

Report

Monitoring of acid deposition in central Yakutia

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Abstract: The results of monitoring acid precipitations showed that subacid-alkalescent precipitations, acidity of which varies in close limits (pH 5.89–7.36) prevail in Yakutsk region. Acidity of solid precipitation is very similar to acidity of rain precipitations and comprises 6.70–7.22 for operating pH of rain precipitations (6.85 in average) and 5.89–7.36 for solid precipitations (6.71 in average). The most considerable deviations of acidity-alkalinity of solid precipitation from the average value are observed at the beginning and in the middle of winter period. According to the monitoring results we made an evaluation of the value of chemical components fall-out in atmospheric precipitations. Annual inflow of H^+ ions from atmosphere to the earth surface is much less than critical load for the forest and water ecosystems. Maximal values of sulfur compounds (0.51 g/m^2) and nitrogen (2.07 g/m^2) fall-out at the monitoring station fall on June and exceed ecostandard and parameters of ecological emergency situation in a volume of nitrogen precipitations.

key words: Yakutia, atmospheric, acid precipitations, monitoring

1. Introduction

Acid rain (acid deposition) has changed from a curious scientific fact to a serious societal concern and the focus of considerable debate in many countries of the world (North America, eastern and western Europe, China, Korea, Japan) during the last twenty years. Problems associated with possible adverse impacts of acid rain are not confined to restricted areas, but are regional, national and international in nature. Acid deposition, precursor gases and some products of their chemical reaction have a variety of effects. Among the possible environmental consequences are harmful effects on human health, acidification of surface waters and soils, decrease in forest productivity, corrosion and decay of materials, and visibility reduction.

The chemistry of atmospheric deposition is being studied at the Laboratory of Geochemistry of the Melnikov Permafrost Institute.

2. Definition of the problem

Acidity of precipitation is determined mainly by the presence of free hydrogen ions, H^+ .

Of natural agents, CO_2 has the strongest effect on the pH value, because the concentration of hydrogen ions in water depends on the amount of carbon dioxide. All other things being equal, the higher the CO_2 concentration, the higher the hydrogen ion concentration and the lower the pH. In addition to carbon dioxide, other acid-forming substances of natural origin, such as organic acids, sulfur dioxide, hydrogen sulfide, hydrochloric acid, nitrogen oxides and nitric acid, may be present in small quantities in unpolluted atmosphere (Izrael *et al.*, 1983).

The relationship between the concentrations of hydrogen ion and other ions in precipitation (neglecting the contribution of weak organic acids) is expressed as:

$$(\text{H}^+) = 2(\text{SO}_4^{2-}) + (\text{NO}_3^-) + (\text{Cl}^-) - 2(\text{Ca}^{2+}) - (\text{K}^+) - 2(\text{Mg}^{2+}) - (\text{Na}^+) - (\text{NH}_4^+) + 2.5 \cdot 10^{-6}.$$

The remainder term in this relation, $2.5 \cdot 10^{-6}$ mole/l, is the hydrogen ion concentration in equilibrium aqueous solution at average atmospheric carbon dioxide concentration of 330 ppm at temperature of 20°C . At this hydrogen ion concentration the pH is = 5.6, the value normally characteristic of unpolluted precipitation. The pH of rainwater and snowcover ranges from 5.8 to 6.4 over much of Yakutia, indicating a low level of air

