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The Oceanographic Society of Japan

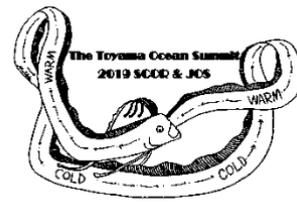
## 19-F8: SCOR-GEOTRACES Joint Session

Biogeochemistry of trace elements and isotopes in the ocean  
- from GEOSECS to GEOTRACES



26 September 2019

TOYAMA INTERNATIONAL CONFERENCE CENTER



2019 Annual meeting, The Oceanographic Society of Japan

19-F8: SCOR-GEOTRACES Joint English Session

**Biogeochemistry of trace elements and isotopes in the ocean  
~ from GEOSECS to GEOTRACES**

Conveners: Jing Zhang, Hajime Obata, and Yuichiro Kumamoto

INTRODUCTION

This session includes 24 interdisciplinary talks related to GEOTRACES and GEOSECS, and serves as a memorial to Wallace Broecker. Needless to say, the success of GEOTRACES today rests on the earlier success of GEOSECS. A few veterans of GEOSECS and related successor programs including WOCE, CLIVAR, GO-SHIP, JGOFS, and SOLAS are represented as well.

GEOTRACES is one of the large-scale international research programs under the auspices of SCOR, and began in 2005 as a succession program of GEOSECS that was conducted in the 1970's. Today, nearly 40 countries are involved, performing cross-basin sections, as well as many process studies in the global ocean, to clarify the role of biogeochemical cycles under on-going global environmental changes using trace elements and isotopes. Facing current rapid climate changes, it is essential to enhance interdisciplinary research and joint ocean surveys integrating physical, chemical, and biological oceanography. Presentations cover a wide view of GEOTRACES and Paleo-GEOTRACES topics in the international and regional oceans, as well as some in the newly established international BioGeoSCAPES program.

# 19-F8: SCOR-GEOTRACES Joint Session

## Biogeochemistry of trace elements and isotopes in the ocean - from GEOSECS to GEOTRACES

**[Oral] 26 September 2019, 9:00-12:00, 14:30-17:00**

- 9:00 INTRODUCTION
- 9:05 1. **WOCE – CLIVAR – GO-SHIP** Masao FUKASAWA (*Invited*)
- 9:30 2. **Tidbits of JGOFS** Chen Chen-Tung ARTHUR (*Invited*)
- 9:55 3. **Comparability of nutrients data and nutrients Certified Reference Materials: from GEOSECS- WOCE to GO-SHIP/GEOTRACES**  
Michio AOYAMA (*Designated*)
- 10:10 4. **Use of man-made geochemical transient tracers to oceanography in the past several decades (from GEOSECS to GEOTRACES)** (*Designated*)  
○Yutaka W. WATANABE , Kenichi SASAKI
- 10:40 5. **Radiocarbon in the deep water and implications for large-scale circulation** (*Designated*)  
Yuichiro KUMAMOTO
- 10:55 6. **US GEOTRACES inception, strategy and outcomes** (*Invited*)  
○Mariko HATTA, Christopher I. MEASURES, Robert F. ANDERSON, William J. JENKINS
- 11:15 7. **Dissolved iron distribution in the subarctic Pacific - HNLC water formation and biogeochemical processes -** (*Designated*)  
○Jun NISHIOKA, Hajime OBATA
- 11:30 8. **Distribution of lead isotopes in the North Pacific** (*Designated*)  
○Kazuhiro NORISUYE, Hajime OBATA, Toshitaka GAMO, Edward A. BOYLE
- 11:45 9. **Nickel and Copper Isotopes in Aerosols and Sinking Particles in the Northern South China Sea**  
○Shotaro TAKANO, Yoshiki SOHRIN, Wen Hsuan LIAO, Tung-Yuan HO
- Poster session (13:00-14:30)
- 14:30 10. **Dissolved organic carbon (DOC) in the Indian Ocean**  
○Masahito SHIGEMITSU, C. YOSHIKAWA, M. WAKITA, A. MURATA
- 14:45 11. **Barium Isotope Geochemistry in a Large Estuarine System: the Pearl River Estuary, China** (*Invited*)  
○Zhimian CAO, Xinting RAO
- 15:05 12. **Exploring marine biogeochemistry of molybdenum and tungsten**  
Makoto TSUJISAKA, Yuta FUJIWARA, Ayumi NAGAE, ○Yoshiki SOHRIN, Masafumi MURAYAMA, Gurumurthy G. PUTTOJIRAO
- 15:20 13. **Dissolved Nd isotope ratios along the GEOTRACES Eastern Pacific Zonal Transect** (*Invited*)  
○Chandranath BASAK, Yingzhe WU, Jesse M. MURATLI, Steven L. GOLDSTEIN, Brian A. HALEY, Leopoldo D. PENA, Louise BOLGE
- 15:40 14. **Tectonically induced formation of the semi-closed Japan Sea inferred from Nd isotopes** (*Designated*)  
○Keiji HORIKAWA, Yukiko KOZAKA, Yoshihiro ASAHARA, Hiroshi AMAKAWA, Yusuke OKAZAKI
- 16:10 15. **Distribution and geochemical cycles of Pt in Ariake Sea, Japan**  
○Asami S. MASHIO, Taiki TANIMURA, Hiroshi HASEGAWA, Teruya MAKI, Shigenobu TAKEDA, Hajime OBATA
- 16:25 16. **Stimulated phosphorus utilization of microbes by zinc and iron addition in the western North Pacific**  
○Tamaha YAMAGUCHI, Kazutaka TAKAHASHI, Mitsuhide SATO, Ken FURUYA,
- 16:40 17. **Global biogeography of giant viruses highlights their interplay with eukaryotic community**  
○Hisashi ENDO, Yanze LI, Romain Blanc-MATHIEU, Hiroyuki OGARA
- 16:55 CLOSING

**[Poster] 26 September 2019, 13:00-14:30**

**P1. The change of material flux via SGD and its impact on coastal ocean**

○Saki KATAZAKAI, Jing ZHANG, Mai SUZUKI, Kazumi ASAI, Kota NOJIMA

**P2. Transport of the upper Kuroshio Intermediate Water from northwestern Pacific to the Sea of Japan: using  $^{137}\text{Cs}$  as a tracer**

○Siteng J. ZHU, Jing ZHANG, Shota KAMBAYASHI, Takeshi MATSUNO, Eisuke TSUTSUMI, Shigenobu TAKEDA, Seiya NAGAO, Mutsuo INOUE, Katsumi TAKAYAMA, Hiroshi OGAWA, Ichiro YASUDA

**P3. Significance of Fukushima-derived radiocesium flux via river-estuary-coastal ocean system**

○Shota KAMBAYASHI, Jing ZHANG, Hisashi NARITA

**P4. Atmospheric Nitrogen Deposition on The Sub-Tropic NWPO and Its Impact**

○Tadateru NOGUCHI, Jing ZHANG, Wenkai GUAN, Bingzhang CHEN, Meixun ZHAO, Yuanli ZHU, Joji ISHIZAKA, Takeshi MATSUNO, Ichiro YASUDA

**P5. Cu-binding organic ligands and dissolved organic matter in coastal waters**

○Wiwit<sup>1</sup>, Hajime OBATA, Kuo Hong WONG, Chia-Jung LU, Hiroshi OGAWA, Hideki FUKUDA, Shigenobu TAKEDA

**P6. Factors affecting radiocesium concentration in sediment off Fukushima: Lateral transport of particles**

○S. OTOSAKA, T. SUZUKI, T. TSURUTA, T. MISONO, Y. MINO, T. ISHIMARU, J. KANDA, C. SUKIGARA, Y. ITO, N. M. SUGIHARA, M.C. HONDA

**Applications of Radium Isotopes to Marine Flux Studies** Guebuem KIM

○Masao Fukasawa<sup>1</sup>

1. JAMSTEC/NIPR

Keywords: Long Hydrography, World Ocean

### 1. Content

The history of Long Hydrographic Observation (LHO) is reviewed

### 2. Before WOCE

The history of LHO may be Meteor's Expedition in the Atlantic Ocean in 1932. An echo sounding was introduced firstly and seven zonal sections were occupied, though interval of stations was so coarse. The main purpose of the expedition was to know the stratification of seawater in the ocean. It is well known that this expedition located Mid-Atlantic Ridge, North Atlantic Deep Water, and Antarctic Bottom Water. Of these findings, Antarctic Bottom Water had attracted attentions of many chemical oceanographers to carry out new program of Geochemical Ocean Sections Study (GEOSECS). GEOSECS expeditions were carried out from 1972 to 1978 over the world ocean. The purpose of GEOSECS was to investigate the thermohaline circulation by measuring chemical tracers and radiotracers. So, the stations were lined up along assumed pathway of NADW and AABW in each ocean. GEOSECS succeeded to show schematic picture of global thermohaline circulation as the first step of global circulation study.

### 3. WOCE

After International Geophysical Year (IGY) from 1957 to 1958, corresponding to the increasing sense of crisis for the climate change or Global Warming, World Meteorological Organization (WMO) started World Climate Program (WCP) in 1979. World Climate Research Program (WCRP) was started in 1980 as a sub-program of WCP sponsored by WMO and International Council for Science (ICSU). IOC participated so late in 1993. Objectives of WCRP were to investigate the predictability of climate and to promote scientific understandings of climate system. World Ocean Circulation Experiment (WOCE) was the stream III of WCRP from 1990 to 2002 with proper objectives to know ocean fluxes in the world ocean (1990-1998) and to develop a model for ocean data assimilation (1998 - 2002 AIMS phase). Former objective was the reason why hydrographic lines were

set to form a "mesh" by land-to-land, surface to bottom sections. There are some special characteristics of WOCE, e.g. 1. Essential Climate Variable (ECV), which includes chemical and radio tracers, was introduced as requirement to measure in hydrographic program of WOCE (WHP). 2. International office was established for each observational method (Data offices and Data Accumulation Center for WHP, XBT, ADCP etc) to adjust observation plans of participating countries, to prepare technical manuals of ECVs measurements in UNESCO technical papers, to synthesis compiled data, and to archive and open data within much shorter period than before.

### 4. After WOCE

Data from WHP were quite "FAIR" supported by DOs and DACs. Based on the "FAIR" characteristic of WHP, World Ocean Atlas (WOA) of NOAA (USA) and eWOCE of Scripps Institution of Oceanography could archive "epoch-making" progress. After WOCE era, the framework of WHP was taken over by CRIVAR and Carbon Hydrographic Program (CCHDP) incorporate with Joint Global Flux Study (JGOFS). In 2007, CCHDP was renewed as Global Ocean Ship-Based Hydrographic Investigation Program (GO-SHIP) under Global Ocean Observing System (GOOS) including biological study so far with a unique objective to develop a strategy for a sustained hydrography program.

