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Water acidification and critical loads: case study European Russia and Western Siberia

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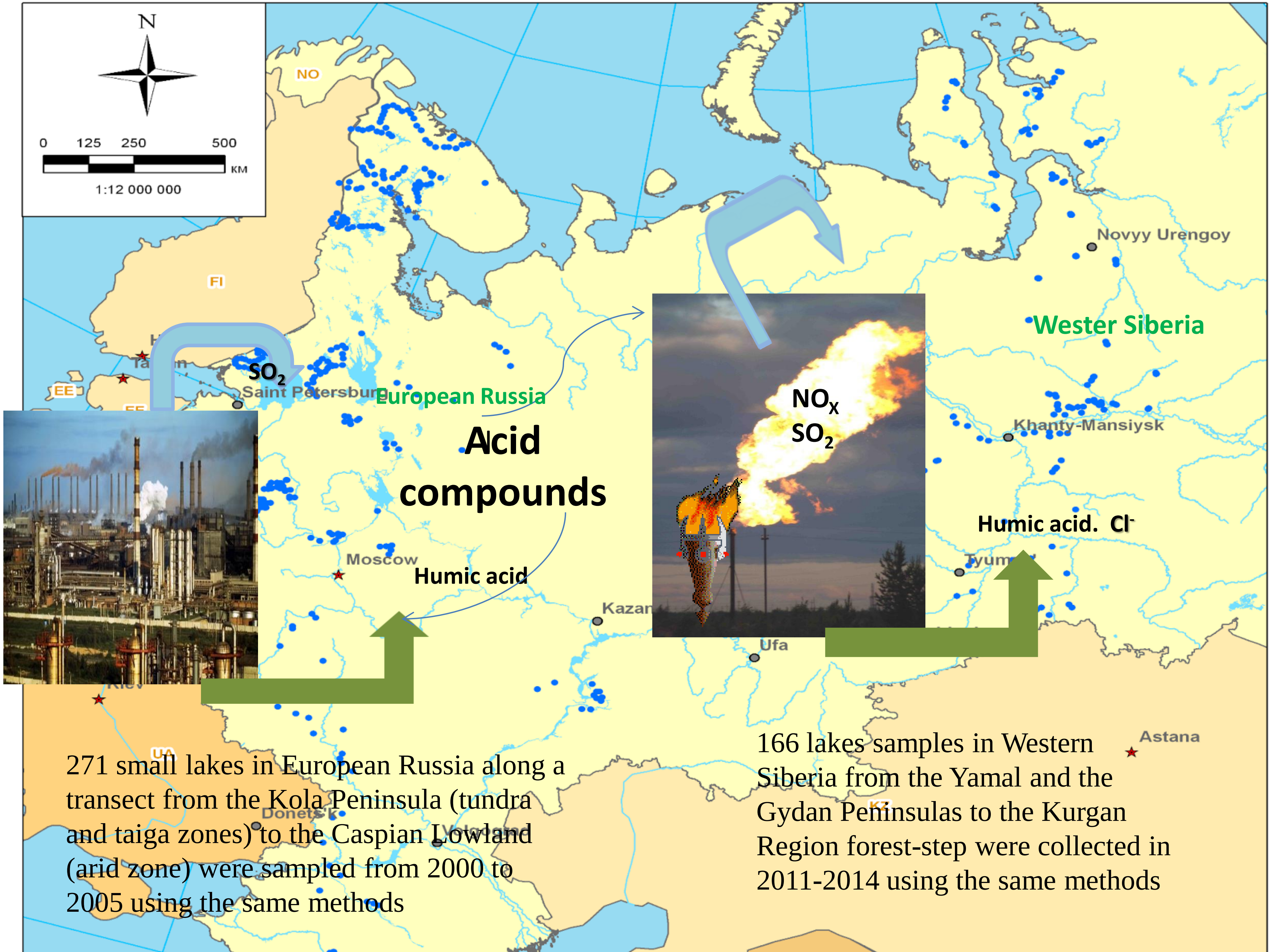
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NO
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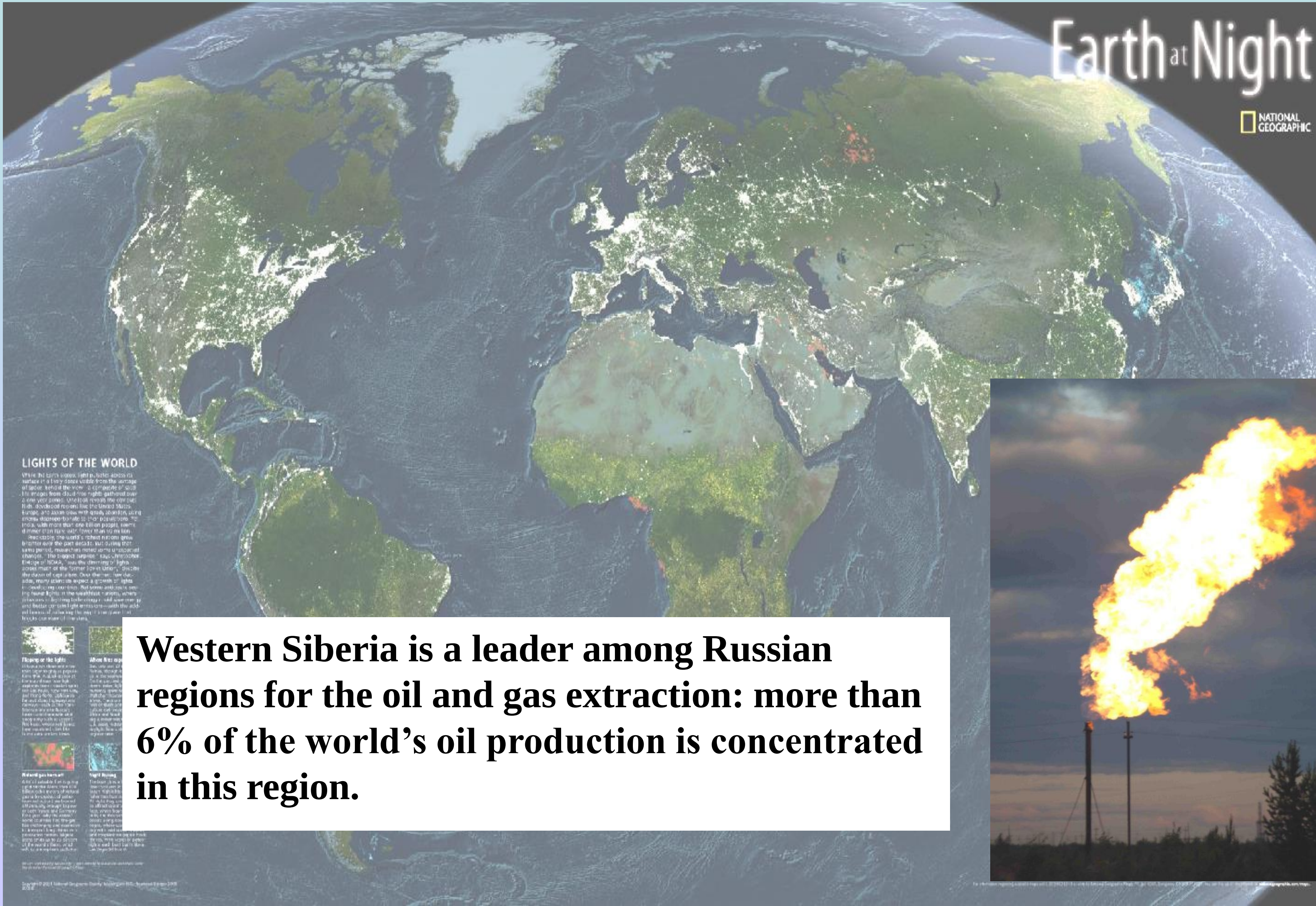
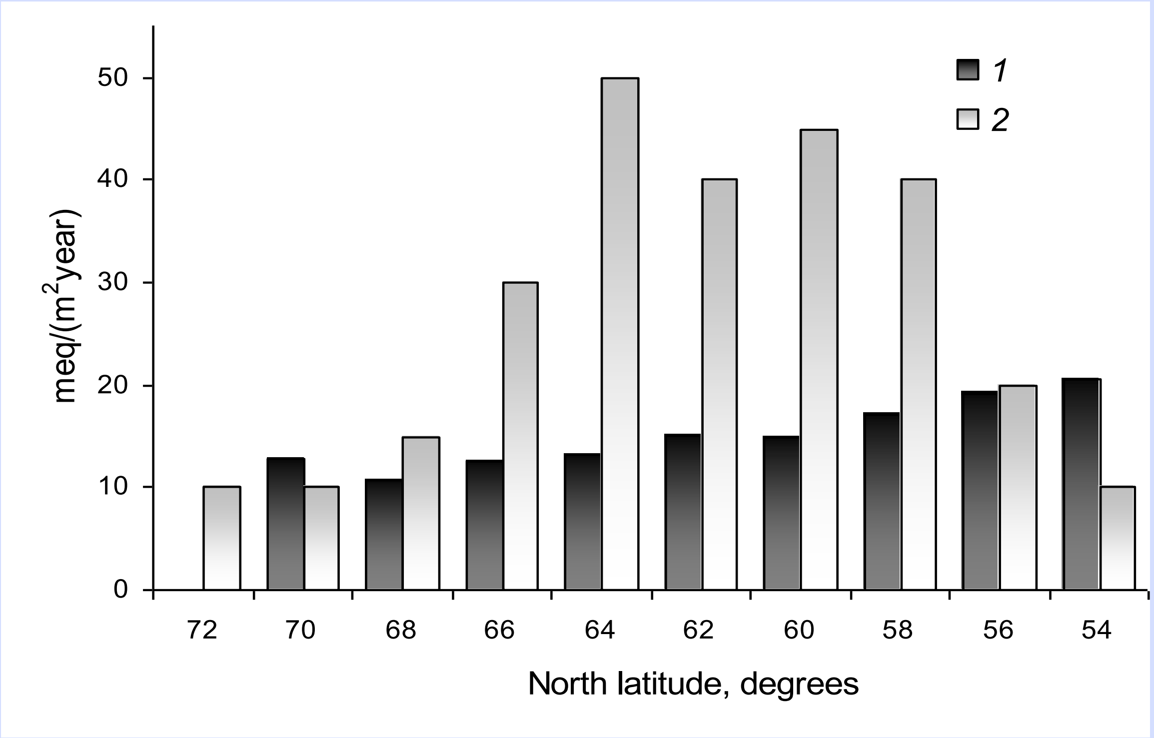
Khanty-Mansiysk
Humic acid. Cl-
Astana
271 small lakes in European Russia along a transect from the Kola Peninsula (tundra and taiga zones) to the Caspian Lowland (arid zone) were sampled from 2000 to 2005 using the same methods
166 lakes samples in Western Siberia from the Yamal and the Gydan Peninsulas to the Kurgan Region forest-step were collected in 2011-2014 using the same methods

