature-inhibited responses of phytoplankton to nutrient shifts.

1 Introduction

Worldwide nitrogen cycle perturbation is the second most important global environmental concern, just after massive extinction of species and even more important than global warming (Rockström et al., 2009; Steffen et al., 2015). The

anthropogenic mobilization of formerly inaccessible nitrogen compartments has more than doubled natural nitrogenase-mediated inputs of reactive nitrogen forms into the global nitrogen cycle (Vitousek et al., 1997). Massive fossil fuel combustion since the industrial revolution, chemical fixation of atmospheric diatomic nitrogen to produce fertilizers since the Second World War and the wide extension of leguminous crops are the most important human sources of nitrogen cycle perturbation (Vitousek et al., 1997). A substantive part of this anthropogenic reactive nitrogen is then spread, air-transported and deposited all over the world with a diverse impact on different ecosystems.

The effects of atmospheric nitrogen deposition on primary production have been documented in the usually nitrogen-limited terrestrial ecosystems (Bobbink et al., 2010; DeForest et al., 2004; Güsewell, 2004; LeBauer and Treseder, 2008), as well as in commonly phosphorus-limited lakes (Bergström et al., 2005). A series of studies all over Sweden and abroad showed atmospheric nitrogen deposition to have turned unproductive lake phytoplankton from natural nitrogen to induced phosphorus limitation (Bergström and Jansson, 2006; Bergström et al., 2005; Elser et al., 2009) when temperature was not a limiting factor (Bergström et al., 2013). Of course, these changes do not only concern primary production limitation, but also primary producer species composition, cascade effects over the food web, secondary production, species interactions, etc. Likewise, these studies showed that it was reasonable to study the relationship between atmospheric nutrient deposition and lake phytoplankton growth limitation independently from biogeochemical processes occurring at the levels of the watershed, runoff and river transport, lake sediments, etc.

Nevertheless, ecological processes are not homogeneous around the World. There is a particular and dynamic geography of reactive nitrogen sources, an atmospheric conveyor belt with a conspicuous structure, an evolving climate with patchy temperature and precipitation changes, and a multiplicity of lake districts with distinct individual lakes in them. If it is true that climatic and atmospheric nutrient deposition models have helped a lot to describe this geography, the latter ones lack empirical measurements for some regions of the world, which might undermine their regional spatial reliability in comparison to climate models (Fagerli et al., 2019; Gauss et al., 2019; Lamarque et al., 2013; Mahowald et al., 2008). Moreover, not all lake districts of the world have been studied with the same intensity, so certain processes might be overlooked and the limnological paradigms might be site-biased (Marcé et al., 2015). In this study, we analysed the snowpack in the West Sayan mountains (south central Siberia) in order to gauge atmospheric nitrogen, phosphorus, sulphate and spheroidal carbonaceous particles (SCPs) deposition rates. As far as we know, no such measurements had been pursued in this site before, so they might be useful to contrast and inform world deposition models. Besides, we have also assessed lake phytoplankton nutrient limitation regime and discussed the potential influence of nutrient deposition on it.

According to published global models (IPCC, 2013; Lamarque et al., 2013), the West Sayan mountains, in south central Siberia, correspond to a low atmospheric nitrogen deposition area with a cold but increasingly warming climate in the last decades. Our aim was to corroborate it because in case it was confirmed, it would be an adequate site to study the effects of global warming on ecosystems with a minimal interference of atmospheric nitrogen deposition. In other words, identifying and studying such areas could help disentangle warming and nitrogen fertilization as drivers of ecological change. It could also contribute to assess the worthiness to implement global nitrogen cycle policies, besides climate ones.

2 Methods

2.1 Study site and sampling

West Sayan mountain range is located in south central Siberia (fig. 1). It has a central position in the Altay-Sayan mountain system, in between the Altay mountains (to the west) and East Sayan mountains (to the east), which are constituents of the Sayan-Baikal mobile fold belt south the Siberian craton (Logatchev, 1993). West Sayan orogeny occurred in the ancient Paleozoic, by folding Paleozoic and Precambrian deposits, during the Baikal tectogenesis and in the Cenozoic era (namely during the Pliocene-Pleistocene Epochs) (Chernov et al., 1988). With a north-west orientation and heights from 400 to 2700 m.a.s.l., West Sayan mountains combine old eroded with typical glacial reliefs, carved during the Pleistocene glaciation in the highest ridges. The source of Yenisei river, the first Siberian river in terms of discharge, is located in West Sayan mountains and its headwater tributaries are also Sayanic.

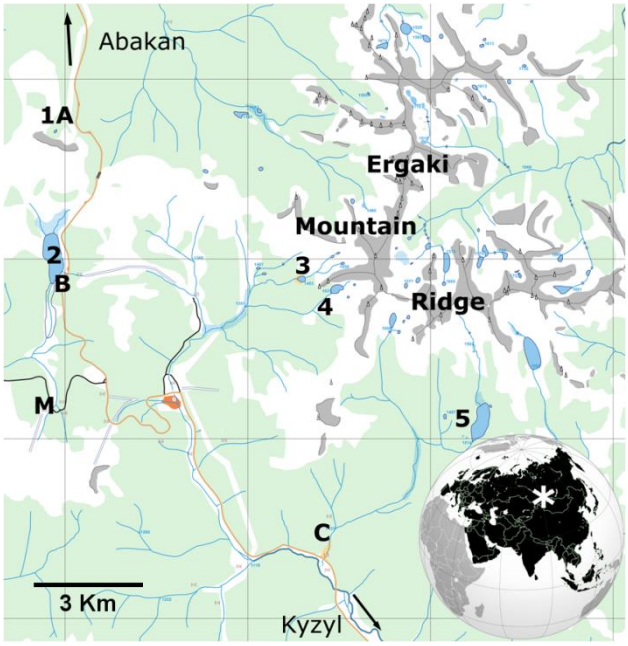


Figure 1. Distribution of sampling points in the Ergaki Natural Park. Snow cores: Tsirkovoe (A), Oiskoe (B) and Tushkan (C); Lakes: Tsirkovoe (1), Oiskoe (2), Raduzhnoe (3), Karovoe (4), Svetloe (5); Olenya Rechka metereological station (M). Ergaki location in Eurasia. Mountain ridge (grey), open spaces (white), forest and bushes (green), three lane federal road (yellow). Source: http://www.shandl.narod.ru/map.htm and Wikipedia CC BY-SA 3.0

The present study was performed in the Ergaki Natural Park, in the West Sayan mountains. With an altitude range from 700 to 2466 m.a.s.l., this park is well known for the glacial landscapes of both Ergaki and Aradan ridges embedded in a boreal mountainous taiga matrix, that extends far to the north. The landscape is spattered with monumental and pictoric granite-syenite rocks, and the general geology is rich in granitoids (Voskresenskii, 1962). South from the park, sub-boreal larch

taigas and central Asian steppes develop. The closest gardens and agricultural fields are located downhill more than 35 Km north from the northernmost sampling point and constitute a modest patch within the taiga matrix. Meteorological conditions in the Ergaki Natural Park are characterized by high precipitation (1243 mm) and extreme temperatures, ranging from -36.8 to +33.3°C (fig. 2 a). From a geobotanical point of view the park is located in the holarctic kingdom, circumboreal region and Altai-Sayan province (Takhtadzhyan, 1978). An exhaustive floristic description is available at (Stepanov, 2016), where our study area corresponds to the L3 district.

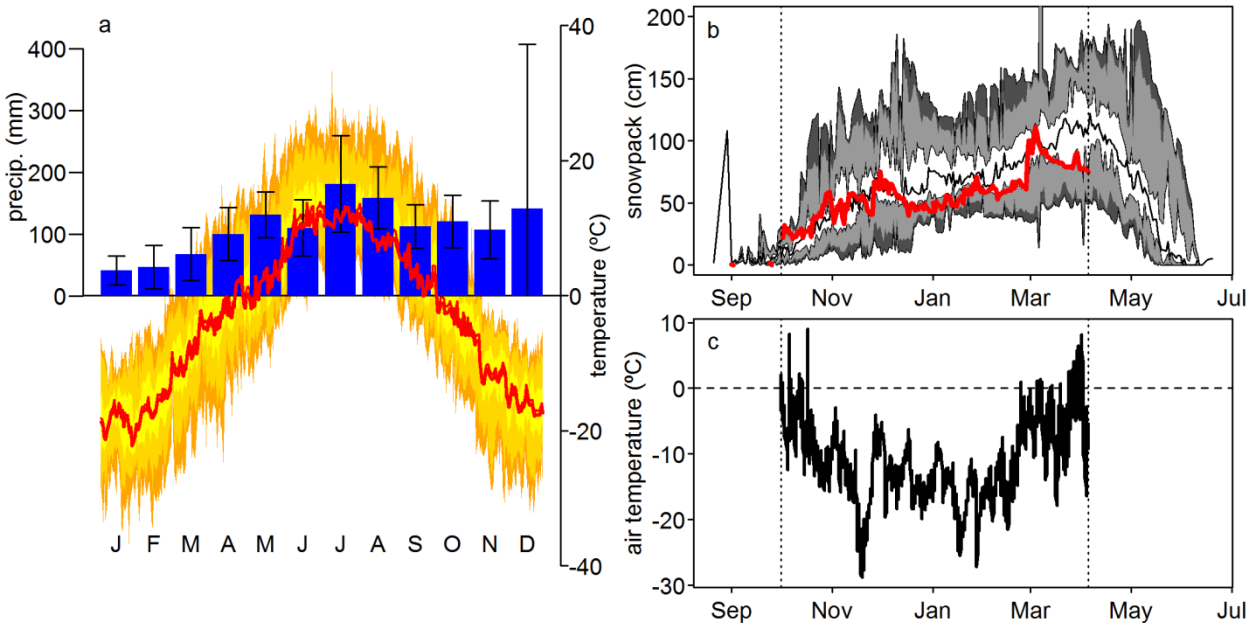


Figure 2. Records at Olenya Rechka meteorological station. a: Climograph (1 February 2005 - 30 April 2019). The median yearly precipitation was 1242.975 mm, with a winter (2nd October to 5th April) and summer precipitations of 464.95 mm and 778.025 mm, respectively. Temperature: median (red), interquartile range (yellow band), 5th to 25th percentiles and 75th to 95th percentiles (lower and upper golden bands), below the 5th percentile and above the 95th percentile (lower and upper orange bands). b: Snowpack thickness (2005-2017): median (black), interquartile range (white band), 5th to 25th percentiles and 75th to 95th percentiles (lower and upper light gray bands), below the 5th percentile and above the 95th percentile (lower and upper dark gray bands). The red line corresponds to the 2016-2017 snowpack thickness record until the snow sampling date. c: Air temperatures measured all the 3 hours during the time period when analysed snowpacks were laying on their respective locations (2016-17).