### 5. Remark

There have been quite a few innovations in ocean observation. Argo float is one of such innovations. Now, Argo may be the most appropriate measuring platform of ocean monitoring. However, it should be noted here that ship based hydrography continues to give all oceanographers unrestricted possibility to understand ocean and seawater state INTERDISCIPLINARY with HIGHEST ACCURATE data which will be a historical record of our ocean and the Earth

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Keywords: JGOFS, SCOR, IGBP, Carbon cycle, climate change

### 1. Abstract

The oceans contain about 50 times as much CO<sub>2</sub> as the atmosphere. As a result, even a two percent change in the oceanic carbon budget would cause a 100% change in the CO<sub>2</sub> concentration in the atmosphere. Yet, in the early eighties, marine geochemists and biologists were concerned that the physical transport model available at the time would be inadequate to determine the role of the ocean in the atmospheric carbon budget and hence the prediction of climate change. The Scientific Committee of Oceanic Research (SCOR) took the problem into its hands and initiated the Joint Global Ocean Flux Study (JGOFS) programme in 1987 to study the fluxes of carbon between the atmosphere and ocean, and within the ocean interior. In 1989 JGOFS became one of the early core projects of the International Geosphere Biosphere Programme (IGBP).

The objectives of JGOFS were:

- To determine and understand on a global scale the processes controlling the time-varying fluxes of carbon and associated biogenic elements in the ocean, and to evaluate the related exchanges with the atmosphere, sea floor and continental boundaries
- To develop a capacity to predict on a global scale the response to anthropogenic perturbations, in particular those related to climate change.

As a result of these two projects as well as a global network of

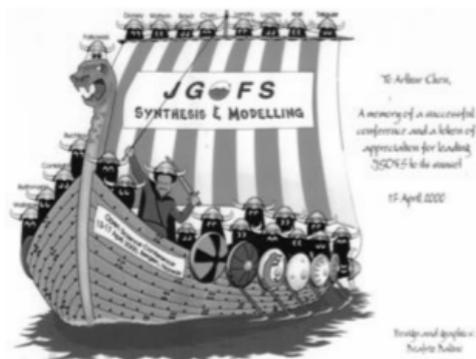
observations temporal increases of oceanic CO<sub>2</sub> concentration and inventory, but a decrease of pH, are quantified. JGOFS was completed in 2003 and left the following legacy in the eyes of IGBP.

- The role of the Ocean Carbon Cycle in Global Change. Fasham, Michael J.R. (Ed.) Springer Verlag, Heidelberg, Germany, 2003, 297 pp. (A synthesis of JGOFS science).

- The Changing Ocean Carbon Cycle: A midterm synthesis of the Joint Global Ocean Flux Study. Hanson, R.B., Ducklow, H.W. and Field, J.G. (eds). IGBP Book Series No. 5. Cambridge University Press, UK, 2000, 520 pp.

- Ocean Biogeochemistry and global change, 2001. IGBP Science no. 2 (A popular summary of JGOFS main achievements).

In addition, before JGOFS the conventional wisdom was that the continental margins are sources of CO<sub>2</sub> to the atmosphere. The late S. Tsunogai was among the first to point out otherwise based on the study in the East China Sea. To tackle the controversial problem JGOFS teamed up with the Land Ocean Interactions in the Coastal Zone project (LOICZ) of IGBP in 1994 to form the JGOFS/LOICZ Task Team on Continental Margin Studies. Partly due to the effort of the Task Team now we know that outside of estuaries most continental margins are actually sinks of CO<sub>2</sub>.



# Comparability of nutrients data and nutrients Certified Reference Materials: from GEOSECS- WOCE to GO-SHIP/GEOTRACES

19-F8-3

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Keywords: words: Nutrients, CRM, WOCE, hydrography

## 1. Introduction

In seawater, nitrogen, phosphorus and silicon exist as so-called nutrients e. g. nitrate, phosphate and silicate, and spatial distribution and temporal variation of nutrients regulate the productivity of the ocean. Therefore, nutrients had been measuring as an important parameter of oceanography for long time. In addition, because it is closely linked to the carbon cycle through biological activities such as photosynthesis and respiration via the C: O: N: P stoichiometry, so-called Redfield ratio, nutrients are also regarded as important from the viewpoint of global warming and ocean acidification. In addition, nutrients are also linked to the oxygen circulation through same C: O: N: P stoichiometry as well as carbon cycle. Oxygen, like nutrients, is an essential part of life in the ocean, and not only is it necessary for each of the organisms to live, but also the circulation of the nutrients and carbons on the earth. The global nutrient data set GND13 ([http://www.godac.jamstec.go.jp/resource/data\\_catalog/GND13/GND13.zip](http://www.godac.jamstec.go.jp/resource/data_catalog/GND13/GND13.zip)), which was created based on the nutrients data of which traceability and comparability are ensured published by the author, may give us more accurate ocean general circulation pattern in deep layers of the Pacific Ocean. Therefore it is very important to keep comparability and traceability of high quality nutrients, carbonate system parameters and dissolved oxygen data, those enable us to study changes and variability of carbon, nutrients and dissolved oxygen and C: O: N: P stoichiometry accurately.

## 2. History of effort to keep comparability and traceability of nutrients concentration

GEOSECS was carried out 1972-1978 and pre-WOCE and WOCE era was late 1980s to 1990s. Nutrient CRM was needed during the WOCE era but no one could supply natural seawater base nutrients CRM while IAPSO salinity standards and Dickson's DIC standards were available and had been working well at that time.

Inter laboratories comparison exercises of nutrients measurements were carried out by ICES since 1965 until 1993, and WHPO encouraged participants of WOCE cruises to participate the IC exercises to improve comparability of nutrients data in the world instead of using CRMs. Some European laboratories also used fresh deep sea water as tracking standard solution. MRI/JMA, JMATEC and KANSO also started to produce nutrients RM since 1993. Aoyama et al. reported at the OSM2002 about new seawater base nutrient RM of which life is four years and have good homogeneity, the number of bottles per lot was 300 bottles. Some guy told me that "I cannot believe". Although certification of the RM was not available in 2002, we pointed out about the issue of who and how to certify them. The IPCC 2007 reported, however, that inability to study nutrient variability in the deep ocean is due to lack of comparability of nutrients data (Bindoff et al., 2007). Aoyama at MRI started to use RM in cruises conducted 2000s until now. Aoyama also organized IC exercise since 2003 until 2012. Hereafter IOCCP-JAMSTEC IC exercises were carried out 2014/15 and 2017/18.

3, SCOR-JAMSTEC CRM, KANSO CRM and NMIJ CRM

Now SCOR-JAMSTEC CRM, KANSO CRM and NMIJ CRM are available and people can use CRMs more globally in the cruises of GO-SHIP and GEOTRACES. IOCCP encouraged the use of CRM for nutrients in 2017 (Tanhua et al., 2017). Recent IC results indicated that comparability of nutrients data in our world becomes better especially for nitrate and phosphate, but we need to do more to improve comparability for silicate. It is also important to have SI traceability throughout carbon, nutrients and dissolved oxygen.

# 19-F8-4 Use of man-made geochemical transient tracers to oceanography in the past several decades (from GEOSECS to GEOTRACES)

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Keywords: transient tracers, CFCs, SF<sub>6</sub>

## 1. Abstract

Time-dependent tracers are important tools to clarify the ocean physical dynamics along with ocean biogeochemical cycles. Especially, man-made geochemical transient tracers such as tritium (<sup>3</sup>H), bomb-radiocarbon (bomb-<sup>14</sup>C), chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF<sub>6</sub>) can allow us to elucidate the ocean physical and biogeochemical dynamics on decadal time-scale.

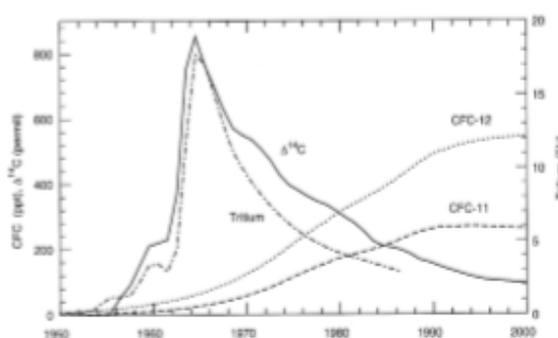
In the 1970s, the Geochemical Ocean Section Study (GEOSECS) as the first global ocean survey for the three-dimensional distributions of physical/biogeochemical properties was carried out. GEOSECS used <sup>3</sup>H and <sup>14</sup>C as transient tracers [Broecker and Peng, 1982] although these data were sparse due to their complicated measurements.

In the late-1980s, developing the analytical method of CFCs in seawater [Bullister and Weiss, 1998] made it possible to enforce the extensive ocean field survey to study detailed water movements such as the World Ocean Circulation Experiment (WOCE). Especially, using the CFCs data with their atmospheric time history and solubilities could evaluate the apparent ages of water mass from when the water mass left the surface during the past decades, bringing many collaborations with physical and chemical oceanographers (Fig. 1).

However, due to the world-wide ban on the production of CFCs in industrial countries, the atmospheric increasing rate of CFCs after the mid-1990s have been gradually decrease, so that it was almost impossible to use CFCs dating techniques. To overcome this problem, it is essential to use SF<sub>6</sub> as a potential time-dependent ocean tracer [Law et al., 1994]. Furthermore, SF<sub>6</sub> was focused by biological oceanography in the iron fertilization experiment [e.g., Tsuda et al., 2003], as a tracer of iron-injected surface water mass.

Recently, these tracer observation data are used in order to study the ocean carbon dynamics and to evaluate

the changes in ocean ventilation and circulation due to climate change. We will introduce some examples using



CFCs and SF<sub>6</sub> in our presentation.

**Fig.1:** The atmospheric time history of anthropogenic geochemical transient tracers [Sarmiento and Gruber, 2006]

## 2. Reference

Broecker WS, Peng TH (1982). Tracers in the Sea. Elgigio Press, New York.

Bullister JL, Weiss RF (1988). Determination of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in seawater and air. Deep-Sea Res. 35: 839-853.

Law CS, Watson AJ, Liddicoat MI (1994). Automated vacuum of analysis of sulphur hexafluoride in seawater: derivation of the atmospheric trend (1970-1993) and potential as a transient tracer. Mar. Chem. 48: 57-59.

Sarmiento JL, Gruber N (2006). Ocean Biogeochemical Dynamics. Princeton University Press, New Jersey.

Tsuda A et al. (2003). A mesoscale iron enrichment in the western subarctic Pacific induces a large centric diatom bloom. Science 300: 958-961.

