GEOTRACES-CHINA GP09 wNP Section Study

Cruise Report

R/V Tan Kah Kee (KK1903)

April 25, 2019 – June 13, 2019

Chief Scientists: Yihua Cai and Kuanbo Zhou
State Key laboratory of Marine Environmental Science, Xiamen University

June 13, 2019

Contents

1. Executive Summary

The Chinese GEOTRACES GP09/KK1903 Cruise was conducted aboard R/V Tan Kah Kee from April 25th to June 13th, 2019, in the western North Pacific Ocean. The cruise was led by the State Key Laboratory of Marine Environmental Science of Xiamen University (MEL) and Peking University (PKU), and was joined by scientists from Second Institute of Oceanography of Ministry of Natural Resources of China (SIO), Ocean University of China (OUC), Shanghai Jiaotong University (SJTU), Tianjing University of Science and Technology (TUST) as well as scientists from international institutes, including University of Maine, The University of Western Ontario, GEOMAR Helmholtz Centre for Ocean Research, and University of Toyama.

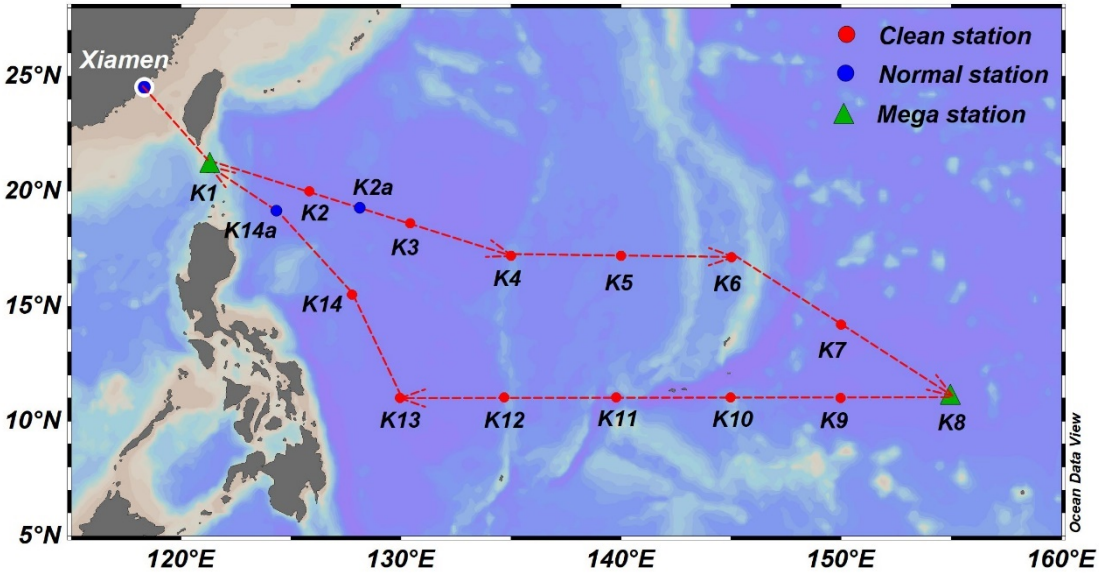


Figure 1. GP09/KK1903 Cruise track

The North Pacific Subtropical Gyre (NPSG) is globally the largest oligotrophic regime and ecosystem, occupying roughly 30% of the world's ocean surface. Macronutrients are thought to play a significant role in shaping the structure and function of ecosystem in the NPSG, therefore regulating the marine carbon cycles and global climate change.

Compared to the eastern part of the North Pacific Ocean, in which two section cruises (GP02 and GP15) have been successfully executed and ongoing time-series investigation are conducted at the ALOHA station, the western (sub)tropical North Pacific Ocean remains largely undersampled and understudied to date.

The GP09 section is situated in the western (sub)tropical North Pacific Ocean and was designed to explore the biogeochemistry of trace elements and isotopes (TEIs) in the western North Pacific (wNP), covering the study area between 10-21°N and 118.5-155°E with a set of 16 stations, including 2 Mega Stations, 12 Clean Stations, and 2 Normal Stations. The main purposes of the GP09 Section Cruise are to obtain the full water column distribution of TEIs and to improve the understanding of sources, sinks and internal cycling of TEIs in the wNP as part of the international GEOTRACES program. The coupling between TEIs with macronutrients and the relation of trace element cycling in the wNP to the oceanic carbon cycle and global environmental and climatic change will be examined as well. Specifically, the major scientific objectives of this cruise are as follows:

1) To examine the vertical profiles of TEIs and their spatial distribution in the wNP;
2) To fingerprint the sources and transport of TEIs in the wNP;
3) To constrain the nutrient (co)limitation of nitrogen fixation and primary production in the wNP;
4) To investigate the regeneration of micro- and macro-nutrients in the wNP;
5) To understand the TEIs biogeochemical cycling in the wNP with the integration of regional biogeochemical models.