Snowpack cores were sampled at three sites of the Ergaki Natural Park: next to lake Tsirkovoe (Цирковое), next to lake Oiskoe (Ойское) and on a forest glade close to Tushkan stream (Тушкан) (fig. 1, table 1). Snow sampling was conducted the 5th of April 2017, integrating a snowfall period of 6 months and 5 days according to precipitation data recorded in the closeby Olenya Rechka metereological station (http://rp5.ru). The 1st and 24th September 2016 snowfalls thinner than 0.5 cm and 2 cm respectively were registered but they melted the following day. The first important snowfall occurred the 1st October 2016 evening and left a 22 cm pack that was not significantly reduced anymore until the sampling day (fig. 2 b). Air

temperatures recorded in the mentioned meteorological station during this time window were mostly below zero, with positive temperatures only for some hours around midday during the first and last weeks (fig. 2 c).

					Distance in m to local pollution sources		
	Symbol in the map	latitude	longitude	Altitude (m)	road	cottage	inflow from houses
Tsirkovoe	1, A	52°52'28.3"N	93°14'53.1"E	1428	466	-	-
Oiskoe	2, B	52°50'28.3"N	93°14'46.0"E	1418	251	229	288
Tushkan	C	52°46'16.9"N	93°21'17.0"E	1125	725	471	-
Raduzhnoe	3	52°50'08.4"N	93°20'44.5"E	1462	4600	3000	-
Karovoe	4	52°49'57.4"N	93°21'41.6"E	1632	5265	4000	-
Svetloe	5	52°48'02.2"N	93°25'05.4"E	1511	5647	5470	-

Table 1 Sampling sites and distance to local perturbations. Temporary summer camps are present on Svetloe lake shore and used to be on Raduzhnoe's. See Table S1 for lake and watershed cover characteristics.

The snow core sampling was conducted following a modified version of the MOLAR project protocols for atmospheric deposition assessment (Mosello et al., 1997). Sampling areas were chosen on a map to be accessible but as far as possible from local sources of air pollution. Definitive locations were also chosen to represent average snowpack thicknesses by checking it across the sampling areas using a snow probe. Hence, wind- and orography-induced secondary modifications of the snowpack were minimised. An aluminium tube and piston (1m x 2.5 cm inner diameter), plastic shovel, plastic containers and rubber gloves were soaked in ~4% HCl and MQ water rinsed before being used to pick up snow cores. A protective mask and synthetic clothes were worn during sampling. The snow was stored in the plastic containers and kept at -20°C until further analyses. Two cores divided in three segments (0-40, 40-80 and 80-115 cm) were sampled at Tsirkovoe, whereas three cores divided in two segments (0-60 and 60-115 cm) were sampled at Oiskoe and Tushkan.

A selection of five accessible Ergaki mountain lakes was chosen to represent a variety in dimensions, altitude, and watershed vegetation covers (fig. 1, table 1 and S1). Oiskoe and Svetloe (Светлое) lakes are relatively large forest lakes (0.57 and 0.37 Km^2, 21 and 24 m maximum depth) with low water transparency (4 and 8 m average Secchi disk, respectively). Tsirkovoe, Raduzhnoe (Радужное) and Karovoe (Каровое) lakes are located at an alpine landscape and are smaller and shallower (0.02, 0.03, and 0.08 Km^2, respectively; 15, 4 and 7m deep, respectively). Secchi disk was not tested at Tsirkovoe but Raduzhnoe and Karovoe lake beds were visible. Karovoe and Svetloe lakes represent a 7% of the watershed area, Tsirkovoe and Oiskoe, a 5%, and Raduzhnoe is only a 1.4% of its watershed area.

As for vegetation cover, Oiskoe and Svetloe watersheds have a 25 and 28% forest cover whereas the other lakes have less than 10% forest covers. These two watersheds are quite similar in terms of land cover: they have quite equilibrated percentages of forests, shrubs, meadows and scree. Oiskoe is also the watershed with higher peatland cover (6%), followed by Svetloe (3%) and Radushnoe (1.6%). Karovoe and Raduzhnoe watersheds are dominated by scree (73% and 52%,

respectively) and meadows (14% and 24%, respectively), whereas Tsirkovoe watershed is dominated by shrubs (56%) and scree (37%).

Lake water was sampled at different depths (from 1 to 5 separate depths, or composite sample from that depths, depending on the sampling expedition, see table S2) and consequently analysed for chlorophyll and nutrient content in early September 2015 (Tsirkovoe, Oiskoe and Raduzhnoe) and in late August 2017 (Tsirkovoe, Oiskoe and Karovoe). Data from a previously published study integrating June and August samplings 2011-12 (Oiskoe, Raduzhnoe, Karovoe and Svetloe) was also used (Anishchenko et al., 2015). Water samples were sieved *in situ* to remove zooplankton, transported to the field laboratory at 4-10°C in the dark, filtered for chlorophyll analyses and frozen at -20°C for further chemical analyses.

2.2 Chemical analyses

Snow and lake water samples were fully thawed and stirred before analyses. Snow water equivalent (SWE) was calculated by multiplying the snowpack depth and the ratio of melted water volume to sampled snow volume. Samples were gently vacuum filtered for NO_2^-, NO_3^-, soluble reactive phosphorus –SRP– and SO_4^{2-}analyses and filtered with single-use plastic syringes for NH_4^+ analyses. Cellulose filters were used in 2011 and 2012 surveys according to the Russian National Standards (Gladyshev et al., 2015; Tolomeev et al., 2014) and 0.45 µm membrane filters "Porafil" (Macherey-Nagel, Germany) were used in 2015 and 2017. Nitrate was reduced to NO_2^- by the cadmium reduction method. Nitrite was determined by the colorimetric method after reacting with sulphanilamide and α-naphthylamine. Detection limits were 0.001 mg $N-NO_3^-$,·l^{-1}, 0.0002 mg $N-NO_2^-$ ·l^{-1} and 0.011 mg N-NH_4·l^{-1}. Lake water dissolved inorganic nitrogen (DIN) was calculated as the sum of nitrate, nitrite and ammonium. Soluble reactive phosphorus was assessed using the ascorbic acid and ammonium molybdate method. Total phosphorus (TP) was measured the same way after persulfate digestion of unfiltered samples. In the 2015 survey, lake water TP was calculated as the sum of soluble reactive phosphorus and seston particulate phosphorus (PP). The latter was collected on the above-mentioned membrane filters and measured after persulfate digestion. All these analyses were made according to the Russian National Standards (Gladyshev et al., 2015; Tolomeev et al., 2014), which generally coincide to those from APHA (APHA, 1989). In 2015 nutrients were measured using a Flow Injection Analyser Lachat Quickchem 8500 autoanalyzer Series 2 FIA System (Hach Ltd, Loveland, CO, U.S.). The method detection limits (MDL) were 0.0263 mg N-NO_3·l^{-1}, 0.0057 mg N-NO_2·l^{-1}, 0.0479 mg N-NH_3·l^{-1} and 0.0011 mg P-PO_4·l^{-1}. As for SO_4^- analysis, snow and lake water samples were concentrated by heating, $HClO_4$ and HNO_3 mixture was added and evaporated, then an ion-exchange column was used to remove interferences of cations. Samples were titrated with $BaCl_2$ solution in the presence of nitrochromazo until blue color appearance (Kalacheva et al., 2002). Finally, total nitrogen (TN) was digested from total snow and lake water samples using persulfate and boric acids and subsequently transformed into NO_3^- (Grasshoff et al., 1983). The natural light absorption of this nitrate at 210 nm was determined using a Spekol 1300 photometer (Analytik Jena, Germany) and corrected for organic matter interference by subtracting absorption at 275 nm (Slanina et al., 1976).

2.3 Chlorophyll and SCPs analyses

A known fraction of melted snow samples was filtered through GF/C filters to collect SCPs (Mosello et al., 1997). Nitric, hydrofluoric and chlorhydric acids were used to remove organic, siliceous and carbonate material, respectively (Rose, 1994; Yang et al., 2001). Determinate fractions of the samples were mounted on NAPHRAX and counted at 400X under an Axiostar plus microscope (Zeiss). Negative controls and a sediment reference standard were likewise processed to correct final counts for eventual experimental bias (Rose, 2008).

Phytoplankton chlorophyll was assessed according to the UNESCO standard protocols (VA, 1997). Samples had been filtered in the field laboratory through $BaSO_4$-covered 0.45 µm membrane filters "Porafil" (Macherey-Nagel, Germany), folded inwards and frozen. They were then let thaw, dried in the dark, and scraped along with $BaSO_4$ into centrifuge tubes. Pigments were extracted in 100% acetone for 9h in the dark at +4°C. After filtration through 0.2 µm polycarbonate filters, MQ water was added to get pigments dissolved in a 90% acetone solution, f.c. Photometric measurements were used to calculate chlorophyll concentrations (Jeffrey and Humphrey, 1975).