## Radiocarbon in the deep water and implications for large-scale circulation

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Japan Agency for Marine-Earth Science and Technology

Keywords: radiocarbon, deep circulation, GEOSECS, WOCE

### 1. Introduction

The application of  $^{14}\text{C}$  (radiocarbon) for the oceanography is to date objects or to determine various process rates in the ocean. Atmospheric radiocarbon is transferred to the ocean primarily by air–sea gas exchange. Once in the ocean, radiocarbon is subject to the same physical, chemical, and biological processes that affect total dissolved inorganic carbon (DIC). There are two major sources, natural and bombproduced radiocarbon. Natural radiocarbon is produced by cosmic ray and its production rate has been constant in a long time-scale. Bomb radiocarbon was produced mainly in the late 1950s and early 1960s by nuclear weapon testing. In surface water, approximately shallower than 1000m, the distribution of natural radiocarbon has been masked by the bomb radiocarbon. Here I review studies on large-scale circulation in deep water by means of natural radiocarbon in DIC ( $\text{DI}^{14}\text{C}$ ).

### 2. Pre-GEOSECS

Soon after the radiocarbon dating method was developed in the early 1950s, it was applied to seawater samples. During the 1950s and 1960s, most of the seawater samples were limited to the shallow layers owing to the difficulty of deep water sampling. Just After the first subsurface measurements of radiocarbon, one of the primary applications has been the determination of deep ocean ventilation rates. Most of these calculations have used a box model. The first such estimates yielded mean residence times for the various deep and abyssal ocean basins of 350–900 years. A solution of these models generally assumes a steady-state circulation, identifiable source water regions with known  $\text{DI}^{14}\text{C}$ , no mixing between water masses, and no significant biological sources or sinks. Another early approach assumed that the vertical distribution of radiocarbon in

the deep and abyssal ocean could be described by a vertical (1D) advection–diffusion equation.

### 3. GEOSECS

During the 1970s the Geochemical Ocean Sections (GEOSECS) program provided the first full water column global survey of the oceanic radiocarbon distribution. About 2200 data were obtained by radioactivity measurement. When the GEOSECS data became available, box models were again used to estimate residence times and mass fluxes for the abyssal ocean. In this case, the model had only four boxes, one for the deep region of each ocean. Results from this calculation gave mean replacement times of 510, 250, 275, and 85 years for the deep Pacific, Indian, Atlantic, and Southern Ocean, respectively.

### 4. WOCE

In the World Ocean Circulation Experiment (WOCE) conducted in the world ocean in the 1990's, more than 15,000 of seawater samples were collected at 785 stations and  $\text{DI}^{14}\text{C}$  was measured using the accelerator mass spectrometer, which can measure radiocarbon with a sample amount of 1/1000 or less as compared to that for the traditional radioactivity measurement. About seven times larger number of WOCE radiocarbon data clearly show the deep path of the wellknown global thermohaline circulation. As a result, the map of the WOCE radiocarbon was used to assess ocean carbon cycle models and it was found that many of them were inconsistent with the new databased metrics of deep and abyssal radiocarbon. In addition, the WOCE radiocarbon revealed that an observed  $^{14}\text{C}$ -age, which is the time elapsed, is dominated by two equally important components, an elapsed time since a body of water has been in contact with the atmosphere and with a “preformed  $^{14}\text{C}$ -age

○Mariko Hatta<sup>1</sup>, Christopher I. Measures<sup>1</sup>, Robert F. Anderson<sup>2</sup>,  
William J. Jenkins<sup>3</sup>

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Keywords: US GEOTRACES, strategy, trace elements, iron

### 1. Abstract

The assembly of vertical profiles of a large number of trace elements determined in the North Pacific Ocean by Nozaki (2001) depicted visually the variety of ways in which these elements interact with, and thus trace, oceanographic processes. However, those profiles had been collected individually. There had been no large chemistry focused coordinated section program since GEOSECS in the 1970's. It was the need for such a program that brought Catherine Jeandel and Robert Anderson together at a JGOFS meeting in Bergen Norway in April 2000. They were concerned about the slow rate of progress of trace elements and isotopes (TEIs) research and the necessity to build a large program such as "GEOSECS for TEIs" to capitalize on the tremendous advances that had been made in both sampling technology and analytical methodology, therefore it seemed like an appropriate time to launch a new initiative. Six marine geochemists, Gideon Henderson (UK), Martin Frank (Germany), Roger Francois (Canada), Mukul Sharma (USA), Catherine (France) and Robert (USA) initiated the first GEOTRACES meeting (it gained that name later) at a special "Town Hall" at the 2001 Fall AGU. Encouraged by the enthusiastic turnout for this event, the organizers submitted a proposal for a planning workshop to the US National Science Foundation. This in turn led to the first open science workshop held in Toulouse, France (April 2003). Subsequently individual countries formed their own national groups that held planning meetings to raise interest, define goals, and provide volunteers for a 30 person group representing 12 countries that wrote the Science Plan that was approved by the International GeosphereBiosphere Programme and published in 2006. The first International Scientific Steering Committee, convened by SCOR, met for first time in Fall 2006 in San Francisco and organized the

ocean basin planning workshops. The first of these workshops was held in Hawaii in 2007 (Pacific), and this was followed by one in Oxford, UK (Atlantic) and Goa, India (Indian). These workshops, which attracted international participation, established basin priorities, and proposed cruise tracks for each basin. The concept was that individual

countries would then volunteer to occupy various sections depending on national interests and logistical constraints.

The US GEOTRACES SSC prioritized their chosen study regions based on several criteria: scientific interest for TEIs, logistics (cost/length/risks), leaders, links with CLIVAR and other country's plans. The US has now completed 4 basin-scale cruise tracks (North Atlantic zonal transect, Eastern Pacific zonal transect EPZT, Arctic Ocean, and North Pacific Meridional Transect).

An example of the value that the program has brought to understanding of biogeochemical cycles is during the Sept 2018 PMT GP15 cruise, where large water column anomalies of helium isotopes and iron (Fe) concentrations were found at intermediate depths above Loihi Seamount. The observation of the export of these anomalies as far as 1000 km along the 152° W transect provides an insight into the significance of hydrothermal Fe input at intermediate depths in the ocean. Furthermore numerical dye-release modeling predicts that this flux supplies Fe to the dominant upwelling signature off the west coast of N. America, indicating that processes in the middle of the Pacific play a role in supplying this limiting micronutrient.

To date the US GEOTRACES program has funded 79 Principal Investigators (PIs). Each transect accommodated about 40 PIs, many postdocs and students, resulting in 235 publications and 27 dissertations, with more to come.

## Dissolved iron distribution in the subarctic Pacific - HNLC water formation and biogeochemical processes -

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2. Atmosphere and Ocean Research Institute, The University of Tokyo

Keywords: subarctic Pacific, iron, HNLC, biogeochemical processes

### 1. Introduction

It is well known that phytoplankton growth is broadly limited by iron (Fe) availability in the subarctic Pacific. To investigate which Fe sources control the amplitude of seasonal variation in biogeochemical parameters in the subarctic Pacific, we examined the spatial variation in the west-to-east distribution of dissolved Fe (DFe) across the western and eastern subarctic Pacific through the Japanese GEOTRACES program.

### 2. Methods

The KH-12-4 and KH17-3 cruises of R/V Hakuohmaru made zonal vertical section observations from west to east across the subarctic Pacific (around 47°N; GP 02) from August to October 2012 and June to August 2017. To obtain the full depth vertical profiles of DFe, we conducted sampling and sub-sampling in accordance with the GEOTRACES protocol. Hydrographic data and seawater samples were collected using a clean CTD-carousel multiple sampler system, on which 24 acid-cleaned Teflon-coated 12-L Niskin-X bottles were mounted. We connected a 0.2 μm Acropak filter (Pall Corporation) to the Niskin-X spigot, then, the filtrate was collected in acid-cleaned 125-mL LDPE bottles (Nalgene Co., Ltd). The filtrate (<0.2 μm) was adjusted to pH < 2 by the addition of ultrapure HCl and then allowed to stand for approximately 24 h at room temperature. It was then adjusted to pH 3.2 just before the sample measurements. Then, DFe was analyzed onboard by using a flowinjection analysis (FIA) chemiluminescence detection system (Obata et al. 1993, 1997). All sample treatments were performed under laminar flow in the onboard clean-air laboratory.

### 3. Results and Discussion

The vertical section profile of the western subarctic Pacific gyre showed high dissolved Fe concentrations

from the bottom of the surface mixed layer to as deep as approximately 3000 m, suggesting that Fe-rich intermediate water is transported laterally and distributed across the western subarctic gyre, over

2000 km. The section data also indicate that the influence of the western Fe-rich intermediate water does not reach the Alaskan gyre. The profiles of DFe reflect the influence of Fe supplied from several potential external sources (external Fe), such as atmospheric Fe and laterally transported Fe, along with internally recycled Fe (internal Fe), such as remineralization and release of Fe from organic particles settling in the water column. Therefore, to understand the controlling sources of Fe in the subarctic Pacific, it is necessary to evaluate both external and internal Fe sources. We used the Fe\* concept for quantitative evaluation of the spatial pattern of the contributions of internal and external DFe in a section profile.

$$\text{Fe}^* = \text{external DFe} = [\text{DFe}]_{(\text{observed})} - [\text{PO}_4]_{(\text{observed})} \times \text{RFe:P}$$

The Fe\* index distribution clearly indicates that the western Fe-rich intermediate water is well explained by external sedimentary Fe sources and water transport systems from a subpolar marginal sea, the Sea of Okhotsk, and the continental margin. The spatial pattern of Fe to nutrient stoichiometry supplied from the intermediate water to the surface, in comparison with reported Fe and nutrient demand in surface phytoplankton, quantitatively explains the differences in surface macronutrient consumption between the western and eastern gyre as well as the formation of the high nutrient and low chlorophyll region in the whole subarctic Pacific.

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Keywords: Lead isotopes, GEOTRACES, Pacific Ocean, biogeochemical cycles

### 1. Purpose

Humans have been injecting lead (Pb) to the marine environment through mining, smelting, burning of fossil fuels and consumption of leaded gasoline for more than a century (Boyle et al., 2014). Anthropogenic Pb overwhelms that of natural origin in the modern ocean. Pb globally dispersed as such is a tracer for anthropogenic contaminants in the ocean and assigned as a key parameter in the ongoing international GEOTRACES program. Ratios of four isotopes ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ) are especially useful in characterizing anthropogenic sources and investigating mutual transformation of Pb isotopes between particulate and dissolved forms (Sherrell et al., 1992). Pb isotope ratios display characteristic values in mode water masses (Lee et al., 2015), which play an important role in heat transfer between surface ocean and lower atmosphere. Pb isotopes in the Atlantic and Indian Oceans have been investigated (Echegoyen et al., 2014; Noble et al., 2015), while knowledge of Pb isotopes in the deep Pacific is sparse partly because analysis is difficult for Pacific deep waters with high silicate contents (Boyle et al., 2012). We have been developing a new method for preconcentration and separation of Pb isotopes to obtain distributions of Pb and Pb isotope ratios in the vast area of the North Pacific. In this presentation, we will describe the distribution of Pb isotope ratios in the North Pacific determined by the method.