Seawater, particles, and aerosol samples were collected in this cruise for the determination of TEIs as well as biological and chemical auxiliary parameters, including nutrients, DIC, DO, pigments, etc. A series of on-deck incubation experiments were also conducted with emphases on the interactions between ecosystem functions and macro- and micro-nutrient supply. Turbulence dissipation rate,

hydrological parameters (T, S, Turbidity, etc), and meteorological parameters were measured at stations and/or underway. Seawater samples were collected with a conventional CTD and a trace metal clean CTD, respectively, while particles were collected by McLane In-Situ Pumps with a SBE37IM CTD attached to each pump. Near-surface underway seawater samples were also collected from a towed fish sampling system for multiple purposes, including TEIs, nutrients, Chla, and on-deck incubations. Nutrient profiles, including nanomolar level phosphate and nitrate in shallow water column, were analyzed aboard for each station. GEOTRACES key trace elements and isotopes in collected samples will be analyzed after the cruise in shore-based laboratories. In addition, some other elements and isotopes, including REEs, ^{234}Th, ^{210}Pb-^{210}Po, and silicon and barium isotopes, will be analyzed after the cruise as well.

We sincerely acknowledge Captain Long Yin, the crew, and the marine technical support team of the R/V Tan Kah Kee for their invaluable and successful support of all shipboard operations. Sincere thanks are also given to the Office for Research Vessel Operation Center of Xiamen University for its flawless logistic support to the cruise. We specially thank Robert F. Anderson (Columbia University), Gregory Cutter (Old Dominion University) and the whole international GEOTRACES community for their continual scientific advices and technical instructions to make the cruise possible. Thomas J. Browning (GEOMAR) help proofreading of this cruise report.

2. Principle Programs

Table 1 Principle programs in GEOTRACES GP09/KK1903 cruise

Parameters	Sampling method	Principle Investigator	Affiliation
Fe/Zn/Cd/Cu/ Co/Ni/Pb	TMC CTD In-situ Pump Towed Fish Aerosol	Yihua Cai Kuanbo Zhou Ruifeng Zhang Qian Liu Jing Zhang	Xiamen University Shanghai Jiaotong University Ocean University of China University of Toyama
Al/Mn	TMC CTD Towed Fish Aerosol	Jingling Ren Jing Zhang	Ocean University of China University of Toyama
REEs	TMC CTD Towed Fish Aerosol	Qian Liu Jing Zhang	Ocean University of China University of Toyama
Hg	TMC CTD Towed Fish Aerosol	Yanbing Li Jing Zhang	Ocean University of China University of Toyama
Fe/Cd isotopes	TMC CTD Towed Fish	Ruifeng Zhang	Shanghai Jiaotong University
V/Mo	TMC CTD Towed Fish Aerosol	Alan M. Shiller Jing Zhang	University of Southern Mississippi University of Toyama
Pb isotopes	TMC CTD	Kuanbo Zhou	Xiamen University
Nd isotopes	Conventional CTD	Qian Liu Jing Zhang	Ocean University of China University of Toyama
^{14}C-DIC/ H_2O isotopes	Conventional CTD	Liping Zhou	Peking University
Bottle Salinity/ (Nanomolar) Nutrient	TMC CTD Conventional CTD	Minhan Dai	Xiamen University
^{15}N-NO_3	Conventional CTD	Jingyu Yang Shuh-Ji Kao	Xiamen University
DO/DOC/ Carbonate system	Conventional CTD	Minhan Dai	Xiamen University
Si/Ba isotopes	Conventional CTD	Zhimian Cao	Xiamen University
^{234}Th/POC/ ^{13}C-POC	Conventional CTD In-situ Pump	Minhan Dai	Xiamen University
^{210}Po-^{210}Pb ^{230}Th/^{232}Th	Conventional CTD	Yihua Cai	Xiamen University

Pigments	Conventional CTD	Bangqin Huang	Xiamen University
Primary Production/ Diazotroph composition	Conventional CTD	Dalin Shi	Xiamen University
Anions/Nutrients/ S isotopes	Aerosol	Jing Zhang	University of Toyama
Amino Acids/ Nutrient/Major Ions	Aerosol	Tiantian Tang Shuh-Ji Kao	Xiamen University
pico-plankton abundance/ pigment absorption	Conventional CTD	Fei Chai	Second Institute of Oceanography
Turbulence	VMP	Zhiyu Liu	Xiamen University
On-deck incubation	Conventional CTD Towed Fish	Dalin Shi Shuh-Ji Kao Mark Wells Charles Trick Fei Chai Thomas Browning	Xiamen University University of Maine University of West Ontario Second Institute of Oceanography GEOMAR