Gas flaring during of oil production in Western Siberia leads to air pollution by oxides of nitrogen, sulfur, chlorine.



Western Siberia is a leader among Russian regions for the oil and gas extraction: more than 6% of the world's oil production is concentrated in this region.

Deposition



Deposition of strong acids (meq/m^2year) by the latitudinal gradient **in European territory of Russia - 1** (EMEP, 2000) and **in Western Siberia - 2** (Semenov, 2002)

pH of precipitation

Region	pH of precipitation	
	Min	Max
North and North-West of ER	3.1 3.4	6.2 6.3
Center of ER	3.2	7.0
South of ER	3.1	7.1
Urals and the Urals region	4.0	7.2
Center of Western Siberia northern coast and north-eastern seas	3.6	7.0

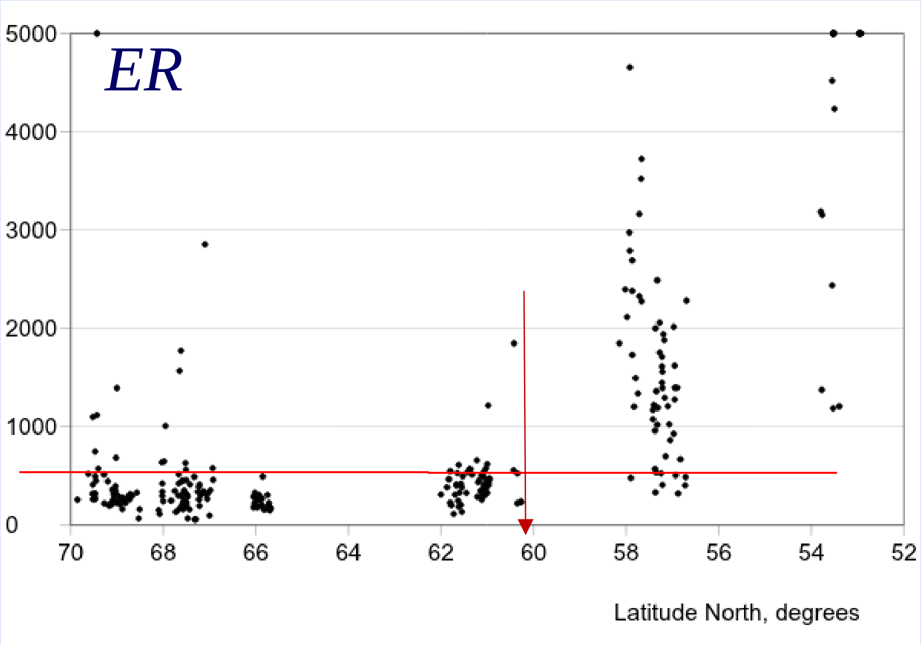
Protasov et al., 2000

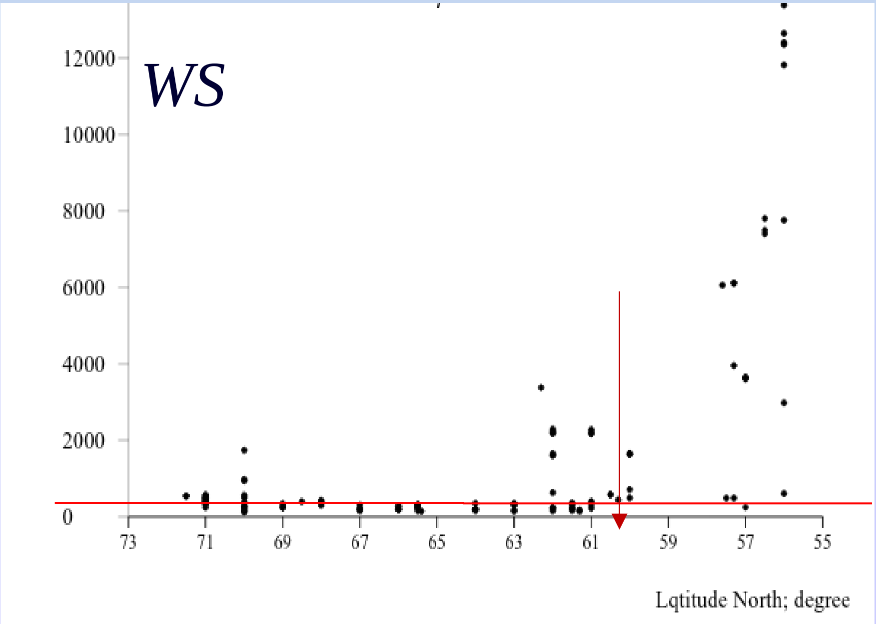
Buffer capacity

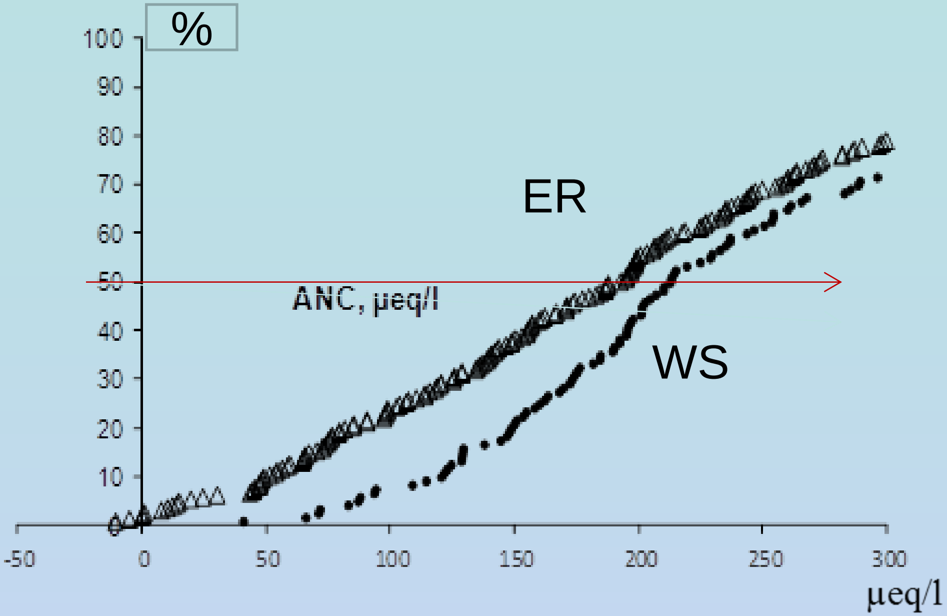
The main feature of both regions is **an increase of cations and alkalinity concentrations** in water towards the south: for ER - 55-60 °, for WS - 55-60 ° North latitude. The lakes of forest-steppe zones in ER and WS are highly resistant to acidification. Therefore, further discussion of these lakes was excluded.

Buffer capacity of northern and middle taiga region of ER and WS connect with the features of geology.