2.4 Air mass retrotrajectory analysis, maps and statistics

The retrotrajectories of air masses flowing on the three snow sampling sites were obtained using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HYSPLIT) model for archive trajectories (Rolph et al., 2017; Stein et al., 2015) of the National Oceanic and Atmospheric Administration Air Resources Laboratory (NOAA, USA). A total of 187 daily retrotrajectories embracing the sampled period of atmospheric deposition were reconstructed as the snowpack bulk deposition airshed. Each trajectory started three days back in the past. It recorded a per hour latitude, longitude and altitude coordinates and ended up at the snow sampling coordinates, at 0 m above model ground level at 24h of consecutive days. All the analyses were performed within the R environment (R Development Core Team, 2017). Total retrotrajectory length and average wind speed the hour before getting to the sampling point were calculated using the Vincenty (ellipsoid) distance method within the geosphere package (Hijmans, 2017). The openair package was used to determine wind direction and to draw wind roses (Carslaw and Ropkins, 2012). The number of per hour coordinates at 0 m above model ground level was calculated to characterise the direct interaction of each air mass with the Earth crust. Retrotrajectories were mapped using the ggmap package (Kahle and Wickham, 2013). One-way ANOVA comparing sites and Pearson correlation analyses of chemical and wind variables in the seven analysed snow core sections were performed using built-in functions of the R statistical environment.

Detailed watershed land cover/land use maps were manually defined for each lake. Polygons were defined using QGIS 3.14.16-Pi on the basis of Google Satellite and Open Street Map XYZ tiles at a resolution that distinguished single trees. Lake, whole watershed and different vegetation and land cover areas were calculated using ellipsoidal project.

3 Results and discussion

3.1 Potential fragmentation of nutrients by snow melting

The three sampled snow cores were 115 cm deep, but had different snow water equivalent (SWE): 25±1 cm in Tsirkovoe, 27±1 cm in Oiskoe and 12±0.3 cm in Tushkan. First of all, the snowpack temperature profile was measured to determine if snow melting could have occurred before sampling. Major snow thawing can be discarded in any of the 3 sampling sites because snow temperature was not around 0°C but always lower. Nevertheless, the deepest snowpack layers fall within the range between -2 and 0°C: Oiskoe at 110 cm deep, Tsirkovoe from 90 to 110 cm, and namely Tushkan from 60 to 110 cm deep. This indicates that snow melt was either about to occur or could have even started in these particular layers, triggering a sequential elution of solutes (Mosello et al., 1997). In that hypothetical case, snowpack-based atmospheric deposition estimates would be biased. In order to discard such a case, solute concentrations in the upper and colder snow layers were compared to those in the deeper and warmer ones (fig. 3, table S3).

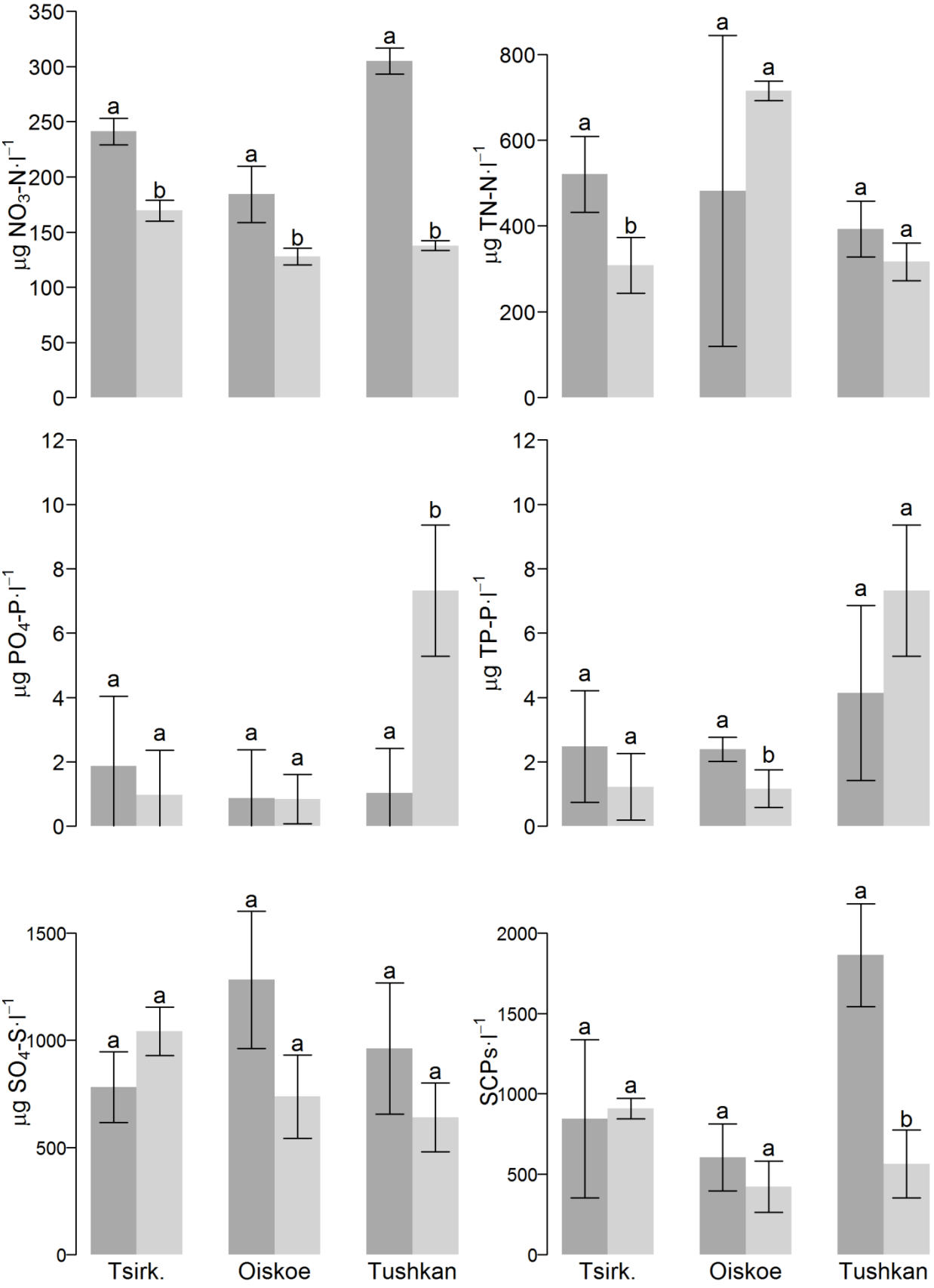

µg NO3-N·l−1
µg TN-N·l−1
µg PO4-P·l−1
µg TP-P·l−1
µg SO4-S·l−1
SCPs·l−1
Tsirk.
Oiskoe
Tushkan
Tsirk.
Oiskoe
Tushkan

Figure 3 Chemical composition of upper (dark grey) and lower (light grey) layers of the 2016-17 snowpack in Ergaki mountains. All values are in μg·l^{-1} except SCPs (counts·l^{-1}). Bars represent mean values and whiskers, standard deviation. The two upper layers were averaged in Tsirkovoe, where the snow core was divided into three layers. Column pairs with "a" and "b" letters are significantly different (one-way ANOVA, p-v<0.05 in the case of nitrate; t-tests in the other cases; n=3 except in Tsirkovoe, where upper layer n=4 and lower layer n=2).

The hypothesis was that deeper and warmer layers, suspect of possible melting, would show lower solute concentration in case of important melting, preferentially in those solutes that elute firstly during snow melting. Yet, because the first centimetres of snowpack were formed much faster than the rest of the snowpack, it is conceivable that the deep layers were originally poorer in airborne chemicals and particles, which would bother the initial hypothesis. Indeed, the first third of snowpack thickness at Olenya Rechka meteorological station deposited in only 19 days (from 10/01 to 10/19), whereas it took 39 days (from 10/01 to 11/08) to attain half of its thickness at sampling date (i.e. 187 days after initial snowpack formation). It is likely that the deepest Tsirkovoe, Oiskoe and Tushkan snow core segments (80-115 cm in the first case and 60-115 cm in the others) would have formed in about 19 and 39 days, respectively. Nevertheless, if precipitation rate had a determinant effect on the vertical distribution of solutes and particles content, the lower values in deeper layers should be expectable in all the measured variables, and it was not the case (fig. 3).

Thus, no significant differences were found between the upper and deeper layers in any of the measured variables except for nitrate, with lower values in the deep layers (ANOVA, p-value= 7.75×10^{-5}). The other significant differences between upper and deeper snow layers (TN in Tsirkovoe, SRP in Tushkan, TP in Oiskoe and SCPs in Tushkan; t-tests) were not consistent across sampling sites (fig. 3). Besides, sulphate also had slightly lower concentrations in the deep snow layers but this difference was not statistically significant. This is especially explanatory because preferential elution of ions during snow melt occurs either in the sequence SO_4^{2-}>NO_3^->NH_4^+ (Kuhn, 2001) or SO_4^{2-}>NH_4^+>NO_3^- (Wang et al., 2018a), but sulphate always elutes preferentially to inorganic nitrogen species, according to the literature (Cragin et al., 1996; Kuhn, 2001; Stottlemyer and Rutkowski, 1990; Williams and Melack, 1991). In other words, higher proportions of sulphate are released during early snow melting steps as compared to nitrate or ammonium. As a result, only significantly lower values of sulphate should be observable in incipient thawing snow layers whereas both sulphate and nitrate would be significantly leaked at a more advanced thawing stage. Therefore, we suggest that the only observed differences in nitrate concentrations between layers might not be due to snow melting. Even if it is true that sulphate also tends to be lower at deep warm snow layers, the fact of being non-significant allows us to discard thawing as a cause, and entails sulphate load estimates would not be thaw-biased nor any of the other solutes, which should elute at a later stage. As a conclusion, snowpack-based estimates of atmospheric deposition should always be cautiously considered, but major elution of solutes due to snow melting was not detected in the present study, probably thanks to the consistently negative temperatures along almost the whole integrated time period.

