C-2 Studies on the impacts of acid pollutants to the aquatic environment

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1. Introduction

While environmental pollution and destruction of nature are expanding on a global scale, it is becoming ever more important to comprehend the human activities on the global environment.

Although we know that drastic and disproportionate increases in the consumption of natural and non-renewable resources have greatly altered the biosphere, reliable data on the actual levels of pollution are scarce or lacking. Especially, in the regions of East Asia, rapidly expanding human activities have led to increase of emission of acidic pollutants such as sulfur dioxide, sulfuric acid, nitrous oxide, nitric acid and ammonia as a source of nitric acid. This situation will continue for another several ten years.

In East Asia, for example, in Tokyo, massive emission of nitrogen oxide, nitric acid and carbon particles from automobiles pollute the air in this several ten years. Then emitted nitrogen oxide is transported to hill and mountain area of Kanto district as acid and nutrient followed by nitrogen saturation of forest ecosystems. However the details on the effects of nitrogen saturation in forest ecosystems and its impacts to stream water quality and rivers have not been revealed.

Furthermore, long-range transport of air pollution from the continental Asia is currently important issue especially in regions susceptible to acidification due to low buffering capacity such as Niigata prefecture, located on the west coast of central Japan. However, direct chemical evidence on the transport of pollutants from continental Asia to Japan is scarce. In addition to this, recent experimental studies on the behavior of salmon families shows slightly acidic water as range of pH 6 is depress pre-sawning behavior. However the data on the acidification of water in mountain streams and its effects on the distribution and behavior of salmonid fish including Japanese char

(Salvelinus leucomaenis) is lacking.

2. Research Objective

The main aim of this study is to get the data on water quality including cations, anions, pH, acid buffering capacity and aluminum compounds and to clarify the chemical and biological effects of acid pollutants on the mountain streams, which located in the Miomotegawa river in northern Niigata prefecture where the impacts of long-range transport of pollutants are susceptible, western Kanto prefecture where there is severe nitrogen oxide pollution and northern Hokkaido prefecture as background area of nitrogen pollution in Japan. Together with these field studies we aimed to get direct chemical evidence on the long range transport of pollutants from continental Asia using lead isotopes and to establish continuous water monitoring system on mountain rivers in heavy snow area, especially in Niigata prefecture.

Research areas

(1) Miomotegawa river

Miomotegawa river is one of the most important salmon rivers in Japan. Several hundred thousand salmon returns to this river every year. Also the bedrock of the upstream areas is mostly granite and the water has very low acid buffering capacity. The past monitoring data of Miomotegawa river for 12 years (1988-1999) showed average concentration of T-N and T-P and pH were 0.25, 0.007 mg/l and 6.5-7 respectively. Miomotegawa river basin is also famous for the heavy snow deposition reaching several meters in winter.

(2) Western Kanto area

In the western part of Tokyo, the study was conducted in N-saturated forest and the streams flowing out from the watershed. The main soil covering the area is volcanic ash from Mt. Fuji.

(3) Northern Hokkaido area

In northern Hokkaido area, the study was conducted in the watersheds of Nakagawa experimental forest, Field Science Center for Northern Biosphere, Hokkaido University. In this area, about 40% of the precipitation falls as snow, mainly from December to march. The forest floor is covered by dense stands of Sasa bamboo. The predominant bedrock and soil are Cretaceous sedimentary rock and Dystric Cambisols

3. Research Method

(1) In Miomotegawa river, stream waters were sampled intermittently. About 50 sampling sites were settled in the upstream, downstream and dam of Miomotegawa river.

Water samples were filtered through GF/F filter. Concentrations of anions and cations were analyzed by ion chromatography and also metals in the water were analyzed by inductively coupled plasma atomic emission spectrometry. Dissolved organic carbon, total inorganic carbon and stable isotope ratios of water were also analyzed. Acid buffering capacity was measured by pH decreasing after adding 1 ml of sulfuric acid (0.001N, 0.01N and 0.1N respectively) To 100ml of water samples.

To determine the sum of inorganically and organically complexed forms of Al (fraction 1), stream waters of these watersheds were sampled intermittently from 2000 to 2003. Samples were filtered through a membrane filter with a 0.4 μ m pore size. Each filtered sample was analyzed by HPLC (Sutheimer and Cabaniss, 1995), and also by the lumogallion method (Koshikawa et al., 2002) to determine the sum of fraction 1 and the aquo and hydroxy forms of Al (fraction 2). The concentrations of inorganically complexed Al were also calculated, using the concentrations of inorganic anions and the equilibrium constant, and found to be negligible. From these results, concentrations of inorganic monomeric Al (the sum of aquo and hydroxy forms), organically complexed Al, and reactive Al (the sum of inorganic monomeric and organically complexed forms) were derived.