### 2. Method

Water samples were collected during the R/V Hakuho-Marui KH-12-4 cruise and R/V Shinsei-Marui KS-13-T3 cruise using a CTD carousel multi-sampling system and Niskin-X samplers. Samples were filtered through a 0.2  $\mu\text{m}$  AcroPak

cartridge filter, transferred to HDPE bottles and acidified with ultra-high purity HCl after the sampling. The samples were brought to our laboratory and chemical separation was carried out: briefly, acetic acid/acetate buffer solution was added to 400 g of the acidified seawater samples. The sample solution of pH 4.75 was passed through a chelating resin column (NOBIAS CHELATE PA-1F, Hitachi-High Technologies, Japan) to preconcentrate and separate Pb from interfering elements. After the elution of Pb with nitric acid solution, secondary column procedure was carried out to attain complete removal of the interfering heavy metals and almost quantitative recovery of Pb isotopes. The final solution was evaporated to dryness, Pb in the residual was redissolved with dilute nitric acid and Tl standard solution was spiked to the solution (NIST 997 with a certified  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio of 2.3871). Pb isotope ratios in the final solution were measured with Neptune multi-collector ICPMS. Reliability of our method was verified using intercalibration samples.

### 3. Results and discussion

The concentration of Pb in the North Pacific is generally high in subsurface water and decreases with depth, comparable to previous results in the North Pacific (Wu et al., 2010; Zheng et al., 2019).  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios increase with depth and are lower than the values for hemipelagic sediments ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.2117$ , Jones et al., 2000) due to the dominant anthropogenic influence on the water column, consistent with the previous study (Zurbrick et al., 2017). We will discuss regional difference of Pb isotope ratios between the western, central and eastern North Pacific and compare our dataset with coral time series data (Inoue and Tanimizu, 2008).

## Nickel and Copper Isotopes in Aerosols and Sinking Particles in the Northern South China Sea

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Keywords: source identification, aerosols, biogenic particles

### 1. Introduction

Nickel and Copper are bio-essential trace metals in the ocean. The oceanic cycle of Ni and Cu is controlled by biogeochemical processes. Sinking particles play an important role in biogeochemical cycling of trace metals by transporting them from the surface to the deep ocean, and provide a direct information on the oceanic sink of trace metals. Recent advances of mass spectrometers and chemical separation techniques have enabled us to determine isotope ratios of trace metals in geochemical samples. The isotope ratios of trace metals are powerful tools to identify sources and transformation processes. Here, we present the isotope ratios of Ni and Cu in sinking particles, aerosols, and seawater collected in the Northern South China Sea.

### 2. Method

Sinking particle samples were collected from April 2014 to March 2015 at the SouthEast Asian Time-series Study (SEATS) station located at 18.0°N, 116.0°E in the Northern South China Sea. Seawater samples were collected at the same station in October 2006. Aerosol samples were collected from January to December 2011 at Dongsha Atoll, which is located at 20.7°N, 116.7°E with a distance of 300 km from the SEATS station. Isotope ratios of Ni and Cu in the seawater samples were determined using a previously published method (Takano et al., 2017): Ni and Cu in the samples were pre-concentrated and purified by chelating extraction and anion exchange, and their isotopic ratios were measured using MC-ICPMS. For the analysis of Ni and Cu isotopes in sinking particle and aerosol samples, we have modified the previous method to remove Al, Fe, and Mn. These elements are enriched in aerosols and sinking particles. The isotope ratios of Ni and Cu are expressed in  $\delta^{60}\text{Ni}$  and  $\delta^{65}\text{Cu}$  as follows:

$$\delta^{60}\text{Ni} = \left[ \frac{(^{60}\text{Ni}/^{58}\text{Ni})_{\text{Sample}}}{(^{60}\text{Ni}/^{58}\text{Ni})_{\text{NIST SRM 986}}} - 1 \right] \times 1000$$

$$\delta^{65}\text{Cu} = \left[ \frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{Sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST SRM 976}}} - 1 \right] \times 1000$$

### 3. Results and Discussion

In the aerosol samples,  $\delta^{60}\text{Ni}$  is in a range from  $-0.08$  to  $+0.56\%$  and  $\delta^{65}\text{Cu}$  is in a range from  $-0.33$  to  $+0.83\%$ . These are largely different from those of lithogenic materials, suggesting that Ni and Cu in the aerosols are dominated by anthropogenic sources. In the sinking particle samples,  $\delta^{60}\text{Ni}$  is in a range from  $+0.01$  to  $+0.54\%$  at a depth of 2000 m and from  $-0.18$  to  $+0.54\%$  at a depth of 3500 m.  $\delta^{65}\text{Cu}$  is in a range from  $+0.15$  to  $+0.35\%$  at a depth of 2000 m and from  $+0.01$  to  $+0.35\%$  at a depth of 3500 m. We estimate sources of Ni and Cu in sinking particles based on a combination of their isotope ratios and elemental ratios to Ti, Mn, and P. The  $\delta^{60}\text{Ni}$  in the sinking particles is linearly correlated with the P/Ni ratio, suggesting two sources for Ni in sinking particles. One of the sources has low  $\delta^{60}\text{Ni}$  and P/Ni, which is considered to be lithogenic particles supplied via resuspension of marine sediments off the southwest Taiwan. The other source has high  $\delta^{60}\text{Ni}$  and P/Ni. The candidate for this source is biogenic particles, which preferentially adsorb heavy Ni isotopes on their surface. For Cu,  $\delta^{65}\text{Cu}$  and P/Cu in the sinking particles are between those of marine sediments and labile fractions of suspended particles. The previous study suggested that Cu in the labile fractions is associated with organic matter (Little et al., 2018). Therefore, Cu in sinking particles is derived from resuspended marine sediments and biogenic particles as well as Ni. The correlation between Cu and P is weaker than that for Ni, suggesting the Cu concentrations in biogenic particles are not constant due to scavenging of Cu through the water column.

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# 19-F8-10 Dissolved organic carbon (DOC) in the Indian Ocean

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Keywords: DOC, Indian Ocean, Indonesian throughflow

## 1. Introduction

In the meridional overturning circulation, the Indonesian throughflow (ITF) enters the Indian Ocean from the Pacific and moves to the Atlantic, and this inflow influences basin-scale biogeochemistry (Talley and Sprintall, 2005).

Dissolved organic carbon (DOC) is the largest reservoir (~662 Pg C) of reduced carbon in the ocean (Hansell et al., 2009), and understanding the basin-scale behavior is important.

In this study, we aim to gain insights into the amount of DOC transported via the ITF from the Pacific to the Indian Oceans. To this end, we measure DOC concentrations for the seawater samples obtained in a revisit cruise along the World Ocean Circulation Experiment Hydrographic Programme (WHP) section I10 between Indonesia and Australia (Figure). Then, we estimate the velocity field across the I10 section using a geostrophic inverse box model. Finally, the DOC flux to the Indian Ocean through the ITF is estimated, with the velocity field and the DOC data.

## 2. Methods

We conducted a revisit cruise along the WHP section I10 from December 2015 to January 2016. At each station, a CTD profile was obtained with temperature, salinity and pressure, and bottle sampling was also carried out. Concentrations of DOC were measured by using a Shimadzu TOC-L for the water samples, and the repeatability of DOC was ~1.0 μmol kg<sup>-1</sup>. In addition to our data, we also used the data from the WHP section I5 conducted from March 2009 to May 2009 (Figure). The data of temperature, salinity, pressure and DOC were downloaded from the Carbon Hydrographic Data Office (CCHDO) website (<http://cchdo.ucsd.edu/>).

In order to estimate the velocity fields across the sections, the steady geostrophic box inversion was considered:

$$\sum_j \rho(j,q) b_j \delta_j \Delta a(j,q) - \rho_i w_i A_i + \rho_{i+1} w_{i+1} A_{i+1} + n_i - \sum_j \rho(j,q) v_2(j,q) \delta_j \Delta a(j,q) - \sum_j F_j^E$$

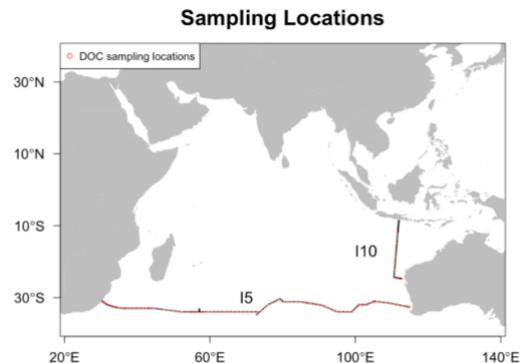
where  $\rho(j,q)$  is the density in station pair  $j$  at depth interval  $q$ ,  $b_j$  is the reference-level velocity,  $\Delta a(j,q)$  is the area in depth interval  $q$  in station pair  $j$ ,  $\delta_j$  is the unit normal ( $\pm 1$ ) for pair  $j$  for

the volume under consideration, and  $v_R$  is the thermal wind velocity.  $\rho_i$ ,  $w_i$ , and  $A_i$  are the density, pseudo-vertical velocity and corresponding horizontal area across each isopycnal layer, respectively.  $n_i$  is the noise, and  $F_j^E$  is the Ekman mass flux. The Ekman transport was calculated from an average wind stress of NCEP/NCAR reanalysis (Kalnay et al., 1996) over the period 1981 to 2010. All unknowns,  $b_j$ ,  $w_i$ , and  $n_i$  were estimated by using the Gauss-Markov estimator (Wunsch, 1996).

## 3. Results

Along the section I10, DOC concentrations ranged from ~38 μmol kg<sup>-1</sup> in the deep waters to ~80 μmol kg<sup>-1</sup> in the shallow waters.

Using the steady geostrophic box inversion, the ITF was estimated at 12±8 Sv. With the measured DOC concentrations and the estimated volume transport of ITF, the DOC flux via the ITF was estimated at 573 ± 223 kmol/s. In the presentation, we will discuss the sources and sinks of DOC associated with the biogeochemical processes in the Indian Ocean.



## Barium Isotope Geochemistry in a Large Estuarine System: the Pearl River Estuary, China

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Keywords: stable barium isotopes, estuarine mixing, sediment pore-water, proxy

### 1. Abstract

Barium (Ba) is a widely used proxy in oceanography for tracing water mass mixing, river inputs, and biological productivity. Recent success in the determination of stable Ba isotopic compositions provides a novel tool to study the biogeochemical cycling of Ba and evaluate the reliability of the Ba proxy for reconstruction of paleosalinity and paleoproductivity. In this study, we present a new dataset of dissolved Ba (DBa) isotopes ( $\delta^{138/134}\text{BaDBa}$ ) in the water column and sediment pore-water from the upper reaches to the lower seaside of the Pearl River Estuary (PRE) in Southern China.

