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HYDROGEN ION CONCENTRATION IN THE PRECIPITATION AND SNOWPACKS IN YAKUTIA

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Abstract

Acidity-alkalinity of meteoric water (rain and snow) in Yakutia was studied. This vast area in north-eastern Asia is characterized by low pollution of the atmosphere, and the background acidity of precipitation varies within a pH range of 5.8 to 6.4. The increased pH values up to near-neutral and alkali were observed in the coastal areas and the zones affected by industrial activities. A decrease in the pH of meteoric water to 5.0-5.4 was detected in the areas where sulfide rich geologic formations occur. Temporary acidification of meteoric water was observed in western Yakutia which is attributed to long-range transport of sulfur from the Norilsk area.

KEYWORDS: *hydrogen ion concentration, precipitation, snowpack*

1. Introduction

In the last 20-30 years acid precipitation observed in many regions of the world (North America, Europe, China, Korea and Japan) has transformed from the intriguing scientific fact into the issue of much public concern and considerable discussion. The problems associated with its potential adverse impacts are not restricted to certain localities, but regional, national and international scale. A wide variety of effects is related to acid precipitation, precursor gases and products of their chemical reactions. Potential environmental impacts include harmful effect on human health, acidification of surface water and soil, decrease in forest productivity, erosion and corrosion of industrial materials and deterioration of atmospheric transparency. Deposition of chemical pollutants from the atmosphere is one of the most serious environmental problems. However, the large areas in north-eastern Asia, including Yakutia, are still "white spots", as virtually no data exist about acidity-alkalinity of the meteoric water in these vast expanses.

2. Methodology

Observations of the chemical composition of meteoric water, including field and long-term monitoring studies, have been conducted since the early 1980s. Rain samples are collected in plastic flasks during the rain period. Snow samples were taken from the entire layer of snowpack at the end of the cold season (March 15-25) before snowmelt. In the present study,

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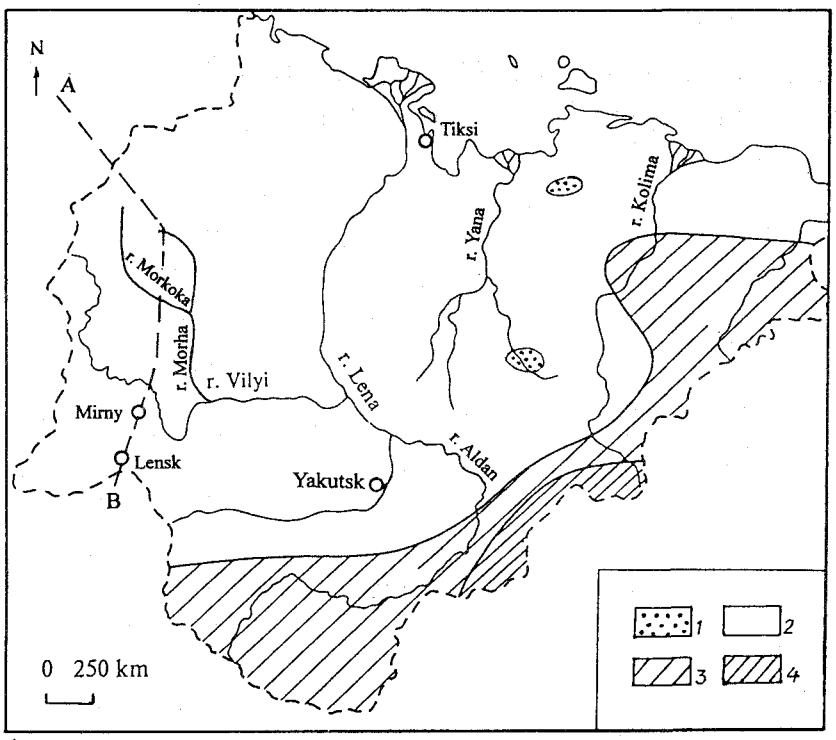

