# Study on transportation and characteristics of organic materials from river to coastal sea

Md.J.Alam D-1
Supervised by Seiya Nagao
Associate professor
Laboratory of Geosphere Science
Devision of Geoscience

**Abstract**

The transportation and characteristics of organic materials were studied in the Ishikari River and the Tokachi River including estuary and coastal sea. DOC concentration for the Ishikari samples ranged from 1.51 mg/l to 2.98 mg/l and POC concentration were 1.81 mg/g-5.4mg/g from April to December in 2004. For the Tokachi River samples DOC concentration ranged from 0.01 mg/l to 4.41 mg/l and POC concentration were from 1.3 mg/g to 4.0 mg/g during the period of April to September in 2003. Variations were found in the DOC and POC concentrations at both river systems. POC flux at both rivers showed maximum in April. DOC flux at the Ishikari River was different from the Tokachi River. These results indicate that transportation behaviors of organic materials are different from the Ishikari and the Tokachi River because of the differences in watershed size and environments and variation in water discharge.

## 1. Introduction

Aquatic organic materials play an important role in geochemical reactions and act as a major reservoir of carbon in an aquatic environment (Aiken et al., 1985).The annual global transport of organic carbon from river to ocean is $0.4\times10^{15}$g (Meybeck, 1982) of which 60% of dissolved and 40 % of particulate forms (Spitzy and Ittekkot,1991). Transport behavior of organic materials depends on climate, watershed conditions, soil types, terrestrial plantations and size of aquatic environment. It may change several times physically or chemically in a year. During the transportation organic materials face to the complex interactions with hydrological - chemical factors and significantly altered sometimes (Raymond et al., 2001). The transportation of organic materials is poorly understood due to complicated processes, inherent complexity multiple components and low quantity of dissolved and particulate organic carbon. Its characterization is not easy and time consuming by single scan methodologies. The estimation of dissolved organic matter (DOC) and particulate organic matter (POC) fluxes is needed through a year on basis of field experiments for the transportation of organic materials. Characterization of POC and DOC is also an important matter to understand migration behavior of organic materials from watershed to river.

The objective of this study is to understand the behavior of organic materials during transportation through different aquatic environments. Two river systems were chosen to study factors controlling the transport of organic materials from river to ocean.

## 2. Materials and methods

### 2.1 Sampling

The Ishikari River main stream is 268 km and drainage area is 14330 $km^2$.The Tokachi River is 156 km long and drainage area is 9010 $km^2$. Water discharge increased through April to May for the Ishikari River and the Tokachi River has two maximum peaks April-May and August-September. (Ministry of Land ,Infrastructure, and Transport, Japan).

Sampling sites are shown in Fig. 1. Samplings for the Ishikari River samples were carried out at Iwamizawa bridge from April to December in 2004. The Tokachi River samples were collected at Moiwa bridge from April to November in 2003. The estuary samples were collected in August in 2003 and coastal sea water samples were collected in April 2004. Water samples were collected by a 5L polythene beaker, filtered by GF/F filters and stored in a freezer. POC samples were isolated from 30~100 L the water samples by continuous centrifuging in our laboratory.