DBa concentrations in the surface waters of the PRE showed non-conservative distributions along salinity gradients in both summer (July 2015) and winter (January 2017). A maximum concentration of DBa ( $\text{DBa}_{\text{max}}$ ) was observed in both seasons with values of 224.7 and 230.3 nmol kg<sup>-1</sup> corresponding to salinities of 2.3 and 4.9, respectively. After  $\text{DBa}_{\text{max}}$ , DBa concentrations decreased linearly with increasing salinity till the sea end. Surface  $\delta^{138/134}\text{BaDBa}$  signatures overall increased from the river water ( $\sim 0.20\text{‰}$ ) to the seawater endmember ( $\sim 0.60\text{‰}$ ), generally mirroring the distribution of DBa concentrations.  $\delta^{138/134}\text{BaDBa}$  also behaved conservatively against salinity after the  $\text{DBa}_{\text{max}}$ , suggesting that Ba isotopes are a potential new tracer of paleosalinity in proximity to large river plumes. We speculate that particle adsorption of Ba preferentially removes lighter Ba isotopes, which results in relatively low DBa concentrations and heavy  $\delta^{138/134}\text{BaDBa}$  signatures for the river water endmember at zero salinity of the PRE.

In the winter season of January 2017, pronounced depth-dependent variations of pore-water  $\delta^{138/134}\text{BaDBa}$ ,

generally showing a shift to lighter values from the topmost layer down to 15 cm depth, were observed in the PRE surface sediments. These gradients primarily results from Ba isotope fractionation caused by various solution-solid phase interactions. Both formation of authigenic barite and Ba precipitation associated with the redox cycling of manganese preferentially remove light Ba isotopes from the pore-water. These processes induce the heaviest  $\delta^{138/134}\text{BaDBa}$  (0.5-0.7‰) in the topmost pore-water, which, however, does not significantly contribute to the bottom waters of the PRE characterized by lighter  $\delta^{138/134}\text{BaDBa}$  (0.1-0.3‰). This contrast suggests that Ba isotopes in sediments are potentially a more robust proxy of paleosalinity than Ba concentrations because even considerable benthic fluxes of Ba would not significantly influence the conservative  $\delta^{138/134}\text{BaDBa}$ -salinity relationship in the water column of estuaries. On the other hand, barite dissolution in sulfate-depleted sediments and subsequent precipitation of authigenic barite most likely alter the original sedimentary Ba isotopic compositions, implying that in this case the Ba isotope proxy data need to be considered with caution.

## Exploring marine biogeochemistry of molybdenum and tungsten

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Keywords: Stable isotopes, Biogeochemical cycle, Paleoceanography, GEOTRACES

A Group 6 element molybdenum (Mo) form molybdate  $\text{MoO}_4^{2-}$  and is conservatively distributed with a concentration of  $\sim 107$  nmol/kg in the oxic modern ocean<sup>1</sup>. In sulfidic waters,  $\text{MoO}_4^{2-}$  is transformed into thiomolybdate  $\text{MoO}_x\text{S}_{4-x}^{2-}$ , which is fixed in sulfidic sediments<sup>2</sup>. Since the sulfide concentration causes a large shift in the concentration and stable isotope ratio of Mo in sediments, Mo has been extensively studied as a proxy for paleoceanography<sup>3,4</sup>.

Tungsten (W) is located just below Mo on the periodic table. Although W forms tungstate  $\text{WO}_4^{2-}$  and is conservatively distributed in the oxic modern ocean as well as Mo, the concentration of W is as low as  $\sim 49$  pmol/kg<sup>5,6</sup>. Since the transformation of  $\text{WO}_4^{2-}$  into thio tungstate  $\text{WO}_x\text{S}_{4-x}^{2-}$  requires about a ten times higher concentration of sulfide than that for  $\text{Mo}^{2+}$ , W and Mo are significantly fractionated in marine environments, such as hydrothermal systems<sup>7</sup> and estuarine<sup>2</sup>. Thus, we expect that the Mo/W concentration ratio and the stable isotope ratio of W will be promising proxies for paleoceanography.

To establish a reliable proxy in paleoceanography, it is essential to understand the biogeochemical cycles of Mo and W in the modern ocean. So far we have developed an analytical method to determine the isotopic ratio of dissolved Mo in seawater<sup>8</sup> and proved that Mo isotopes are uniformly distributed in the modern ocean<sup>1</sup>. Now we are developing a new analytical method to determine the isotopic ratio of dissolved W in seawater.

For solid samples, such as sediments and rocks, we have developed a method for precise analysis of the concentration and isotopic composition of Mo and W<sup>9</sup>. In this method, we realized an effective and simple removal of interfering elements by using a combination of chelating extraction and anion exchange. Now we are

applying this method to paleoceanographic study on marine sediment cores that had been collected from the Sea of Japan and the northeastern Arabian Sea. We will report the present status and overview of our study in the presentation.

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19-F8-13

## Dissolved Nd isotope ratios along the GEOTRACES Eastern Pacific Zonal Transect

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Keywords: GEOTRACES, EPZT, Ocean Circulation, Neodymium

The GEOTRACES Eastern Pacific Zonal Transect (EPZT, GP 16) encompasses a wide variety of ocean environments including a near shore oxygen minimum zone and Earth's most active ocean ridge, thereby offering a unique opportunity to study the biogeochemical cycling of Nd and the impacts on Nd isotopes. We report dissolved Nd isotopes with emphasis on whether it behaves as a conservative water mass tracer in the region, and the effects of hydrothermal input.

The EPZT can be broadly divided into two segments east and west of the mid-ocean ridge. The eastern segment shows  $\epsilon_{Nd} \sim -2$  from the surface to 1000 m, with values decreasing to  $\epsilon_{Nd} \sim -4$  to  $-5$  with increasing depth. The western segment shows slightly lower  $\epsilon_{Nd}$  values of  $\sim -3$  in upper 1000 m. Below 1000 m, like the eastern segment,  $\epsilon_{Nd}$  generally decreases with depth, typically to values of  $\sim -5$  to  $-7$ . However, western profiles, both over the ridge and farther west, show a prominent increase at 3000 m depth of  $\sim 1$   $\epsilon_{Nd}$ -unit, both at the ridge and along the western segment.

The surface signal can be attributed to particle contributions from continent and/or dust. Within the subsurface to upper 1000 m the  $\epsilon_{Nd}$  data can be explained as variable mixtures of Equatorial Subsurface Water ( $\sim -1.6$ , ESW) and Antarctic Intermediate Water ( $\sim -7$ , AAIW) with ESW dominating majority of the stations. Pacific Deep Water ( $\sim -4$ ) and Lower Circumpolar Deep Water ( $\sim -8$ ) dominate at depths  $>1000$  m. The higher  $\epsilon_{Nd}$  values within the upper 1000 m of the western segment suggest higher proportions of AAIW. The input of hydrothermal Nd to the ocean is generally considered to be

negligible due to scavenging at the ridge. The EPZT results indicate that hydrothermal Nd can alter the seawater Nd isotope composition near the ridge.

## Tectonically induced formation of the semi-closed Japan Sea inferred from Nd isotopes

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Keywords: Lead isotopes, GEOTRACES, Pacific Ocean, biogeochemical cycles

### 1. Abstract

Abstract The Japan Sea in the western North Pacific was connected to the deep Pacific via deep seaways before it became a semi-closed marginal sea. However, the timing of the semi-closure and its cause(s) remain debatable. To further constrain the timing, for the first time we analyzed Nd isotopic compositions of fossil fish teeth and fish debris deposited in the Japan Sea (Integrated Ocean Drilling Program [IODP] Site U1425, ~2000 m water depth) over the past 10 m.y. Neodymium isotope values ( $-4.5$  to  $-3.2$   $\epsilon$ Nd) in the Japan Sea prior to 4.5 Ma illustrate that the deep Japan Sea was composed of an admixture of less-radiogenic Lower Circumpolar Deep Water (avg.  $-4.3$   $\epsilon$ Nd) and more-radiogenic North Pacific Deep Water (avg.  $-2.2$   $\epsilon$ Nd), potentially with

inflow from the Okhotsk Sea. At 4.5 Ma,  $\epsilon$ Nd values fell to  $-5.5$   $\epsilon$ Nd within a span of 140 k.y., suggesting that the deep-water communication between the Japan Sea and the North Pacific rapidly declined. We argue that active mountain building in the northern Japan arc, initiated by accelerated Pacific plate motion from the late Miocene to mid-Pliocene, caused the shallowing/narrowing of the Japan Sea–Pacific seaways and rapidly made the Japan Sea semi-closed at 4.5 Ma. As a result, the Japan Sea circulation patterns were realigned; a cyclonic circulation was developed and drew less-radiogenic Amur River–influenced Okhotsk Sea water into the Japan Sea.

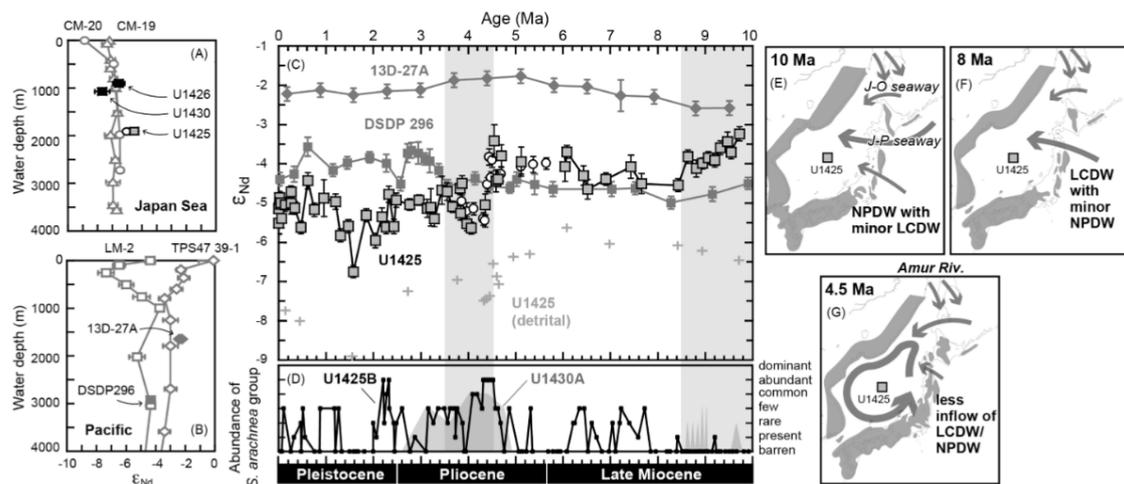


Fig. 1 C: Ten-million-year Nd isotope records from IODP Site U1425 and DSDP Site 296 and Fe-Mn crust 13D-27A (van de Flierdt et al., 2004). Detrital  $\epsilon$ Nd from Site U1425 is also shown. D: Semiquantitative abundance of radiolarian *Siphocampe arachneae* group from cores at Sites U1425B (black line) and U1430A (blue shading) in Japan Sea (Kamikuri et al., 2017). E–G: Schematic paleogeographic maps (modified from Sato, 1994), with intermediate- and deep-water circulation patterns inferred from Nd isotope records.