Figure 1. Hydrogen ion concentration (1:pH≤5.5, 2:5.5<pH≤6.5, 3:6.5<pH≤7.0, 4:7.0<pH≤7.4) in snowcover in Yakutia since the early 1980s (Makarov,1990). A broken line (A-B) is a part of the path for obtaining the geochemical profile of snowcover shown in Fig.4.

the results of the chemical analysis of snow samples from the entire thickness of snowpack were used. Hydrogen ion concentrations were measured by the I-120, I-type pH meter with sensitivity of a 0.01 pH value. In addition, a full chemical analysis of rain and snowmelt water with determination of a wide range of macro- and microelements was made using ion chromatography and atomic absorption spectrophotometry.

3. Results

It is well known that acidity of precipitation is determined by free hydrogen ion(H^+) concentration. Among the natural agents CO_2 has the greatest effects on the pH, since hydrogen ion concentration in water depends on the CO_2 content. All other conditions being the same, the larger is the CO_2 concentration, the larger is the hydrogen ion concentration, and the lower is the pH. For the mean CO_2 concentration in the air the pH is 5.5-5.6 (Drozdova *et al.*, 1964; Vasilenko *et al.*, 1985). These pH values are characteristic of the unpolluted precipitation. Besides cabon dioxide, some other natural acid-forming substances may be present in the atmosphere in small amounts such as organic acids, sulfur dioxide, hydrogen sulfide, hydrochloric acid, nitric oxides and nitric acid (Izrael, 1983).

Relation between the hydrogen ion concentration and the concentration of other ions in

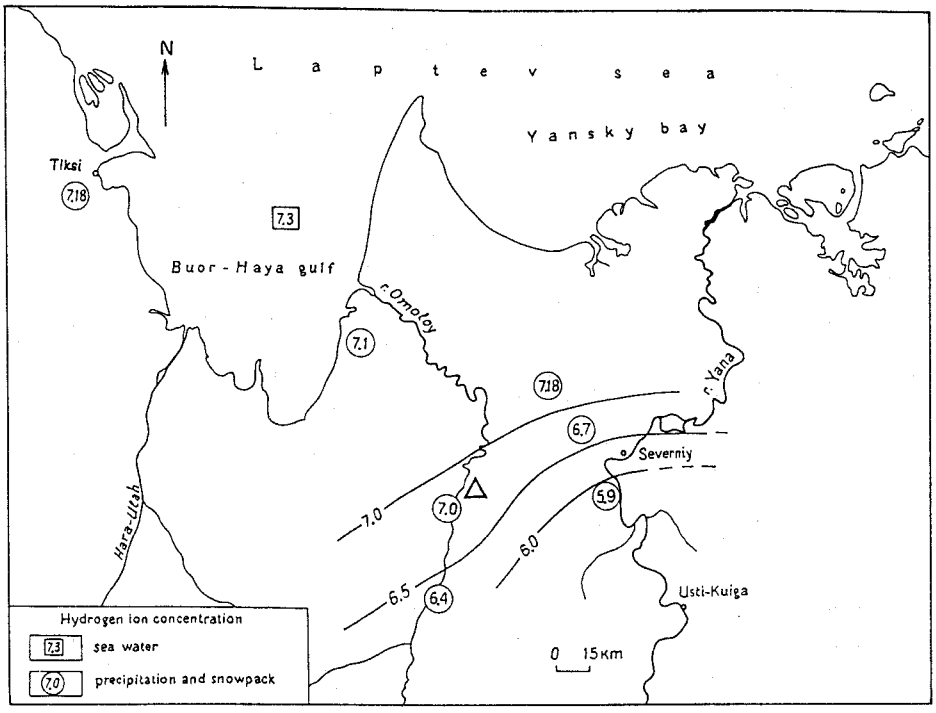

Figure 2. Changes in pH value in precipitation in the Laptev coastal zone (1996). Triangle (△) shows the sampling place (Fig.3) in 1981.