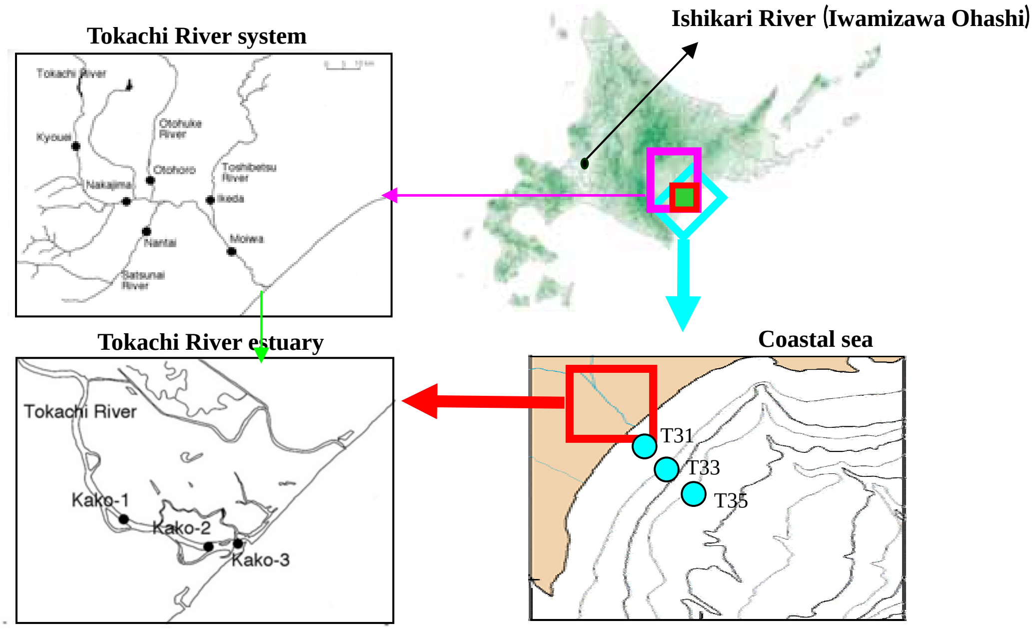


Fig.1 Sampling location

### 2.2 Analytical methods

DOC and POC concentrations were determined by TOC analyzer. The characterization of DOC was carried out by three dimensional fluorescence spectroscopy because this method is a very sensitive, convenient rather than other methods which was applied to characterize organic materials. Three dimensional excitation emission matrix (3D-EEM) spectra provide numbers, types, sources and concentration (intensity) of fluorephores. Our obtained 3D-EEM spectra were compared with these of IHSS standard samples for Suwannee River humic and fulvic acids. The DOC concentration of fulvic acid (DOC-FA) were calculated on the basis of 3-D EEM data. The estimation was carried out as follows: RFI of fulvic acid, isolated from a river water sample in the Bekanbeushi River which is similar watershed environment, at Ex 320/Em 430 nm is equal to the DOC concentration of 5 mg/l.

The flux of DOC and POC was calculated from multiplying DOC and POC concentrations by average water discharge of every month respectively.Water discharges at Iwamizawa bridge (1999-2000) from the Ishikari River and at Moiwa bridge (1990-1998) from the Tokachi River were taken from the data of Ministry of Land, Infrastructure and Transport, Japan.

## 3. Results and discussion

Transport of POC and DOC

DOC and POC concentrations are shown in Fig. 2. There are differences in variations of DOC and POC concentrations between the Ishikari and the Tokachi River samples. Higher DOC and POC concentrations in the Ishikari samples may be caused by its bigger watershed and higher water discharge. Both of the samples DOC and POC concentrations increased with time. The averaged water discharge in April were in the highest value for both of the river. Generally when the water discharge increase, the load of suspended substances also increase (Thurman, 1985). Often dramatically, the POC content decreases because organic materials are diluted by minerals and clays (Thurman, 1985). Therefore, DOC and POC concentrations in snow–melt season were lower than the other seasons.

The variations in POC and DOC fluxes are shown in Fig. 3. The Ishikari River shows two peaks of DOC flux in April and July. On the other hand DOC flux of the Tokachi River increases linearly. The highest POC flux was observed in April at the Ishikari River and the Tokachi River. These results indicate that the transport of DOC and POC is different from each other. It appears that the variations in the fluxes are related to the water discharge and may be considered to be due to the concentration of other factors.

