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TEMPORAL VARIATION IN ANTHROPOGENIC NITROGEN INPUTS TO THE ACTIVE LAYER IN YAKUTSK, RUSSIA

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Nitrogen is an essential nutrient for all living organisms. This paper discusses the results of investigation on migration of mineral nitrogen compounds into the active layer and permafrost in the residential and industrial zones of the city of Yakutsk. Concentration of nitrogen compounds as nitrogen is relatively uniform in perennially frozen Cenozoic alluvial deposits on the Lena River terraces. Concentration of nitrogen compounds in the active layer distinctly correlates with the time length of anthropogenic impact. The flux of nitrogen compounds to the active layer of the residential areas has been relatively constant over the 300 years of anthropogenic impact. In the industrial zone, accumulation of nitrogen compounds in the active layer increases by more than one order of magnitude.

Keywords: *active layer; anthropogenic; nitrogen; permafrost; variation*

1. INTRODUCTION

Nitrogen is the most abundant chemical element in the atmosphere and a less common element in the Earth's crust. It is an essential nutrient for all living organisms, ranging from viruses and microorganisms to higher organisms such as animals and humans. The geochemical role of nitrogen-containing compounds in permafrost landscapes is still poorly known. For example, a recent experimental study suggests anomalous acceleration of the rate of HNO_2 oxidation in the range of subfreezing temperatures [1]. This paper discusses the results of investigation on migration of mineral nitrogen compounds into the active layer in the Yakutsk area (Fig. 1).

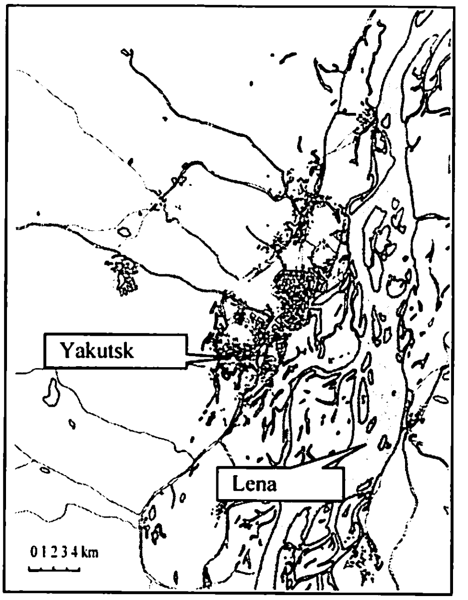


Fig. 1 Map of Yakutsk area.

2. GEOLOGICAL PROPERTIES OF YAKUTSK AREA

Yakutsk is one of the oldest cities in north-eastern Russia. It is the capital of the Republic of Sakha with a population of about two hundred thousand people. There are two power plant and 24 district boiler stations. Anthropogenic nitrogen is emitted from these plants (Table 1).

Yakutsk was founded in 1632 and some of its districts have been developed for 350-370 years (Fig. 2). This long history of anthropogenic impact on permafrost allows us to assess the temporal dynamics of nitrogen input and concentration in the active layer within the urban area.

Geologically, the Yakutsk area is in an ancient trough of the Siberian Platform. The trough is filled with Mesozoic marine rocks (conglomerates and sandstones) overlain by Neogene and Quaternary sediments (sands and loess-like silts).

Yakutsk is located in the ancient erosional-aggradational plain that encompasses the floodplain and the first and second low terraces with elevations ranging from 85 to 105 m above sea level. The terraces are covered by chernozem-meadow and meadow-chernozem soils. Sod-meadow alluvial soils occur occasionally on the first terrace. The soils in most parts of the city are saline.

Permafrost at Yakutsk is 200 to 250 m in thickness. Alluvial deposits of the Lena River terraces at Yakutsk were frozen approximately 10,000 years ago. Radiocarbon dating of vegetation debris from the lower part of the first-terrace section indicates that the permafrost in the depth interval 9-12 m is 9,600-11,600 years old [2]. Ground temperatures depend on the age of urban development and, at a depth of 10 m, vary from -2º to -8ºC. The active layer is 1.5 to 3.5 m thick. Prior to the pre-industrial stage of the city development, ground temperatures at Yakutsk had been close to those in natural environments. The increased building density, expanded infrastructure, and increased municipal effluents in the recent period have resulted in temperature changes in the active layer. Perennially frozen alluvium of the Lena River low terraces at Yakutsk is primarily composed of fine and very fine sands.

Urban soils near the surface (0.10-0.20 m) mainly consist of sands and sandy silts, highly variable in chemical composition. The various parts of the city are dominated by chloride, sulfate or carbonate salts. Soil salinities range from 0.021% to 3.24% in the older districts. The chemical composition of the upper soil layer is given in Table 2 [3].