## Distribution and geochemical cycles of Pt in Ariake Sea, Japan

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Keywords: Platinum, semi-closed sea, river water, sediment, fractional dissolution

### 1. Purpose

Platinum (Pt) belongs to the least abundant group of elements (platinum group elements, PGEs) in the earth's crust (Wedepohl, 1995). Due to its specific and chemical properties, Pt has been used in a variety of industrial and medical applications, including automobile catalysis and anticancer drugs. At present, anthropogenic Pt has been emitted and dispersed to the environment at a global scale.

Vertical profiles Pt in coastal seawaters indicated increasing concentrations from surface to bottom (Mashio et al., 2017). Dissolved Pt might be supplied from seafloor sediment to seawater. However, the process how Pt is supplied to seawater from sediment has remained unsolved.

In this study, our purpose was to reveal the geochemical cycles of Pt between seawater and sediment in Ariake Sea. Ariake Sea is a semi-closed sea where we can examine the interaction among seawater, sediments and river water.

### 2. Methods

Seawater and sediment samples in this study were collected from Tachibana Bay and Ariake Sea in Kyushu area, Japan using Kakuyo-Maru (May 8 to 10, 2012, May 18 to 20, 2015, May 7 to 9, 2018). Moreover, we collected river water samples flowing into Ariake Sea just before the 2018 sampling time. We applied fractional dissolution of sediments to understand the chemical form of Pt in sediments. Chemical sequential extraction method included 5 steps (Tessier et al., 1979). We determined sub-picomolar levels of dissolved Pt using isotope-dilution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after column preconcentration with an anion exchange resin (Suzuki et al., 2014).

### 3. Results and Discussion

Pt concentrations ranged from 0.61 to 10.2 pmol/L in this study area. The highest Pt concentration, 10.2 pmol/L, was observed at the deepest St. A7. Pt concentrations at all stations were higher than those of open ocean seawater (about 0.2 pmol/L; Suzuki et al. 2014). The concentrations increased with depth toward the bottom. We observed decreasing concentration trend from the Hayasaki-Seto Strait to inner central area in Ariake Sea. Pt concentrations in river water samples were about 0.2 pmol/L at the same level as those of open ocean seawater. Higher Pt contents were found in exchangeable phase (E4; 0.43 ng/g) or bound to Fe & Mn oxide phase (A11; 1.26 ng/g) of the sediments. Pt contents in residual phases were 0.96 and 0.87 ng/g, respectively.

Since there was little supply of dissolved Pt from river to in Ariake Sea, most of Pt was estimated to be supplied from sediments. Loosely adsorbed Pt onto sediment might be desorbed by complexing with chloride and emitted to seawater.

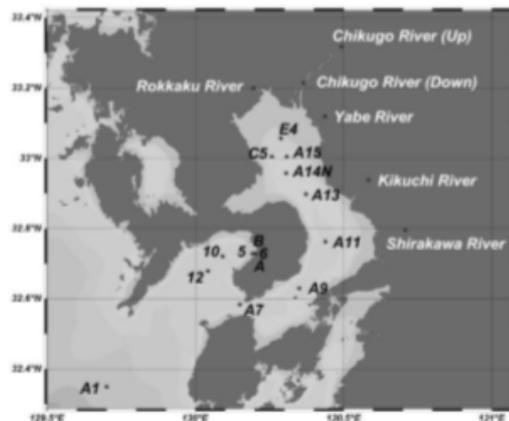


Figure 1 Sampling points

## Stimulated phosphorus utilization of microbes by zinc and iron addition in the western North Pacific

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Keywords: alkaline phosphatase activity, phosphorus, trace metal, co-limitation

### 1. Purpose

Phosphorus is one of the major growth limiting factors of marine microbial communities in the ocean. Thus, under phosphate depleted conditions, microbes express a metalloenzyme alkaline phosphatase in order to facilitate phosphorus acquisition from dissolved organic matters. Because alkaline phosphatase superfamily enzymes require either zinc or iron as a part of their reaction center, co-limitation of phosphate and zinc/iron is likely to occur in the surface layer of oligotrophic oceans, although the involvement of trace metals in the marine phosphorus cycle is not well understood. In this context, we aimed to elucidate effects of zinc/iron addition on phosphorus acquisition of microbial communities in the subtropical North Pacific Ocean.

### 2. Materials and Methods

On-board enrichment incubation experiments were conducted at 4 stations along a 23°N transect during the R/V Hakuho-maru summer cruise (Figure 1). Either 2 nM of zinc, 2 nM of iron, or 200 nM of phosphate was added to each of 5-L water samples pre-filtered with 100- $\mu$ m mesh, and the samples were incubated for 2 days in an on-deck running seawater bath. Alkaline phosphatase activity (APA), dissolved inorganic and organic phosphorus concentrations were measured, and microbial community structure was examined by flow cytometry.

### 3. Results and Interpretation

Initially, phosphate was severely depleted (< 3 nM) at the two western stations A and B, accompanied by increasing APA towards the west. APA was suppressed after phosphate addition at these stations, indicating

phosphate limitation in these regions. The most significant positive response to zinc/iron addition of APA (maximum 2.5/1.5 folds higher than control) was observed at Stn. B. Moreover, enhancement of APA by a single addition of iron and zinc was also observed at Stn. A and C, respectively. These results suggest that limiting factors of APA gradually shifted from iron to zinc along with distance from the Asian Continent. However, no obvious changes in nutrient concentrations or microbial community structures were observed in association with such enhancement of APA, except for an increase in heterotrophic bacteria abundance after zinc addition at Stn. B. Such ambiguous results may be attributable to the short incubation period or deficiency of other essential elements. In conclusion, we report the putative co-limitation of phosphate and trace metals on microbial communities for the first time in the western North Pacific Ocean. Our results suggest that phosphorus consumption in this region will be stimulated by sporadic supply of trace metals, leading to a progress in oligotrophication.

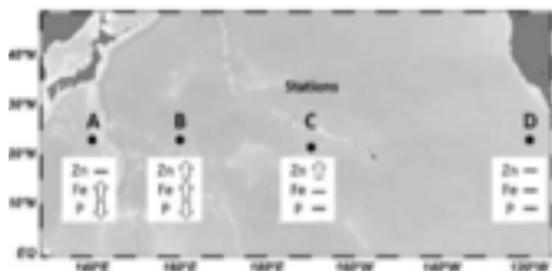


Figure 1 Station locations and the effect of reagent addition on APA. White arrows show either significant increase or decrease of APA in each treatment ( $p < 0.05$ ), whereas black bars show insignificant responses.

# Global biogeography of giant viruses highlights their interplay with eukaryotic community

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Keywords: Nucleocytoplasmic large DNA viruses (NCLDV), Biogeography, Metagenome, Arctic Ocean

## 1. Introduction

Nucleocytoplasmic large DNA viruses (NCLDVs) constitute a monophyletic viral group infecting a wide variety of eukaryotic lineages (Koonin and Yutin, 2012). NCLDVs are ubiquitous in marine environments with extremely high species richness (Hingamp et al., 2013; Li et al., 2018, Mihara et al., 2018). However, their ecological and geographical characteristics are poorly understood, due to the lack of knowledge about the global patterns of distribution, diversity, and host association. Here, we explore the distribution and the host association of NCLDV community using the Tara Oceans metagenomic data collected from the global biomes.

## 2. Data and Methods

Metagenomic samples were collected from the Tara Oceans expedition (2008–2013; Peasant et al., 2015) and the Tara Oceans Polar Circle (TOPC) (2013; Gregory et al., 2019). We used the latest version of the non-redundant gene catalog of ocean metagenomes (OM-RGC.v2; Salazar et al., submitted), which includes the samples from Tara Oceans projects (0.2– 1.6/3.0 and <0.2  $\mu\text{m}$  size fractions). We identified 7,020 NCLDV-derived B type DNA polymerase (polB) genes from OM-RGC.v2 using pplacer (Matsen et al., 2010). To evaluate the diversity of NCLDVs in each sample, Shannon's entropy was used. Non-metric multidimensional scaling (NMDS) based on Bray-Curtis similarity was employed to assess compositional variation among samples. In addition, Partial Mantel test (removing the effect of spatial autocorrelation) was performed to evaluate the associations between NCLDV and eukaryotic community.

## 3. Results and Discussion

Community and phylogenetic analyses suggest that the marine NCLDVs were composed mostly of algae-infecting lineages in the families Megaviridae and Phycodnaviridae in all sampling

sites and depths. Although almost NCLDV phylotypes were shared across world ocean, the Arctic Ocean had higher proportion of unique NCLDVs, likely reflecting the distribution of their specific host species. Consequently, NCLDV communities in the Polar biomes (Arctic and Antarctic Oceans) were clearly distinct from others. The Shannon diversity of NCLDVs peaked in tropical and subtropical regions and declined toward the poleward, and this trend agreed well with that of their known host community (Ibarbalz et al., in revision). Significant correlations were found between the community structures of NCLDVs and their known hosts, especially phytoplankton lineages such as chlorophytes and haptophytes, indicating the strong interplay in structuring these communities. Our results suggest that the NCLDVs follow the distribution of their hosts, but would have significant roles on controlling the local microbial structure in the ocean.

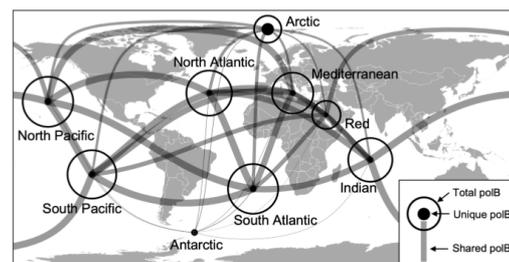


Figure 1. A synthesis map showing the numbers of total and unique NCLDV polB phylotypes in each region. The numbers of shared phylotypes between two regions are also shown.

## The change of material flux via SGD and its impact on coastal ocean

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Keywords: Submarine Groundwater Discharge(SGD), Climate Change, Nutrient and Carbon flux

### 1. Introduction

Submarine Groundwater Discharge(SGD) is one of the processes of water and nutrient transport from the land to the ocean, and it is recognized worldwide that it is important for basic production of the coastal ocean. In Toyama Bay, Fresh SGD supply a large amount of dissolved nutrients to coastal ocean, which have been indicated to contribute significantly to primary activities on surface ocean (Hatta and Zhang, 2013). However, in recent years, it reported that, the amount of snowfall decreased in the Hokuriku region including Toyama Prefecture, while the amount of rainfall has increased (Japan Meteorological Agency, 2015; Yasunaga and Tomochika, 2017). As a result of this change, the amount of SGD in Toyama Bay increased by up to 30% in 30 years (Zhang et al. 2017). This quantitative change of the seafloor springs is considered to bring about a qualitative change at the same time. The aims of this study are (1) to understand the changes of water quality associated with climate change, and (2) to evaluate the impact on material supply to the coastal ocean in Toyama Bay.