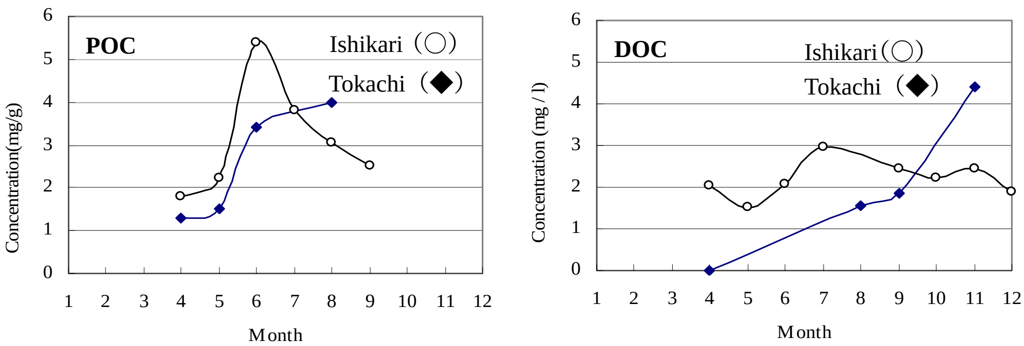


Fig. 2 Variations in organic carbon concentrations

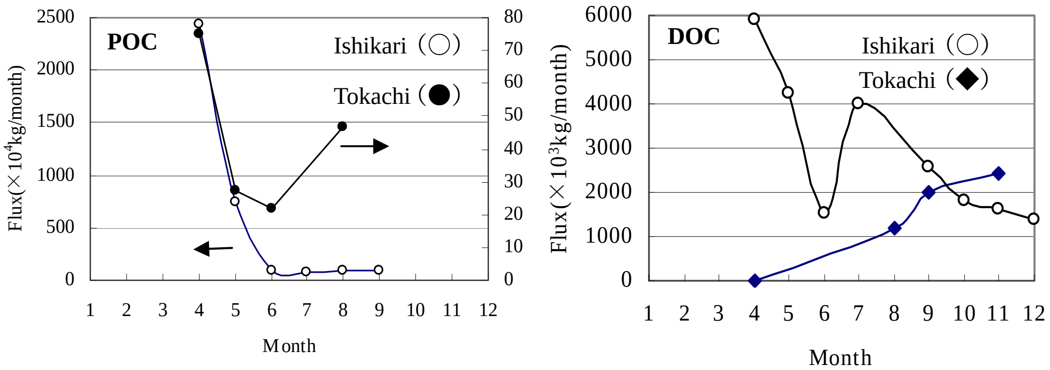


Fig.3 Variations in the flux of POC and DOC.

Characterization of DOC

The 3D-EEM spectra for the Tokachi River system were shown in Fig. 4. The Tokachi River samples have two peaks at Ex 230-235nm and Em 410-420nm, and Ex 310-330nm and Em 425nm. The estuarine samples were also found two peaks at Ex 230-235nm and Em 420-430nm, and Ex 320 nm and Em 420-425 nm. In the coastal sea samples one type peak was detected at Ex 305-310 nm Em 400-405 nm. The peak at Ex 320 nm and Em 430 nm corresponds to fulvic like materials and at Ex 230 nm Em 430 nm also corresponds to humic like materials (Coble, 1996).

The relative fluorescence intensity (RFI) are shown in Fig.5. The RFI increased from 6.9 at the upstream to 19.1 at the downstream. In the estuary samples RFI held 14.00-to 24.90. The coastal sea samples show the lowest value of 4.62-3.09. The RFI of coastal sea waters decreased to seaward. This is a dilution effect.

In the Moiwa bridge DOC concentration of fulvic acid (DOC-FA) was almost constant but DOC concentration of organic materials varied with season. The percentage of DOC-FA was 60 % at summer season and 20 % at autumn.

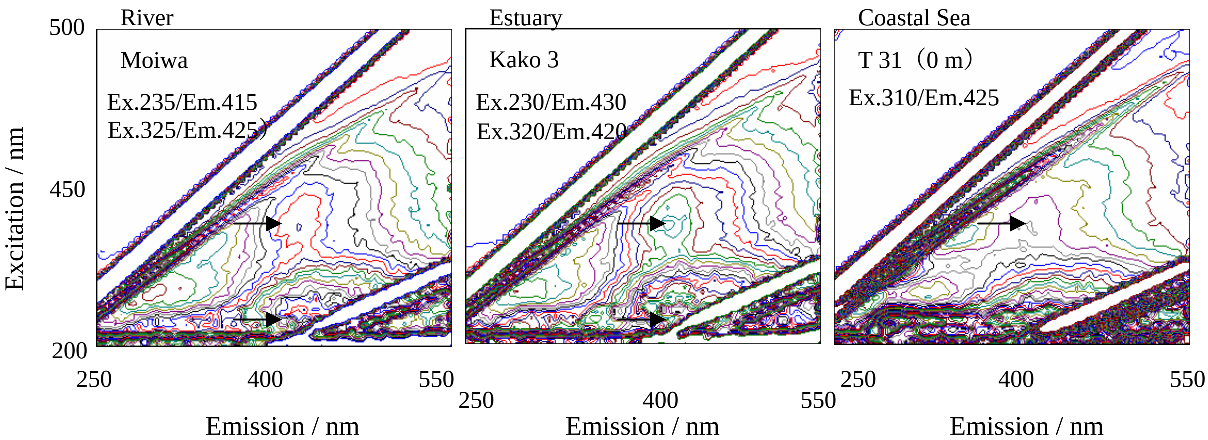


Fig.4 Typical 3D-fluorescence spectra of water samples from the Tokachi River, estuary and the coastal sea off Tokachi River.