the precipitation (neglecting contribution of weak organic acids) is expressed in the form:

$$[H^+] = 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] - 2[Ca^{2+}] - [K^+] - 2[Mg^{2+}] - [Na^+] - [NH_4^+] + 2.5\times10^{-6}.$$

The remainder term in this expression, 2.5×10^{-6} mol ℓ^{-1}, corresponds to the hydrogen ion concentration in an equilibrium water solution at the mean atmospheric carbon dioxide concentration of 330 ppmv at 20 °C. When the hydrogen ion concentration is 2.5×10^{-6} mol ℓ^{-1}, pH value is 5.6. This value is generally characteristic of unpolluted precipitation.

Figure 1 shows the spatial distribution of hydrogen ion concentration(pH) in snowcover in Yakutia (Makarov *et al.*, 1990). In the major portion of Yakutia, the pH of snowpacks ranges from 5.8 to 6.4, which attests to low pollution of the winter atmosphere. Larger deviations from these values are indicative of severe pollution. As mentioned later, industrial waste products released into the atmosphere cause most commonly an alkaline reaction. Hence, the precipitation and snowpack in those areas have increased pH values. On the other hand,in the areas far off the industrial facilities precipitation and snowpacks may be acidified due to long range transport of sulfur and nitrogen compounds, and pH values of snow water are lower. Relatively high pH values near neutrality (pH 6.5-7.2) are found in snowpacks in south-eastern and eastern Yakutia attributable to transport of cold air mass from the Pacific basin.

The effect of the sea basin on precipitation chemistry is observed in the Arctic coastal area though to a lesser extent. Figure 2 shows the distribution of pH values in precipitation in the Laptev coastal zone. Weak-alkali and near-neutral pH values (7.1-7.18) close to the sea water

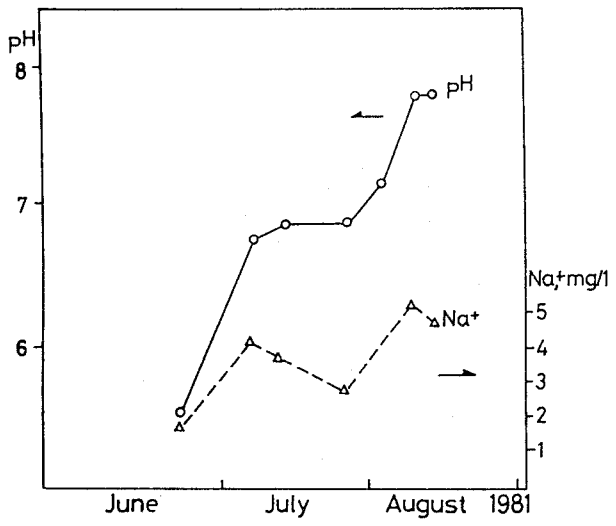

Figure 3. Changes in pH value and Na^+ concentration (mg ℓ^{-1}) in precipitation on the banks of the river Omoloy in summer in 1981 (Makarov,1989).

values (the Laptev Sea, Buor-Haya Bay, pH= 7.3) are found in the precipitation (rain and snow), and the snowpack at a distance of 50 to 60 km from the shoreline, while at a distance of 90-100 km from the Laptev coast, the pH of the precipitation is close to the background values of interior Yakutia (5.9-6.4).

There is a known correlation between the chemical composition of atmospheric aerosols and the underlying ground surface (e.g., Chemistry of the Lower Atmosphere, 1976; Weiss, 1973). Vernadsky(1960) suggested that the average chemical composition of precipitation in any region should be relatively constant and largely dependent on the chemical composition of the land surface. This is supported by the accumulation of tin, copper, lead, zink, i.e. specific elements of the regional geologic formations, in the precipitation in some areas of eastern Yakutia (Makarov, 1989). An increase in the atmospheric transport of the components of sea salts (for example, Na^+) during the warm season with a decrease in the continuity of the ice cover of the Laptev Sea may result in increasing alkalinity of precipitation near the coast shown in Figure 3. Sulfides released into the atmosphere from the land surface in the form of aerosols, and their oxidation in the air causes apparently acid rains which are relatively local. In these areas, the pH value of precipitation (rain, wet snow and snow) may drop to 5.0-5.4.

