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Non-free ionic transport of sodium, magnesium, and calcium in streams of two adjacent headwater catchments with different vegetation types in Japan

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ABSTRACT

Sodium (Na), magnesium (Mg), calcium (Ca) are usually believed to occur mostly as free ions in the fresh water and consequently little is known about their chemical species. To understand the importance of non-free ionic fractions (NIF) of major metals in freshwater streams, Na, Mg, Ca, silicon (Si), and fulvic acid-like materials (FAM) were measured in streams of mountainous adjacent headwater catchments dominated by different vegetation types (planted evergreen coniferous forest and natural deciduous broadleaf forest). During both no rainfall periods and rainstorms, the proportion of NIF relative to total elements was lower in the coniferous catchment than in the deciduous catchment, although it sometimes accounted for half or more of the total concentrations of Na, Mg, and Ca in both catchments. The solubility of metal compounds was higher than the measured maximum concentrations of Na^+, Mg^{2+}, and Ca^{2+} to the extent that inorganic bonding was hardly possible. During no rainfall periods when FAM was slightly produced into the streams, the fluxes of NIF and Si were highly correlated ($r > 0.92$, $p < 0.0001$, $n = 30$) in both catchments. During a small rainstorm, the flux of NIF correlated weakly with that of Si but did not correlate with that of FAM in both catchments. In contrast, during a heavy rainstorm, the flux of NIF correlated strongly ($r \geqslant 0.83$, $p < 0.0001$, $n = 26$) with that of FAM in the deciduous catchment where relatively deep soil water compared to near-surface water was the predominant component of stream water. However, during the heavy rainstorm in the coniferous catchment, only the flux of NIF originated in the quick-flow component (i.e., surface or near-surface water) in stream water (ΔNIF) correlated strongly ($r \geqslant 0.81$, $p < 0.0001$, $n = 22$) with that of FAM. These findings imply that heavy rainstorms may enhance the bonding of the major metals with humic substances mainly in the deciduous catchment; and also exhibit that, in the headwater catchments, both water flow pathways resulted from the different vegetation types play a very important role to promote the bonding of major metals with humic substances in stream water.

1. Introduction

Major metals such as sodium (Na), magnesium (Mg), and calcium (Ca), which are the vital elements involving the metabolism and physiological function of life, are thought to occur mainly (>98%) as free ions in freshwater environments (e.g., Mantoura et al., 1978). On the contrary, the biogeochemical implication (i.e., bonding) of the major metals, humic substances, and nano-scale phyllosilicates represented by clay minerals (Wilson et al., 2008) has been mentioned in particular in the laboratory and modeling studies (e.g., Choppin and Shanbhag, 1981; Livens, 1991; Romkens et al., 1996; Majzik and Tombacz, 2007; Takahashi et al., 1999, 2002). This discrepancy regarding major metal species implies that little is known about their transport forms (i.e., chemical species) in freshwater environments.

In contrast, as described by Tipping (1993), the information regarding the effect of environmental factors (topography, geology, climate, hydrology, vegetation, etc.) on metal bonding must be very useful to allow the calculation and modeling of chemical speciation under natural condition in freshwater environments. Furthermore, the insights related to the interaction between aquatic and terrestrial biogeochemistry will also facilitate a better

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understanding of controls on humic substance production, consumption, and flux across whole landscapes and biomes (McDowell, 2003). However, the effects of environmental factors on bonding possibility of major metals to humic substances and nano-scale phyllosilicates and consequently the transport in bonding in stream water are as yet unclear.

Accordingly, characterizing the bonding of major metals to humic substances and nano-scale phyllosilicates in field sites must provide useful information about the chemical regimes in stream catchments, and besides, give a novel knowledge in catchment hydrology. If the free ions of major metals combined with humic substances and nano-scale phyllosilicates, the relationships between the fluxes of combined materials (i.e., non-free ionic fraction of the major metals), humic substances, and nano-scale phyllosilicates can be the good indices to explore broadly both the implication as represented by the bonding of Na, Mg, and Ca and consequently the characteristics of bonding resulted from the environmental factors.

Thus we measured Na, Mg, Ca, and silicon (Si) in streams of two mountainous adjacent headwater catchments composed of differing vegetation. Fulvic acid-like materials (FAM), representative of dissolved organic matter (DOM) in the streams that we observed (Terajima and Moriizumi, 2013) and usually accounts for 60–99% of DOM in stream or ground water (Thurman, 1985; Malcolm, 1990; Artinger et al., 2000), were also measured to understand the interaction among the major metals, clay minerals, and humic substances. Additionally, FAM and dissolved organic carbon (DOC) was measured for soil extracts from both catchments to determine where FAM and DOC are stored in the soil profile and examine water flow pathways along the slopes. Subsequently we broadly estimated how stream water chemistry (i.e., bonding possibility) was provided and how slope hydrology depending on differing vegetation (i.e., environmental factor) affected the transport of major metals.