(2) Nitrogen addition experiment and gross nitrogentransformation in soil

In northern Hokkaido area, 50 kgN ha^{-1} of ammonium nitrate (NH4NO3) was added manually in particulate form to the experimental basin. Given the difficulties associated with walking through the dense Sasa dwarf bamboo (1.5-2.0 m in height) during the growing season, the application of NH4NO3 in the basin was conducted once in early April of 2002 during the latter stages of snowmelt. Eleven personnel took two hours to carry out the application of nitrogen. The amount of nitrogen applied corresponded to twenty times amount derived from extant rates of atmospheric deposition.
Stream water was collected from the lower slopes of the treated and control basins at intervals of approximately 1-2 weeks from June 2001. The stream was gauged (90℃, V-notch) at the lowest position of the whole experimental watershed (6.0 ha) and the water height was measured 10 minutes interval using a pressure transducer and data logger at the V-notch station. We assumed that the runoff from each sub-basin was equivalent to the total for the whole watershed. This was quantified from water height and the empirical relationship between the observed discharge and water height (Q-H curve). Tension lysimeters (DAIKI Co Ltd. DIK-8390) were installed to collect soil solutions from depths of 5 cm at ridges, and the middle and lower slopes of each sub-catchment, with four replicates taken for each sub-catchment on August 2001. A three-plate lysimeter (42 x 200 mm) was installed under the organic layer to collect leachate at ridge, middle and lower slopes in each basin. Soil leachate from the organic layer and soil solutions from the mineral soil were collected and analyzed monthly when there was no snowfall. All water samples were filtered (GF/F, Whatmann Co. Ltd.) and

analyzed for concentrations of nitrate (NO3), ammonium (NH4) (Ion chromatography, DIONEX DX-500, Japan Dionex Co Ltd.), dissolved total nitrogen (Total nitrogen analyzer, TN-100, Mitsubishi Chemicals Co Ltd.) at the chemical laboratory of the Northern Forestry and Development Office, Field Science Center for Northern Biosphere, Hokkaido University. Net nitrogen mineralization and nitrification rate in organic (Oe/Oa) and mineral top soil (0-10cm) was determined by laboratory incubation at 25℃ for 30 days. Inorganic nitrogen content before and after incubation was analyzed using flow injection analyzer (FI-500V, Aqua Lab Co. Ltd.) after the extraction using 2M-KCl..

15N as a tracer for laboratory incubation was used to determine the gross rate of nitrogen immobilization, nitrification and mineralization (Davidson et al. 1991; Wakamatsu et al. 2004). Samples collected from the Oa/Oe and A horizons (0-10 cm) were used for laboratory incubation. 1.8 mgN kg soil^{-1} of (15NH4)2SO4 and Na15NO3 was supplied for 10 g (dry weight) of soil from the Oa/Oe horizon, respectively. Similarly, 3.0 mgN kg soil-1 of (15NH4)2SO4 and Na15NO3 was supplied for 20 g (dry weight) of soil for the A horizon, respectively. Each sample was incubated for 15 minutes, 24 hours, 1 day and 1 month at 25℃, respectively, and sample moisture was controlled manually (Soil:Water = 1:1.25 for Oa/Oe horizon, 60% of field capacity for A horizon) using distilled water during the incubation period. After the incubation period, samples were extracted using 2N-KCl for isotope analysis. 15N in the extracted solutes was trapped using a combination of procedures of diffusion and Teflon-bag methods. Isotope ratios were determined using a mass spectrometer (Finnigan, MAT252) and an element analyzer (ThermoQuest, NC2500) in the chemical laboratory of Nagoya University. Gross nitrogen transformation (mineralization, nitrification and immobilization) was calculated based on the isotopic nitrogen budget during the incubation.

(3) Effects of Water Chemistry of Mountain Stream on the Distribution and Behavior of Salmonid Fish:

[1] Experiments using artificial 2-way flow through channels in which water of neutral and various pH levels were allowed to flow were conducted in order to observe the effects of acidic water on upstream migratory behavior of salmonid fish. [2] Investigations of the relationship between the distribution of Japanese char and the water quality including pH were carried out in a naturally acidified river, Kurosawa, Tochigi prefecture. [3] Signs of acidification due to acid precipitation and the effects on the distribution of Japanese char were observed in Miomote River, Niigata prefecture. [4] Acid tolerance of Japanese char in tributaries of Miomote River was compared by observing the blood chemical parameters.