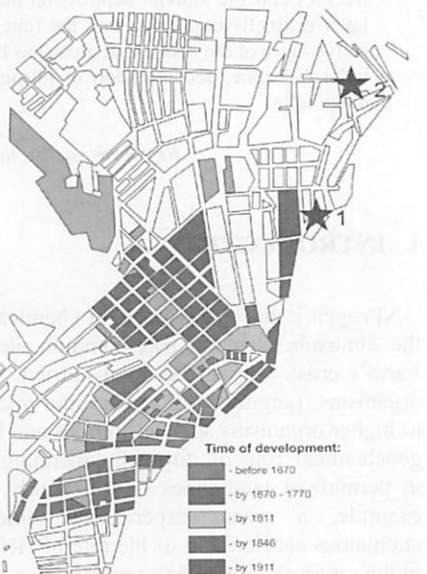
Table 1 Power facilities in Yakutsk, 2007.

Source	Output [MW]	NO_X emissions [Ton]	Fuel used
Yakutsk TPS	320	2677	Natural gas 100%
Yakutsk CHP plant	12	518	Natural gas 100%
District boiler stations (24)		543	Natural gas 92% Coal 8%
Total emissions		3738	

Table 2 Chemical composition of soils at Yakutsk. (0.10-0.20 m depth, n=161).

(C_{av} : averaged value, C_{min} : minimum value, C_{max}: maximum value)

	Unit	C_{av}	C_{min}	C_{max}
pH	-	7.9	6.45	9.99
Eh	mV	355	121	478
Electrical conductivity	mS/m	735	52	952
Salinity	%	0.31	0.021	3.24



(1: Yakutsk TPS, 2: Yakutsk CHP Plant)

Fig. 2 Development in Yakutsk city.

3. MEASUREMENT METHOD FOR NITROGEN CONCENTRATION

Mineral nitrogen compounds concentration (ammonium, nitrate, and nitrite salts) were measured in thawed and frozen ground (active layer and permafrost). To this end, boreholes were drilled to depths of 10 to 15 m in the residential and industrial zones of the city. Development ages of the drilling sites varied from 30 to 300 years. Boreholes were located on the flat surface away from the modern local sources of contamination by domestic waste. The dry drilling method was used with continuous core sampling [3]. Concentrations of nitrogen compounds in the active layer were measured by water solution portion soils.

The core samples were analyzed by the electrophoretic methods (Instrument "Kapel-105M") at the Permafrost Institute's laboratory (analysts L.Y. Boitsova and O.V. Shepeleva). The determination limit for nitrogen compounds was:

Nitrogen compound	NH_4^+	NO_3^-	NO_2^-
Determination limit, mg/kg	$3 \cdot 10^{-5}$	$0.5 \cdot 10^{-5}$	$0.2 \cdot 10^{-5}$

Atmospheric concentrations of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) were measured at Yakutsk from July 25 through August 8, 1993 [4], and from July 20 through August 8, 1994 and from July 22 through August 24, 1995. In the measurement, NO_2 and SO_2 were collected on reagent soaked filters by diffusion sampling. After the sampling, nitrite and sulfite were extracted with distilled de-ionized water. The nitrite concentrations were analyzed by the Saltzman method. The sulfate concentrations were determined by Ohta et al. [4].

4. RESULTS AND DISCUSSION

The present-day concentration of nitrogen compounds in the top 0.10-0.20 m of soil varies from 0.0024 to 1.393 mg-eq., averaging 0.062 mg-eq (Makarov, 2010). The variance of concentration is greatest for nitrate nitrogen (0.0002 to 1.128 mg-eq.). Ammonium forms of nitrogen are more evenly distributed (0.002 to 0.130 mg-eq.). Nitrate forms are dominant in the soils, comprising 72% of total nitrogen. Nitrogen forms rank in the following order (% concentration is shown in brackets):

$$NO_3^-(72) > NH_4^+(26) > NO_2^-(2).$$

Table 3 Concentration of nitrogen compounds and nitrogen in permafrost, 10^{-5} mg/kg (at depths from 4 to 15 m).

Distribution	NH_4^+	NO_2^-	NO_3^-	N_{tot}
Minimum	2.5	0.1	0.1	1.9
Maximum	36.0	0.4	9.0	28.0
Mean	15.7	0.2	2.7	
$N_{mean.}$	12.2	0.1	0.6	12.9

Concentration of nitrogen compounds as nitrogen is relatively uniform in perennially frozen Cenozoic alluvial deposits of the low terraces and varies within one order of magnitude, 1.9 to 28 × 10^{-5} mg/kg, averaging 12.9 × 10^{-5} mg/kg (Table 3).