### 2. Data and Methods

SGD samples were collected at the water depth of about 8 m. We also conducted shallow groundwater and the upstream rivers in the Katakai River Alluvial Fan linked to SGD. In addition, in order to understand the overview of the water and material transport from the land to Toyama Bay, we investigated five First-class rivers. SGD was collected directly by scuba diving and about 1L sample was successfully collected by suctioning with the syringe attached to the device shown in figure 1.

Samples of SGD, groundwater, and river water were immediately measured for water temperature, pH, and electrical conductivity at the each sites, and the

concentrations of major chemical components (nutrients, cations, anions, etc.) were measured in the laboratory. We also measured hydrogen and oxygen stable isotopes( $\delta D$ ,  $\delta^{18}O$ ) using water isotope ratio analyzers (Picarro L2120-i, L2130-i) owned by the Research Institute for Humanity and Nature.

### 3. Results and Discussion

Comparing the past (2000-2003) and present (2017-2018), it was confirmed that the concentration of bicarbonate increased, while the nutrient concentration decreased. In addition, the isotope values ( $\delta D$ ,  $\delta^{18}O$ ) of SGD, shallow groundwater, and river water also decreased. These results mean that the residence time was more shorter, which was supported by the results of tritium concentration.

Furthermore, we calculated the amount of material supply from the land to Toyama Bay via the river and SGD using the results of previous studies and this study. As a result, nutrient flux decreased by from 40 to 80% and the carbon flux increased two times over the past 10 years.

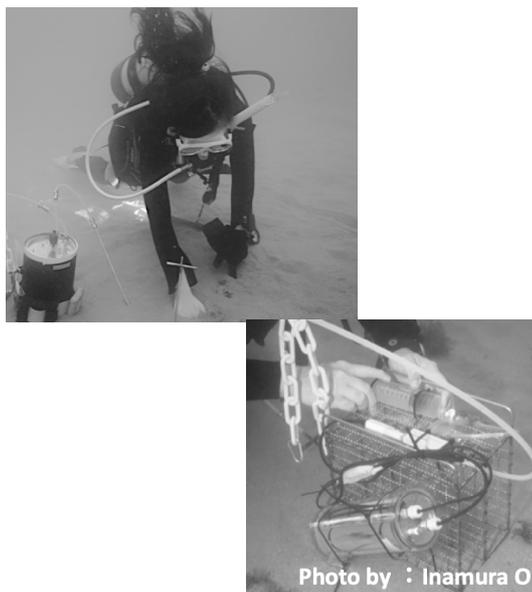


Fig1. Sampling for SGD

# Transport of the upper Kuroshio Intermediate Water 19-F8-P2 from northwestern Pacific to the Sea of Japan: using $^{137}\text{Cs}$ as a tracer

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Keywords:  $^{137}\text{Cs}$ , subtropical mode water, water masses, KIW, nutrients

## 1. Abstract

Kuroshio is the western boundary current of the Pacific providing abundant nutrients from its intermediate water (KIW). However, vary lack research, especially using direct chemical tracers to track the transport and quantify the nutrients flux of the KIW, which contains abundant nutrients, was in the previous studies.  $^{137}\text{Cs}$  in the subtropical mode water (STMW) that originated in the Fukushima Dai-ichi Nuclear Power Station (FDNPS) accident is an excellent tracer and it can also be useful to research the transport of the KIW. In this study, transport of the upper Kuroshio intermediate water from northwestern Pacific to the Sea of Japan was shown approached using the direct evidence  $^{137}\text{Cs}$ .

Data and water samples were collected from the Hakuho-Maru KH-17-5 Cruise and Nagasaki-Maru 464 Cruise in November and July 2017 respectively. Data from KH-17-5 Cruise was used for the study of area around the Luzon Strait and those of the Nagasaki-maru 464 Cruise was used for the study of area around outer shelf region of the East China Sea (ECS) and the Tsushima Strait. The  $^{137}\text{Cs}$  active concentration was analyzed by the  $\gamma$ -Ray spectrometry after preconcentration. The turbulence intensity was measured using TurboMAP and VMP2000.

$^{137}\text{Cs}$  from the FDNPS accident inked onto the STMW in the North Pacific at a depth of 300-400 m, and then STMW was observed in the Luzon strait after mixing with the origin of the Kuroshio through diffusion and vertical mixing which is consistent with Vigan Mensah's research. The KIW is transported from Luzon Strait northward to Tokara Strait via the continental shelf margin of the East China Sea, and part of it is transported to the Sea of Japan via Tsushima Strait traced using  $^{137}\text{Cs}$ . The water mass with the maximum value of  $^{137}\text{Cs}$  was identified as STMW, the upper layer of KIW, and its depth gradually decreases from 400 m in Luzon to 150

m in ECS, and finally about 100 m in Tsushima Strait. The Tsushima warm current in depth of 100 m can be identified as KIW, rich in nutrients, by our analysis of  $^{137}\text{Cs}$  and potential density. The flux and contribution of KIW to the west channel of the Tsushima warm current and to the whole Tsushima warm current were calculated using current velocity and nutrients data in the same season, which is about 22% and 8% of the DIN in Tsushima warm current from KIW. It is the first time that the transport of the upper Kuroshio intermediate water from northwestern Pacific to the Sea of Japan was intuitively shown

## Significance of Fukushima-derived radiocesium flux via river-estuary-coastal ocean system

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Keywords: Fukushima-derived radiocesium; Submarine groundwater discharge; Recycled saline groundwater discharge; Export flux into the ocean

### 1. Introduction

Riverine input is a major pathway for discharge from land to the ocean. Furthermore, submarine groundwater discharge (SGD) has been recognized as an important source flowing into the ocean. The concentration of radionuclides in SGD are often dramatically higher than in river water. Moreover, Charette et al. (2013) raised the possibility that the SGD-derived radiocesium flux to the ocean increases due to seawater intrusion driven by tidal pumping or seasonal changes in the hydraulic gradient. However, few reports have been published on subsurface pathways as a source of radiocesium. The major goals of this study are to explore the distribution of Fukushima-derived radiocesium in river-estuary-coastal ocean system and to evaluate the export flux from land to coastal ocean, including SGD. To accomplish these goals, we investigated activity concentration of radiocesium in Matsukawa-ura Lagoon, the largest lagoon in Fukushima.

### 2. Materials and Methods

Water samples (river water, groundwater and estuarine water) were collected from October, 2014 to October, 2016. The salinity was also measured with a sensor. Water samples were filtered through a 0.45- $\mu\text{m}$  membrane filter. In addition, sediment samples (from surface to 5 cm below lagoon bottom) for obtaining pore water were collected on October, 2016. Sediment samples were squeezed by a centrifuge (3,000 rpm, 30 min). After centrifugation, a pore water sample was filtered through a 0.20- $\mu\text{m}$  membrane filter. Dissolved radiocesium was concentrated on ammonium phosphomolybdate (AMP). The activity concentration was measured with Ge detectors. All of the activity concentration values were decay-corrected to the sampling date.

### 3. Results and Discussion

Activity concentration of dissolved  $^{137}\text{Cs}$  showed excess from low to intermediate salinity (<0.1 - 18) in the estuarine water. This increase in activity concentration of dissolved  $^{137}\text{Cs}$  was most likely the result of desorption from particles when the riverine particles mixed with seawater. In the polyhaline and euhaline zone (> 18.0), the activity concentration of dissolved  $^{137}\text{Cs}$  gradually decreased due to dilution caused by seawater. These results suggest that dissolved radiocesium behaved non-conservatively via river-estuary-coastal ocean system. Moreover, activity concentration of  $^{137}\text{Cs}$  in pore water was much higher than in overlying water, suggesting that a significant amount of radiocesium in sediment desorb into pore water. From results of mass balance model, dissolved  $^{137}\text{Cs}$  flux from lagoon bottom such as recycled saline groundwater discharge (RSGD) is about 15 times greater than riverine input including desorption from particles. This result implies that RSGD is the major radiocesium source flowing into the lagoon. Moreover, the export fluxes of dissolved  $^{137}\text{Cs}$ , including RSGD from the Pacific coast of eastern Japan to the coastal environment, were estimated to be up to 4 times greater than the sum of the values for riverine input and ongoing release from the Fukushima Daiichi Nuclear Power Station harbor. Thus, RSGD plays an important role in the system of radiocesium discharge from land to coastal ocean.

# Atmospheric Nitrogen Deposition on The Sub-Tropic NWPO and Its Impact

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Kyusyu University, 6. The University of Tokyo

Keywords: Pacific ocean • Aerosol • Phytoplankton • Nutrients

## 1. Introduction

It has been suggested that aerosols (particulates in the atmosphere) such as continent-derived loess and anthropogenic dust carried by the monsoon wind and the westerly wind play a very important role in surface ocean primary production (Yuan et al., 2006). Previous study report that spring dust events in Asia increase the base production of the western North Pacific by more than 70% (Yoon et al., 2017). There is a need to evaluate the impact of aerosols on marine phytoplankton and the marine environment. However, there are not many observation researches at these sites today, and there are few observations especially on the ocean. Observation research in the field is important for model creation and the model's accuracy improvement. Therefore, in this study, we aimed material transport between the atmosphere and the ocean focusing on nutrients deposition and surface primary production.

## 2. Methods

In this study, aerosols and surface seawater were collected during the R/V Hakuho-maru KH-17-5 cruise (2017.11.14-12.18). Nutrients and REEs in the aerosol sample. The aerosols were collected using a high volume air sampler (SHIBATA HV1000-F). Major chemical components, nutrients and rare earth elements in the aerosol, were extracted into MilliQ water and measured. Surface water was collected using a pump during the cruise. The Chl-a samples were extracted using D MF after filtering during the cruise, and later were measured using a fluorometer (Turner designs 10-AU). The biomarkers were measured at the Ocean University of China.

## 3. Results & Discussions

Analyses of REEs in the aerosols showed that the atmospheric dust (aerosol) is a mixture of loess, coal smoke and sea salt. Their ratios were calculated as 60%, 26%, and 14%, respectively. From this, it was inferred that the majority of aerosols flying to the Pacific Ocean originated from or passed through the Chinese continent rich in loess and dust, and the actual amount of sedimentation could be quantified.

A positive correlation was found between TDIN deposition and the surface Chl-a concentration ( $R=0.89$ ).

