

## 論文の内容の要旨

論文題目 Dynamics of Terrigenous Dissolved Organic Matter in the Marine Environments  
(海洋環境中における陸起源溶存態有機物の動態)

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### Introduction

Dissolved organic matter (DOM) in the ocean is one of the largest reservoirs of organic matter on the earth, and it plays the important role in the marine systems. Terrigenous dissolved organic matter (tDOM) in the ocean is transported by river input, and it is a small fraction of bulk DOM in the ocean. However, tDOM still plays an important role in the marine biogeochemical cycles due to this accompanies with bioactive trace metals, such as iron, and tDOM may act the organic ligands for trace metals in the ocean. Lignin is a phenolic polymer common to vascular plants and a useful biomarker of tDOM in the marine environment (Hedges et al., 1997; Opsahl and Benner, 1997). Chromophoric dissolved organic matter (CDOM) is ubiquitous in the ocean and has been widely studied in DOM sources and sinks (Coble 2007; Yamashita et al., 2013). The good linkages between lignin phenols and CDOM optical properties indicate the distributions and transformations of tDOM (Hernes and Benner, 2003; Fichot and Benner, 2012). In the present study, measurements of lignin phenols and CODM were used to trace tDOM in seawater from coastal area to open-ocean environment. The tDOM decomposition experiment was conducted with river water to investigate photodegradation and biodegradation of lignin and CDOM.

In this study, the following questions will be discuss in each chapter,

- 1) The removal mechanism of tDOM should be various and this supposes depend on the environmental condition. Numerous of tDOM studies focus on the plumes of the major rivers in the world (Opsahl et al., 1999; Benner and Opsahl, 2001; Amon et al., 2012; Fichot and Benner, 2014; Ward et al., 2013; Mann et al., 2014). However, most of the estuarine environment is not in large spatial scale as like the major large rivers.
- 2) Numerous studies pointed out that photodegradation is primarily responsible for losses of the lignin phenols components of tDOM (Opsahl and Benner, 1998; Herne and Benner, 2003; Stubbins et al., 2012; Benner and Kaiser, 2011). However, recently studies have demonstrated biodegradation is the main removal process of lignin phenols in rivers and river-influenced ocean margin (Ward et al., 2013; Fichot and Benner, 2014). Those investigations results imply the effect of biodegradation is possible ignored or underestimated in previous incubation experiments, especially when the water residence time in *in-situ* environment is longer than laboratory incubation time.

- 3) The good linkage between lignin and CDOM is based on lignin phenol concentrations and CDOM optical properties. It is still unclear regarding the linkage of removal or degradation pathway between lignin and CDOM, especially lignin is a chemical characteristic and CDOM is an optical property analysis.
- 4) Is it possible or not tDOM can transport to more open-ocean environment, such as North Pacific Intermediate water (NPIW) in the North Pacific Ocean?
- 5) A notable hypothesis of tDOM is organic ligands for trace metal in the ocean, however, a directly evidence is lacking. It is well known the concentrations of humic substance, dissolved organic carbon and dissolved Fe were high in NPIW layer (Nakatsuka et al., 2004; Yamashita and Tanoue, 2008; Nishiola et al., 2013). Therefore, lignin analysis is important to test this hypothesis.

## Material and Methods

In river-influenced coastal environment, samples were collected in Otsuchi Bay, Japan and three rivers in this catchment basin during 2012-2013. Water samples from the rivers were collected using a bucket, and seawater from the bay was collected at the surface and near the bottom using a Niskin bottle. Open-ocean samples were collected from the western North Pacific Ocean on the KH-12-3 cruise of R/V *Hakuho-Maru* in 2012. Seawater and river samples were filtered through Whatman<sup>®</sup> polycarbonate filter (1- $\mu$ m) and tDOM fraction including lignin were extracted by solid phase extraction on C18 cartridge, and lignin-derived phenols were produced by the CuO oxidation method following the previous studies (Louchouart et al., 2000; Kaiser and Benner, 2012). Eleven lignin phenols (including *p*-hydroxy, vanillyl, syringyl and cinnamyl phenols) were measured as the total dissolved lignin phenol concentrations using GC-MS. The ratios of each kind of phenols were also calculated and present in this study.

CDOM samples were filtered through Whatman<sup>®</sup> GF/F filter then stored frozen in the dark until analysis. Absorption measurement was measured from 200 nm to 800 nm of wavelength at 0.5 nm intervals using a dual-beam spectrophotometer (UV-1800, Shimadzu) to convert absorbance to Napierian absorption coefficient (Yamashita and Tanoue 2009). Absorption coefficient,  $a(350)$ , spectral slope coefficient,  $S_{275-295}$ , and  $E_2/E_3$  (ratio of absorbance at 250 nm and 365 nm) were used as indicators of tDOM characteristic in this study.

A lignin decomposition experiment was conducted with the Unosumai River water and *in-situ* microbial assemblages exposed to natural sunlight or kept in the dark for two months to investigate tDOM degradation processes in aquatic environment. Subsamples were collected after 3, 10, 20, 41 and 62 days, and those were analyzed for lignin phenols and CDOM absorbance following the same approaches for the *in-situ* samples.

## Result and Discussion

In tDOM decomposition results, lignin phenols and CDOM removed rapidly and substantial in the light treatment during the first 3 days. However, biodegradation was responsible for 67% of total lignin phenols decomposition, and 33% of those was due to photochemical processes during 62-day incubation. In Otsuchi Bay results, lignin phenol concentrations and CDOM absorption coefficients declined with increasing salinity and indicated an influence from river input. The physical mixing of river and seawater played an important role in controlling the concentrations and distributions of lignin phenols and CDOM optical properties in the bay. Photochemical transformation of fresh riverine tDOM can be significant in the early stages of plume dispersal and mixing with surface water in the bay, and biodegradation will be the dominant process in the coastal ocean.

Although ocean margin could be the important and major hot spot of tDOM transformations (Hedges et al., 1997; Opsahl and Benner, 1997), tDOM is possible to be transported to more open-ocean. In the western North Pacific Ocean, lignin phenol concentrations increased with decreasing salinity, and lignin phenol concentrations were maximal at 750 m. The

maximal values of lignin phenol concentrations were consistent with the depth of NPIW (Yasuda et al., 2001; Hernes and Benner, 2002; Nishioka et al., 2013) and those distributed over subarctic to subtropical region. Therefore, NPIW is successfully traced by lignin phenols in this study and our results are more evident to indicate the distributions of NPIW. This result also highlights the potential of tDOM may act the organic lignds for bioactive trace metals in the marine environment.

### **Conclusion**

This study results indicates the removal mechanism of tDOM is various and this is depend on the environmental condition. tDOM is highly affected by photochemical processes in a river system, and then the influence of biodegradation will increase in the coastal area. Meanwhile, physical mixing of freshwater and seawater also plays an important role in tDOM transformation in the coastal area. Finally, biodegradation will be the major degradation process of tDOM in the open ocean, and tDOM will become fairly refractory in seawater. Additionally, a long distance transportation of tDOM was investigated in this study, and provided us a good evidence of organic ligands in the ocean.