3. Cruise Participants

Table 2 Participants in GEOTRACES GP09/KK1903 cruise

Name	Shipboard Duties	Email	Affiliation
Yihua Cai	Chief Scientist TMC CTD operation	yihua_cai@xmu.edu.cn	Xiamen University
Kuanbo Zhou	Chief Scientist In-situ Pump operation	kbzhou@xmu.edu.cn	Xiamen University
Yaojin Chen	FIA analyst/Deck/ Towed fish	yj_chen@xmu.edu.cn	Xiamen University
Liping Ye	TMC CTD Supertech	lpye@xmu.edu.cn	Xiamen University
Yaqian Zhou	FIA analyst	1534038715@qq.com	Xiamen University
Xin Wang	^{230}Th/^{210}Po-^{210}Pb	851823968@qq.com	Xiamen University
Hao Jin (4.25-5.9)	TMC CTD sampling/ Aerosol	996317793@qq.com	Xiamen University
Lifang Wang	Nutrients	lifang@xmu.edu.cn	Xiamen University
Junhui Chen	POC/In-situ Pump	cjh@xmu.edu.cn	Xiamen University
Kan Zhang	In-situ Pump Supertech	1043638089@qq.com	Xiamen University
Yifan Ma	^{234}Th/In-situ Pump	yivanma@stu.xmu.edu.cn	Xiamen University
Jing Liu	Nutrients/Deck	liujing@stu.xmu.edu.cn	Xiamen University
Yangyang Zhao	DO/Carbonate	yyzhao@stu.xmu.edu.cn	Xiamen University
Yating Li	BSi/Ba	liyating@stu.xmu.edu.cn	Xiamen University
Zixiang Yang	In-situ Pump/Aerosol	644976706@qq.com	Xiamen University
Siqi Wu	N_2 fixation incubation	715263726@qq.com	Xiamen University
Feipeng Xu	Pigments	448761535@qq.com	Xiamen University
Zuozhu Wen	On-deck incubation/ towed fish	wenzuozhu2014@ stu.xmu.edu.cn	Xiamen University
Wenfang Lin	On-deck incubation	lwf@xmu.edu.cn	Xiamen University
Rongbo Dai	On-deck incubation/ Towed fish	dairongbo@stu.xmu.edu.cn	Xiamen University
Ruifeng Zhang	Towed fish/TMC CTD/ On-deck incubation	ruifengzhang@sjtu.edu.cn	Shanghai Jiaotong University
Zhan Shen (5.15-6.13)	Towed fish/TMC CTD/ On-deck incubation	oucshenxiaozhan@163.com	Shanghai Jiaotong University
Yuanli Zhu	Towed fish/ Conventional CTD/ On-deck incubation	zyl0218@163.com	Second Institute of Oceanography
Qiang Hao	Towed fish/ On-deck incubation	haoq@sio.org.cn	Second Institute of Oceanography

Yuanyuan Feng	On-deck incubation	yfeng@tust.edu.cn	Tianjing University of Science and Technology
Mark Wells	Towed fish/ On-deck incubation	mlwells@maine.edu	University of Maine
Charles Trick	On-deck incubation	trick@uwo.ca	University of West Ontario
Qian Liu	REEs/Nd Isotopes/ Towed fish	liuqian@ouc.edu.cn	Ocean University of China
Siteng Zhu	REEs/Nd Isotopes/ Aerosol	542222670@qq.com	University of Toyama
Chang Liu	Hg/Deck	nmgtllc@163.com	Ocean University of China
Yongrui An (4.25-5.9)	^{14}C-DIC/H_2O isotopes	yongrui@pku.edu.cn	Peking University
Na Qian (5.15-6.13)	^{14}C-DIC/H_2O isotopes	qianna@pku.edu.cn	Peking University
Tom Browning	On-deck incubation	tbrowning@geomar.de	GEOMAR
Xuewen Wu	Chief Marine technician	wxw790726@xmu.edu.cn	Xiamen University
Jiannan Cai	Marine Technician	jncai@xmu.edu.cn	Xiamen University
Chengmiao Ye	Marine Technician	yecm@xmu.edu.cn	Xiamen University
Xirong Chen	Marine Technician	136847419@qq.com	Xiamen University
Peng Tan	Marine Technician	648506177@qq.com	Xiamen University

4. Sampling and parameters

4.1. Conventional CTD

4.1.1. Instrument information (By Xirong Chen)

Table 3 Instrument information

Instrument	Parameters	Station Number	Cast Number
Regular CTD (SBE 911 plus)	Temperature	16	79
	Conductivity/Salinity		
	Pressure/Depth		
	Oxygen		
	Fluorescence		
	Beam Transmission		
	PAR/Irradiance		

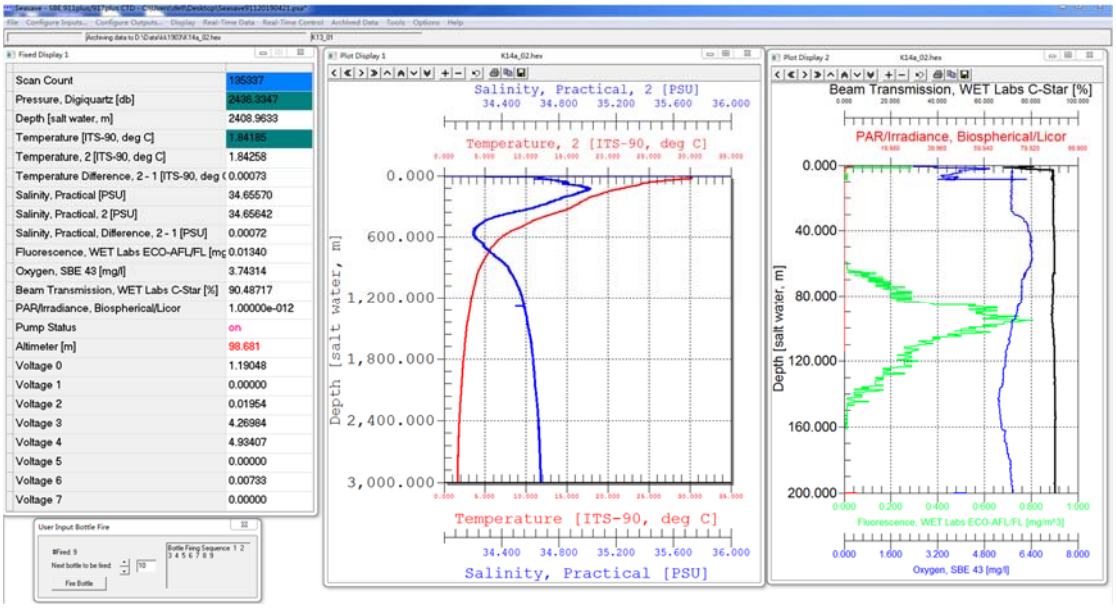


Figure 2. Vertical profiles of CTD parameters at station K14a

4.1.2. Pigments (By FeiPeng Xu, Bangqin Huang)

Analytical Methods:

- Chlorophyll-*a* concentration: 500 mL seawater collected with the regular CTD from

each depth (5m, 15m, 25m, 50m, 75m, 100m, 120m, DCM, 140m, 160m, 180m, 200m) was filtered onto Machery Nagel GF/F filter papers and extracted for 16-20 hours with 10 mL 90% analytical reagent grade acetone in a -20 °C freezer in the dark before measurement on a Turner Designs fluorometer following the method of Welschmeyer (1994).

- High Performance Liquid Chromatography (HPLC): 4-6 L seawater collected with the Regular CTD from each depth (5m, 15m, 25m, 50m, 75m, 100m, 120m, DCM, 140m, 160m, 180m, 200m) was filtered onto Machery Nagel GF/F filter papers and placed directly into a -80 °C freezer. Pigment concentrations will be analysed following the method of Gibb et al. (2000). Chlorophyll-*a* concentrations determined by HPLC will be used to verify those determined by fluorimetry.
- Analytical flow cytometry: 1.8 mL of seawater is mixed with 20μL 16% paraformaldehyde yielding a final paraformaldehyde concentration of 1%. Samples were mixed by hand and left for 10 minutes at room temperature in the dark before transferring to a -80°C freezer. Samples will be analysed on a FACSort flow cytometer following the method of Davey et al. (2008) with the intention of analysis for nanophytoplankton, picophytoplankton, and total bacterial cell counts.

Table 4 The dates/times (all Beijing time) of sample collection

Station	Date	Time
K1	2019.4.27	10:17
K1	2019.4.30	1:57
K2	2019.5.2	13:02
K3	2019.5.4	21:55
K2a	2019.5.5	16:37
K4	2018.5.20	0:34
K5	2018.5.21	22:22
K6	2019.5.24	12:01

K7	2019.5.26	17:20
K8	2019.5.28	6:01
K9	2019.5.31	8:09
K10	2019.6.2	4:23
K11	2019.6.3	23:45
K12	2019.6.6	3:17
K13	2019.6.7	1:49
K14	2019.6.8	2:31
K14a	2019.6.10	21:00

References

Davey, M., Tarran, G. A., Mills, M. M., Ridame, C., Geider, R. J., and La Roche, J. 2008. Nutrient limitation of picophytoplankton photosynthesis and growth in the tropical North Atlantic. Limnol. Oceanogr. 53: 1722-1733, doi:10.2307/40058292.

Gibb, S. W., Barlow, R. G., Cummings, D. G., Rees, N. W., Trees, C. C., Holligan, P., and Suggett, D. 2000. Surface phytoplankton pigment distributions in the Atlantic Ocean: an assessment of basin scale variability between 50 degrees N and 50 degrees S. Prog. Oceanogr. 45: 339-368, doi:10.1016/S0079-6611(00)00007-0.

Welschmeyer, N. A. 1994. Fluorometric analysis of chlorophyll a in the presence of chlorophyll b and pheopigments. Limnol. Oceanogr. 39: 1985-1992, doi：10.4319/lo.1994.39.8.1985.

4.1.3. Ancillary hydrochemical parameters, ^{234}Th, and non-traditional isotopes (By Yangyang Zhao, Lifang Wang, Jing Liu, Junhui Chen, Yifan Ma, Yating Li, Xiaolin Li, Zhimian Cao, Minhan Dai)

4.1.3.1. Salinity

Samples for salinity were collected into 125 mL polyethylene bottles from 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a conductivity-temperature-depth (CTD) recorder (Sea-Bird SBE911 plus), at Stations K1, K3, K4, K6 and K8-K14 with full depth profiles. Salinity will be measured with

the Autosal (Model 8410A, Guildline Intruments Ltd.) Laboratory Salinometer and calibrated using the IAPSO standard seawater.

4.1.3.2. Dissolved oxygen (DO)

Duplicate samples for DO were collected from 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. The DO concentration in discrete samples were measured on board within ~4 hours using the spectrophotometric Winkler method (Pai et al., 1993), with a precision of ±1 μmol kg^{-1}.

Samples for DO were collected into BOD bottles with a volume of ~60 mL and overflowed by at least one bottle volume, avoiding the introduction of bubbles. Immediately after seawater subsampling, 0.5 mL of $MnCl_2$ solution and 0.5 mL of NaI-NaOH solution were successively added to the sample bottles. The sample bottles were capped and shook upside down at least 20 times to fully fix the DO in seawater as $MnO(OH)_2$ precipitate. After incubation in a 25±0.1 °C water bath for several hours to allow for precipitates to settle down to the bottom of the bottle, ~0.5 mL of 28% (v/v) H_2SO_4 was added to the precipitation to release I_2. The I_2 concentrations were then measured with the spectrophotometer (Model UV-1800, Shimadzu Suzhou Instrument, Mfg Co., Ltd.) and calibrated by standard curves using KIO_3 standard solutions.