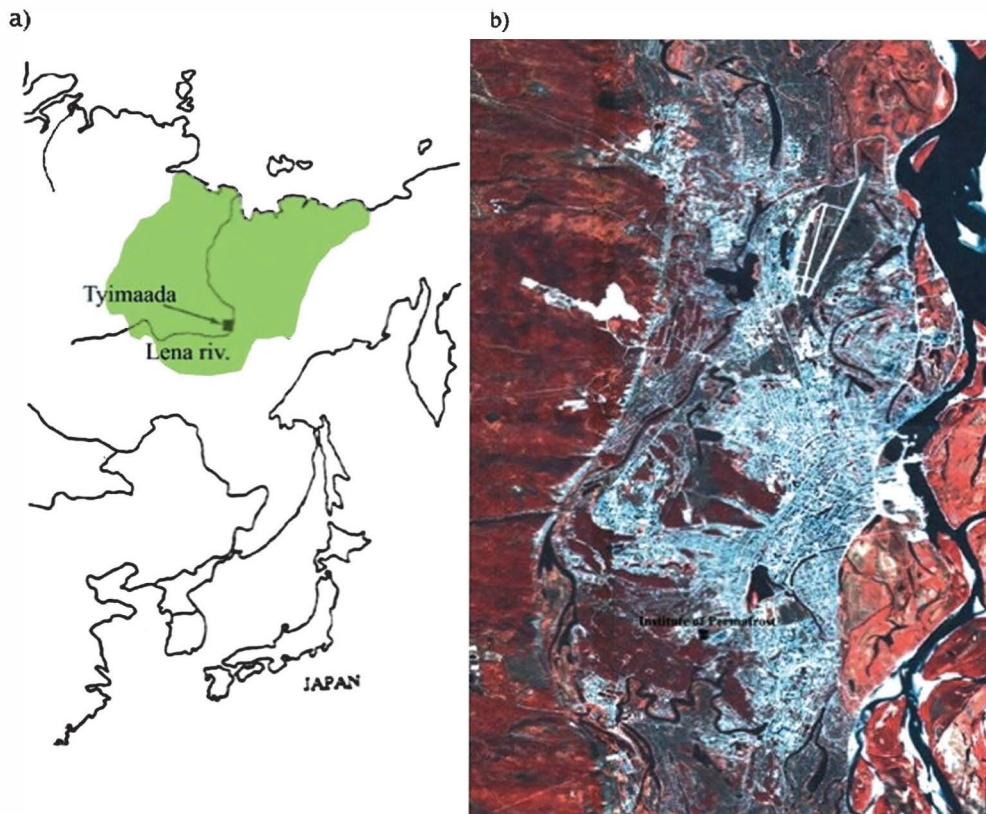


Fig. 1. Location of the study site. a) Tyimaada valley, b) Yakutsk city.

pollution in the region.

Any significant deviations from this range indicate deterioration trends. Emissions from industrial sources in Yakutia commonly produce an alkaline reaction, therefore precipitation and snowcover in the vicinity of the sources have increased pH values (Makarov *et al.*, 1990). On the other hand, acidification of precipitation and snowcover may occur in areas remote from the sources due to long range transport of sulfur and nitrogen compounds.

In order to investigate acid precipitation in Central Yakutia, a deposition collection apparatus provided by the Hokkaido Institute of Environmental Sciences, Japan, was installed in the southwestern fringe of Yakutsk (Fig. 1).

3. Methods

The investigations reported here are conducted as a part of the international acid deposition monitoring program, using common methodologies and devices. The joint monitoring is based on the Survey Manual for Acid Deposition developed by the Environmental Agency of Japan (Survey Manual for Joint Monitoring of Acid Deposition, 1999) and is carried out in compliance with the following basic criteria:

- 1) Sample collection is carried out by as simple a method as possible.
- 2) Measured components and analytical methods can be compared and evaluated mutually, and provide the member regions with common information.
- 3) Common devices are used for collecting liquid and solid (snow) precipitation (Fig. 2).

The merits and demerits of the acid deposition sampling method and matters that demand attention in using it are given in Table 1.



Fig. 2. Acid deposition sampler (winter).

Table 1. *Merits, demerits and special features of the filter type sampling method.*

| Merits | Cautions |
|---|--|
| <p>It collects all depositions.</p> <p>As evaporation is controlled, it permits to estimate precipitation volume.</p> <p>It causes minimum gas absorption from the air.</p> <p>It saves filtering work in the analytical laboratory and saves time.</p> <p>Its filtering and insulating light reduce changes in quality caused by micro-organism.</p> | <p>Care is needed not to cause cracks to funnel (glass ware can also be used).</p> <p>For filter materials, use of quartz fiber is advisable.</p> <p>It is necessary to analyze components of the washing water after washing the device such as funnel and insoluble substances (residues).</p> |
| Demerits | |
| <p>It is unable to eliminate dry depositions and thus specify deposition forms.</p> <p>Because meshes tend to clog and precipitation remains in the filter immediately after precipitation.</p> <p>It is unable to prevent insects from entering.</p> <p>Its collection efficiency is low for dry samples.</p> | |

Table 2. *Parameters analyzed and their importance.*

| Parameter | Importance |
|-------------------------------|---|
| SO ₄ ²⁻ | Major cause of acidity (sulfur loading) |
| NO ₃ ⁻ | Major cause of acidity (nitrogen loading) |
| NH ₄ ⁺ | Nitrogen loading |
| Cl ⁻ | Substances of marine origin |
| Na ⁺ | Substances of marine origin |
| Ca | Substances of soil origin (prevent acidification) |
| pH | Basic measure of acidity |
| Electrical conductivity | Measure of the total amount of dissolved substances |
| Eh | Redox potential |

The sampling period is one month. Sufficient sample amount for analysis is collected in the filter sampling device during this period. Samples are collected on first Monday of month.