Concentration of cations (Ca+Mg+K+Na), μeq/l, in smalls lakes



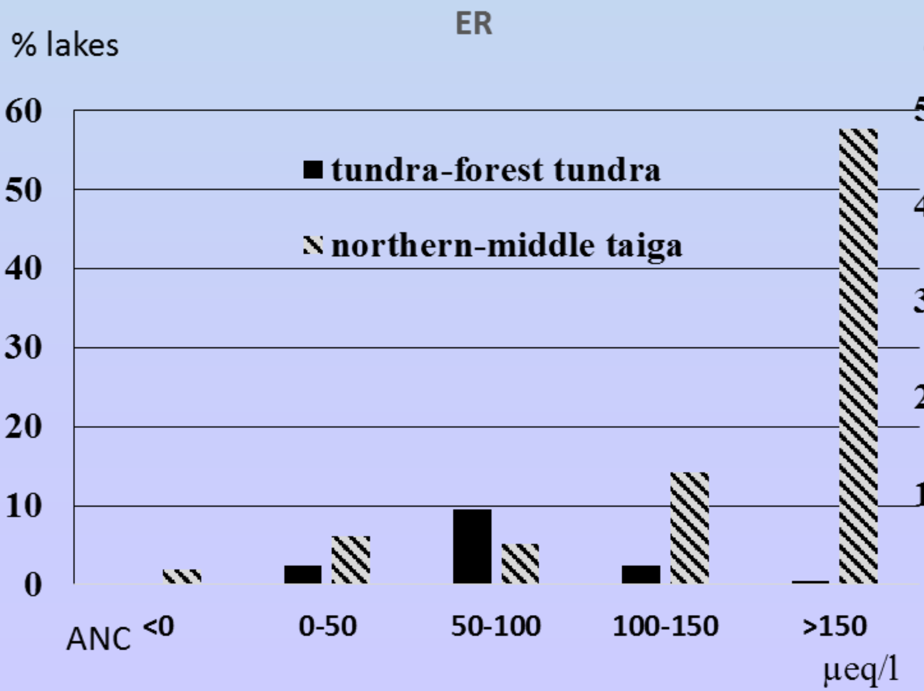


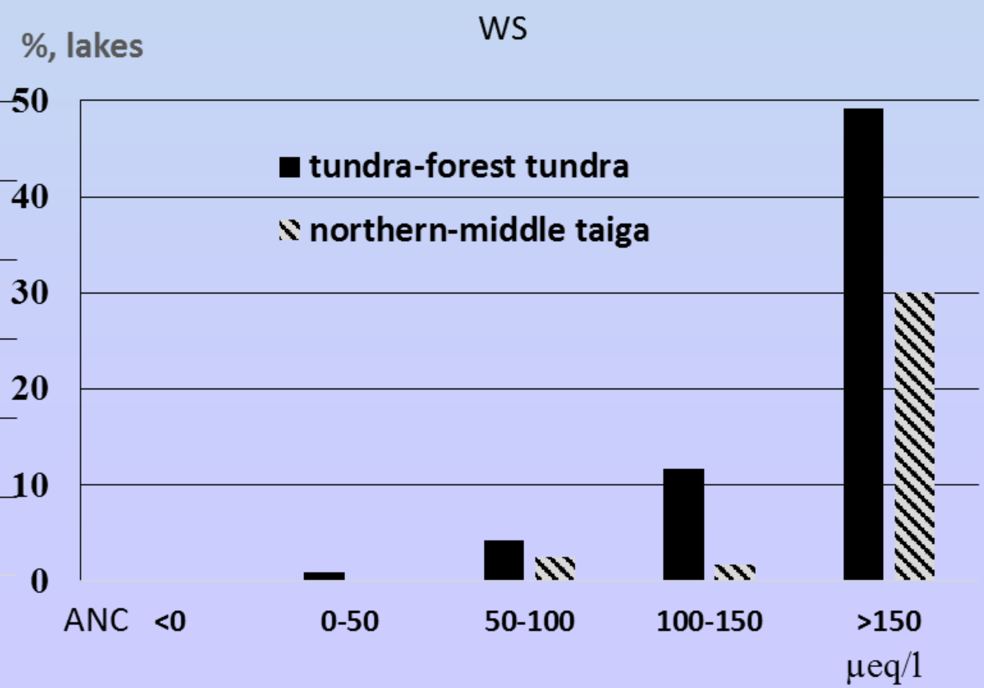


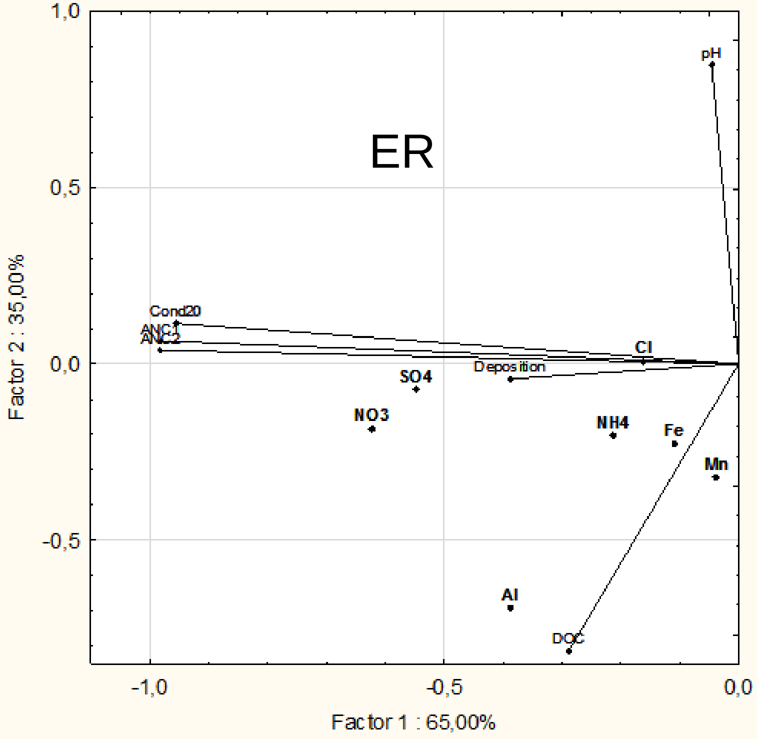
The acid neutralizing capacity of water (ANC, µeq/l) is used to estimate the anthropogenic acidification as a difference between cations and anions of strong acids (Henriksen et. al., 1992)