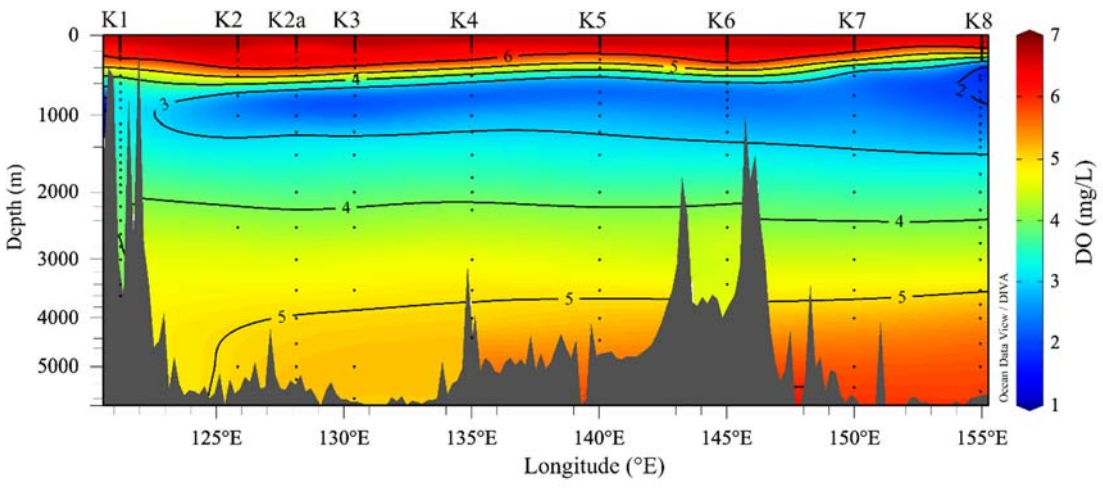


Figure 3. Distribution of dissolved oxygen along the north section from Stations K1 to K8

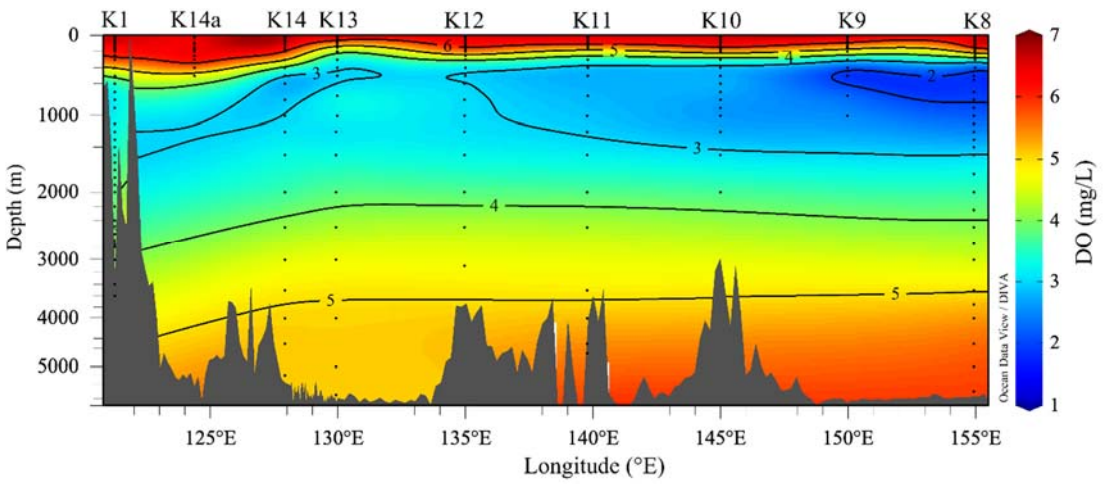


Figure 4. Distribution of dissolved oxygen along the south section from Stations K8 to K14a

References

Pai, S. C., G. C. Gong, and K. K. Liu. 1993. Determination of dissolved oxygen in seawater by direct spectrophotometry of total iodine. Mar. Chem. **41**: 343-351, doi:10.1016/0304-4203(93)90266-Q.

4.1.3.3. Dissolved Inorganic Carbon (DIC)

Samples for DIC were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. Samples for DIC analysis were overflowed by at least one bottle volume, stored in 250 mL PYREX® borosilicate glass bottles, and poisoned with 50 μL of $HgCl_2$-saturated solution upon sample collection. The DIC concentration will be measured by acidifying ~0.5 mL of water sample and subsequently quantifying released CO_2 using an infrared CO_2 detector (Apollo ASC-3) with a precision of ±2 μmol kg^{-1} (Cai et al., 2004). DIC will be calibrated against certified reference material provided by Dr. A. G. Dickson at the Scripps Institution of Oceanography, University of California, San Diego.

References

Cai, W. J., and others. 2004. The biogeochemistry of inorganic carbon and nutrients in the Pearl River estuary and the adjacent Northern South China Sea. Cont. Shelf Res. 24: 1301-1319, doi:10.1016/j.csr.2004.04.005.