3.2 Snow nutrients and pollutants composition

Nutrient concentrations in Ergaki snowpack (table 2, table S3) generally take intermediate positions in comparison with other snowpack studies around the world. For instance the average 191±35 µg NO_3-N·l^{-1} in Ergaki is comparable to an old record in the Pyrenees (115±106 µg NO_3-N·l^{-1}, Catalan 1989) but lower than a later one in the same mountains (280 µg NO_3-N·l^{-1}, Felip et al. 1995). It also takes an intermediate position relative to the Alps: lower than in Tyrolean Alps in the early 1990s (308 µg NO_3-N·l^{-1}, Felip et al. 1995) but higher than most sampling points in the French Alps in a more recent study (Dambrine et al., 2018). Finally, nitrate concentration in Ergaki snow was in between that of the Bothnian Bay of the Baltic sea (480 ±130 µg NO_3-N·l^{-1}, Rahm et al. 1995) and the lake Tahoe basin in Sierra Nevada (14-138 µg NO_3-N·l^{-1}, Pearson et al. 2015). Note that, paradoxically, the former is considered a low atmospheric nitrogen deposition region (Bergström and Jansson, 2006) whereas the latter has been reckoned as an airborne nutrient enriched area (Sickman et al., 2003) where atmospheric nitrogen deposition has shifted phytoplankton limitation from N and P colimitation to persistent P limitation (Jassby et al., 1994).

		NH_4-N	NO_2-N	NO_3-N	TN	PO_4-P	TP	SO_4-S	SCPs
Average concentration in snow (µg·l^{-1})		n.d.	n.d.	191 (34)	483 (165)	2.55 (2.13)	3.33 (2.42)	864 (106)	805 SCPs·l^{-1} (275)
Half year deposition (mg·m^{-2})		n.d.	n.d.	40 (16)	97 (56)	0.43 (0.15)	0.58 (0.13)	190 (91)	159 × 10^3 SCPs·m^{-2} (48)
Deposition rate (~time) (mg·m^{-2}·y^{-2})		n.d.	n.d.	79 (47)	191 (132)	0.84 (0.48)	1.13 (0.60)	372 (236)	312 × 10^3 SCPs·m^{-2}·y^{-1} (174)
Deposition rate (~precipitation) (mg·m^{-2}·y^{-2})		n.d.	n.d.	119 (71)	288 (198)	1.26 (0.73)	1.71 (0.91)	560 (356)	470 × 10^3 SCPs·m^{-2}·y^{-1} (262)
Modelled deposition rates (mg·m^{-2}·y^{-2})	For year 2000			c. 100 (Lamarque et al., 2013)		0.1-0.5 (Mahowald et al., 2008)	c. 2 (Mahowald et al., 2008)	100-200 (Lamarque et al., 2013)	
	For year 2030			50-200 (Lamarque et al., 2013)				50-200 (Lamarque et al., 2013)	

Table 2. Average concentrations, half year depositions and estimated yearly deposition rates, as averaged by the 3 sampled sites (µg·l^{-1}, mg·m^{-2} and mg·m^{-2}·y^{-1}, respectively) (SCPs in counts·l^{-1}, 10^3 counts·m^{-2} and 10^3 counts·m^{-2}·y^{-1}). Mean values are shown, standard deviation in parenthesis, "n.d." means non detected. Yearly deposition rates were estimated on the basis of measured winter depositions and either assuming a constant deposition rate (time weighted estimate, row 3) or a precipitation-dependent deposition rate (precipitation-weighted estimate, row 4). See section 3.3 for further discussion.

Total nitrogen and total phosphorus in Ergaki snowpack (table 2) were higher than in the first mentioned Pyrenean study but lower than in the Baltic: 194±135 and 1054±363 µg TN-N·l^{-1}, and 2.38±0.59 and 9.3±5.1 µg TP-P·l^{-1}, respectively. Total phosphorus concentration also was within the lowest range of that measured around lake Tahoe (3-109 µg TP-P·l^{-1}, Pearson et al. 2015). Nevertheless, ammonium and nitrite were undetectable in the present study but detected in most of the previous studies in the snowpack (e.g. Catalan 1989; Pearson et al. 2015). Ammonium was also detected in the snow surrounding the city of Krasnoyarsk by our own lab, using the same analytical method as here (unpubl.). It is very likely that ammonium concentrations in the present study were under the detection limit, as nitrate values were more than five-fold lower than in the Krasnoyarsk city snow samples, where ammonium had been detected. Finally, nutrient bioavailability is an attribute of the Ergaki snowpack as 73±12% TP was in the form of phosphate and about 44±19% TN was nitrate.

Besides ammonium and nitrite, sulphate concentrations in Ergaki snowpack were also unusual. Sulphate was the most abundant of the measured ions. It doubled that in the Pyrenees in the late eighties (401±106 µg SO_4-S·l^{-1}, Catalan 1989) and quadrupled that on lake Tahoe (Pearson et al., 2015). Sulphate concentration in Ergaki snowpack was only similar to the highest values in the literature for non-urban areas, such as on the south coast of lake Superior in the eighties (828±216 µg SO_4-S·l^{-1} in average, Stottlemyer and Rutkowski 1990). Altogether, nitrogen and phosphorus concentrations reached intermediate-low values but sulphate concentration was remarkably high in Ergaki snowpack.

The organic nitrogen in Ergaki snowpack represented a 56±19% of the total nitrogen, which is a high but reasonable value as compared to the literature. The relative share of organic to total nitrogen in the snowpacks of the Pyrenees, Alps and Sierra Nevada (USA) mountains, and on the Baltic sea were 10±9%, 41±13% ,49±17% and 21±12%, respectively (Catalan, 1989; Clement et al., 2012; Pearson et al., 2015; Rahm et al., 1995). Organic nitrogen has been reported elsewhere to be higher in snowpack records than in wet deposition because dry deposition of organic nitrogen is integrated in the snowpack and because microbial uptake and assimilation of inorganic nitrogen might occur in the snowpack (Clement et al., 2012; Pearson et al., 2015). In the case of microbial conversion from inorganic to organic nitrogen, it could be hypothesised that deeper and older snow layers should have higher organic nitrogen shares. Such a pattern was only observed at Tushkan (ANOVA, p-value= 0.0178) whereas no significant differences were found in the percentatge of organic nitrogen between upper and lower snow layers at Oiskoe and Tsirkovoe sites. We, therefore, hypothesise that a different combination of phenomena might be responsible for organic nitrogen dominance at different sites.

3.3 Atmospheric deposition load

Roughly half year cumulative deposition corresponding to the snow season -187 days- is summarized in table 2 (second row; see table S3 for original measurements). Unfortunately, snow-free season depositions were not measured in the present study and, consequently, yearly deposition rates could not be determined. Nevertheless, preliminary estimations were conducted assuming either a constant deposition rate along the year –time-weighted estimate– or a precipitation-weighted deposition rate (table 2, 3rd and 4th rows, respectively). These assumptions entail different simplifications concerning the seasonal pattern of emission, transport and deposition of the different chemical species in this particular part of the world. The precipitation-weighted estimate should be, *a priori*, a more accurate estimate because wet deposition is known to be the main contributor to total deposition in wet climates like that in West Sayan mountains. Indeed, the accumulated precipitation registered in Olenya Rechka meteorological station during the studied snow season was 419 mm, whereas almost the double (819 mm) were registered during the following months up to complete a year. Note that the 2016-17 seasonality was slightly more prominent than the median 2005-2019 seasonal precipitation (fig. 2 a). Nevertheless, both estimations neglect the emission seasonality, which might turn the constant deposition estimate into the most credible option in some cases. To evaluate our different estimates, we compared them to seasonal depositions in the literature and discussed their likely seasonal emissions.

The precipitation-dependent estimate of atmospheric phosphorus deposition (table 2, 4th row) was probably the closest to the actual yearly load, although it might be an underestimate. That is because two thirds of the yearly precipitation and biogenic aerosols –mainly pollen– co-occur during the snow-free season and pollen represents an important share of atmospheric phosphorus sources in low-atmospheric-phosphorus taiga landscapes like Ergaki (Banks and Nighswander, 2000; Doskey and Ugoagwu, 1992; Mahowald et al., 2008; Wang et al., 2015). In order to evaluate the magnitude of our underestimation, we checked similar studies with seasonal resolution in cold forest landscapes including the lake of Bays (ON, Canada) (Eimers et al., 2018), lake Simcoe (ON, Canada) (Brown et al., 2011), and a Tibetan forest (Wang et al., 2018b). Phosphorus loads during the snow period were about 9, 11 and 18 times larger than in Ergaki, snow-free season atmospheric phosphorus depositions, 2.4, 5 and 7.4 times higher than in the snow season, and snow-free season precipitations, 0.88, 0.91 and 9.1 times that of snow season, respectively. Thus, in the hypothetical case that phosphorus deposition seasonality strictly depended on the yearly phosphorus load, the seasonal factor for Ergaki should be much lower than 2.4. On the other hand, if it depended on precipitation seasonality alone, Ergaki precipitation seasonality (1.95) would correspond to a phosphorus deposition seasonality of about 5.5. If we applied these factors (2.4 and 5.5) to estimate snow-free season phosphorus deposition and added it to measured snow season deposition, the yearly deposition rates they would be: 1.972 mg TP-P· $m^{-2}\cdot y^{-2}$ and 1.462 mg PO4-P· $m^{-2}\cdot y^{-2}$, and 3.77 mg TP-P· $m^{-2}\cdot y^{-2}$ and 2.795 mg PO4-P· $m^{-2}\cdot y^{-2}$, respectively. The latter factor (5.5) would definitely provide an overestimation of snow-free season phosphorus deposition. The former one (2.4) resulted in slightly higher values than our precipitation-dependent estimate and it is not certain if that would either over- or underestimate the actual value.