Samples are analyzed for SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, Na⁺, Ca²⁺, pH, and electrical conductivity (EC). The reasons for selecting these parameters are given in Table 2.

4. Results and discussion

Monitoring observations at the site located near the Permafrost Institute were begun on 31 July 1996 at 1530 LT and have been carried out continuously during 8 years.

The pH of atmospheric deposition has predominantly been in the range of 6.8 to 7.4 over the period of observations. Acidic deposition with a pH less than 6 were observed

in April 2001 (pH=5.48), July 2002 (pH=5.88), and September and October 2004 (pH =5.86–5.89). Alkaline deposition with a pH greater than 8 occurred in October 2003 (pH=8.62). Since 2003, the acidity/alkalinity range of atmospheric deposition has notably increased compared to the earlier years. Average acidity values are virtually identical for rain and snow.

Monthly trends in the concentration of main acid deposition constituents over 8 years are illustrated in Fig. 3.

Average, minimum and maximum values of measured acid deposition components for the year (2004), and for warm and cold seasons are presented in Table 3.

The electrical conductivity which characterizes the total amount of dissolved substances and the concentrations of most components of atmospheric deposition are more than twice higher during the warm season. Maximums of the electrical conductivity are observed in the first half of the warm season, in May and June, being 44.1 and

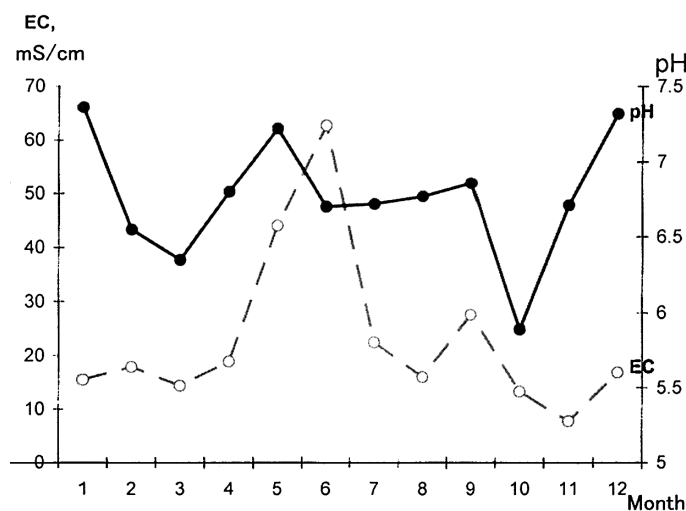


Fig. 3. Change in pH and electrical conductivity of atmospheric deposition.

Table 3. Seasonal variation in acid deposition chemistry in 2004, in $\mu\text{g}/\text{ml}$.

| Component | 2004 | | | Warm season | | | Cold season | | |
|-------------------------------|------|------|-------|-------------|------|-------|-------------|------|------|
| | Avg | Min | Max | Avg | Min | Max | Avg | Min | Max |
| pH | 6.77 | 5.89 | 7.36 | 6.85 | 6.70 | 7.22 | 6.71 | 5.89 | 7.36 |
| Ec, ms/cm | 23.1 | 7.8 | 62.7 | 34.6 | 16.0 | 62.7 | 15.0 | 7.8 | 18.9 |
| Eh, mV | 391 | 337 | 452 | 400 | 367 | 452 | 384 | 337 | 427 |
| SO ₄ ²⁻ | 3.53 | 1.80 | 5.70 | 4.34 | 2.70 | 5.70 | 2.86 | 1.60 | 4.11 |
| NO ₃ ⁻ | 4.42 | 1.03 | 16.85 | 6.59 | 3.10 | 16.85 | 2.86 | 1.03 | 6.60 |
| Cl ⁻ | 1.02 | 0.62 | 2.10 | 1.30 | 0.90 | 2.10 | 0.82 | 0.62 | 0.93 |
| Ca ²⁺ | 2.66 | 0.90 | 5.60 | 3.86 | 2.50 | 5.60 | 1.81 | 0.90 | 2.35 |
| Na ⁺ | 0.39 | 0.04 | 0.83 | 0.81 | 0.79 | 0.83 | 0.09 | 0.04 | 0.25 |
| NH ₄ ⁺ | 0.89 | 0.10 | 4.20 | 0.98 | 0.10 | 4.20 | 0.85 | 0.20 | 1.60 |