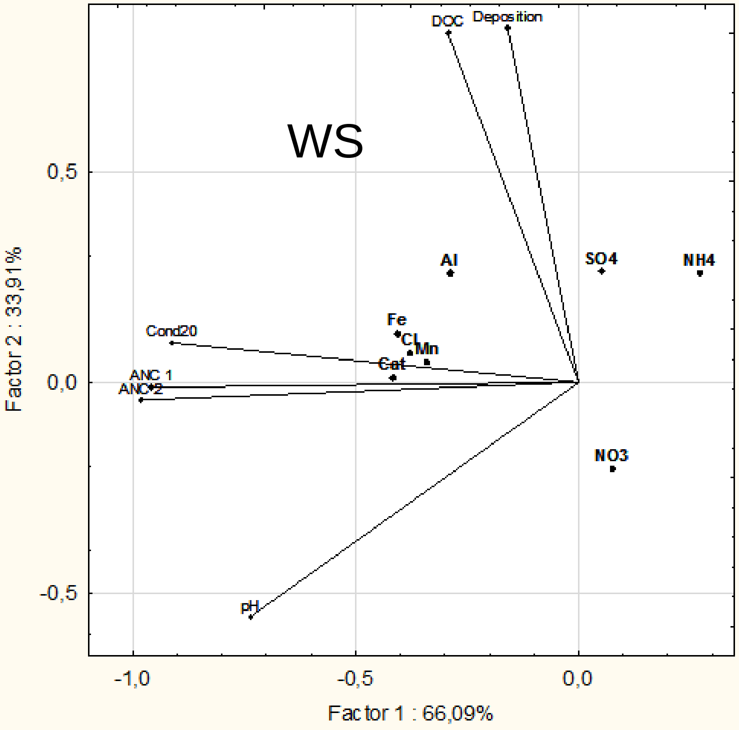
1. ANC1=$Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}-SO_4^{2-}-NO_3^{-}$

2. ANC2=$HCO_3^{-}+A^{n-}-H^{+}-Al^{3+}$







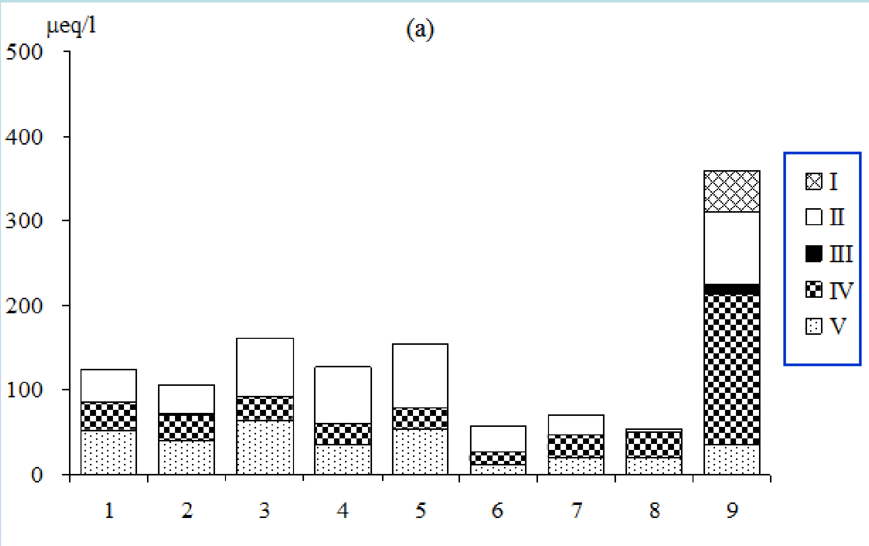


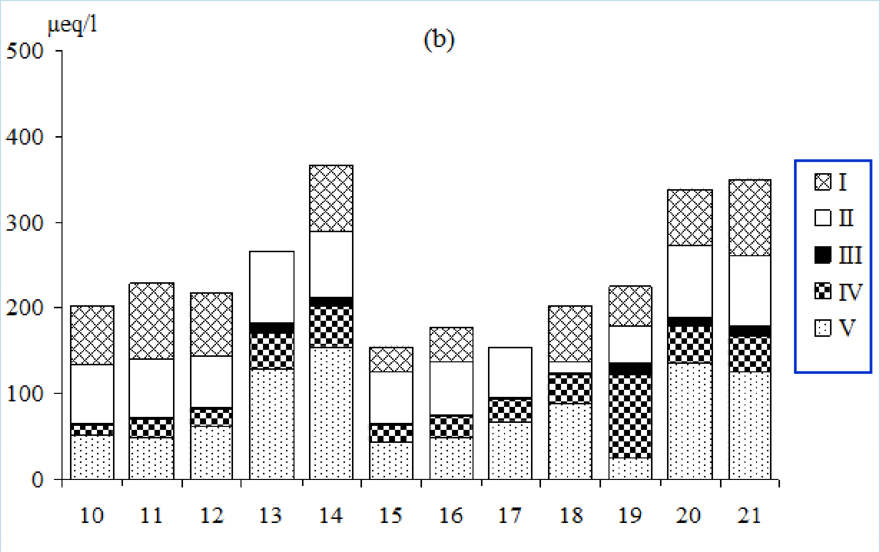
According to the results : **ANC 1 and ANC 2 are very close** that means the reliable of analyzes.