The best atmospheric nitrate deposition estimate was the precipitation-dependent estimate (table 2, 4th row), according to its seasonal distribution in other natural forested sites in the literature. The Ergaki autumn-winter nitrate deposition was four and five times lower than in a Chinese "background" and a south Bohemian forest site, respectively (Kopáček et al. 2011b; Xu et al. 2018). Nevertheless, HNO3 and total inorganic nitrogen species atmospheric concentrations were stable along the year in the Chinese background site, and only particulate NO3 was slightly higher in autumn-winter than spring-summer. In the south Bohemian forest, the April to September precipitation and nitrate deposition were only 15% and 5% higher than in October-March, respectively. Therefore, atmospheric nitrogen concentration was also fairly stable at this site, with just slightly higher atmospheric nitrate concentrations in the autumn-winter semester that would be mainly counterbalanced by a lower precipitation. In the light of these observations, it is likely that atmospheric nitrate concentration in Ergaki during the snow season was either similar to or slightly higher than in the snow-free season. In case of invariable atmosphere nitrate concentrations along the year, higher precipitation during the snow-free season would trigger also a higher nitrate deposition, and our precipitation-dependent estimate (table 2, 4th row) would be our best estimate. In the hypothetical case where the proportion between snow and snow-free season atmospheric nitrate concentrations was the same as in the Chinese site (1.24), and taking into account the higher snow-free season precipitation in Ergaki (1.95), the resulting snow-free nitrate deposition would be about 1.6 times higher than that measured in the snow season and the yearly load would be about 104±62 mg NO_3-N·m^{-2}·y^{-1}. In conclusion, the actual yearly nitrate deposition should be somewhere in-between the time-dependent and the precipitation-dependent estimates but closer to the latter estimate.

Time-based sulphate atmospheric deposition estimate was better than the precipitation-dependent estimate. Winter atmospheric sulphate depositions were higher than in summer both in the pristine Canadian Rocky Mountains (2-5 times) and in a Japanese site receiving sulphate from Chinese coal combustion (3.5-4 times) (Ohizumi et al., 2016; Wasiuta et al., 2015). Unexpectedly high seasonality in the pristine location was due to much higher precipitation in winter but the atmospheric sulphate concentration was relatively constant along the year. On the other hand, sulphate deposition seasonality in the polluted site was attributed to higher coal burning and emissions in winter. As winter atmospheric sulphate deposition in Ergaki (190±91 mg SO_4-S·m^{-2}) was about four times higher than the background values in the Canadian Rocky mountains (≤ 50 mg SO_4-S·m^{-2}) and 11-12 times lower than in a Japanese site, it is likely that winter atmospheric sulphate concentrations in Ergaki were also higher than in summer. In this case, the precipitation-weighted yearly deposition estimate would be an overestimation but we cannot rigorously determine if the actual value would lay above or below the time-weighted estimate. At most, we could assume a linear relationship between yearly sulphate deposition load and its seasonality. Then, a seasonality 11-12 times lower than in the Japanese site form the literature would imply a yearly deposition load of 251 mg SO_4-S·m^{-2} in Ergaki. Accordingly, our time-dependent estimate would be our best estimate but still an overestimate. In conclusion, for the sake of a simpler discussion, we will only consider the time-weighted estimate of yearly sulphate deposition and precipitation-weighted estimates of phosphorus and nitrate depositions. Nevertheless, these estimates must be interpreted cautiously: Whereas nitrate and sulphate deposition estimates might be slightly overestimated, phosphorus would be underestimated.

The selected yearly deposition rate estimates (table 2, 3rd and 4th rows) were compared to global model predictions from the literature (table 2 5th row). A global deposition model predicted c. 100 mg NO_3-N·m^{-2}·y^{-1} and 100-200 mg SO_4-S ·m^{-2}·y^{-1} loads on West Sayan mountains for year 2000, whereas it forecasted ranges from 50-200 mg NO_3-N·m^{-2}·y^{-1} and 50-200 mg SO_4-S·m^{-2}·y^{-1} in 2030, according to different scenarios (Lamarque et al., 2013). The EMEP wet deposition model reported similar values (50-100 mg oxidized N·m^{-2}·y^{-1} and 50-200 mg oxidized S·m^{-2}·y^{-1}, including SO_2 and SO_4, and HNO_3, HONO and NO_3, respectively) for year 2017 on the limits of their geographical prediction, at a location about 200 Km west of our sampling site (Fagerli et al., 2019; Gauss et al., 2019). Therefore, our 2016-17 nitrate deposition estimate roughly fitted the models, whereas sulphate deposition was clearly higher than expected. In the case of phosphorus deposition, our TP estimate was slightly lower than predicted (c. 2 mg TP-P·m^{-2}·y^{-1}), although uncertainties linked to pollen contribution could make the actual TP-P deposition match or even surpass the modelled values. On the other hand, the phosphate fraction would be clearly higher than expected (0.1-0.5 mg PO_4-P ·m^{-2}·y^{-1}, Mahowald et al. 2008).

In conclusion, the atmospheric nitrate deposition in Ergaki mountain ridge is at the very low range and is between 5 to 20 times lower than in polluted areas of the world. Nevertheless, it is clearly above the background deposition of 0-50 mg NO_3-N·m^{-2}·y^{-1}, as it used to be the case of most Siberia in 1850 or the Antarctica and unpolluted parts of the oceans in 2000 (Lamarque et al., 2013). As for total phosphorus deposition, the uncertainty linked to non-measured spring-summer biogenic and wildfire contributions, makes it hard to position the studied site within a World ranking. Our estimate excluding these important biogenic and wildfire contributions (1.71 mg TP-P· m^{-2}·y^{-2}) and our literature-based estimate including them (1.972 mg TP-P· m^{-2}·y^{-2}) would be lower than any terrestrial measurement, according to a worldwide review (≥3 mg TP-P· m^{-2}·y^{-2}) (Tipping et al., 2014). Nevertheless, it is also possible that pollen and wildfires accounted for a larger contribution and that the present study site exceeded the latter value. In any case, atmospheric phosphorus deposition in Ergaki would be above the background values corresponding to the poles and the oceans (≤1-2 mg TP-P· m^{-2}·y^{-2} and ≤0.5 mg PO_4-P· m^{-2}·y^{-2}), excluding the Atlantic strip downwind of the Sahara (Mahowald et al., 2008). Finally, our yearly sulphate deposition estimate should be cautiously considered, as it could be overestimated due to regionally widespread coal combustion for heating during winter (see section 3.5). In any case, it would positively exceed the background values of 0-50 and 50-100 mg SO_4·m^{-2}·y^{-1} typical in the polar areas and southern hemisphere oceans, respectively (Lamarque et al., 2013).

3.4 SCPs deposition rate

The calculated SCPs deposition rate in Ergaki Natural Park (312±174×10^3 SCPs·m^{-2}·y^{-1}) was high above the background rates recorded in Baikal middle basin (57×10^3 SCPs·m^{-2}·y^{-1}), Svalbard islands (13×10^3 SCPs·m^{-2}·y^{-1}) and Nevada Rocky mountains (1.3±0.8×10^3 SCPs·m^{-2}·y^{-1}) (Reinemann et al., 2014; Rose et al., 1998). Indeed, it is also far below the records in more polluted areas such as the case of lake Paione Superiore in western Alps as it used to be during the more polluted times of 1980s and early 1990s (40900×10^3 SCPs·m^{-2}·y^{-1}) or a set of north African lakes (1098-23694×10^3 SCPs·m^{-2}·y^{-1}), where production of electricity by thermal means has increased in the last years (Rose et al., 1999b, 2003). In comparison to a couple of lakes sampled in 1992 in the Khamar-Daban mountains (Southern Siberia) (262 and 780×10^3 SCPs·m^{-2}·y^{-1}), the

SCP deposition rate in Ergaki was more similar to the lake that was relatively farther from Irkutsk city pollution source (Rose et al., 1998). Our data also falls in the lower range of Tatra mountains (225-5240×10^3 SCPs·m^{-2}·y^{-1}) and the Pyrenees (229-630×10^3 SCPs·m^{-2}·y^{-1}) in the mid-1990s (Rose et al., 1998, 1999a; Šporka et al., 2002). An interesting and paradoxical case to compare with is lake Grånästjärn in 1980, with a very similar SCP deposition (300×10^3 SCPs·m^{-2}·y^{-1}) but sulphate and nitrate deposition rates 2.6 and 1.8 times higher than in Ergaki (Bergström et al., 2005; Wik and Renberg, 1996). This may lead to think that our SCP, sulphate and nitrate data didn't match. Nevertheless, at least sulphate depositions differing up to c. 40% have been observed at a particulate low SCP deposition rate (Rose and Monteith, 2005). Additionally, sulphate measurements in Sweden might include a higher percentage of marine sulphate than in the heart of Eurasia. Finally, apart from this single Swedish lake where the proportion of nitrate to SCPs differs so much from ours, both SCP and nitrate deposition measured in this study are generally comparable to the low range of values in the literature.

3.5 Spatial distribution and origin of atmospheric depositions

The spatial distribution of deposited chemical species showed two different patterns. On the one hand, phosphorus forms and SCPs showed even distribution between sampling sites. On the other hand, NO_3, TN and SO_4 depositions were significantly higher on Tsirkovoe and Oiskoe than on Tushkan (fig. 4). Even distribution of phosphorus deposition suggests a common source of atmospheric phosphorus for all Ergaki sites. Under very low atmospheric phosphorus deposition, like in Ergaki mountain ridge, biogenic and combustion origins are more important than mineral (Mahowald et al., 2008). This is supported by several evidences in our case. Firstly, even if the predominant western air mass retrotrajectories partly traverse Kazakhstan steppe a percentage of days, they hardly ever cross central Asian deserts (fig. 5 a and b). Moreover, direct contact between air mass retrotrajectories and the Earth crust occurs more often in the taiga ecoregion (yellow dots, fig. 5 a and b). Finally, the percentage of TP which is soluble in our snow samples (79%) is comparable to European aerosols (50-100%), but much higher than Saharan dust (8-25%) (Mahowald et al., 2008), so it suggests that phosphorus aerosols in Ergaki were not of desert origin. Thus, Ergaki mountain lakes differ from Baikal lake, which can be influenced by dust originating at the Gobi desert (Jambers and Van Grieken, 1997).