4. Result and discussion

(1) Miomotegawa river

In Miomotegawa River, K (261kg), Na (49kg), P (179kg), and Ca (10kg) were returned from sea to the basin every year by the returning salmons, being comparable to 0.03%, 0.000064%, 3.1%, and 0.0004%, respectively, of the amount of elements drained as river-borne elements. In the snowy area such as the Miomotegawa River basin, pH of the river water usually becomes the lowest in the early spring thaw. However, such data are limited, we measured the pH continuously by the automatic monitoring systems at 2 sites in the branches of Miomotegawa River. Although the pH values in no rainy season were kept at approximately constant around 7, the short-term decrease blow 6 was also observed after the acid rain, which may have been the influential level on salmon families. Stream waters in Japan (pH, 6.5-8.5) are not yet acidified, but stream waters in granite area of bedrock in Miomotegawa River drainage basin have low pH after the acid rain and salmon families already have received effects of the behavior in short-term.

Inorganic monomeric Al was found to be dominant (90%-100%) in stream waters with low concentrations of reactive Al(0.40-3.27μM). This trend is opposite to that observed in acidified systems. In spite of the variation in the range of reactive Al in the four watersheds (Miomote, 0.03-3.27μM; Tsukuba, 0.07-0.40μM; Dorokawa, 0.10-0.51μM; Tama, 0.03-0.38μM), the entire date set for reactive Al could be expressed as a function of the ratio of dissolved organic carbon (DOC) and calsium (Ca): [Reactive Al (μM)]=0.12[DOC/Ca (mol/mol)]+0.14 (r=0.86).

In most sites the alkalinity was less than 0.5meq/L, and especially that of Iidasawa site was about 0.1meq/L. It was suggested that Miomote river has relatively low buffering capacity for acid substances. One of the main reasons might be due to the fact that the bedrock of the survey area consisted of granite. Seasonal changes of alkalinity were observed in most sites, where the alkalinity was lower in winter than those in other seasons.

In summer, when pH value decreased, EC value also decreased, and the timing of both decrease corresponded with timing of the rainfall. Ion concentrations in the river water might be diluted by rainfall.

Typical change of the water quality which can be evaluated as acid shock in snow-melting period was observed in the continuous monitoring data. (Fig.1)

When air temperature increased abruptly on March 10th, pH value decreased and EC value increased. And also at the timing of remarkable rainfall on May 11th, pH value more decreased and EC value more increased too. In this case it was considered that much snow-melting water flowed into the river by much rainfall.

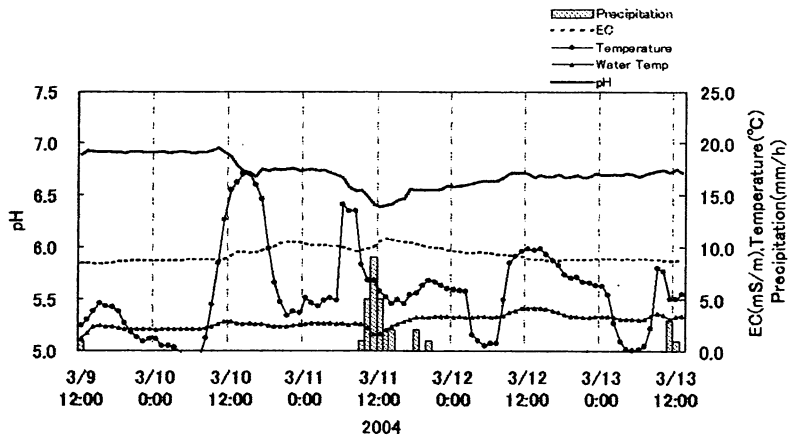

Fig.1 The change of the water quality in snow-melting period

Analysis of precipitation filters collected over three years (1999 to 2002) from Murakami on the west coat of central Japan showed seasonal periodicity in particulate lead deposition, with highest deposition in winter and spring (November through May) each year. Computation of 72-hour back trajectories over this period strongly indicated continental Asia, most likely northeast China as the source of lead, following long range transport. Analysis of stable lead isotope ratios in the filters supported this conclusion since some samples had 'thorogenic' (excess 208Pb/206Pb) ratios, since thorogenic ratios can be diagnostic of Chinese of Russian sourced lead. Tree bark pockets isolated from the atmosphere between 1972 and 1982 had lead isotope ratios close to those quoted for Japanese sourced lead whilst current (2003) bark had significantly different thorogenic ratios. The result is consistent with the scenario of decreasing Japanese sourced lead emissions and increasing long range transport of pollution from continental Asia, signifying the threat of transboundary air pollution to the region. Thorogenic lead isotope ratios were also measured in tree bark collected at high altitude in the area.

(2) Western Kanto area

Although stream water NO3 concentration showed an increasing trend in the eastern watersheds along a Tama River transect in general, the hilly region, most close to downtown, acted as a zone where NO3 concentration was decreased due to denitrification.

