The chemical link of forest and sea by river: materials supply from land-used soil and transport by river with reference to fulvic-Fe complex

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Abstract
In order to investigate the transport of iron-fulvic complex from forest to sea, water at 13 sites was sampled along the 88 km of Obitsu River in Chiba, Japan. The importance of the relationship between dissolved organic matter and iron (Fe) was proved. Concentrations of dissolved organic carbon (DOC) as fulvic acid and dissolved Fe in river water and surrounding soils were analyzed. In addition to investigate each major element in water, fulvic characters in DOC were analyzed by fluorescence spectrophotometer. Net production tends to decrease with increasing forest area toward midstream region and after that increasing in the downstream region. A characteristic peak of the fluorescence spectra originating from fulvic acid occurred at 440 nm with excitation 335 nm and its intensity is proportional to DOC. Concentration of DOC in soil decreased toward downstream regions, but dissolved Fe was constant. These trends indicate that abundant iron-fulvic acid complex produced in forest soil of the upstream region and forests have a greater effect on the ecosystem in the downstream region.

Key Words
Fulvic acid, iron, materials transport, land use, leaching.

Introduction
Iron is an essential element for plant growth. Iron is converted into an insoluble form because of pH change, and some recent studies suggested that dissolved iron in seawater might be limiting factor for primary production in ocean (Shibata *et al.* 2004). Fulvic acid and low molecular weight organic acids produced in forest and marsh lands are responsible for dissolving Fe from minerals in rocks or parent material in soil, and for helping to keep it soluble in water. Rivers play an important role in transport of the complex to the sea because of their source region is in mountains and they run through various lands to reach the sea. Recent research on transport of iron in Amur River has been performed as the Amur-Okhotsk Project (Shibata *et al.* 2004). Also a tree-planting program is progress in many regions in Japan which will produce fulvic acid. However, qualitative and quantitative processes of iron transport with fulvic acid from terrestrial to sea are not well understood. To gain better understanding transport mechanisms of fulvic acid from the forest to the sea, we analysed water and soil sampled along the Obitsu River using a fluorescence spectrophotometer method.

Methods
Sampling of river water and soil
Obitsu River (88 km in length and 267 km^2 in basin) is located in southern Chiba, Japan (Figure 1), it runs into Tokyo Bay and has mudland at the mouth of the river. Sampling was performed at 13 points numbered from upstream to downstream and nearby area (mudland, dry field, bamboo grove, paddy field, golf course, and forest). River water was sampled by 3 bottles (500 mL), and soil was sampled 20 cm in depth and 5cm in diameter by a polyvinyl chloride tube.

Estimating of land-use
Investigation of land use: Drainage course and integrated value of land-use area are shown in Figure 1 and Figure 2, respectively. Drainage course was analyzed by GTOPO030 and basin contribution of each water sampling point was calculated using that data. Land use was analyzed by Global Land Cover Characterization and was determined by reference to Fujii *et al.* (1987).

Analysis methods
1) River water: Current speed, river width, water depth was measured in the field. Analyzed elements in laboratory include dissolved organic carbon (DOC), total Nitrogen (T-N), phosphoric acid in the phosphorus (PO_4-P), dissolved iron (Fe), and dissolved silica (Si). In addition to evaluation of water quality, three-

dimensional fluorescence spectra of samples were obtained using a SHIMADZU RF-5300PC fluorescence spectrophotometer. The relative fluorescence intensities of the sample aliquots were reported in quinine sulfate unit (QSU) for excitation 350 nm and 455 nm using 10 μg/L quinine sulfate in 0.05M H_2SO_4. Measurement range was Ex 220~ 500 nm / Em 250 ~ 600 nm and sampling width was 5 nm. The peak of fulvic acid was determined according to *Nagao et al.* (1997).

2) Soil: Each sample from characteristic lands, which was cut into 5 cm lengths, and separated upper 5cm (0~5 cm in depth) as surface layer and lower 5 cm (15~20cm in depth) as subsoil layer. These were analyzed texture, organic matter content, and grain density. 7.0 g samples were shook with ion-exchanged water for 24 hour. The DOC and dissolved Fe in 350 mL leach liquid removed from samples were determined by SHIMADZU AA-6200 atomic absorption spectroscopy and SHIMADZU total organic carbon analyzer TOC-V_{CSH}. Major elementals were determined with X-ray fluorescence (XRF) using a RIGAKU 3491 X-ray fluorescence spectrometer.