In **ER** lakes SO4, Cl and NO3mostly have an affinity for Cond. This is due to increased population density and industrial at the same time with increase cations and buffer capacity of water, The direct connection of the deposition and pH (lake ER) confirms the greatest acid deposition in an areas with steady geological formations to acidification.

In the water **WS** Cl have an affinity for Cond because increased salt content of watersheds toward the South. WS is located on the site of paleo area and Quaternary rocks: contain a amount of chloride. SO4 have an affinity for Deposition despite the higher sulfate concentrations in waters ER. The nitrate is inert to the selected axes because has the technological and natural origin.

The anionic composition (I – Alk. II - A^{n-}. III – NO_3^-. IV – SO_4^{2-}. V – Cl^-) of the water lakes with **pH <5** on the ER (a) (1 - in the tundra, 2-8 - in the northern taiga, 9 - in the middle taiga) and WS (b) (10-12 in the tundra, 13-14 - in the northern taiga, 15-21 - in the middle taiga).





Water acidification due to anthropogenic sulfate is characterized of ER.
In the acidic lakes of WS the water contained: chlorides, nitrates and sulfates.
Chlorides (lakes 13. 14. 20. 21) are dominated in majority lakes, but in same lake sulfates are dominated (lake 19).
Concentration of nitrates in water WS are higher in compared to the waters of ER.

NO^-_3

i) Delivery with the marsh waters, wetland and marsh is widely developed in the WS

(Nорг = 49.7·DOC – 114. (r=0.87. n=120);

i) the gas flaring forms the nitrogen oxides;

Cl^-

i) WS is located on the site of paleosee area and Quaternary rocks contain a amount of chloride (Arkhipov et al.. 1987).

ii) The chlorides are present in the waters of WS as part of pollution of the oil and gas fields development (Kiriushin et al.. 2013).

Organic compound (A^-)

Natural humus acids enters with the marsh waters.

Natural humus are characterized by a dual nature: weak and strong acids

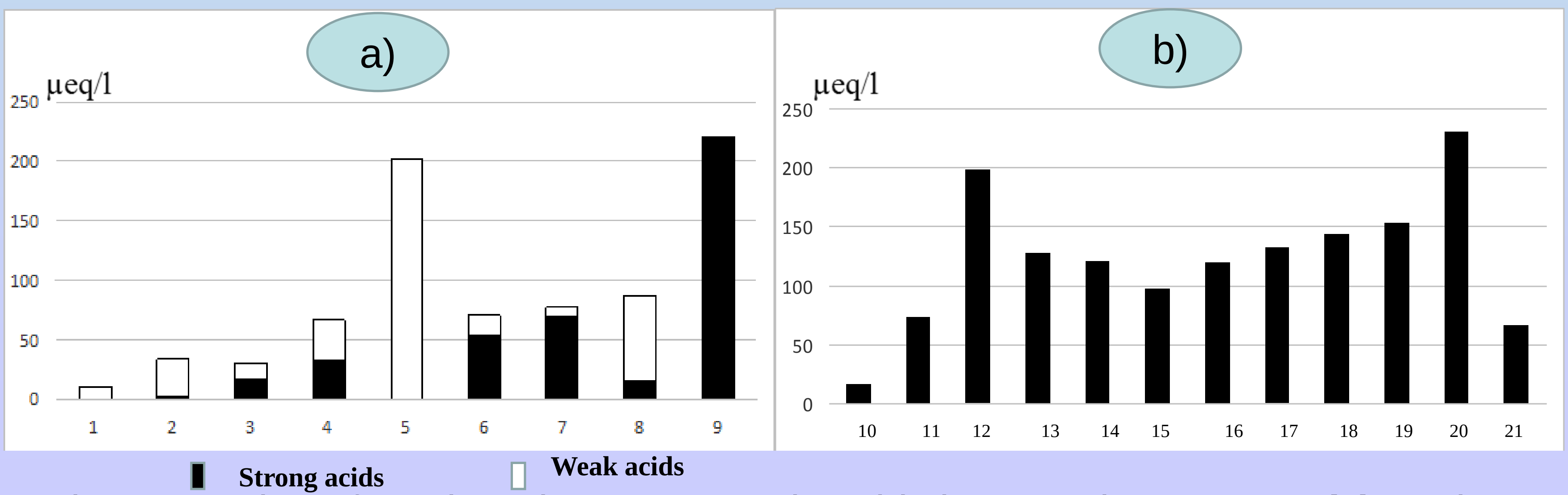
(Evans, Monteith et al.. 2008)

We calculated part of strong and week acids in water for acidify lakes in ER and WS based on method (Evans, Monteith, et.al. 2008). We used date about material balance of water chemical composition in each lake. The calculation algorithm takes into account the whole structure of the cationic and anionic groups including carbonates and bicarbonates.

$$OrgA_{strong} = Ca^{2+} + Mg^{2+} + Na^{+} + NH_4^{+} + K^{+} + Al_{inorg} - SO_4^{2-} - Cl^{-} - NO_3^{-} - Alk$$

$$OrgA_{weak} = A^{n-} - OrgA_{strong}$$

(Evans, Monteith et al.. 2008)



*The proportion of weak and strong organic acids in natural waters ER **(a)**: 1 - in the tundra. 2-8 - in the northern taiga. 9 - in the middle taiga and WS **(b)**: 10-12 in the tundra. 13-14 - in the northern taiga. 15-21 - in the middle taiga*

RESULTS FOR DISCUSSION

In table:

Black color without parentheses is the average ANC classics:

1. $ANC1=Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}-SO_4^{2-}-NO_3^{-}$

2. $ANC2=HCO_3^{-}+A^{n-}-H^{+}-Al^{3+}$

Red color with parenthese is the average ANC* with used of organic weak and strong acids

1. $ANC{*}1=Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}-SO_4^{2-}-NO_3^{-} - A_{strong}^{n-}$

2. $ANC{*}2=HCO_3^{-}+A_{weak}^{n-}-H^{+}-Al^{3+} - Fe^{3+} - A_{strong}^{n-}$

pH	Color, °Pt-Co scale					
	<10	10-30	30-60	60-100	>100	*n*
European Russia, 220 lakes, ANC*, μeq/l						
4-5	-5.0 (-20)	7 (25)	-	4 (-7)	130 (-9)	*10*
5-6	43 (31)	270 (187)	250 (149)	310 (279)	410 (222)	*34*
6-7	69 (54)	220 (176)	235 (168)	235 (131)	260 (108)	*141*
7-8	234 (233)	380 (335)	-	400 (305)	373 (269)	*35*
Western Siberia, 120 lakes, ANC*, μeq/l						
4-5	40 (-5)	62 (3.5)	140 (5.3)	175 (6.2)	250 (6.2)	*18*
5-6	150 (4.8)	170 (4.0)	230 (10)	300 (11)	350 (15)	*54*
6-7	300 (10)	375 (9.7)	350 (6.5)	-	400 (5.5)	*35*
7-8	472 (153)	1142 (8)	1100 (220)	1450 (75)	1560 (606)	*13*

Critical Loads and its exiding

$$CL = ([BC_o^*] - [ANC_{limit}])\, Q - BC_d^*$$

$$BC_o^* = [BC^*]_t - F\,\Delta([SO_4^*] + [NO_3]) = [BC^*]_t - F\,(([SO_4^*]_t + [NO_3]_t) – ([SO_4^*]_o + [NO_3]_o))$$

$$F = \sin(\pi/2)\, [BC]_t / S$$

$$[SO_4]_{0^*} = 15 + 0.16[BC_t)\ *$$ (Henriksen et al., 1992)

European Russia

$$\mathbf{BC_o = [BC]_t - F\,(([SO_4]_t - [SO_4]_o)}$$

Zones of tundra, forest-tundra and northern taiga (Kola Peninsula):

$[SO_4^*]_o = 15.3 + 0.02\,[BC^*]_t$. $r = 0.71$. $p < 0.001$;

Zone of the middle taiga (Karelia):

$[SO_4^*]_o = 15.4 + 0.11\,[BC^*]_t$. $r = 0.64$. $p < 0.001$;

Zone of mixed forests:

$[SO_4^*]_o = 15.2 + 0.05\,[BC^*]_t$. $r = 0.68$. $p < 0.001$.