62.7 mS/cm respectively. Higher concentration in warm season atmospheric deposition is exhibited by the ions of marine origin, Na^+ , which in the Yakutsk area are commonly associated with carbonates, but not with chlorides. An exception is the concentration of nitrates which are the major cause of acidity related to nitrogen loading. They have increased concentrations during the cold season.

The pH values obtained at Yakutsk are close to those observed at Ulan-Bator, Mongolia. The pH values at this site which is also located in continental Asia are in the range of 6.36 to 8.12.

The increased pH values of atmospheric deposition are caused by the high concentration of carbonates in particulate matter in the Tyimaada valley. For example, the Ca and Mg ion concentrations in particulate matter are tens and hundreds times higher in Central Yakutia than in central areas of Alaska. This is due not only to urban activities and the predominance of carbonates in industrial emissions, mainly from construction facilities and power plants, but also to the geochemistry of the geological profile influenced by the predominance of carbonate and halogenic formations within the zone of hypergenesis (Makarov, 1985).

The acidity/alkalinity of atmospheric deposition observed at the monitoring site is not an analog of the acidity of precipitation (rain or snow), since the pH of total deposition is influenced by particulate deposition. The greater the amount of particulate matter in atmospheric deposition, the greater the pH difference between total deposition and wet deposition. The difference may be positive or negative depending on the chemical composition of depositions (Table 4). The pH of total deposition is considerably higher than that of wet deposition virtually throughout the entire winter (October–April). The two coldest months (December–January) are an exception when the pH of wet and total deposition are approximately equal. In the warm season (May–September), the pH of dry deposition is approximately equal to the pH of wet deposition.

The inherent and consistent relationship between the pH value and the concentra-

Table 4. Variation in acidity/alkalinity of precipitation and atmospheric deposition over 8 years.

| Month | pH of total atmospheric deposition | pH of wet deposition | $\text{pH}_{\text{total}} - \text{pH}_{\text{wet}}$ |
|---------|------------------------------------|----------------------|---|
| 1 | 7.36 | 7.35 | 0.01 |
| 2 | 6.55 | 7.62 | -1.07 |
| 3 | 6.35 | 7.18 | -0.83 |
| 4 | 6.80 | 7.63 | -0.83 |
| 5 | 7.22 | 7.19 | -0.03 |
| 6 | 6.70 | — | — |
| 7 | 6.72 | 6.66 | 0.06 |
| 8 | 6.77 | — | — |
| 9 | 6.86 | 6.87 | -0.01 |
| 10 | 5.89 | 7.09 | -1.20 |
| 11 | 6.71 | 7.27 | -0.56 |
| 12 | 7.32 | 7.07 | 0.25 |
| Average | 6.77 | 7.17 | -0.40 |

tions of dissolved and particulate substances in atmospheric deposition was noted earlier (Makarov *et al.*, 1990). A shift in the acidity/alkalinity of atmospheric deposition to the alkaline range is a sensitive indicator of atmospheric pollution. A negative correlation between acidity/alkalinity and redox potential of precipitation can be another indicator of anthropogenic pollution of the atmosphere.

Atmospheric deposition on the earth's surface (P) for the sampling period was calculated using the formula:

$$P = \frac{CV}{1000} \times \frac{100^2}{\pi r^2} \times \frac{30}{D} \text{ mg/m}^2/30 \text{ days,}$$

where: C -concentration in the sample solution, mg/ml; V -sample volume, ml; r -radius of the sampling tap, mm; D -number of sampling days.

Levels of atmospheric deposition to the earth's surface were estimated on an annual basis.

The averages, minimums and maximums of deposition levels of components and the total deposition for the year, warm season and cold season in 2004 are given in Table 5.