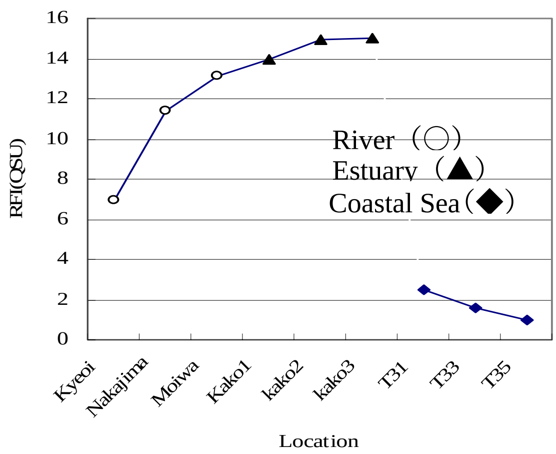


Fig.5 Relative fluorescence intensity (RFI)of the Tokachi River systems.

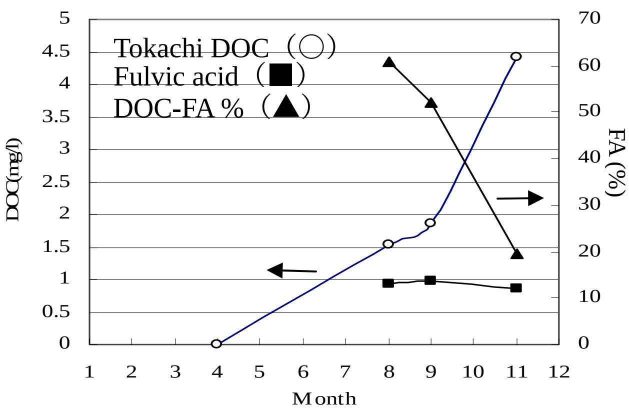


Fig.6 DOC, DOC-FA and DOC-FA % of the Tokachi River water from Moiwa

## 4. Summary

The purpose of the study is to understand transportation behavior and characteristics of dissolved organic matter in waters from river and coastal sea. This study were obtained following results.

Transportation of particulate organic materials increased in the snowmelt season at the Tokachi and Ishikari River systems. The DOC fluxe also increased in spring season at the Ishikari River, but exhibited the lowest value at the Tokachi River due to the dilution effect. Transportation of organic materials depend on the size and watershed environments of the river system.

Refractory organic materials (humic substances) were analyzed by 3-Dfluorescenc spectrophotometer. Major fractions in the Tokachi River samples were fulvic like materials. DOC-FA is almost constant but the percentage of DOC in FA varied with season (summer 60% and autumn 20%).

## References

1) Aiken, R., McKnigh D. M., Wershaw R. L., MacCarthy P., 1985. Humic Substances in Soil, Sediment and Water. Wiley –Interscience Publication, NewYork.

2) Coble, P. G., 1996. Characterization of marine and terrestrial DOM in sea water. Mar. Chem. 51, 325-346.

3) Meybeck M., 1982. Carbon, nitrogen and phosphorus transport by world rivers. Am. J. Sci. 282, 401-405.

4) Ministry of Land, Infrastructure, and Transport, 2004. http://www1.river.go.jp/.

5) Raymond A., Bauer E., 2001. Use of $^{14}C$ and $^{13}C$ natural abundances for evaluating riverine, estuarine and coastal DOC and POC. Org. Geochem. 32, 469-485.

6) Spitzy A., Ittekkot V., 1991. Dissolved and particulate organic matters in rivers. John Wiley and Sons Ltd., NewYork, pp 5-17.

7) Thurman E. M., 1985. Organic Geochemistry of Natural Waters. Dr W. Junk publishers. Boston.