Ammonium forms of nitrogen are dominant in permafrost, comprising about 95% of total nitrogen, while nitrite forms have very low concentration (0.1%). Nitrogen forms in permafrost rank in the following order (% concentration is shown in brackets):

$$NH_4^+(95) > NO_3^-(5) > NO_2^-(0.1).$$

Since the concentration of nitrogen compounds in the permafrost is relatively constant, concentration changes in the active layer, which is closer to contamination sources, can be evaluated in relation to the length and intensity of urban development. Concentrations of nitrogen compounds in the active layer at Yakutsk range within three (NH_4^+, NO_2^-) to four (NO_3^-) orders of magnitude – from 0.1 to 482.0 × 10^{-5} mg/kg averaging 234 × 10^{-5} mg/kg.

Ammonium forms are dominant in the active layer, comprising 3/4 of total nitrogen. Nitrogen forms rank in descending order of concentration as (%):

$$N(NH_4^+) - 73 > N(NO_3^-) - 25 > N(NO_2^-) - 2.$$

Nitrogen accumulation in the active layer of the residential zone was more or less uniform throughout the "pre-industrial" period and depended primarily on the duration of anthropogenic impact.

Within the residential zone, the concentration of nitrogen is 1.6 to 268 × 10^{-5} mg/kg. Highest concentrations, N_{tot} = 209-268 × 10^{-5} mg/kg, are

Table 4 Nitrogen compound concentrations in the active layer of the residential zone in relation to anthropogenic impact duration, 10^{-5} mg/kg.

Anthropogenic impact duration, years	NH_4^+	NO_2^-	NO_3^-	N_{tot} (as N)
300	220.3	28.3	386.9	268
150-200	129	0.6	482	209
100	73.8	1.2	17	62
80	2	0.1	0.1	1.6
60	39.7	3.4	85.8	52

Table 5 Nitrogen compound concentrations in the active layer of the industrial zone in relation to anthropogenic impact duration, 10^{-5} mg/kg .

Anthropogenic impact duration, years	NH_4^+	NO_2^-	NO_3^-	N_{tot} (as N)
30-40	355.7	43.1	486.5	399

measured in the oldest part of the city where the impact period ranges from 150-200 to 300 years. Lowest concentrations, $N_{tot} = 1.6\text{-}52 \times 10^{-5}$ mg/kg, are found in the areas of recent (less than 80 years) development (Table 4). The northern zone, where power supply plants, airport and other industrial facilities are located, has been subject to heavy anthropogenic impact for the last 30-40 years. In this zone, concentration of nitrogen in the active layer is 399×10^{-5} mg/kg , or 40 times that in the permafrost (Table 5).

Industrial contamination, particularly atmospheric emissions from the power supply facilities, has strongly increased nitrogen input to the active layer. Concentration of nitrogen compounds in the active layer distinctly correlates with the length of anthropogenic impact (Fig. 3). The result of 80 years in Fig. 3 was deleted because of low validity of data from borehole 1. For other time periods, the number of observation points is larger, for example, 9 boreholes for 300 year period.

The flux of nitrogen compounds into the active layer of the residential areas had been uniform, averaging 0.89×10^{-5} mg/kg in year, over the 300 year period of low anthropogenic impact until the mid-20th century. Nitrogen accumulation in the active layer of the residential zone was more or less uniform throughout the "pre-industrial" period and depended

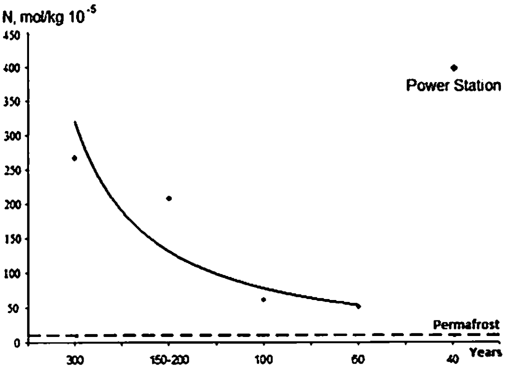


Fig .3 Nitrogen concentration in the active layer of industrial and residential zones in relation to anthropogenic impact duration, the city of Yakutsk (The correlation coefficient is 0.78 at the significant level of 0.63 (10%).).

primarily on the duration of anthropogenic impact. For about 400 years (until the middle of the 20th century) Yakutsk was a large village, without modern infrastructure (no water supply or sewage system, individual wood heating, etc.) and with herds of cattle and horses. The population density had been changing little because of expansive growth of the settlement. Therefore, the flux of nitrogen compounds was uniform and was increasing in the older parts of Yakutsk.