S is 400 μeq / l for the tundra and taiga zones.

S is 1100 μeq / l for mixed ER forests.

$$\mathbf{CL_{ex} = CL – SO_{4\ dep}^* – NO_{3dep} + BC_{dep}^*}$$

Western Siberia

$$\mathbf{BC_o = [BC]_t - F\,(([SO_4]_t - [SO_4]_o) + ([NO_3]_t - [NO_3]_o) + ([Cl]_t - [Cl_{Na}]))}$$

$$\mathbf{[NO_3]_o = 0.118\,[A^{n-}]_t.}$$

(Cl_{Na} is compensated by Na)

Zones of tundra, forest-tundra and northern taiga:

$[SO_4]_o = 2.67 + 0.021\,[BC]_t$. $r = 0.72$. $p < 0.001$;

Zone of the middle taiga:

$[SO_4]_o = 16.9 + 0.015\,[BC]_t$. $r = 0.76$. $p < 0.001$;

Zone of southern taiga:

$[SO_4]_o = 12.4 + 0.002\,[BC]_t$. $r = 0.69$. $p < 0.005$.

S is 500 μeq / l for the tundra and northern taiga zones.

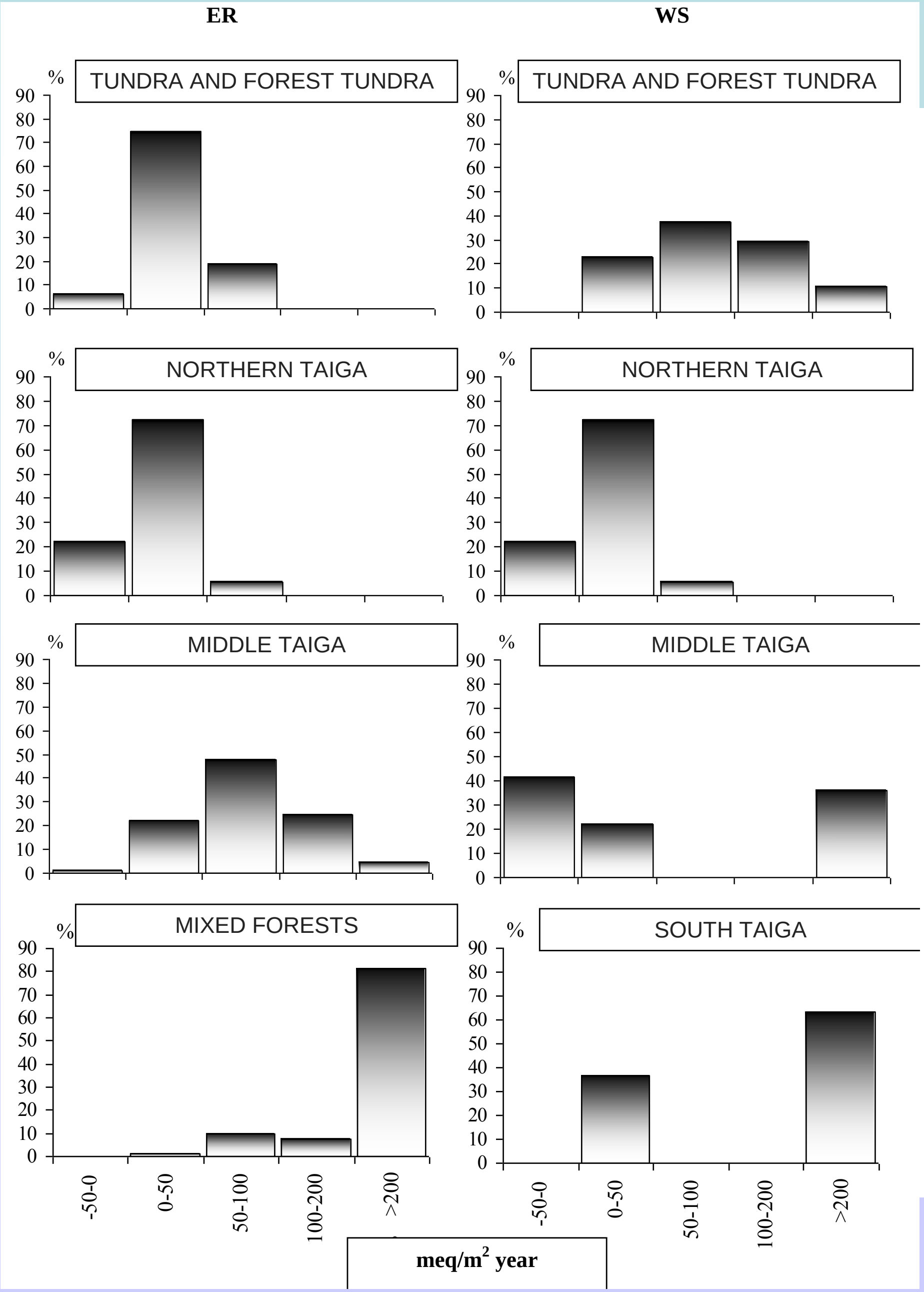
S is 1250 μeq / l for the middle taiga

S is 3000 μeq / l for the southern taiga.