The pH of snowmelt water is basically affected by the processes related to the industrial activities, fossil fuel consumption and emission of large amounts of substances which lead to the formation of strong acids as sulfuric acid and nitric acid. However, in Yakutia there are practically no such industries, and coal from local deposits used for power generation is mainly low-sulfur containing, which leads to small amounts of sulfur emission.

Some acidification of precipitation, probably non-permanent, may occur in the north-western part of Yakutia, where the chemical composition of the snowpack is changed due to long-range transport of atmospheric pollutants, which are mainly nitrogen and sulfur compounds, and heavy metals such as Cu, Cr and Mo, from the Norilsk mining industrial region. Figure 4 illustrates regional geochemical profile of snowcover from Norilsk to Lensk. The hy-

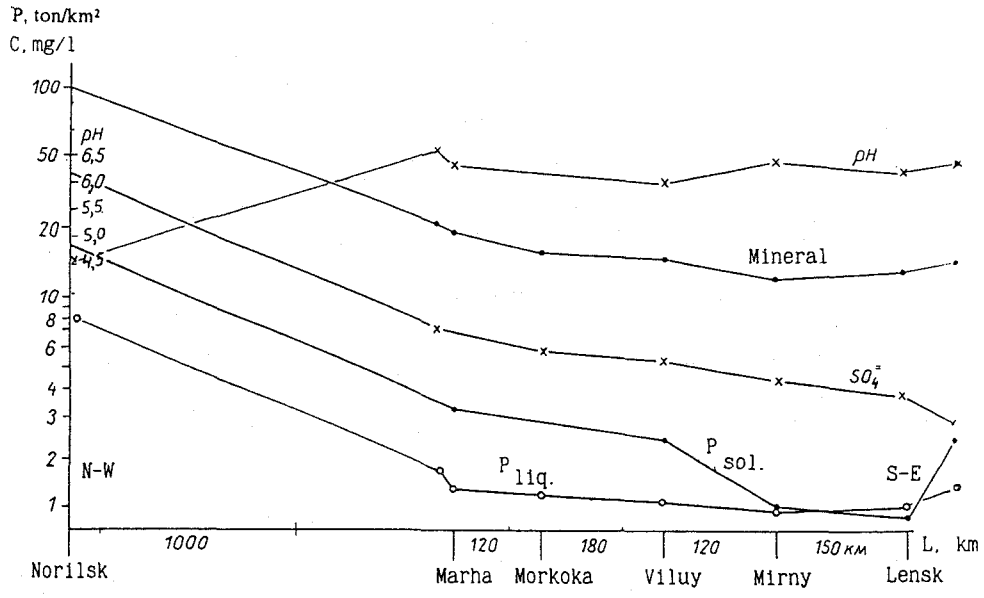

Figure 4. Regional geochemical profile of snowcover from Norilsk to Lensk (1996). Mineral and SO_4^{2-} are the concentrations ($mg\,\ell^{-1}$) of mineral substances and sulfate, respectively, in snow water. Psol. and Pliq. are amounts of mineral substances (tons km^{-2}) deposited from the atmosphere on the surface, respectively, in solid and liquid phases.

drogen ion concentration decreases regularly from the Norilsk area (pH 4.5) to the Markha River basin (pH 6.4-6.6). In the north-western boundary of Yakutia the pH is estimated to be 6.0. An increase in the pH is accompanied by a simultaneous decrease in the concentration of soluble and particulate substances in snowpacks.

Since the pH of meltwater depends on the anion/cation ratio, relatively high pH values of snowpacks are expected in the areas where the compounds (CaO and MgO) with an alkaline reaction are predominant in the industrial emissions. An increase in pH values of snowmelt water with increasing anthropogenic impacts is observed in the industrial areas of the country (Pavlenko *et al.*, 1981; Glazovsky *et al.*, 1983).