Determination of nitrogen migration into the active layer was based on the following considerations. The measurements of nitrogen compound concentrations in the perennially frozen alluvial deposits of the Lena River indicated their variation within an order of magnitude, $1.9\text{-}28.0 \times 10^{-5}$ mg/kg (see Table 3). Considering the high mobility of nitrogen compounds in the zone of weathering, their concentrations in the active layer can not be higher than in the permafrost. The elevated concentrations of nitrogen compounds in the active layer, $52\text{-}399 \times 10^{-5}$ mg/kg (see Tables 4 and 5) are likely to be related to the intensity and duration of anthropogenic impact. Therefore, nitrogen compound concentrations measured within the city in the soils of varying age (268×10^{-5} mg/kg : 300 years = 0.9×10^{-5} mg/kg in year) were used to estimate the migration of nitrogen compounds into the active layer. Data presented in Table 6 indicate that in the residential zone of Yakutsk the migration rate of nitrogen compounds into the active layer had been relatively constant during the pre-industrial period of the city.

Table 6 Flux of nitrogen compounds to the active layer for various anthropogenic impact periods, 10^{-5} mg/kg in year.

Anthropogenic impact duration, years	NH_4^+	NO_2^-	NO_3^-	N_{tot} (as N)
Residential zone				
300	0.70	0.09	1.29	0.9
150-200	0.43	0.01	1.60	1.2
100	0.25	0.01	0.06	0.6
80	0.03	0.01	0.01	0.1
60	0.13	0.01	0.20	0.9
Geometric Average	0.38	0.02	0.630	0.9
Industrial zone				
30-40	12	1.4	16	13.3
Industrial/residential zones	32	70	25	15

In the industrial zone, annual input of nitrogen compounds to the active layer mainly due to atmospheric emissions from two power supply facilities and twenty-four district boiler stations by using mainly natural gas has increased by more than one order of magnitude to 13.3×10^{-5} mg/kg in year (Table 6), leading to a strong increase in nitrogen concentration in the active layer.

The greatest increase in nitrogen input to the active layer of the industrial zone compared to the residential areas is shown by nitrites.

It is interesting to note that the northern, industrial part of the city which is affected by emissions from the power stations is also characterized by maximum atmospheric concentrations of nitrogen dioxide, 4 to 21 ppb and 30-100 times the background values at Radio relay station and forest area shown in Fig. 4 and Table 7 [4) 5)]. Mean NO_2 concentration in summer, winter and yearly were each, 16 mg/m^3, 20 mg/m^3 and 19 mg/m^3 in Yakutsk in 2008. Atmospheric deposition of N into the active layer is related to the development of gas- fueled power generation during the last 50 years. This is supported by the fact that the N anomalies in the soil are mainly observed near the higher-power station (the Yakutsk TPS), where there are no N sources other than atmospheric source. In this area, a relationship is observed between the total emission of nitrogen compounds (NO_2, NO, NH_3) from the power station and the increase in N content in the active layer.

Table 7 Atmospheric concentration of nitrogen dioxide (ppb) from 1993 through 1995 at Yakutsk.

Year	Date and sampling place	NO_2 conc. (ppb)
1993	July 25 – August 8	
	Downtown	6
	Downtown	4
	Downtown	6
	Downtown	10
	Environmental center	6
	the suburbs	2
	Radio relay station	< 1
	Forest	< 1
1994	July 20 – August 8	
	Downtown	15
	Downtown	15
	Downtown	6
	Downtown	5
	Downtown	21
	Downtown	14
	Downtown	6
	the suburbs	3
	Radio relay station	1
1995	July 22 – August 24	
	Downtown	10
	Downtown	5
	Downtown	5
	Downtown	7
	Downtown	6
	Downtown	5
	Downtown	5
	Downtown	9
	Downtown	5
	Environmental center	3
	the suburbs	2
	the suburbs	5
	Radio relay station	< 1

5. CONCLUSIONS

Nitrogen concentrations in the active layer in the industrial and residential zones of Yakutsk have been