$$\mathbf{CL_{ex} = CL – SO_{4dep} – NO_{3dep} – Cl_{dep} + BC_{dep}.}$$

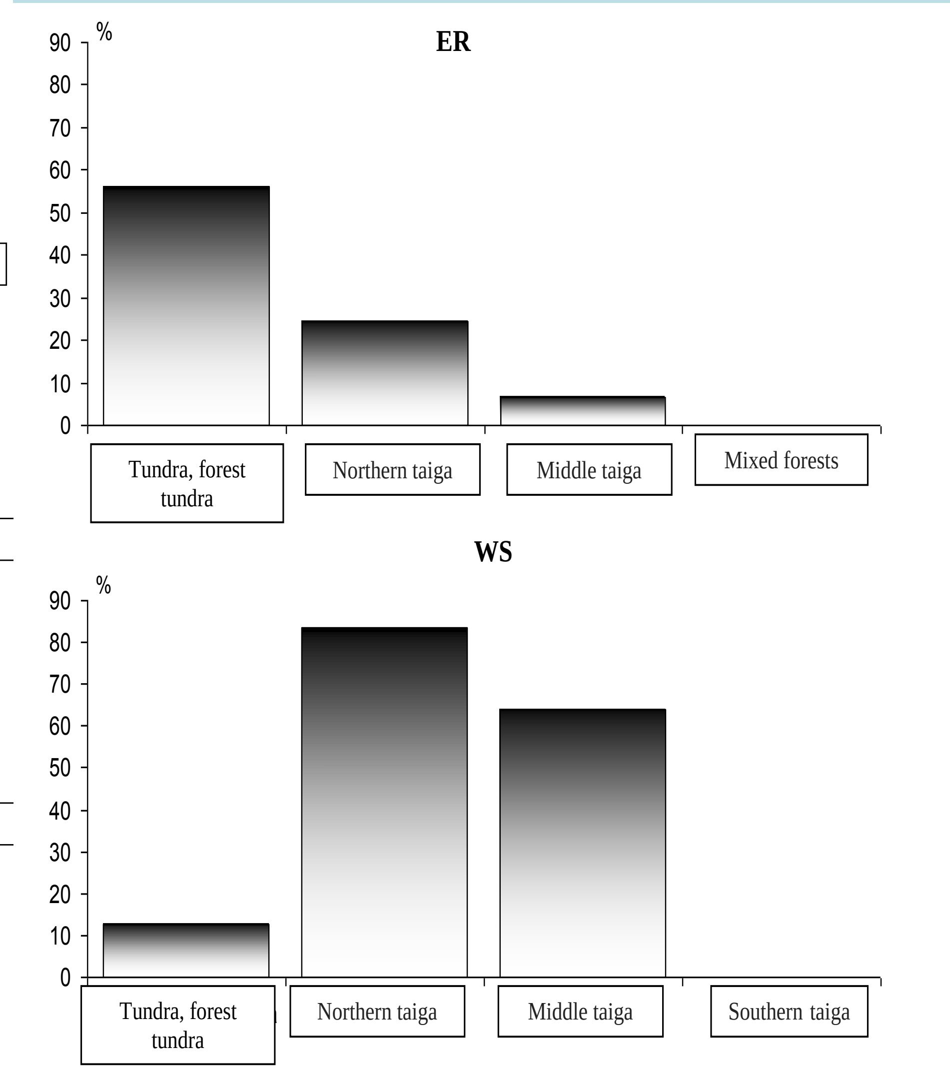
Thus, the necessary date for estimating the flow of cations into water systems ensuring neutralization of anthropogenic acids have been determined. Taking into account the complete and correctly obtained hydro-chemical information. ANClimit was adopted as 50, μeq/l

CL



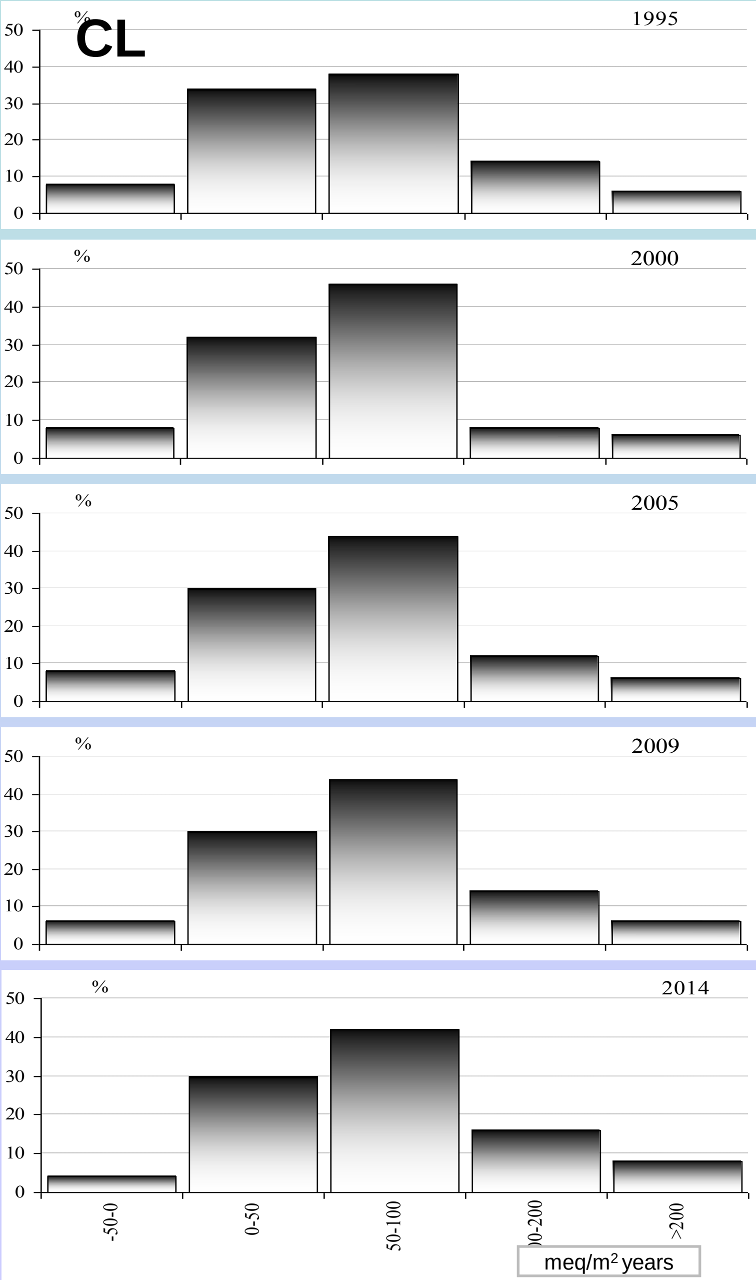
ER
WS
%
TUNDRA AND FOREST TUNDRA
NORTHERN TAIGA
MIDDLE TAIGA
MIXED FORESTS
SOUTH TAIGA
90
80
70
60
50
40
30
20
10
0
-50-0
0-50
50-100
100-200
>200
meq/m2 year