High dust contents in the atmosphere in the areas of anthropogenic impacts, predominance of carbonates, and calcium and magnesium oxides in the industrial emissions, subsequent dissolving the mineral particulates accumulated in snowpacks lead to a sharp increase in pH values being as much as 8.0-9.5 in the mining and development areas. For example in the zones of intensive anthropogenic impacts in Yakutia, pH values of snow water are shifted to the alkaline range being as much as 7.5-9.0 in the towns and settlements (Yakutsk 9.4; Neryungri 7.3; Mirnyui 8.2; Udachny 7.85; Zhatai 7.4 and Abyi 7.25), and 8.0-9.4 in the mining areas (the Mir diamond pipe 9.45; Neryungri coal pit 8.0-9.1 and Elginsk coal pit 7.3). Snowpacks in the areas experiencing high anthropogenic loads are characterized by increased pH values (8-9) which are indicative of low hydrogen ion concentration and an alkaline reaction of melt water. The pH value of snowpacks decreases regularly with increasing distances from the developed and industrial zones. For example, as shown in Fig.5, in Central Yakutia the background pH values are within the range of 6.2-6.5, while in Yakutsk city they are as much as 7.5-9.4.

Figure 6 shows the dependence between the pH and the concentrations of soluble substances

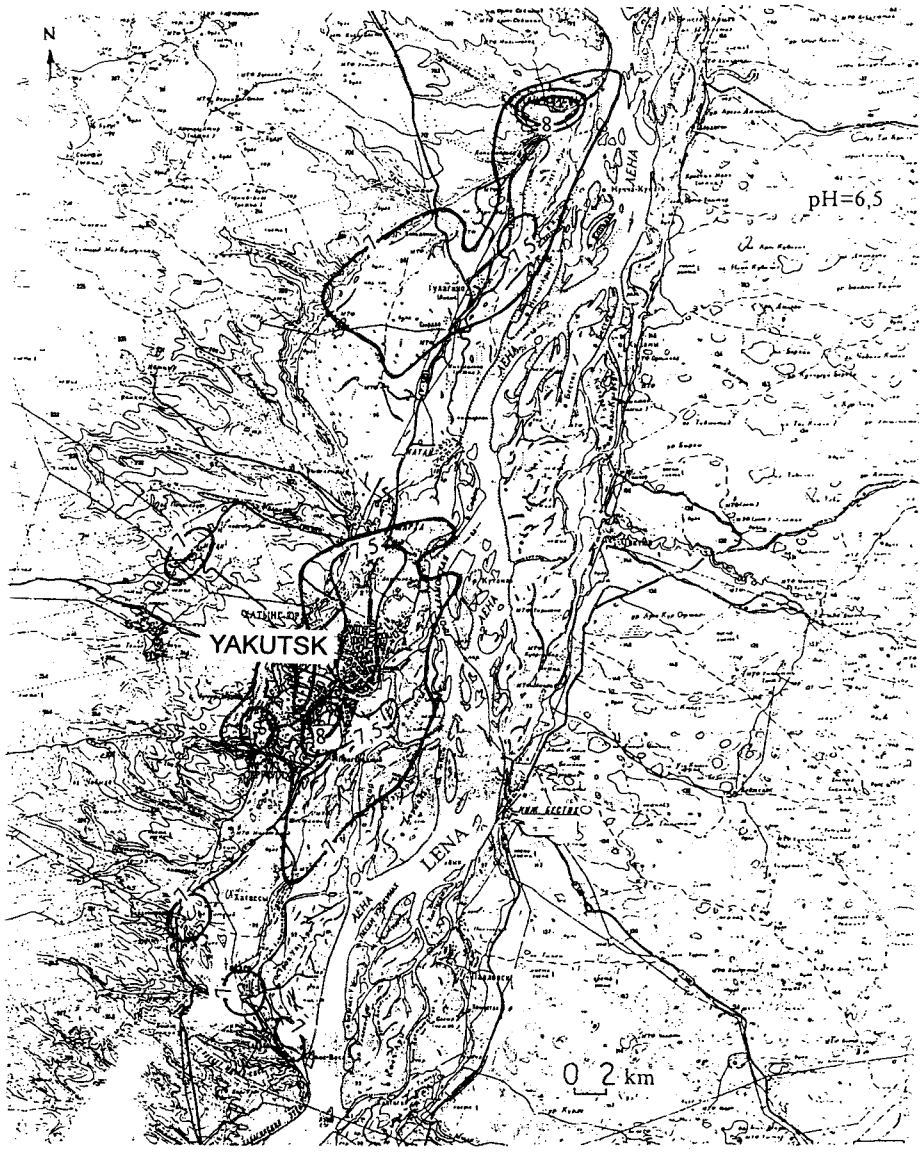

Figure 5. Changes in pH value in snowcover in the Tuymada valley (1997).

