Surface water chemistry in a continuous permafrost region, Central Yakutia, Eastern Siberia

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1. INTRODUCTION

One of distinct features of the ecosystems of central Yakutia, eastern Siberia, is the abundance of thermokarst depressions called "alases," which form by thawing of the upper part of the continuous permafrost. Alases range from several meters to more than 20 m in depth, and in area they range from less than 1 ha to more than 500 ha. Central Yakutia has about 16 000 alases, covering a total area of about 44 million ha (Fedorov and Konstantinov 2003). While many alases are covered by grassland, with or without small ponds, some alases contain sizeable lakes. Another feature of this region is the accumulation of soluble salts in soils and their high alkalinity (Desyatkin 1993, Lopez et al. this volume). The very low annual precipitation of 230 mm and continuous permafrost in central Yakutia inhibit the leaching of soluble weathering products, causing the soils to be highly saline and alkaline. Alases in particular accumulate substantial amounts of salts that had been stored in the permafrost (Desyatkin 1993). This study's aim was to characterize the surface water chemistry in central Yakutia.

2. STUDY AREA AND METHODS

The study area was in central Yakutia (Fig. 1). The annual mean temperature in Yakutsk ($62^{\circ}05'N$, $129^{\circ}45'E$) is $-10^{\circ}C$, and the annual mean precipitation is 230 mm. The soil parent material in the study area is composed mainly of Upper Pleistocene to Holocene alluvial deposits.

In summer 2005 (17 July to 5 August), 33 water samples were collected from tributaries of the Lena and Aldan rivers, and six water samples were collected from alas lakes (Fig. 1).

Total dissolved nitrogen (TDN) was determined by the method of alkaline persulfate digestion with HCl-acidified UV detection. Anions (NO₃⁻, Cl⁻ and SO₄²⁻) and metal cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) were determined by ion chromatography (QIC Analizer; Dionex, Sunnyvale, CA & ICA-2000; DKK-TOA, Tokyo, Japan). NH₄⁺ was determined by colorimetry using the indophenol blue method. Dissolved organic nitrogen (DON) was calculated by subtracting dissolved inorganic nitrogen (DIN, NO₃⁻ + NH₄⁺) from TDN. Total dissolved C and inorganic C were determined with a TOC analyzer (TOC-5000A; Shimadzu, Kyoto, Japan), and dissolved organic carbon (DOC) was calculated by subtracting inorganic C from total dissolved C. pH was measured with a glass electrode.

Symptom of Environmental Change in Siberian Permafrost Region, Eds. Hatano R and Guggenberger G, p 129-134, Hokkaido University Press, Sapporo, 2006 Chemical speciation and the activity of each species were calculated by using the algorithm proposed by Wada and Seki (1994). Alkalinity was calculated by summing the concentrations of HCO_3^- and CO_3^{2-} . Saturation indexes (*SIs*) of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) were calculated as follows:

$$SI_{\text{calcite}} = \log \left[(\text{Ca}^{2+})(\text{CO}_3^{2-}) / K_{\text{calcite}} \right]$$
$$SI_{\text{dolomite}} = \log \left[(\text{Ca}^{2+})(\text{Mg}^{2+})(\text{CO}_3^{2-})^2 / K_{\text{dolomite}} \right]^{1/2},$$

where the activity of each solute is shown within parentheses and K_{calcite} and K_{dolomite} are the solubility constants of calcite and dolomite, respectively.

Student's *t* test was used for comparison between two groups and detection of significant correlation between two variables.



Fig. 1. Sampling locations of surface waters: stream waters (closed circles) and alas lake waters (open circles).

3. RESULTS AND DISCUSSION

We found very high concentrations of some inorganic solutes in surface waters (Fig. 2). Average pH was 8.2, and average concentrations were Na⁺, 1244 μ eq L⁻¹; K⁺, 77 μ eq L⁻¹; NH₄⁺, 10 μ eq L⁻¹; Ca²⁺, 1618 μ eq L⁻¹; Mg²⁺, 2082 μ eq L⁻¹; Cl⁻, 142 μ eq L⁻¹; NO₃⁻, 0.2 μ eq L⁻¹; SO₄²⁻, 72 μ eq L⁻¹; and Si, 57 μ mol L⁻¹. Concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, and Cl⁻ and alkalinity and pH were significantly higher in central Yakutia than values reported by Huh et al. (1998), who measured inorganic solute compositions of 106 river waters in eastern Siberia (*P* < 0.01), while concentrations of SO₄²⁻ and Si were significantly lower (*P* < 0.01) (Fig. 2).