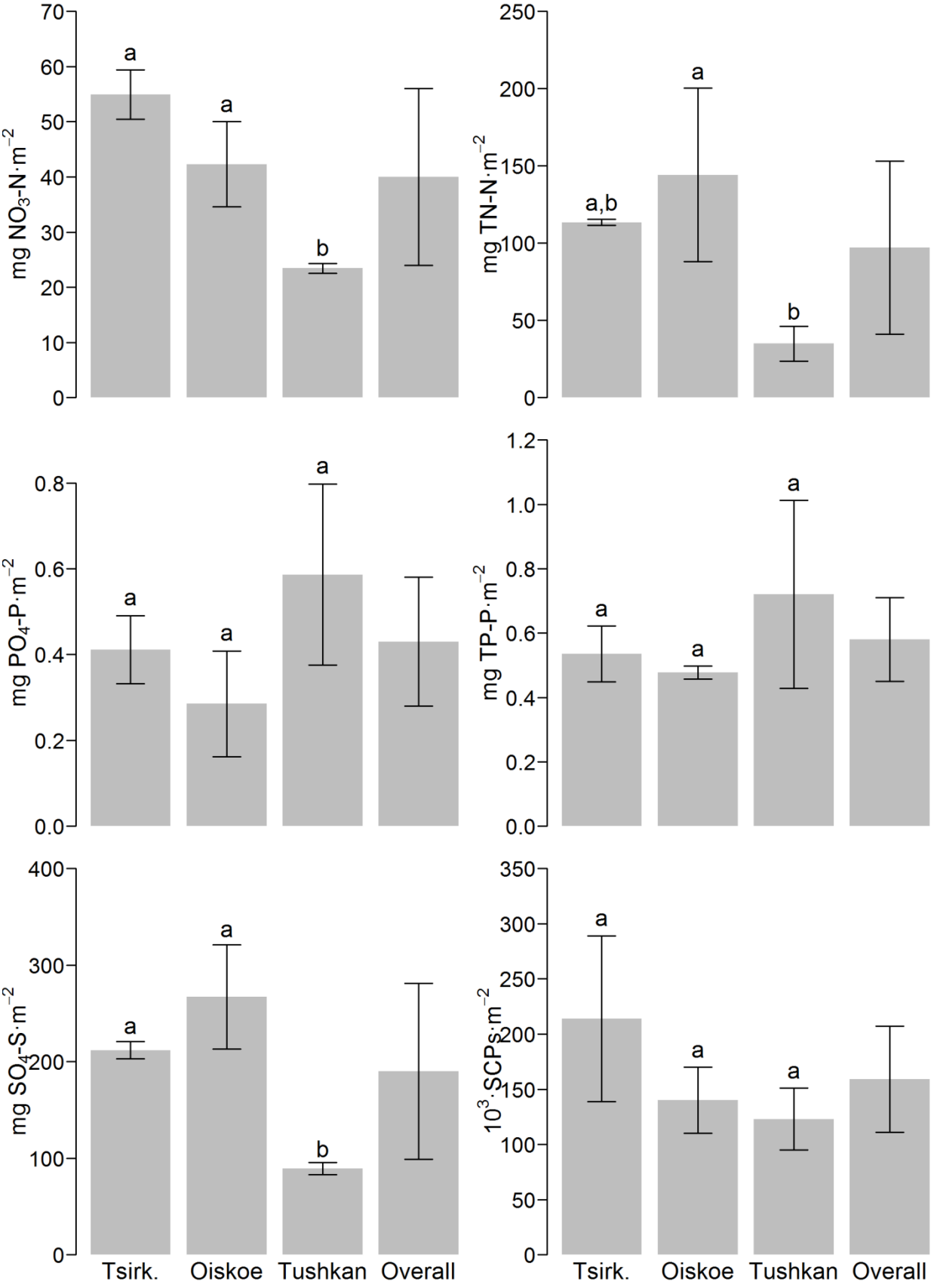
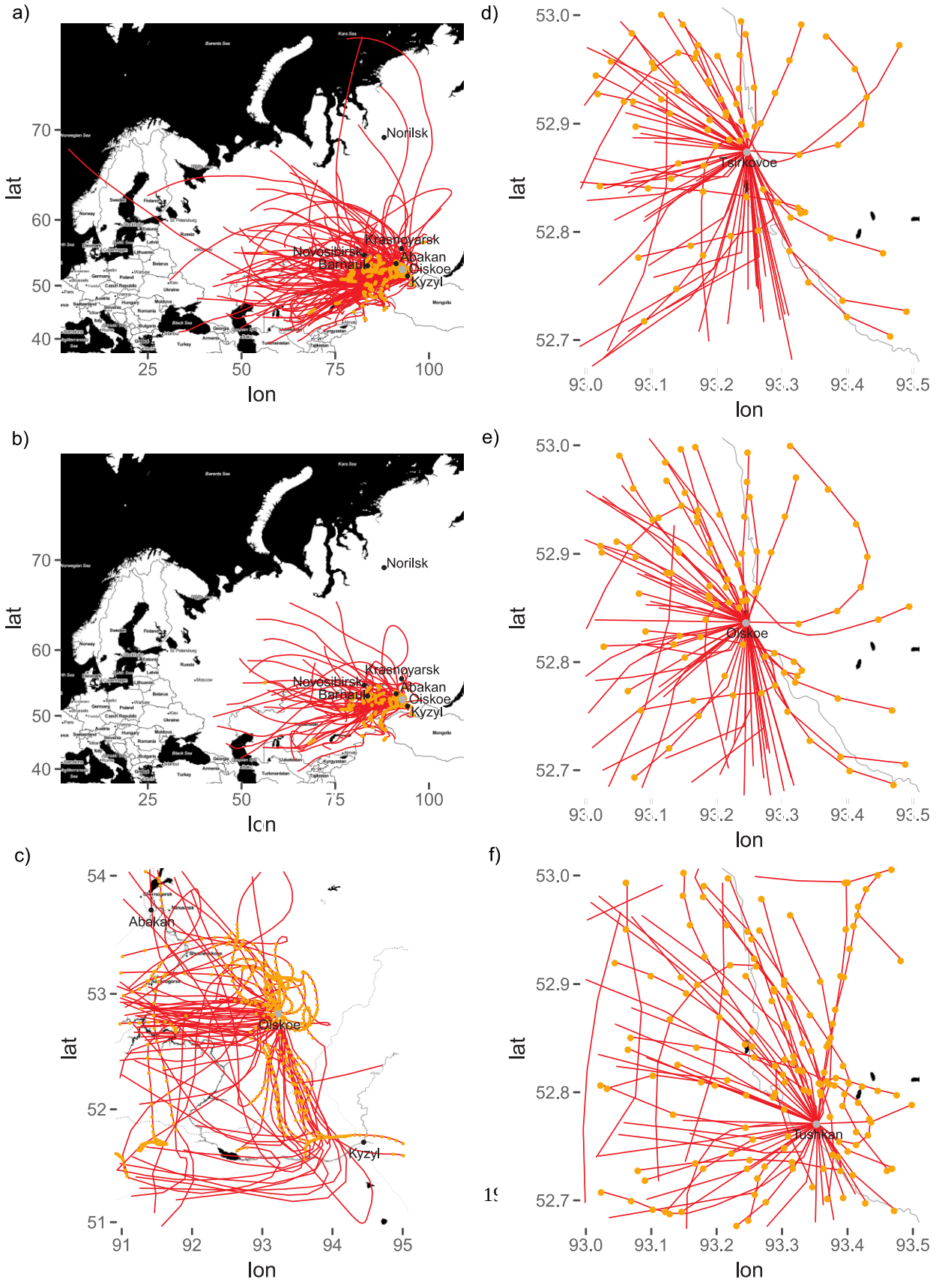

mg NO_3-N·m^{-2}
a
a
b
mg TN-N·m^{-2}
a,b
a
b
mg PO_4-P·m^{-2}
a
a
a
mg TP-P·m^{-2}
a
a
a
mg SO_4-S·m^{-2}
a
a
b
10^3·SCPs·m^{-2}
a
a
a
Tsirk.
Oiskoe
Tushkan
Overall

Figure 4. Half year deposition of some airborne chemical species along with snow at 3 different sites in Ergaki mountain ridge. Bars are average values and whiskers represent standard deviation. Sites with different letters on error bars belong to different groups defined by post-hoc Tukey HSD analysis (one-way ANOVA p-values<0.01).


a)
b)
c)
d)
e)
f)
lat
lon
Norilsk
Krasnoyarsk
Novosibirsk
Barnaul
Abakan
Oiskoe
Kyzyl
Tashtagol
Tashtykan

405

Figure 5. Daily three-day long air mass retrotrajectories flowing onto lake Oiskoe from 1st October 2016 to 5th April 2017 (a). Only retrotrajectories of air masses causing precipitation onto Oiskoe at different zooms (b, c and e) and to Tsirkovoe (d) and Tushkan (f). Yellow dots represent hourly records where the air mass retrotrajectories contacted the Earth crust. Water bodies are in black. Grey lines are either political borders or the road. Sources: Map tiles by Stamen Design, under CC BY 3.0. Data by OpenStreetMap, under ODbL; Airmass retrotrajectories by http://www.ready.noaa.gov.

Nitrate and sulphate are tracers of fossil fuel or biomass combustion (Mahowald et al., 2008). Their spatial correlation (lower in Tushkan than in the other two sites, fig. 4) suggests that alternative nitrate origins like chemical fertilizers or secondary transformations like nitrification/denitrification by microbes in the snowpack might be unimportant. In the same vein, nitrate and sulphate had a relatively high, although not significant, Pearson correlation coefficient (0.63) in the seven analysed snow core sections. The reason for lower nitrate and sulphate values in Tushkan is still unclear. This site is a forest glade located at a 300 m lower altitude than the other two. We argue that this altitude difference is too limited to trigger any differences in nitrate deposition and, in any case, the higher the site, the lower the expected deposition (Dambrine et al., 2018). Nonetheless, shorter distance between Tsirkovoe and Oiskoe and their wind regimes might be more decisive, even if the former is located on the north face and the latter on the south face. The wind speeds there were 3.4 $m \cdot s^{-1}$ and 3.3 $m \cdot s^{-1}$, respectively, whereas in Tushkan, farther from the ridge, it was 3.0 $m \cdot s^{-1}$. Despite wind rose circular correlation between Tsirkovoe and Oiskoe was not significant, their local air mass retrotrajectories were quite more similar than to Tushkan (fig. 5 d, e and f). Perhaps, the two more northern sites might be also more exposed to the dominant snow-forming westerlies that flow between latitudes 52° and 53° and above (fig. 5 c). As for SCPs, which are also originated by combustion, the nitrate and sulphate spatial distribution is not followed. We speculate that the particulate character of SCPs might impose different atmospheric transport properties, so even if SCPs are good tracers of air pollution, slight mismatches between SCPs and chemical pollutants might occur (Rose and Ruppel, 2015; Wik and Renberg, 1996). Anyway, a trend to higher values in the northernmost sites is also observed (fig. 4).