2. Site description

2.1. Topography, geology, and climate

The study area consisted of two mountainous headwater catchments with differing vegetation in the Nariki catchment (35°50′N and 139°10′E at the rain gauge in Fig. 1a), which is about 40 km west of central Tokyo. Slope gradients in the catchment range between 35° and 45°, and Mt. Kuro-yama, at 842 m, is the highest point. The catchment is underlain by sandstone and mudstone bedrock of Jurassic age that also contains some chert. The rock layers dip 60–90° northeast and strike NW-SE (Inosato et al., 1980; Tokyo Prefectural Public Work Institute, 2002).

According to data from the Automated Meteorological Data Acquisition System (AMeDAS) of the Japan Meteorological Agency, the average annual precipitation between 1976 and 2009 at Ohme city (35°47′N, 139°18′E; 10 km southeast of the Nariki catchment and 100 m in elevation) was 1487 mm, and the average minimum, maximum, and annual air temperatures during the same period were −6.7 °C in late January, 36.9 °C in mid-August, and 14.2 °C, respectively. Rainstorms occur mainly from mid-June to late July (the rainy season), and in the typhoon season which lasts from mid-August to mid-October. About 80% of the annual precipitation falls during these periods. Dry conditions prevail in winter, from early December to early March, although snow usually accumulates in the Nariki catchment to a maximum depth of 10–20 cm in February. The stream water temperature of both headwater catchments ranged from 10 °C in winter to 23 °C in summer.

2.2. Experimental catchments

A first headwater stream (first-order stream; 70 m in length) on the north side of the Nariki River (Fig. 1a and b) is densely surrounded by an unmanaged evergreen coniferous forest composed of Japanese cedar (*Cryptomeria japonica*) and Hinoki cypress (*Chamaecyparis obtusa*) which were planted in 1961 (Coniferous catchment: 1.29 ha, 100 m in relief; Fig. 2a). In 2007, the catchment contained 2000–2500 trees ha^{-1}, most with trunk diameters of <20 cm. The forest canopy is mostly closed, with little understory vegetation owing to the weak penetration of sunlight to the forest floor. The litter layer on the forest floor is very thin, and mineral soil is exposed in some places.

A second headwater stream (first-order stream; 70 m in length) on the south side of the Nariki River (Fig. 1a and c) is surrounded by a natural deciduous broadleaf forest (Deciduous catchment: 1.28 ha, 100 m in relief; Fig. 2b). The dominant tree species in this catchment are oak (*Quercus serrata* and *Quercus mongolica*), beech (*Fagus japonica*), chestnut (*Castanea crenatus*), and Japanese maple (*Acer palmatum*). The understory vegetation is dense in comparison to that in the coniferous catchment, and there is a thick litter layer on the forest floor.

The riparian zone (the flat bottomland along the streams) is very small and narrow in both catchments (Fig. 1b and c). Thus the contribution of subsurface and groundwater flow for the stream water generation, which had been involved in the riparian zone before rainstorms, seems to be relatively small compared to those from the slopes.

The boundary between soil and bedrock was determined by cone penetration test to occur at $N_{10} = 50$, and the soil depth ($N_{10} \leqslant 50$) in both catchments was <3 m. The structure of the soil profile (the soil horizons present and their thicknesses) is similar along the slopes of both catchments. In both catchments, the soils are classified as Cambisols (according to the classification by the Food and Agriculture Organization of the United Nations), and soil pH ranges between 3.8 and 5.2 throughout the vertical soil profile in both catchments. The strongly organic-rich soil horizons, the A_0 to AB horizons, are up to 25 cm thick in both catchments, and a gravel rich mineral soil (B horizon) is below 15–25 cm depth. The soil parent material is presumably derived from upslope via soil creep or rock slides because many discrete angular stones and sediment particles in various size are included and mixed intricately throughout the soil profiles. The saturation hydraulic conductivity (K_s) of the soil above 80 cm depth in both catchments ranges mostly between 10^{-2} and 10^{-3} cm s^{-1}. Soil porosity in the coniferous catchment gradually decreases with soil depth, ranging between 70% at 10 cm depth and 45% at 70 cm depth, whereas soil porosity in the deciduous catchment is relatively constant, decreasing from 70% near the soil surface to 53% at 70 cm depth. The gravitational water drainage capacity of the soil in the coniferous catchment is below 5%, except between 0 and 5 cm depth, where it is 28%. In the deciduous catchment, it is constant at 9% throughout the soil profile up to 50 cm depth (Hirano et al., 2008).

A unique high permeable and organic rich layer, the so-called biomat ($Ks > 10^{-2}$ cm s^{-1}; porosity above 70%), consisting of a dense network of fine roots of Japanese cedar and Hinoki cypress within the loose litter and root-permeated zone (Sidle et al., 2007), was common on the slope surface (above 0 cm depth) in the coniferous catchment. Its thickness varied from a few centimeters to 20 cm in the coniferous catchment, but it was rare in the deciduous catchment (Terajima and Moriizumi, 2013). Thus water flow through the biomat (i.e., biomatflow) during rainstorms appeared predominantly in the coniferous catchment (Hirano et al., 2008).

On the basis of the above facts, the characteristics of the environmental factors in the two headwater catchments are briefly