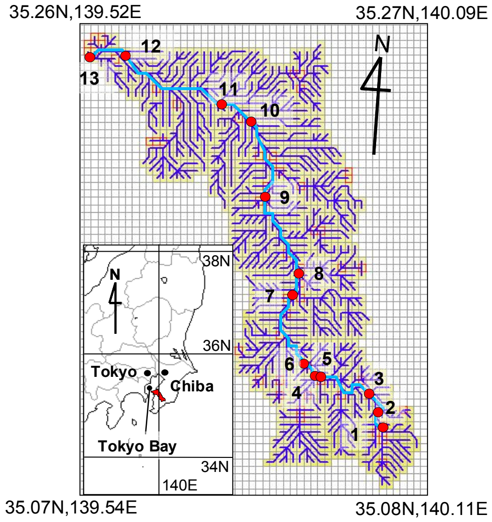

Figure 1. Sampling points (St.1~St.13) and drainage course by GTOPO030 in Obitsu river basin

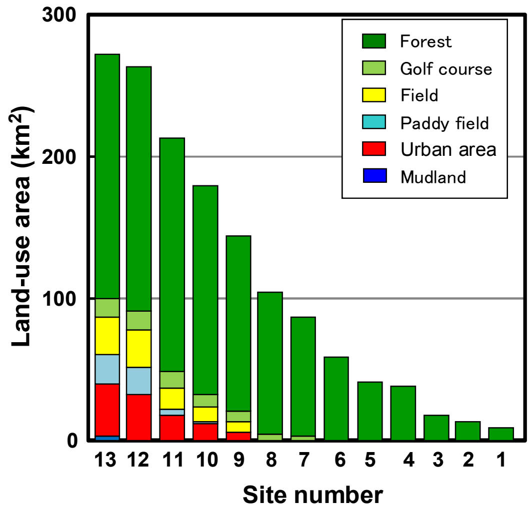

Figure 2. Integrated value of land-use area in Obitsu river basin by Global Land Cover Characterization

Results and discussions

DOC and dissolved Fe in leachate from soil

Concentration of DOC and dissolved Fe in surface and subsoil layers are shown in Figure 3. Concentrations of DOC and Fe suggested that the upstream area contributes to leaching Fe and its complex with fulvic acid. The concentration of DOC in surface soils decreased going downstream, whereas values in subsoil were unchanged except for some points. The concentration of dissolved Fe was unchanged as compared with DOC. Therefore, the ratio of dissolved Fe to DOC increased toward the downstream region, and DOC downstream had an effect on redissolution of Fe. This tendency is contrary to degree of chemical weathering or the ratio of Fe_2O_3 to SiO_2 in soil based on XRF data. This result suggests that upstream soil is likely to be weathering, but in that condition, Fe is not dissolved easily. Also, the surface layer showed higher value of

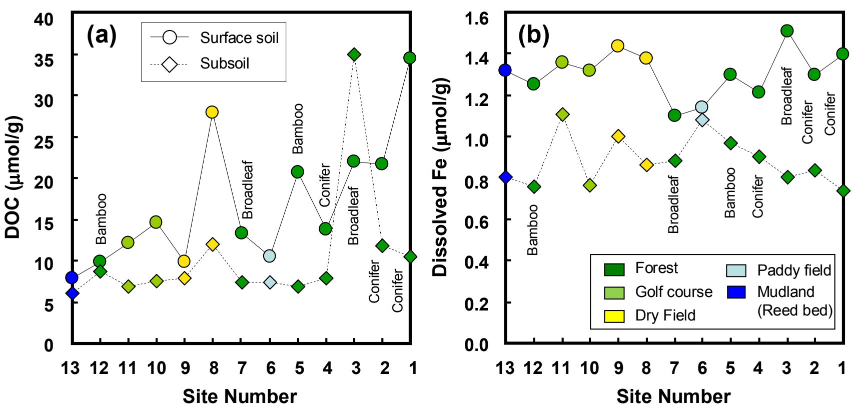

Figure 3. Concentration of DOC (a) and dissolved Fe (b) in leachate from surface and subsoil layers.

DOC than the lower layer in upstream basins, were there are conifer forest, broadleaf forest, and bamboo grove. The reason why such a sequence is found may be attributed to the facts that A-horizon may be thick under the conifer forest, and thin under the broadleaf forest. If the A-horizon is thin, organic matter is insufficient to weather the bed rock beneath, suggesting that dissolution of Fe in the broadleaf forest is more difficult than in the conifer forest. In the paddy field having a strong connection with river water, the subsoil layer showed higher values of dissolved Fe then the surface layer. It can be explained due to the fact that paddy field has oxidation and reduction layers because of separating soil from air (oxygen) by the water, Fe is soluble in the reduction layer. In fact, dissolved Fe is unchanged in both surface and lower layer but the DOC of lower layer is two-thirds as much as in the surface.

Fluorescence characterization of fulvic acid and net production

Figure 4 shows the contour plots of excitation-emission matrix (EEM) spectra for river waters at typical sampling points, and Figure 5 shows the net production of the Obitsu River basin and fluorescence intensity of fulvic acid to DOC 1 mg/L.