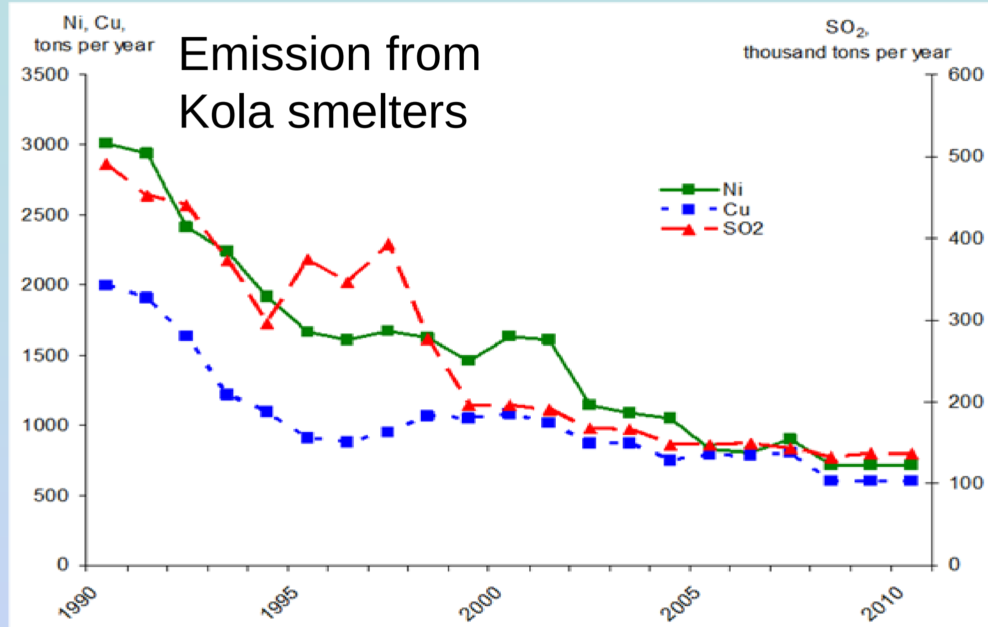
CLex



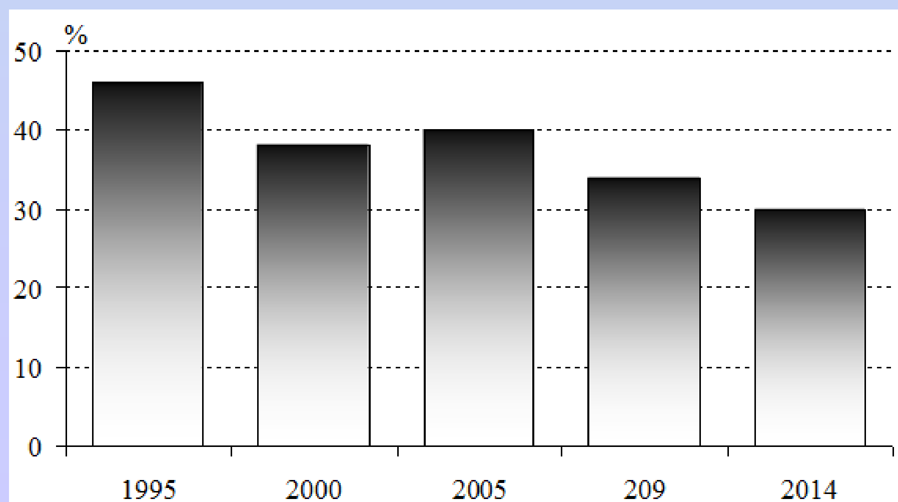
ER
WS
%
90
80
70
60
50
40
30
20
10
0
Tundra, forest tundra
Northern taiga
Middle taiga
Mixed forests
Southern taiga

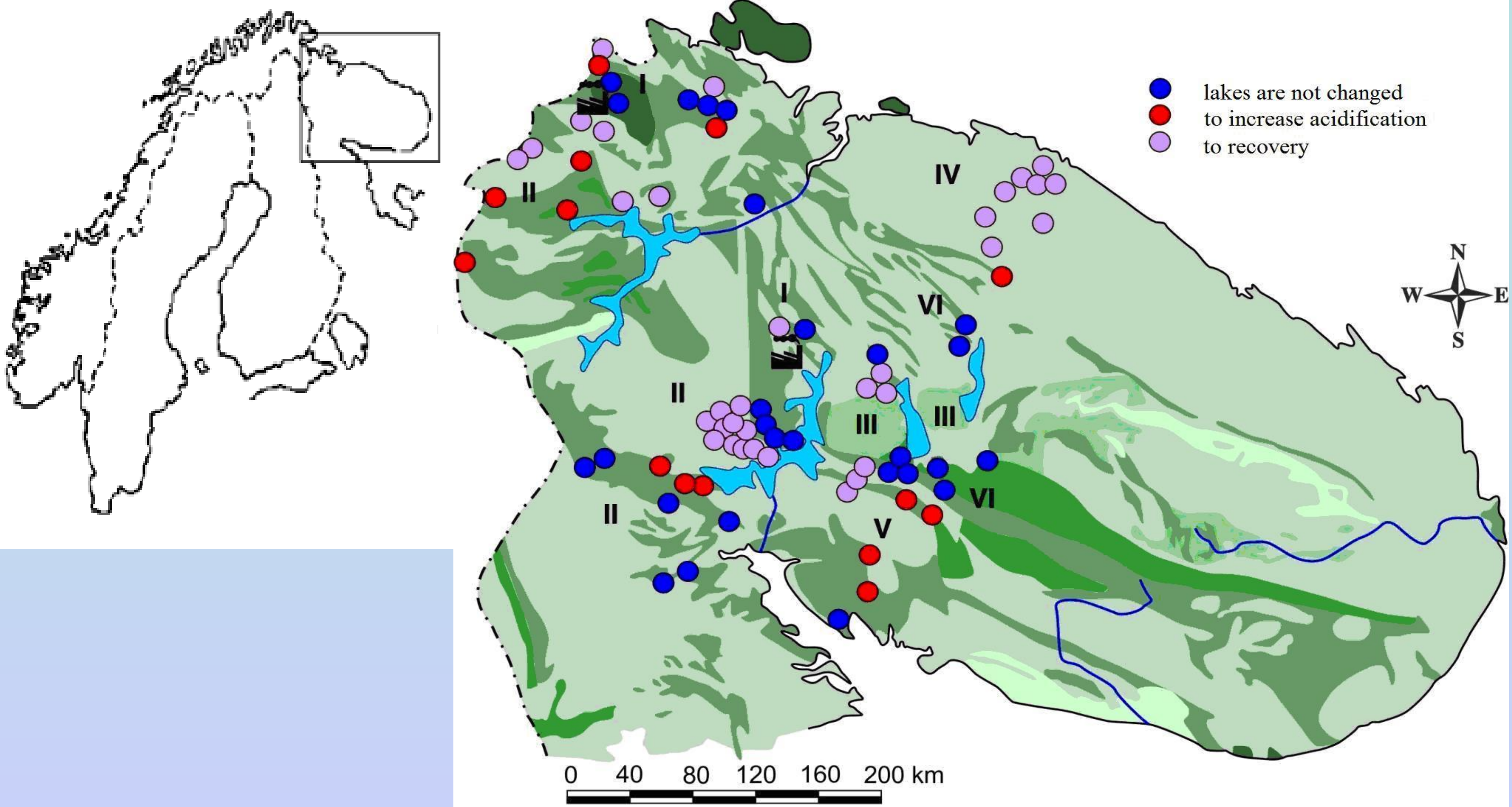
Long-term trends - recovery (Kola region)





Clex





*Water chemistry responses are **not** always proportionate to reductions in sulfate flow. Exists three scenarios of changes water chemistry: i) further water acidification is progressing. ii) pH and alkalinity levels remain the same; iii) lake water chemistry recovers.*

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Character of Spatiotemporal Variations in the Chemical Composition of Lake Water under the Influence of Emission from Copper–Nickel Plants: Prediction of Acidification

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Abstract In this paper, we analyze the influence of variations in the emission of sulfur dioxide and solid substances by the Pechenganikel and Severonikel copper–nickel plants in Murmansk oblast on the chemical composition of lake water and development of acidification. The dynamics of ~100 lakes examined in 1990, 1995, 2000, 2005, and 2009 and response of the chemical composition of the lake waters on the impact of acidifying substances was explored depending on the magnitude of load (distance from the plants), geologically controlled vulnerability of the lake catchments to acid precipitation, and the size of the lakes. Possible further changes in the sulfate concentration and pH values of lake waters were estimated for scenarios assuming an increase or a decrease in sulfur dioxide emission from the plants. It was shown that, in the zone of maximum and high load, a 20% change in sulfur dioxide emission will result in a mean change in sulfate concentration of ±8 μeq/L (which is comparable with the regional background) and a change in pH value of ±0.1 in acid-sensitive lakes and will have almost no effect on these parameters in lakes insensitive to acid precipitation.

Keywords: lakes, anthropogenic sulfates, vulnerability, acidification, load variations, dynamics, prediction
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Thanks for attentions !