4.1.3.4. Total Alkalinity (TA)

Samples for TA were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. Samples for TA analysis are overflowed by at least one bottle volume, stored in 250 mL PYREX® borosilicate glass bottles, and poisoned with 50 μL of a $HgCl_2$-saturated solution upon sample collection. TA will be determined on 25 mL samples using an open-cell setting based on the Gran titration technique (see details in Cai et al., 2010) with a Kloehn digital syringe pump. The analytical precision is ±2 μmol kg^{-1}. TA will be calibrated against certified reference material provided by Dr. A. G. Dickson at the Scripps Institution of Oceanography, University of California, San Diego.

References

Cai, W. J., X. Hu, W. J. Huang, L. Q. Jiang, Y. Wang, T. H. Peng, and X. Zhang. 2010. Alkalinity distribution in the western North Atlantic Ocean margins. J. Geophys. Res.: Oceans 115: C08014, doi:10.1029/2009JC005482.

4.1.3.5. pH

Samples for pH were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. Samples for pH analysis were overflowed by at least one bottle volume, stored in 250 mL PYREX® borosilicate glass bottles, and poisoned with 50 μL of $HgCl_2$-saturated solution upon sample collection. pH will be measured at 25 °C via UV-VIS spectrophotometer (Agilent 8453) using the unpurified meta-cresol purple (mCP) from Acros Origanics on the total hydrogen ion concentration scale (pH_T)

in the seawater. The precision of analysis is better than 0.001 pH units (Dickson et al., 2007).

References

Dickson, A. G., C. L. Sabine, and J. R. Christian. 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3191 pp.

4.1.3.6. Nutrients

Samples for nutrients were collected in 125 mL polyethylene bottles with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus). Samples for nitrate (NO_3^-), nitrite (NO_2^-), soluble reactive phosphate (SRP), and silicate (SiO_3^{2-}) were collected at all stations with full depth profiles, and for NO_3^-, NO_2^- and SRP at nanomolar level were usually collected in depths within upper 150 m. Samples for nutrients were stored at 4 °C and for nutrients at nanomolar level, frozen at -20 °C, until analysis. Nutrients from discrete samples were analyzed onboard with a Four-channel Continuous Flow Technicon AA3 Auto-Analyzer (Bran-Lube, GmbH) according to classic colorimetric methods. NO_3^- and NO_2^- were measured using the copper-cadmium column reduction method, and SRP and SiO_3^{2-} were measured using spectrophotometric methods (Knap et al., 1996). The detection limits for NO_3^-, NO_2^-, SRP and SiO_3^{2-} are 0.04 μmol L^{-1}, 0.04 μmol L^{-1}, 0.08 μmol L^{-1} and 0.16 μmol L^{-1}, respectively. The analytical precision is better than ±1% for NO_3^-, ±1% for NO_2^-, ±2% for SRP and ±2.8% for SiO_3^{2-} (Han et al., 2012; Du et al., 2013). The determination of NO_3^- at nanomolar level was conducted on a continuous flow analysis system combined with a liquid waveguide capillary flow cell (Zhang et al., 2000). The detection limit of NO_3^- is 2.4 nmol L^{-1} and the precision is better than ±5%. SRP at nanomolar level was determined using a flow injection system onboard within 1 day of sampling. The detection limit is 1.4 nmol L^{-1} and the precision is better than ±5% (Ma et al., 2008; Han et al., 2012; Du et al., 2013).