Furthermore, the ratio of different phytoplankton species changed according to the amount of nutrients deposition. The change in the proportion of brassica sterol shows the amount of diatoms increases with  $\text{NO}_3^-$  deposition. The value of  $\text{NH}_4^+$  do not fluctuate. It is suggested that not only the amount of nutrients deposition but also the kind of nutrient influence the composition of phytoplankton species. We focused on the Luzon Strait to compare winter vertical mixing, which is one of the major sources of nutrient supply in the open ocean, and nutrient deposition from the atmosphere. The required amount of nitrogen nutrient determined from the integrated value ( $17\text{-}24 \mu\text{mol} / \text{m}^3$ ) of 0-80 m of the Chl-a concentration was approximately  $2.3\text{-}3.6 \mu\text{mol} / \text{m}^3$ . The amount of nitrogen deposition in the Luzon Strait was  $25 \mu\text{mol} / \text{m}^2 / \text{day}$ . We found that nutrient sedimentation completely met the phytoplankton requirements. These results prove that nitrogen from the atmosphere plays an important role in this area.

## 4. Conclusions

About half of the aerosols in the subtropical area of Northwestern Pacific comes from loess, then 30% and less than 20% from coal smoke and sea salt respectively, estimated by using dissolved Rare Earth Elements in aerosols. A positive correlation was found between the nutrient deposition and Chlorophyll-a concentration in surface sea water. The phytoplankton species composition is influenced by the amount of nutrient deposition and different speciation of nutrients. The estimation of consumed nutrient from C-Chl-a integration (<80m) is  $N=2.2\pm 0.59 \mu\text{mol}/\text{m}^3$ ,  $P=0.13\pm 0.05 \mu\text{mol}/\text{m}^3$  in surface water column. However, the deposition of N from atmosphere into the surface ocean was estimated  $25 \mu\text{mol}/\text{m}^2/\text{day}$  in this study. Furthermore, in the Luzon Strait area, the integrated N (<80m) is 1.7 times higher, where strong vertical mixing observed, comparing with those stations with very weak vertical mixing. In summary, the nutrient deposited from atmosphere plays an important role in the phytoplankton on the surface subtropical western north Pacific ocean.

## Cu-binding organic ligands and dissolved organic matter in coastal waters

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Keywords: organic ligand, dissolved copper, dissolved organic matter, incubation experiments

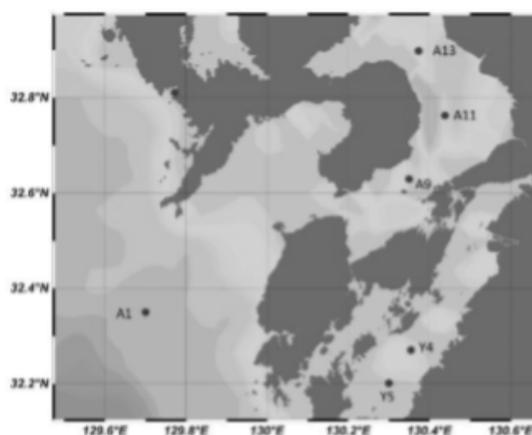
Copper is a bio-essential element to most microorganism at low concentrations, but at high concentrations free copper ( $\text{Cu}^{2+}$ ) can be toxic. Copper in seawater is predominantly complexed by strong organic ligands exuded by phytoplankton to reduce toxic  $\text{Cu}^{2+}$  concentrations. Previous studies showed Cu-binding organic ligands were correlated with terrestrial humic substances in seawater (e.g., Kogut and Voelker, 2001). Therefore, in order to understand how organic ligands for Cu were produced in seawater, we investigated the relationship between Cu-binding organic ligands (concentrations and conditional stability constants) and dissolved organic matter (DOM) by incubation experiments.

Seawater samples used for the incubations were collected from Ariake Sea (A11 in Fig. 1) and Otsuchi Bay, Japan in May 2019. These experiments were conducted at constant temperature ( $20^{\circ}\text{C}$ ) under light and dark conditions. For some samples, adequate amounts of nitrate and phosphate were added. One extra set of the incubation experiment using Otsuchi Bay water was conducted in the presence of zooplankton. The samples were incubated for 1, 3, 5, 7, and 14 days. Copper speciation parameters were determined by competitive ligand exchange adsorptive cathodic stripping voltammetry (CLEadCSV) using salicylaldehyde (SA) as the competing ligand (Campos and van den Berg, 1994; Wong et al., 2018). Chromophoric DOM (CDOM) absorbances were measured at 200–800 nm using a dual beam spectrophotometer, while fluorescent DOM (FDOM) patterns were measured in the range of 250–500 nm and 280–600 nm for the excitation and emission by using a spectrofluorometer.

Preliminary data showed total dissolved copper concentrations gradually decreased with incubation time. CDOM absorption coefficient at 440 nm ( $a_{440}$ ) increased under nutrient-rich condition compared to other samples.

FDOM results for Ariake Sea samples showed that there are four components including two protein-like and two humic-like components. Using CLE-adCSV, organic ligands were detected in both Ariake Sea and Otsuchi Bay samples, whose conditional stability constants were approximately  $10^{14}$ . The relationship between the organic ligands and DOM (CDOM and FDOM) were being investigated in this study.

Fig. 1. Map of the sampling location in Ariake Sea



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## Factors affecting radiocesium concentration in sediment off Fukushima: Lateral transport of particles

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Keywords: Radiocesium, Sinking particles, Seabed sediment, Fukushima Daiichi NPP

### Introduction

The accident of Fukushima Daiichi Nuclear Power Plant (FDNNP) that occurred in March 2011 is an unusual event in which a large amount of radionuclides was released directly to the ocean. At present, accurately understanding the dynamics of the radionuclide in the ocean on a decadal scale and clarifying the factors are one of the issues that marine chemists should be addressed. It is known that a few percent of the radiocesium released to the ocean by the accident has deposited on the coastal seabed. Although the concentration of radiocesium in the seabed showed a gradual decreasing trend with time, the decreasing rate was not always constant, and it is pointed out that various processes affected the behavior of radionuclides near the seabed. In this study, in order to clarify the transport process of suspended radiocesium from the coast to the offshore area, which is one of the processes that change the inventory of radionuclides in sediments, a sediment trap experiment was conducted for one year at the southeast station of the FDNNP.

### Materials and Methods

From May 2017 to June 2018, a time-series sediment trap was deployed 10 m above the seafloor at the station located at about 50 km (37° 00' N, 141° 25' E, bottom depth 210 m) offshore of Iwaki City. Sinking particles for 39 periods were collected at intervals of 5 to 30 days. The activity concentrations of two radiocesium isotopes (<sup>134</sup>Cs, <sup>137</sup>Cs) were measured as accident-derived radionuclides and the major components (biogenic opal, biogenic carbonates, lithogenics, organic matter) and lead-210 (<sup>210</sup>Pb) activity concentrations were measured as indicators of the characteristics of sinking particles. Seabed sediment samples collected from the mooring station and the surrounding area were also analyzed in the same manner as sinking particles. A current meter was installed at the same depth as the sediment trap, and water temperature, current direction, and current velocity were observed during the sampling period.

### Results and Discussion

<sup>137</sup>Cs was detected from sinking particles throughout the observation period, and the <sup>137</sup>Cs activity concentration showed clear seasonal variation. The <sup>137</sup>Cs concentration in the sinking particles showed a

maximum value during the period in December 2017 (110 Bq kg<sup>-1</sup>, decay corrected to March 11, 2011). This concentration was an order of magnitude higher than the <sup>137</sup>Cs concentration in the surface sediment (0-1 cm layer) at the same station. On the other hand, the <sup>137</sup>Cs concentration in summer (May to September) was about 1 to 15 Bq kg<sup>-1</sup>, and showed a similar to or lower than that of surface sediments. Although <sup>134</sup>Cs was below the detection limit in many periods due to the small amount of samples and fast radioactive decay of <sup>134</sup>Cs, most of the radiocesium detected in this study is presumed to be accident-derived. The total mass flux observed with the sediment trap ranged between 143 and 1732 mg m<sup>-2</sup> day<sup>-1</sup>, and several maxima exceeding 1000 mg m<sup>-2</sup> day<sup>-1</sup> occur from March to June were observed. Since the major component of the sinking particles during this period was lithogenics, it can be considered that the high mass flux was mainly due to the supply of riverine particles and the resuspension of sediments. In this season, contentious southward flow was observed near the seafloor. From these results, it was found that <sup>137</sup>Cs-bound particles were laterally transported in this season from coastal area including the vicinity of the FDNNP. From the mass balance of <sup>210</sup>Pb (particle-reactive natural radionuclide) in the water column at the mooring station, it was estimated that the station is located in the area where particles are imported from the surrounding area. Nevertheless, the observed annual <sup>137</sup>Cs particle flux was less than 3% of the <sup>137</sup>Cs inventory in the seabed (1250 Bq m<sup>-2</sup>) at the mooring station. From these results, it can be concluded that the transport of <sup>137</sup>Cs-bound particles from the coastal area has a relatively small effect of changing the abundance of <sup>137</sup>Cs in sediments. Regarding the detailed process, relatively high concentrations of <sup>137</sup>Cs were detected from the settling particles from late fall to winter (November to February). Sinking particles collected in this period had a slightly higher proportion of organic matter. These results are considered to indicate that organic matter particles which incorporate <sup>137</sup>Cs accumulated on the seabed were remobilized by disturbance near the seafloor in late autumn. Although the magnitude is quite small, the transport of radionuclides associated with organic matter is a remarkable process in consideration of the migration of bioavailable radionuclides near the seafloor.

# Applications of Radium Isotopes to Marine Flux Studies

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Keywords: Radium, Ocean, Flux, Elements

## 1. Abstract

Combinations of radium isotopes ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $^{223}\text{Ra}$ ) have been successfully used to trace water mixing and transport in the ocean. Due to their difference in half lives,  $^{224}\text{Ra}$  (half life: 3.4 d) and  $^{223}\text{Ra}$  (half life: 11.3 d) are suitable for application to the coastal ocean, while  $^{228}\text{Ra}$  (5.8 y) and  $^{226}\text{Ra}$  (1622 y) are more useful for basin-scale studies. In the ocean, Ra isotopes are produced primarily from marine sediments enriched with their parents. There are additional sources from groundwater and river water where the isotopes are an order of magnitude enriched relative to open-ocean seawater. Amongst these Ra isotopes,  $^{228}\text{Ra}$  is an ideal tracer of fluxes on a basin scale since its decay and transport/mixing of sedimentary sources produce large

gradients across important oceanic interfaces: cross continental-shelves, upper-deep oceans, and benthic boundary layers. However, such applications of Ra isotopes have been hampered mainly by difficulties resulting from their extremely low-level activities in the ocean. In this study, I demonstrate how we can more efficiently measure Ra isotopes in the ocean and how the scarcity of Ra data can be complemented by extrapolation of available data using an inverse model. Then, I will briefly introduce how we can apply these Ra data (observed and modeled) to hot issues in modern marine biogeochemistry including submarine groundwater discharge, cross-shelf fluxes of chemical constituents, and carbon sequestration in the ocean.