The highly alkaline and saline conditions in the soils of central Yakutia (Desyatkin 1993) are probably the primary cause of the high concentrations of metal cations and high alkalinity in surface waters of this region. Permafrost inhibits the downward leaching of soluble ions in soils, and the very low annual precipitation of 230 mm, which is not high enough to wash soluble ions out of the soil and into the streams by horizontal flow, has led to the accumulation of

soluble ions produced by weathering reactions during soil formation processes (Desyatkin 1991, 1993).

SI values of calcite and dolomite are negative, zero, or positive when a solution containing these minerals is undersaturated, saturated, or supersaturated, respectively. Most surface waters in central Yakutia were saturated or supersaturated with respect to both calcite and dolomite (Fig. 3(a)), but *SI* values were higher in lake waters than in stream waters (P < 0.05), indicating that concentrations of Ca²⁺, Mg²⁺, and CO₃²⁻ in the lake waters had been increased by evaporation, or that these solutes had been diluted in stream waters by rainfall.



Fig. 2. Comparison of inorganic solute concentrations between central Yakutia (gray boxes) and other rivers in eastern Siberia (white boxes), reported by Huh et al. (1998).



Fig. 3. Saturation indexes of carbonate minerals (calcite and dolomite) (a) and phase diagram of silicate minerals (b). Equilibrium constants for silicate minerals adopted by Garrels (1984) were used.

On a stability diagram of silicate minerals (Fig. 3(b)), lake waters fell mainly into the muscovite stability field, whereas stream waters fell into the kaolinite stability field. A possible reason for this difference between lake and stream waters is that the activity ratio $(K^+)/(H^+)$ was increased by K^+ and OH⁻ becoming more concentrated in lake waters as a result of evaporation, whereas it was decreased in stream waters by dilution of K^+ and OH⁻ as a result of rainfall. We speculate that the muscovite–kaolinite weathering reaction, which is located around the boundary between lake and stream waters in the diagram, might be an important control of the silica concentration in surface waters of central Yakutia.

DON was the main form of dissolved nitrogen in surface waters of central Yakutia. The concentration of DON ranged from 1.0 to 5.3 mg N L⁻¹ (mean, 2.2 mg N L⁻¹) and accounted for 68%–100% of TDN. DON was followed in importance by NH₄⁺ (range, 0.0–1.4 mg N L⁻¹; mean, 0.14 mg N L⁻¹) and NO₃⁻ (range, 0.000–0.019 mg N L⁻¹; mean, 0.003 mg N L⁻¹). The DON concentrations were about 10 times previously reported values from the Lena basin: 0.1–0.4 mg N L⁻¹ (mean, 0.2 mg N L⁻¹) from the Lena, Aldan, and Viluy rivers (Lara et al. 1998) and 0.15 mg N L⁻¹ from the Lena delta (Lobbes et al. 2000). The DOC concentration ranged from 21 to 73 mg C L⁻¹ (mean, 43 mg C L⁻¹) and was positively correlated with the DON concentration (r = 0.37, P < 0.05, Fig. 4(a)). The DOC/DON ratio ranged from 14 to 29, and the average was 20; this value was much lower than previously reported values from the Lena basin: 34–68 (mean, 56) by Lara et al. (1998) and 49.2 by Lobbes et al. (2000).



Fig. 4. Correlations between DON and DOC (a), Si (b), alkalinity (c), and Na⁺ (d).

The DON concentration was negatively correlated with the Si concentration (r = -0.38, P < 0.05, Fig. 4(b)). Since it takes longer for Si to reach equilibrium between the soil solid phase and the soil solution than for other solutes in soils, the Si concentration tends to decline during high-flow events, which are dominated by surface runoff and bypass flow in soil macropores

(Drever 1997). Therefore, the negative correlation between DON and Si concentration indicates that surface runoff and bypass flow are important pathways by which DON is transported from organic soil horizons to stream waters. Our result is contrary to the positive correlation between DON and Si concentration obtained by Lara et al. (1998) from the Lena River. These opposite results indicate that the DON concentration in the stream waters of central Yakutia is controlled by a different mechanism compared with other areas of the Lena basin. We also speculate that the much lower DOC/DON ratio in this study compared with previously reported values might be attributed to this distinctive control mechanism for DON in this area.