and dust in snowpacks. The pH values increase with an increase in mineral substances of snow melt water and dust contents in snowpacks. The pH is a sensitive indicator of atmospheric pollution, since the values depend on the magnitude of anthropogenic impacts, and stronger anthropogenic impacts lead to a shift of pH to the alkaline region.

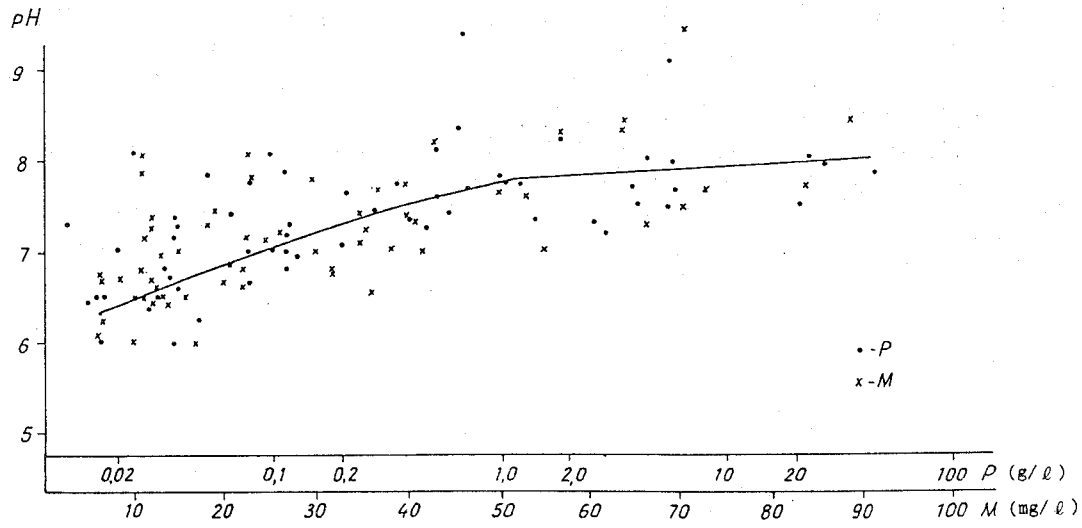

Figure 6. Dependence of pH on snow contamination in the natural and industrial zones in Yakutia (1985-1995). M and P denote the concentrations of dissolved and mineral phase substances, respectively, in the snowpack.

4. Conclusions

The precipitation and snowpacks on the vast areas of north-eastern Asia which are little affected by industrial activities are characterized by a weakly acid pH reaction. Carbonates are predominant in the atmospheric emissions from the few small-size technogenic zones in the area. This leads to the shift of pH of meteoric water to the alkaline region. A decrease in the pH value of meteoric water to 5.0-5.4 is detected in the areas in eastern Yakutia where sulfide-rich geologic formations occur. Temporary acidification of meteoric water observed in large areas of western Yakutia is attributed to the long-range transport of sulfur from the Norilsk area.

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