Finally, local wind speed differences between sites might be a tracer of air mass origin. Generally, faster winds would be capable to deliver chemical species from longer distances. The average retrotrajectory length had a weak, non significant, but still positive Pearson correlation with nitrate (0.47) and negative with phosphate (-0.48), TP (-0.25) and TN (-0.20). This suggests that nitrate deposited on Ergaki mountains might originate at farther distances than phosphorus and particulate nitrogen. To sum up, we hypothesise that northern cities might contribute more to the nitrate deposition than southern ones. These combustion-produced chemicals would be uploaded to the northernmost half of the dominant westerlies conveyor belt flowing directly onto Ergaki mountains, rather than on the southernmost half of the westerlies flow, which mainly traverse Kazakhstan and turn northwards to Ergaki mountain ridge just before reaching the city of Kyzyl (fig. 5 c). These urban sources might not only include those at the local scale (Abakan, Minusinsk, Chernogorsk, rather than Kyzyl in the south) but also those at a regional one (central and eastern south Siberian rather than northern Kazakhstan cities).

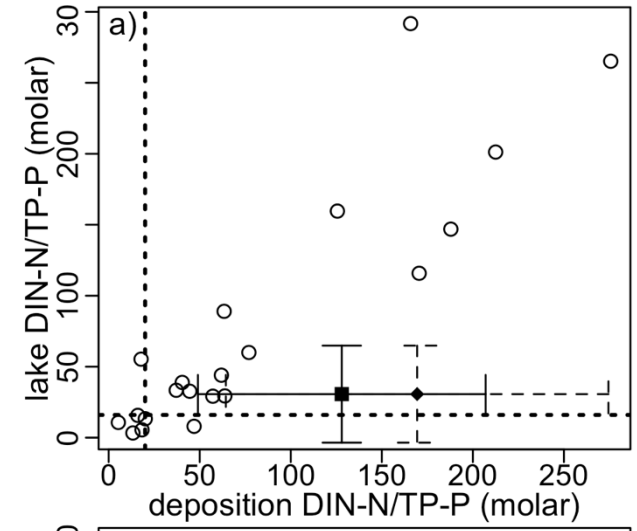
3.6 Nutrient deposition and lake water stoichiometry

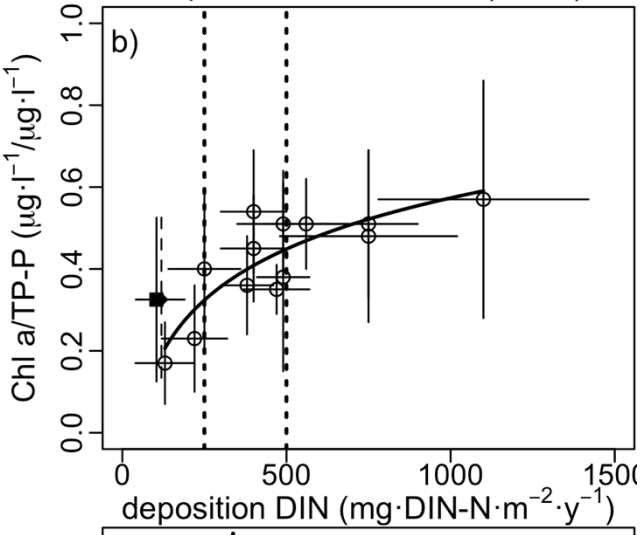
The molar stoichiometry of volume weighted mean concentrations in the snowpack, i.e., the concentrations that would be measured if we had sampled the whole snow core at once, were 169±76 NO3-N/TP-P, 251±134 NO3-N/PO4-P, and 486±357 TN-N/TP-P (mol/mol). The molar stoichiometry of estimated yearly atmospheric nutrient deposition in Ergaki were 169±105 and 128±79 NO3-N/TP-P (mol/mol) according to the precipitation-dependent yearly load estimation and to the abovementioned literature-based corrections, respectively. As no other DIN form but nitrate was detected in our samples, NO3-N/TP-P ratio can be compared to DIN-N/TP-P ratios in the literature. The latter ratio has been previously used to assess nitrogen and phosphorus bioavailability both from deposition and in mountain lake water (Brahney et al., 2015). Total phosphorus was used instead of PO4 because: (1) otherwise, the fast biological uptake of deposited PO4 would lead to underestimate the actual atmospheric load, and (2) organic phosphorus sources are bioavailable to many mountain lake phytoplankton species via extracellular enzyme activity, phagotrophy and osmotrophy (Diaz-de-Quijano, 2014; Medina-Sanchez et al., 2004). Thus, our estimated NO3-N/TP-P deposition molar ratios in Ergaki would belong to the higher quartile, as compared to a set of alpine regions of the world (Brahney et al., 2015) (fig. 6 a). The closest nutrient deposition stoichiometries to that of Ergaki (precipitation-dependent estimates) were recorded at the Sant Nicolau valley in the Pyrenees during the second half of the 1990s (170.5 DIN-N/TP-P, molar) and the Tatra mountains (165.8; calculation based on DIN wet deposition during 1990-94 and average TP wet deposition during 1998-2009) (Brahney et al., 2015; Kopáček et al., 2000, 2011b; Ventura et al., 2000). In the case of the alternative 128±79 NO3-N/TP-P (mol/mol) deposition estimate for Ergaki, southern Sweden lake district was the closest value (125.6). In any case, Ergaki atmospheric nutrient deposition stoichiometry was by far larger than that of northern Sweden (20.1 molar DIN-N/TP-P), the paradigm of pristine areas with very low anthropogenic atmospheric nitrogen deposition and naturally nitrogen limited lakes. This was due to the extraordinary low phosphorus deposition as compared to nitrogen, which was also relatively low but not that much (see section 3.3).

The molar stoichiometry of Ergaki lakes water was on average above the Redfield ratio (30.7±34.2 DIN-N/TP-P, fig. 6 a, table S2), which suggests lake phytoplankton would generally be P limited. Nevertheless, values below the Redfield ratio (16:1), i.e., corresponding *sensu lato* to N limitation, were also frequently observed. All the lakes had DIN-N/TP-P ratios both above and below the Redfield ratio at different surveys with the exception of lake Tsirkovoe, which was always above the Redfield ratio (P limitation) (table 3). Most lakes had DIN-N/TP-P ratios below the Redfield ratio in June and August 2011 and early September 2015, and above it in June and August 2012 and late August 2017. Therefore, no temporal trend can be drawn from our lake water chemistry data set (see table 3). Besides to the Redfield criterion, a previous study determined that DIN-N/TP-P molar ratios of 3.3, 4.9 and 7.5 would correspond to 75%, 50% and 25% probabilities of chlorophyll increase under a N enrichment experiment (Bergström, 2010). According to this more restrictive criterion, only lake Oiskoe would approach the 75% probability of having a positive increase of chlorophyll under N enrichment in the 2015 survey. Nevertheless, it is very likely that this case was due to watershed-level processes. Forest and peat cover (25%

and 6%, respectively) in Oiskoe watershed are more important than in other lakes watersheds and, more importantly, the lake receives an inflow passing by nearby houses (table 1 and S1). A local phosphorus input from nearby houses could have occurred at Oiskoe in 2015 pointing to mesotrophic status of the lake. The high TP values could be also partly due to having calculated TP as the sum of SRP and PP instead of measuring it directly in 2015 but only lake Oiskoe recorded unprecedentedly high values, which might be due to the mentioned human activities in its watershed. In conclusion, lake water nutrient stoichiometry suggests a variable, but slightly P-dominated, nutrient limitation regime.

In conclusion, a decoupling between atmospheric deposition and lake water nutrient ratio was observed in Ergaki as compared to many other mountain regions of the world (fig. 6 a). We argue that this was due to the extraordinarily low absolute values of nutrient, and especially phosphorus, atmospheric deposition on Ergaki mountain ridge. Accordingly, the sum of other biogeochemical processes occurring at the watershed soils, run-off, rivers, water column, sediments, etc. would be sufficient to modify the original stoichiometry of air-borne nutrients.


a)
lake DIN-N/TP-P (molar)
0
50
100
200
300
0
50
100
150
200
250
deposition DIN-N/TP-P (molar)


b)
Chl a/TP-P (µg·l⁻¹/µg·l⁻¹)
0.0
0.2
0.4
0.6
0.8
1.0
0
500
1000
1500
deposition DIN (mg·DIN-N·m⁻²·y⁻¹)

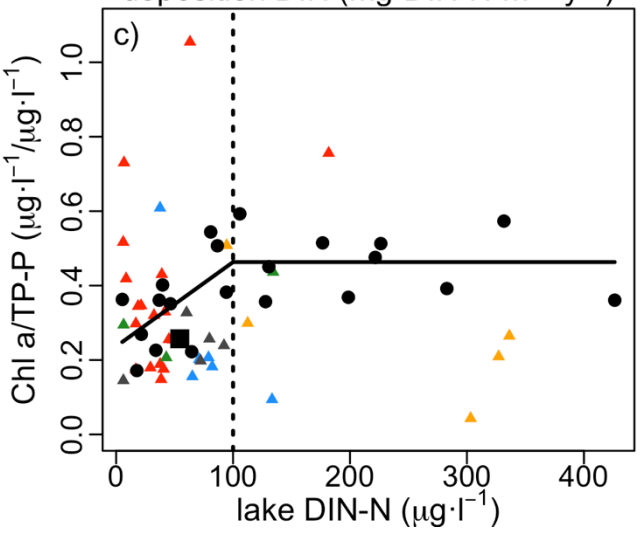

c)
Chl a/TP-P (µg·l⁻¹/µg·l⁻¹)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
lake DIN-N (µg·l⁻¹)