Forest soil profile of NO3 content was studied down to > 3 m depth in a variety of areas in Kanto, Kansai and Hokkaido districts having different soils and stream water NO3 concentrations. The results of soil NO3 profile showed a good correspondence to stream NO3 levels. In the watersheds with low stream water NO3 concentration, NO3 contents decreased sharply just below the soil surface and remained negligible throughout the profile. In contrast, the soil NO3 content in the watersheds with high stream NO3 concentration was much higher at all the depths; near the soil surface,

around 1 m (a maximum rooting zone), and deeper horizons. The soil profile provides clear evidence of nitrogen excess situations in the watersheds.

Slightly decreased pH values were observed in streams in the region of elevated N levels compared with other regions. The alkalinity/ Σ anion ratio also tended to decrease in this region, being lower the world average and Japanese average. Although a correlation was found between Ca^{2+} + Mg^{2+} concentration and NO3 concentration in streams, the increase in Ca^{2+} + Mg^{2+} concentration showed a decline in higher NO3 concentration range, suggesting a limited ion exchange reaction in watershed soils under an elevated N level.

Along with a possible ground water movement studied from the hydrological research, dissolved components in ground water samples collected from piezometers showed a systematic change representing weathering; increases in SiO_2, HCO_3^-, Na^+, Ca^{2+}, and Mg^{2+} concentration, and a decrease in pH. Excellent correlations were found among these constituents, suggesting a consistent weathering process in the watershed. From the relationships between these components, a stoichiometry of Na^+, K^+, Ca^{2+}, and Mg^{2+} solubilization during weathering were estimated as 0.24, 0.01, 0.32, and 0.14 mol per 1 mol of SiO_2, respectively.

(3) Northern Hokkaido area

Approximately 90 % of ammonium labeled by ^{15}N-NH_4^+ was retained as an organic form during the 24 hours in the Oe/Oa horizon, while only 50% of ^{15}N-NH_4^+ was retained as organic form in the mineral soil during the same period.

Nitrate concentration in stream water increased sharply just after the addition of ammonium nitrate in the treatment basin. However, concentration of nitrate, ammonium and dissolved organic nitrogen in stream water reached same level between control and treatment watershed about two months after the treatment. Annual nitrogen export from the treatment sub-catchment was more than two times higher than that in the control basin during first year after the treatment. While dissolved organic nitrogen was dominant nitrogen species in stream water in the control basin, nitrate was dominant as dissolved nitrogen in the stream water in the treated basin. It was suggested the initial increase of nitrate concentration just after the addition contributed to increase the nitrate export in the treated basin. Nitrogen budget indicated that approximately 90 % of added nitrogen was retained in the watershed against sum of the ambient bulk nitrogen deposition (2.3 kgN ha^{-1} y^{-1}) and experimentally added nitrogen (50 kgN ha^{-1} y^{-1}). In northwestern Europe region, significant nitrate has been leached from the forest soil where receive 30-50 kgN ha^{-1} y^{-1} of atmospheric N deposition. Our results indicated that the current forest ecosystem has high ability to retain the deposited nitrogen in the ecosystems. Since ecosystem function to retain nitrogen and the stage of nitrogen saturation are thought to shift temporally, more continuous monitoring and investigation will be need to understand the temporal response of forest ecosystem against

anthropogenic nitrogen deposition.

(4) Effects of water chemistry of mountain stream on the distribution and behavior of salmonid fish

Upstream migratory behavior of mature Japanese char and brown tout (*Salmo trutta*) in a 2-way flow through channels were significantly inhibited by weakly acidified water of pH below 6.0 even if the water was their natal stream.

A volcanic acidified stream, Kurosawa, Tochigi prefecture has 2 highly acidified tributaries in the upper part and 2 neutral ones in the lower part. Water pH gradually increased downstream form 4.96 to 7.72. Concentration of aluminum reversely decreased form 1.27 to 0.026 mg/l. Japanese chare sere caught by electrofishing only in the lower part of the stream whose pH was above 6.14. The estimated density of the fish in the area around the confluence of Kurosawa and a neutral tributary (8.8/100m^2) were lower than in the neutral tributary (12.2/100m^2). Number and diversity of aquatic insects, especially acid-sensitive *Ephemeroptera* were lower in acidic than neutral streams.

At the present, Miomote River, Niigata prefecture, was not revealed to be always acidified by acid precipitation. Japanese char were caught in every tributary we investigated. However, measurement of alkalinity as well as stepwise acidic neutralizing capacity[1)] of the water suggested that some tributaries were weakly acidified temporally and locally.

Japanese char in a tributary which has low acidic buffering capacity were comparatively acid tolerant. This suggested that the char had experienced weakly acidic environment temporally. These results and our previous studies indicate that if water pH of mountain stream in Japan decrease approximately below 6.0 due to acid precipitation, Japanese char should lose their habitants and spawning areas.