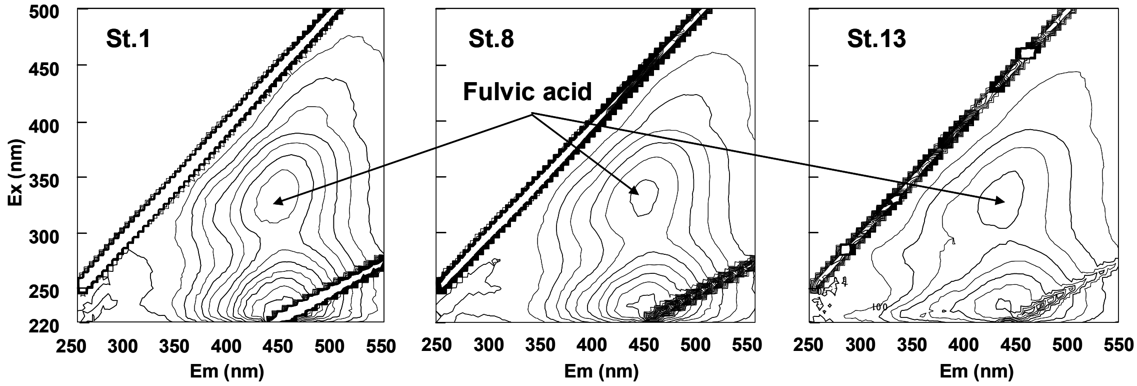

Figure 4. The contour plots of excitation-emission matrix (EEM) spectra for river waters of typical sampling points (St.1, 8, and 13).

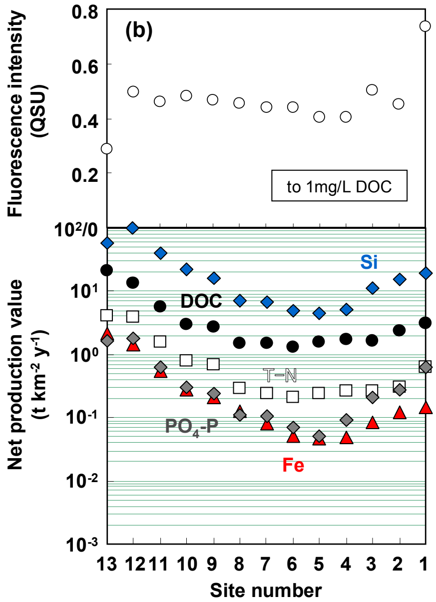

Figure 5. Net production of DOC, dissolved Fe, PO4-P, T-N and dissolved Si (a) and fluorescence intensity to 1 mg/L DOC (b) in Obitsu river water.

In fluorescence analysis, the characteristic peak originating from fulvic acid occurred at 440 nm with excitation 335 nm. Fluorescence intensity is proportional to DOC, the ratio of fulvic acid to 1 mg/L DOC is high at St. 1, the conifer forest. According to *van Hees et al.* (2005), coniferous trees supply organic acids such as citric, malonic, and oxalic acid. In most cases, forest soil produces aliphatic fulvic acid and river water produces aromatic fulvic acid. Therefore, dissolution of Fe occurs by aliphatic acid in the upstream region, and remains soluble due to aromatic fulvic acid in the downstream region.

Net production tends to decrease toward the midstream region (St. 5 or 6), and increase in the downstream region. Upstream (St. 13 to 11) and downstream regions have productivity at the same level. Dissolved Fe was expected to change similarly to DOC, T-N is unchanged similarly to DOC at midstream. This result suggests that the tendency of leaching or holding Fe is stronger than for run off from the surface in upstream region, and solution may discharge as groundwater at St. 6. Because natural gas and ancient seawater (brine water containing high concentration of fulvic acid) are mixed in the region of St. 5 and St. 6, there is a possibility that mixing of groundwater is responsible for this. In the downstream region from St. 7, net production increased with increases in other areas except for forest. Soil of the downstream region tends to have high productivity and release materials easily. At St. 13, dissolved Si and PO_4-P decreased dominantly. Dissolved Fe is also expected to decrease because of adsorption into organism living in mudland, the dilution effect or pH change mixing with sea water. It is suggested that mudland is another production region of fulvic-Fe complex.

Conclusions

(1) Net production values for fulvic acid tend to decrease as forest area increases towards the midstream region and increases in the lower river region.
(2) In fluorescence analysis, the peak of fulvic acid occurred at 440 nm with excitation at 335 nm and its intensity was proportional to DOC. The ratio of dissolved Fe to DOC in soil increased downstream and DOC downstream has an effect on re-dissolution of Fe.
(3) These results prove that abundant iron-fulvic acid complex produced in forest soil in the upstream region and forests may have a great effect on the ecosystem in the sea.

Acknowledgements

This work was supported by the Ocean Policy Research Foundation and the Japan Science Society.

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