Figure 6. The relationship between atmospheric nutrient deposition, nutrient bioavailability and phytoplankton biomass in Ergaki lakes (black square) in the context of different world data sets. a: Atmospheric deposition versus lake DIN-N/TP-P molar ratios of several alpine regions of the world, as reproduced from (Brahney et al., 2015), including Ergaki means and standard deviations: precipitation-dependent estimates (rhombus and dashed lines) and literature corrected estimate (square and solid lines). Vertical dashed line represents the referential north Sweden value (20.1). Horizontal dashed line represents the Redfield ratio (16). b: Yearly atmospheric DIN-N deposition versus Chl a/TP-P ratio of 13 Swedish regions, as reproduced from (Bergström and Jansson, 2006; Bergström et al., 2005), including Ergaki means and standard deviations (as before). Dashed lines represent approximate limits of N, N-P and P limitation areas, according to the authors (250 and 500 mg DIN-N·m^{-2}·y^{-1}). c: Lake DIN-N concentration versus Chl a/TP-P ratio of different lake districts in the world (black circles) and its segmented regression fit as reproduced from (Camarero and Catalan, 2012), including Ergaki medians (black square) and particular observations from the following lakes (triangles): Tsirkovoe (yellow), Oiskoe (red), Raduzhnoe (blue), Karovoe (grey) and Svetloe (green). Dashed line represents limit between N and P limitation conditions, according to the authors.

Year	month	Lake	DIN-N/TP-P (mol/mol)	TN/TP (mol/mol)	Limiting nutrient
2011	early June and August	Oiskoe	4.3		N
		Svetloe	4.3		N
		Raduzhnoe	16.2		N-P
		Karovoe	6.5		N
		mean	7.9		N
2012	early June and August	Oiskoe	109.2		P
		Svetloe	49.5		P
		Raduzhnoe	42.1		P
		Karovoe	29.6		P
		mean	57.6		P
2015	early September	Oiskoe	3.7	11.6	N
		Raduzhnoe	10.5	30.9	N
		Tsirkovoe	23.6	82.8	P
		mean	12.6	41.8	N
2017	late August	Oiskoe	6	56.6	N
		Karovoe	25.8	61.9	P
		Tsirkovoe	97.9	164.1	P
		mean	43.3	94.2	P

Table 3. Lake water N:P ratios along the studied years and limiting nutrient according to nutrient availability (DIN-N/TP-P) and the Redfield ratio.

3.7 Atmospheric input and lake phytoplankton biomass limitation

Atmospheric nitrogen deposition rate was lower in West Sayan mountains than in the most pristine areas in Sweden during the period 1995-2001, and two orders of magnitude lower than the most impacted Swedish region (Bergström et al., 2013, 2005; Bergström and Jansson, 2006) (fig. 6 b). The Swedish atmospheric deposition gradient was used to establish the new paradigm, according to which the natural state of phytoplankton growth in many unproductive lakes (≤25 µg TP-P·l^{-1}) would be nitrogen limitation, when atmospheric deposition is below c. 250 mg DIN-N·m^{-2}·y^{-1}. According to that, the West Sayan mountain lakes (79-119 mg DIN-N·m^{-2}·y^{-1}) would clearly belong to the potential atmospherically induced N limitation domain, where slight increases in atmospheric nitrogen deposition trigger larger phytoplankton biomass shifts. In a further study, Camarero and Catalan reckoned the upper threshold of N limitation of phytoplankton growth regime as ~100 µg DIN-N·l^{-1} in lake water (Camarero and Catalan, 2012) (fig. 6 c). Despite some of our measurements fell above the threshold, the median of 54 µg DIN-N·l^{-1} would confirm potential N limitation in most of the sampled lakes (table S2). Nevertheless, the potential character of that nitrogen limitation should be highlighted. If we combine all the mentioned pieces of evidence, it is understandable that atmospheric nutrient deposition was so low (fig. 6 b) that it led to a decoupling between atmospheric deposition and lake water nutrient stoichiometries (fig. 6 a). In the end, the lake water DIN concentration was low enough to allow the occurrence of phytoplankton growth N limitation events (fig. 6 c), but their occurrence was alternated with phosphorus limitation periods (table 3).

The future dynamics of DIN and TP concentrations in Ergaki lakes are likely to determine changes in phytoplankton biomass and species composition because the observed stoichiometries suggested a switching regime between N and P limitation events. That would promote alternatively low-P- and low-N-adapted species. Moreover, in the case of N, we found that shifts resulting in DIN concentrations ranging from zero to the double of the average registered values would trigger important phytoplankton biomass responses (fig. 6 c). During our survey, nutrient concentrations in lakes were not majorly connected to atmospheric deposition (fig. 6 a), but future dynamics of atmospheric nutrients deposition in West Sayan mountain lakes are uncertain. On the one hand, the observed high snow sulphate concentrations and the wind analysis, made us suggest coal combustion in cities of central and eastern south Siberia to be the main winter atmospheric nitrate source. Additionally, predicted winter precipitation in this region under the RCP4.5 scenario (IPCC Representative Concentration Pathway scenario assuming 4.5 W·m^{-2} radiative forcing by 2100) would increase 10-30% in 2016-2035 and up to 20-30% in 2081-2100 (IPCC, 2013). Therefore, it is likely that atmospheric nitrogen deposition increased even in a scenario where actual emissions did not change. On the other hand, wild forest fire events in south central Siberia have multiplied and intensified during the last decades and are expected to follow this trend in the 21st century as well (Brazhnik et al., 2017; Malevsky-Malevich et al., 2008). Their effect on atmospheric nutrient dynamics will be complex. Apart from modifying the sources of phosphorus rich biogenic aerosol particles, wildfires themselves used to be considered as a nitrogen volatilization pulse that left phosphorus on the burnt land (Hungate et al., 2003; Raison, 1979). Nevertheless, a recent study unveiled their relevance as a source of atmospheric phosphorus too (Wang et al., 2015). To sum up, uncertainties on the magnitude and timing of

future fossil fuel combustion, precipitation and wildfire regimes make it difficult to predict the details of future atmospheric nutrient deposition on West Sayan mountains. Nevertheless, it is very likely that deposition rates will increase and, perhaps, represent a sufficient input to finally couple the nutrient ratio of deposition inputs and lake water and/or to promote an increase in phytoplankton biomass.

Finally, the sensitiveness of lake phytoplankton to nutrient availability might likely depend on temperature too as it was the case in the pristine Swedish north (Bergström et al., 2013). Low values of atmospheric nitrogen deposition in that region triggered a low DIN availability and a regional N limitation of lake phytoplankton growth. Nevertheless, the authors found clear phytoplankton responses to experimental NH_4NO_3 additions only in warm enough and N-limited lakes. As summer lake water temperatures were roughly 5-18 °C there and 5-14 °C here in West Sayan lakes, it is conceivable that the phytoplankton response to nutrient availability shifts was temperature-mediated in Ergaki mountain lakes. Of course, the predicted warming in the region (IPCC, 2013) would decrease the system resilience, as eventual changes in nutrients availability could not be temperature mitigated and would be directly reflected in phytoplankton biomass and species composition changes.

4. Conclusions

The Ergaki Natural Park in the West Sayan mountains was reckoned as an above-background but low atmospheric nutrient deposition area. Our atmospheric total phosphorus and nitrate deposition estimates reasonably fitted those predicted by global deposition models, whereas sulphate and phosphate proved to be higher than expected. While nitrogen values were comparable to the lowest records in other mountain areas of the World, phosphorus deposition was likely at the very lowest range ever measured on terrestrial ecosystems before. Nevertheless, any conclusions regarding yearly atmospheric phosphorus deposition loads from this study should be contrasted with further year-long measurements in West Sayan mountains, including the presumably important biogenic and wildfire contributions during spring and summer seasons.

The atmospheric reactive nitrogen deposition load on Ergaki Natural Park was similar to that in northern Sweden, so low enough to potentially induce nitrogen limitation in lake phytoplankton. However, the strongly mismatching nutrient ratios in atmospheric deposition and lake water suggested a decoupling between the two compartments. The stoichiometry of atmospheric nutrient deposition was highly determined by the extremely low phosphorus deposition and the biogeochemical processes occurring at the watershed level would easily modify the nutrient ratio of the tiny and unbalanced atmospheric input. Under such conditions, a succession of N and P limitation events was observed rather than the expected N limitation. Thus, we hypothesise that the recently suggested paradigm of nitrogen limitation of lake phytoplankton growth in natural pre-industrial conditions might apply for Sweden and other regions with a minimal atmospheric phosphorus deposition but maybe not for large areas in Siberia. A larger number of lakes distributed over Siberia and whole year long atmospheric nutrient deposition, including spring and summer seasons, should be studied to contrast that hypothesis.

Finally, the West Sayan mountain range constitutes an excellent pristine area to study the effects of past global warming with a minimal influence of atmospheric nitrogen and phosphorus deposition. The studied mountain lakes are also good sensitive sentinels for upcoming climate warming and atmospheric nutrient deposition dynamics. The expected increase in precipitation and wildfires and future fossil fuel combustion, could finally couple these lakes to the atmospheric nutrient deposition and, if climate warming unlocked the phytoplankton response to it, promote a phytoplankton biomass increase and species composition change.

Data availability

The data sets presented in this study are available as supplementary tables S1 and S2 at the repository of the library of the Siberian Federal University: http://elib.sfu-kras.ru/handle/2311/135098**.**

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Author contribution

DD and EAI designed the snow sampling, DD and AVA performed it and DD and OVA analysed snow samples. All the authors participated in sampling and sample analyses of lake water. DD prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

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