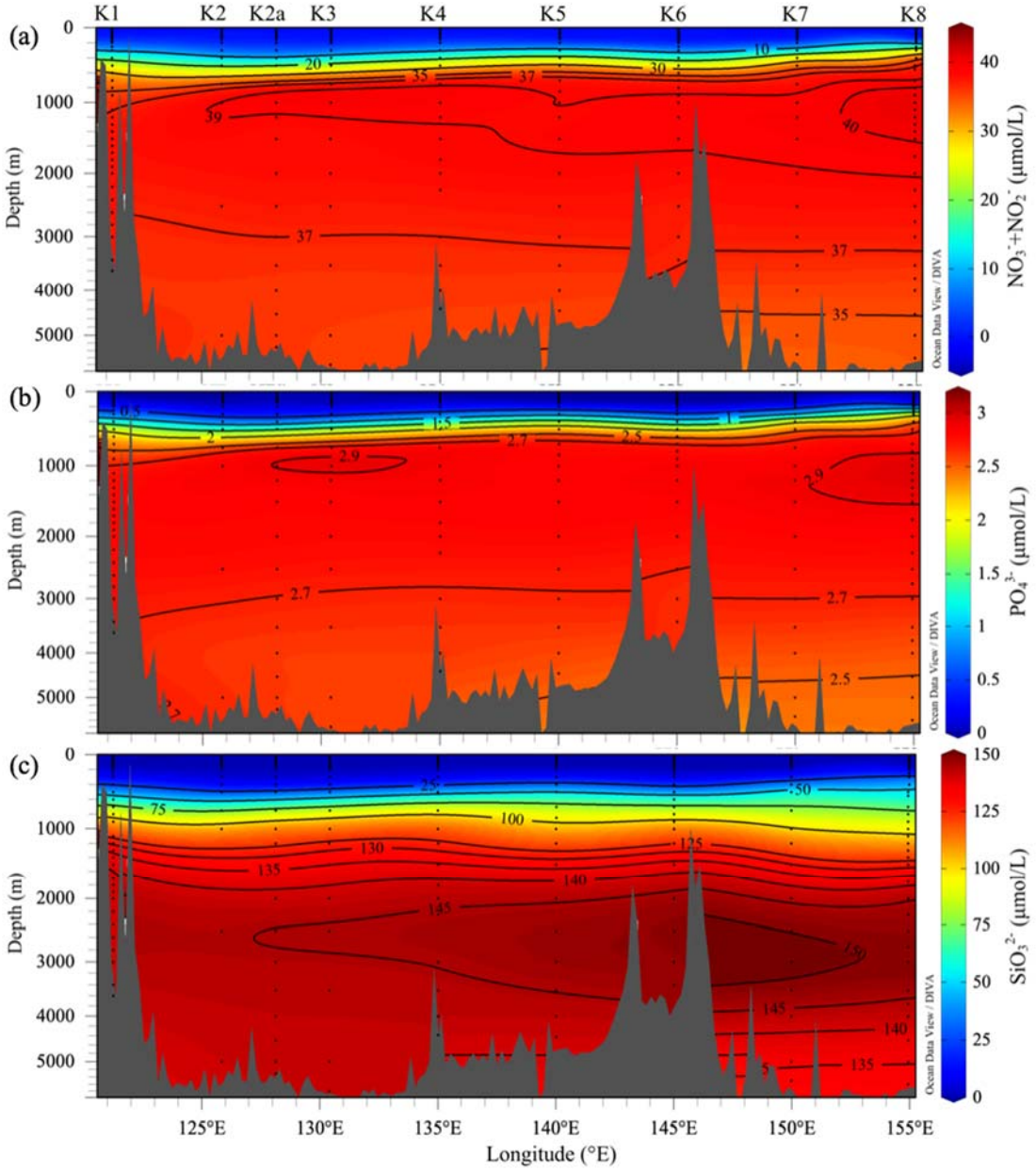


Figure 5. Distributions of (a) nitrate+nitrite ($NO_3^-+NO_2^-$), (b) SRP (PO_4^{3-}) and (c) silicate (SiO_3^{2-}) along the north section from Stations K1 to K8