The highly alkaline and saline soils predominating in central Yakutia probably mainly account for the extremely high DON concentrations in surface waters of this region. A ligand exchange reaction on surfaces of Fe and Al oxide/hydroxide minerals is one of the most important reactions affecting the retention of dissolved organic matter (DOM) in soils (Kalbitz et al. 2000). Maximum adsorption of DOM by ligand exchange occurs at pH 5, and adsorption decreases as pH increases owing to desorption of DOM through ligand exchange with OH⁻ under alkaline conditions (Tipping 1981, Kalbitz et al. 2000). The positive correlation between DON concentration and alkalinity in the stream waters (r = 0.71, P < 0.01, Fig. 4(c)) indicates that desorption of DOM occurred in the alkaline soils. The valence of cations in soil solution is another important factor determining retention of DOM in soils (Kalbitz et al. 2000). While polyvalent cations such Ca²⁺ and Al³⁺ make stable complexes with DOM, leading to subsequent precipitation of metal–DOM complexes, monovalent cations such as Na⁺ induce dissolution of DOM (Skyllberg and Magnusson 1995, Kalbitz et al. 2000). This effect of monovalent Na⁺ was confirmed by the positive correlation found between DON and Na⁺ concentrations in surface waters (r = 0.76, P < 0.01, Fig. 4(d)).

4. CONCLUSIONS

The chemical compositions of surface waters collected from tributaries of the Lena and Aldan rivers and alas lakes were analyzed. The pH and alkalinity and the concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, and Cl⁻ were significantly higher than values previously measured in eastern Siberia. The highly alkaline and saline soils predominating in central Yakutia are probably responsible for these high concentrations. DON (1.0–5.3 mg N L⁻¹) was the major species of dissolved nitrogen, followed by NH₄⁺ (0.0–1.4 mg N L⁻¹) and NO₃⁻ (0.00–0.02 mg N L⁻¹). The DON concentration was 10 times previously reported DON concentrations (0.1–0.4 mg N L⁻¹) from the Lena basin. The extremely high DON concentration in surface waters in this region is attributed to inhibited retention of DON by soils owing to the highly alkaline and saline soil conditions.

REFERENCES

Desyatkin RV (1991) Soil formation in alases. Soviet Soil Sci. 23, 9–19.

- Desyatkin RV (1993) Syngenetic soil salinization during thermokarst alas formation. *Eurasian Soil Sci.* 25, 38–46.
- Drever JI (1997) *The geochemistry of natural waters—surface and groundwater environments* (3rd ed.). Prentice Hall, Upper Saddle River, NJ, USA.
- Fedorov A, Konstantinov P (2003) Observations of surface dynamics with thermokarst initiation, Yukechi site, central Yakutia. In: Phillips, Springman, Arenson (eds) Proceedings of the Eighth International Conference on Permafrost, pp 239–243.

Garrels RM (1984) Montmorillonite/illite stability diagrams. Clays Clay Miner. 32, 161–166.

Huh Y, Panteleyev G, Babich D, Zaitsev A., Edmond JM (1998) The fluvial geochemistry of the

rivers in eastern Siberia: II. Tributaries of the Lena, Omoloy, Yana, Indigirka, Kolyma, and Anadayr draining the collisional/accretionary zone of the Verkhoyansk and Cherskiy ranges. *Geochim. Cosmochim. Acta* **62**, 2053–2075.

- Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Sci.* **165**, 277–304.
- Lara RJ, Rachold V, Kattner G, Hubberten HW, Guggenberger G, Skoog A, Thomas DN (1998) Dissolved organic matter and nutrients in the Lena River, Siberian Arctic: characteristics and distribution. *Marine Chemistry* 59, 301–309.
- Lobbes JM, Fitznar HP, Kattner G (2000) Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean. *Geochim. Cosmochim. Acta* 64, 2973–2983.
- Skyllberg U, Magnusson T (1995) Cations adsorbed to soil organic matter—a regulatory factor for the release of organic carbon and hydrogen ions from soils to waters. *Water Air Soil Pollut.* **85**, 1095–1100.
- Tipping E (1981) The adsorption of aquatic humic substances by iron-oxides. *Geochim. Cosmochim.* Acta **45**, 191–199.
- Wada S, Seki H (1994) A compact computer code for ion speciation in aqueous solutions based on a robust algorithm. *Soil Sci. Plant Nutr.* **40**, 165–172.