Table 5. Atmospheric deposition of components to the earth's surface in 2004, in g/m²yr.

| Component | 2004 | | | Warm season | | | Cold season | | |
|------------------------------------|------|-------|------|-------------|-------|------|-------------|-------|-------|
| | Avg | Min | Max | Avg | Min | Max | Avg | Min | Max |
| H ⁺ (10 ⁻⁴) | 0.71 | 0.073 | 3.72 | 0.54 | 0.14 | 0.86 | 0.82 | 0.07 | 3.72 |
| SO ₄ ²⁻ | 0.92 | 0.16 | 1.54 | 1.33 | 1.17 | 1.54 | 0.59 | 0.16 | 1.12 |
| NO ₃ ⁻ | 1.15 | 0.17 | 4.55 | 2.00 | 0.82 | 4.55 | 0.54 | 0.17 | 1.03 |
| Cl ⁻ | 0.26 | 0.087 | 0.57 | 0.41 | 0.24 | 0.57 | 0.15 | 0.09 | 0.33 |
| Ca ²⁺ | 0.69 | 0.22 | 1.47 | 1.22 | 0.91 | 1.45 | 0.32 | 0.22 | 0.52 |
| Na ⁺ | 0.13 | 0.005 | 0.42 | 0.27 | 0.19 | 0.42 | 0.026 | 0.005 | 0.072 |
| NH ₄ ⁺ | 0.20 | 0.019 | 1.13 | 0.26 | 0.024 | 1.13 | 0.16 | 0.019 | 0.25 |

Both the averages and the maximums of deposition levels for all analyzed components are notably higher during the warm season (see Table 5).

The deposition levels of measured components, H⁺, Ca²⁺, Na⁺, NH₄⁺, SO₄²⁻, NO₃⁻ and Cl⁻, and their relationship to precipitation amount are illustrated in Fig. 4.

Of interest are the deposition rates of regulated components: sulfur, nitrogen and hydrogen ions. The H⁺ deposition levels have remained significantly below the maximum allowable concentration throughout the observation period. The annual average deposition flux of other components which impact terrestrial vegetation and aquatic ecosystems (nitrogen: N and sulfur: S) notably exceed the air pollution criteria (RF Ministry of Environmental Protection, 1992).

Changes in the atmospheric deposition fluxes over the period of observations (since 1997), including in terms of sulfur and nitrogen, are shown in Table 6.

The atmospheric deposition fluxes for a number of important components, Ca²⁺, SO₄²⁻ and NO₃⁻, in 2003 were highest over the seven years of observation. In 2004, the atmospheric deposition on the earth's surface decreased for Ca²⁺ and SO₄²⁻ and in-