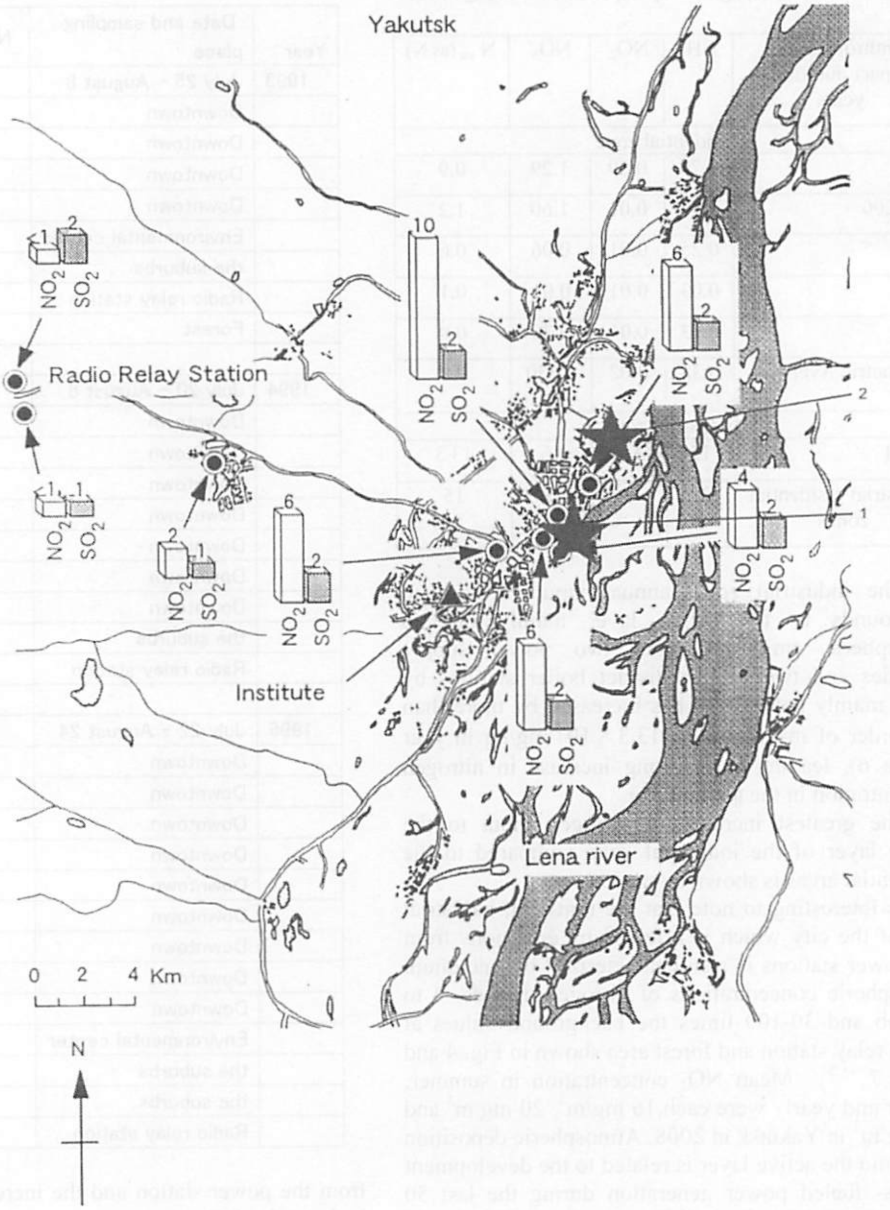


Fig. 4 Atmospheric concentrations of nitrogen dioxide (NO_2) and sulfur dioxides (SO_2) in ppbv in 1993 at Yakutsk.

found to distinctly correlate with the length of anthropogenic impact. Concentration of nitrogen compounds as nitrogen is relatively uniform in the perennially frozen Cenozoic alluvial deposits and varies within one order of magnitude, 2 to 28×10^{-5} mg/kg.

The flux of nitrogen compounds to the active layer of the residential areas had been relatively constant, averaging 0.89×10^{-5} mg/kg in year, over the 300 year period of low anthropogenic impact until the mid-20th century. Nitrogen accumulation in the active layer of the residential zone was more or less uniform throughout the "pre-industrial" period and depended primarily on the duration of anthropogenic impact.

In the industrial zone, input of nitrogen compounds to the active layer has increased by more than one order of magnitude to 13.3×10^{-5} mg/kg in year, leading to greater nitrogen concentrations compared to the residential zone.

Ammonium forms of nitrogen are dominant in both in the active layer and permafrost, comprising 3/4 of total nitrogen. However, the mechanism by which the nitrate forms are transformed into the ammonium forms in the active layer is not clearly understood, but supposed to be related to ammonification. This process occurs when nitrification is inhibited due to insufficient aeration and low temperatures in the active layer, requires further research.

Emissions from the power stations characterized the maximum atmospheric concentrations of nitrogen dioxide, 4 to 21 ppb and 30-100 times those in background area.

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