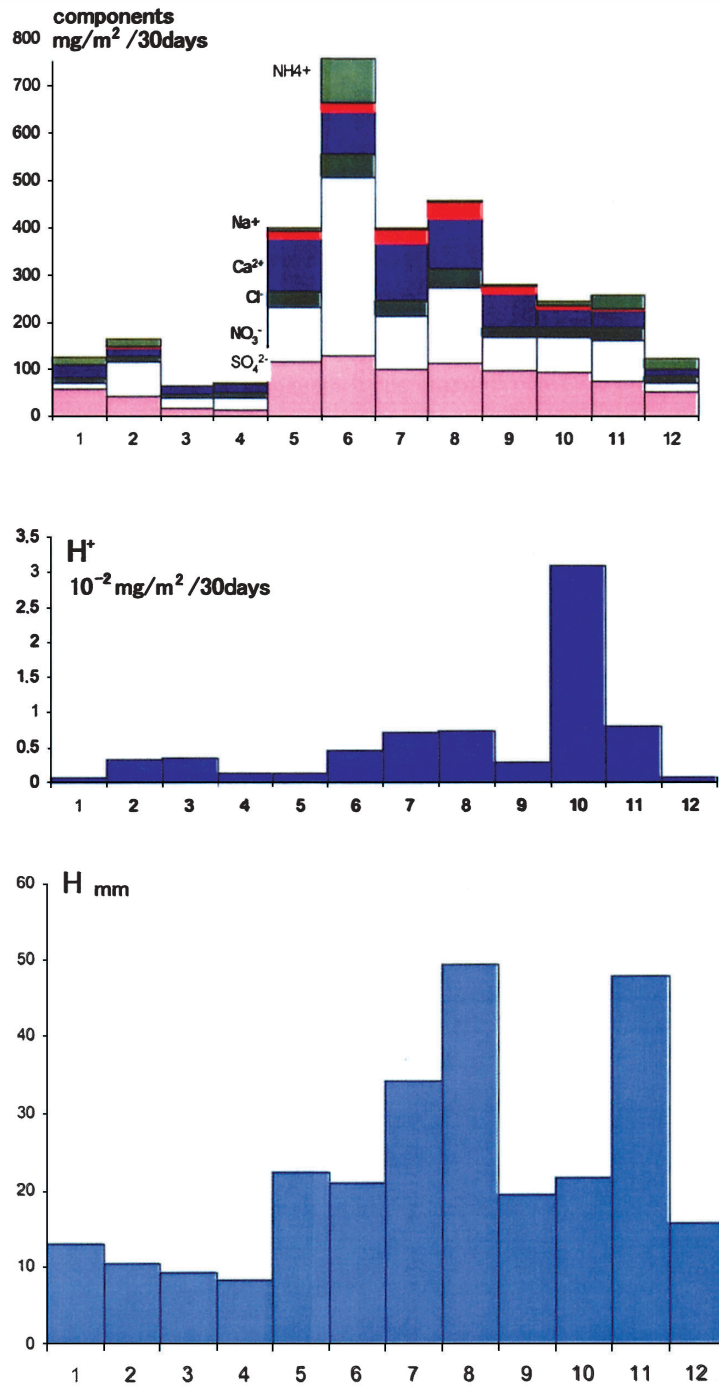


Fig. 4. Atmospheric deposition fluxes of major components, pH, and precipitation amount in 2004.

creased for H^+ , while NO_3^- deposition was highest for the five-year period starting in 2000. Higher values for NO_3^- were observed only in 1999. It should be noted that the concentrations of sulfates and nitrogen compounds in atmospheric deposition and, correspondingly, sulfur and nitrogen deposition levels show a clear increasing trend

Table 6. Changes in annual average atmospheric deposition flux over the period 1997–2004, $g/m^2/yr.$

| Component | Year | | | | | | | |
|---------------------|------|------|-------------|------|------|-------|--------------|-------------|
| | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 | 2004 |
| H^+ (10^{-4}) | 0.18 | 0.26 | 0.20 | 0.17 | 0.16 | 0.101 | 0.443 | 0.71 |
| SO_4^{2-} | 1.00 | 0.66 | 0.70 | 0.61 | 0.51 | 0.691 | 1.445 | 0.92 |
| NO_3^- | 0.15 | 0.20 | 0.90 | 0.19 | 0.17 | 0.844 | 1.156 | 1.15 |
| Cl^- | 0.30 | 0.38 | 1.02 | 0.30 | 0.48 | 0.252 | 0.557 | 0.26 |
| Ca^{2+} | 0.64 | 0.70 | 0.75 | 0.75 | 0.74 | 0.629 | 1.015 | 0.69 |
| Na^+ | 0.09 | 0.06 | 0.13 | 0.05 | 0.12 | 0.080 | 0.084 | 0.15 |
| NH_4^+ | 0.14 | 0.12 | 0.52 | 0.08 | 0.13 | 0.143 | 0.122 | 0.20 |
| S | 0.33 | 0.22 | 0.23 | 0.18 | 0.17 | 0.23 | 0.501 | 0.30 |
| N | 0.14 | 0.14 | 0.61 | 0.11 | 0.14 | 0.30 | 0.355 | 0.46 |
| Precipitation, ml | 309 | 269 | 342 | 292 | 181 | 189 | 356 | 274 |

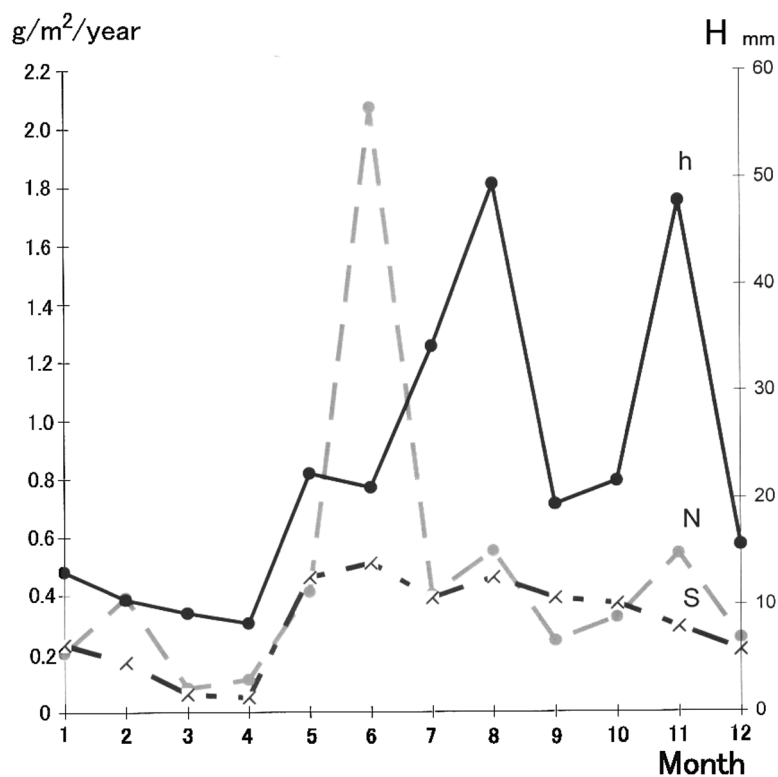


Fig. 5. Atmospheric deposition of sulfur (S), nitrogen (N) and precipitation amount (h) in 2004.

Table 7. Ecological estimate of deposition levels of atmospheric pollutants in 2004.

| | Sulfur, g/m ² /yr | Nitrogen, g/m ² /yr | Hydrogen ions 10 ⁻⁴ g/m ² /yr |
|---------------------------------|---------------------------------|-----------------------------------|--|
| Average | 0.30 | 0.46 | 0.71 |
| Maximum | 0.51 | 2.07 | 3.72 |
| Ecological standard* | <0.32 | <0.28 | <20 |
| Ecological emergency situation* | >3.0 | >2.0 | 200–300 |

* RF Ministry of Environmental Protection (1992).

during the last four years (since 2000). The atmospheric deposition flux has increased by 67% for sulfur compounds and by a factor of 4.6 for nitrogen compounds between 2000 and 2004 (Fig. 5).

The estimated atmospheric deposition levels of chemical components based on monitoring data are close to the estimates obtained earlier from snowcover geochemistry studies in the Tuymaada valley and in Yakutsk (Makarov, 1997). An exception is the deposition level of nitrogen compounds which has notably increased during the monitoring period.

In 2004, the annual average atmospheric deposition of nitrogen and the maximum deposition of sulfur exceeded the ecological standards by 59% for S and by 64% for N (Table 7). The maximum value of atmospheric deposition of nitrogen measured at the monitoring site in June, 2.07 g/m², reached the parameters of ecological emergency situation: >2.0 for N compounds (RF Ministry of Environmental Protection, 1992). Of nitrogen compounds, ammonium compounds are prevailing, which account for about 60% of the total nitrogen deposition. The highest values of atmospheric deposition of sulfur and nitrogen compounds that significantly exceed the ecological standards occur in the warm season and the early winter (May through September).

5. Conclusions

The results of acid deposition monitoring have shown that atmospheric deposition in the Yakutsk area is predominantly weakly acidic to weakly alkaline with a narrow pH range of 5.89 to 7.36. The acidity of atmospheric deposition has very close values in the warm season (pH=6.70–7.22 with an average of 6.85) and the cold season (pH=5.89–7.36 with an average of 6.71). Largest deviations of the cold season acidity/alkalinity from the average values are observed in the early and middle winter: October—maximum acidity (pH=5.89) and December–January—maximum alkalinity (pH=7.32–7.36).

The increased pH values of atmospheric deposition are caused by high carbonate concentrations in particulate matter in Central Yakutia. The Ca and Mg carbonate contents in particulate matter in this area are tens and hundreds times higher than, say, in central Alaska. This is due to the specific geochemistry of anthropogenic processes and to the high carbonate and halogen concentrations in natural particulates resulting from the predominance of carbonate and halogenic formations in the geological profile.

Based on monitoring data, the atmospheric deposition of chemical components has

been estimated. Annual atmospheric inputs of H^+ ions to the earth's surface are considerably lower than the critical loads on forest and aquatic ecosystems. The maximum values of atmospheric deposition for sulfur compounds (0.51 g/m^2) and nitrogen compounds (2.07 g/m^2) at the monitoring site are observed in June and exceed the environmental standards, with the nitrogen deposition level reaching the environmental emergency values.

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