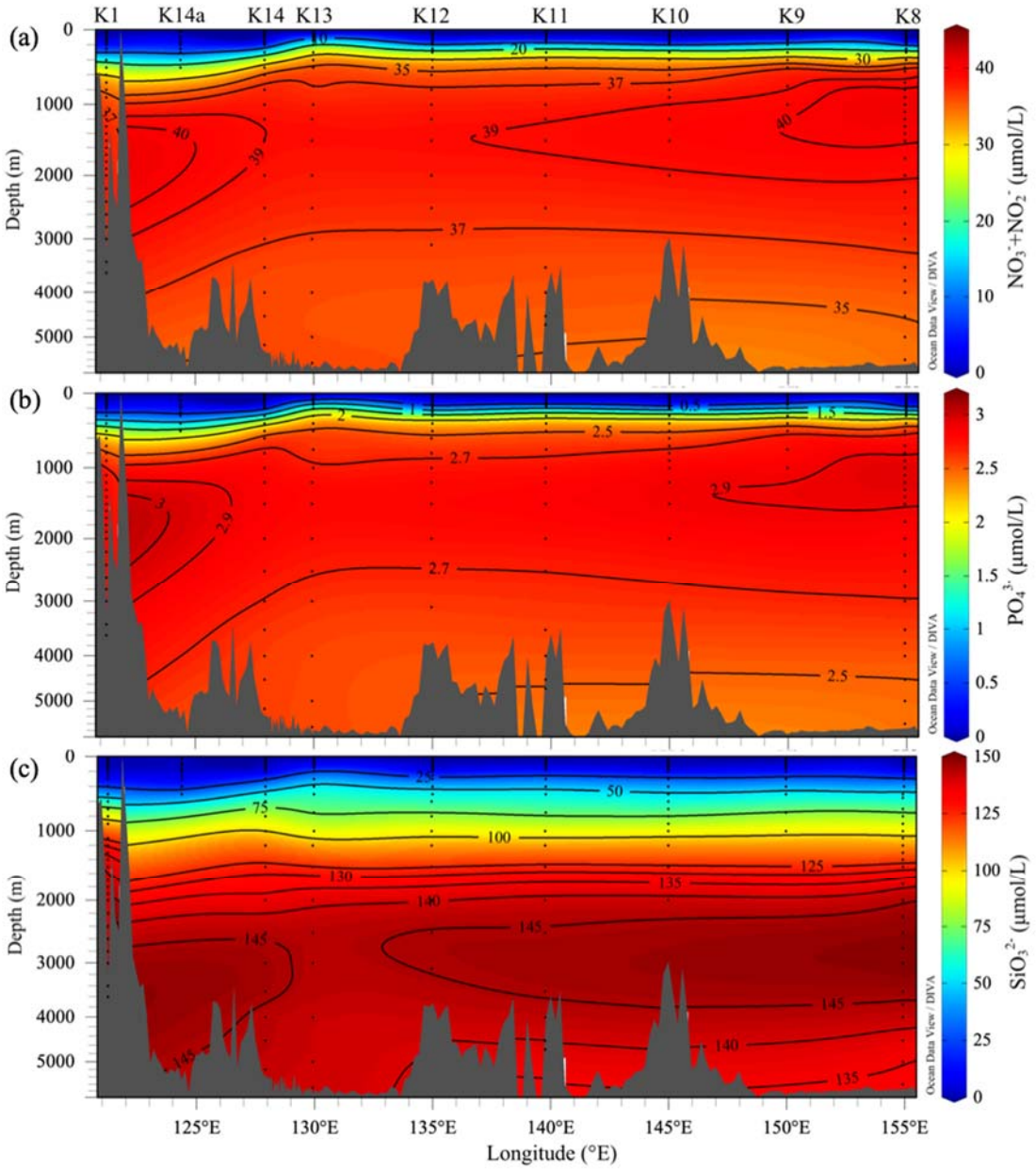


Figure 6. Distributions of (a) nitrate+nitrite ($NO_3^-+NO_2^-$), (b) SRP (PO_4^{3-}) and (c) silicate (SiO_3^{2-}) along the south section from station K8 to K14a

References

Du, C., and others. 2013. Impact of the Kuroshio intrusion on the nutrient inventory in the upper northern South China Sea: Insights from an isopycnal mixing model. Biogeosciences 10: 1-14.

Han, A., and others. 2012. Nutrient dynamics and biological consumption in a large continental shelf system under the influence of both a river plume and coastal upwelling. Limnol. Oceanogr. 57: 486-502, doi:10.4319/lo.2012.57.2.0486.

Ma, J., D. Yuan, and Y. Liang. 2008. Sequential injection analysis of nanomolar soluble reactive phosphorus in seawater with HLB solid phase extraction. Mar. Chem. 111: 151-159.

Knap, A., A. Michaels, A. Close, H. Ducklow, and A. Dickson. 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements, p. 43-90. JGOFS Report No. 19, vi + 170 pp. Reprint of the IOC Manuals and Guides No. 29, UNESCO 1994.

4.1.3.7. Dissolved Organic Carbon (DOC)

The collection and measurement of samples for DOC follow the JGOFS protocol (Benner and Strom, 1993; Sharp and Peltzer, 1993). Duplicate samples for DOC were collected from 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. For the depths within the upper 200 m, filtered samples were also collected using on-line filter holder packaged with 450 °C baked GF/F membrane to eliminate the contribution from particulate organic carbon. Samples for DOC analysis were collected into 40 mL borosilicate glass bottles and stored at -20 °C until analysis. DOC will be measured using a total organic carbon analyzer (Model TOC-V_{CPH}, Shimazu Co., Ltd.) with the method of high temperature combustion (HTC) followed by quantitative measurements of the CO_2 produced by non-dispersive infra-red (NDIR) analysis. The precision is ±1 μmol L^{-1}. DOC will be calibrated against certified reference material provided by Dr. Hansell, D.A. at the University of Miami.

References

Benner, R. and M. Strom. 1993. A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation. In: Measurement of Dissolved Organic Carbon and Nitrogen in Natural Waters (eds. Hedges and Lee). 41:153-160.

Sharp, J., and E.T. Peltzer. 1993. Procedures subgroup report. Mar. Chem. 41:37-49.

4.1.3.8. Dissolved Organic Phosphorus (DOP)

Duplicate samples for DOP were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus) at K7 - K14a stations within the upper 200 m. These samples are collected into 125 mL HDPE bottles and stored at -20°C until analysis. Total dissolved phosphorus (TDP) will be determined by converting phosphorus compounds into orthophosphate at sub-boiling temperature after 3h of digestion time, followed by addition of ascorbic acid to eliminate free chlorine generated from the saline sample and subsequent addition of the ammonium molybdate reagent for detection by UV-Vis spectrophotometry (Ma et al., 2017). DOP is then calculated by subtracting dissolved inorganic phosphorus from TDP.

References

Ma, J., Y. Yuan, T. Zhou, and D. Yuan. 2017. Determination of total phosphorus in natural waters with a simple neutral digestion method using sodium persulfate. Limnol. Oceanogr.: Methods 15: 372-380.

4.1.3.9. Total Thorium-234 (^{234}Th)

4-L samples for total ^{234}Th were collected into FLPE bottles with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. ^{234}Th is co-precipitated with MnO_2 and filtered through a QMA filter (25 mm, 1.0 μm). All samples for total and particulate ^{234}Th are dried and mounted on plastic discs with two layers of aluminum foil and one layer of Mylar film. ^{234}Th is counted for at least 12 h until 2500 counts is obtained using a gas-flow proportional low-level RISØ beta counter. A second count will be carried out after 6 months later to get the background value. The ^{234}Th recovery is monitored by adding ~10 dpm ^{230}Th and analyzed using the demounted total ^{234}Th samples from the ^{230}Th spike on QMA filters after beta counting. The ^{230}Th is monitored using ^{229}Th, purified using iron precipitation and anion column exchange, and finally diluted in 2%

(v/v) HNO_3. The ratios of ^{229}Th and ^{230}Th were measured with Inductively Couple Plasma-Mass Spectrometry (ICP-MS).

References

Cai, P. H., D. C. Zhao, L. Wang, B. Q. Huang, and M. H. Dai. 2015. Role of particle stock and phytoplankton community structure in regulating particulate organic carbon export in a large marginal sea. J. Geophys. Res.: Oceans 120: 2063-2095.

4.1.3.10. Particulate Organic Carbon (POC)

8-L samples for POC were collected into FLPE bottles with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus) at K1, K8, K10 and K14a stations within the upper 1000 m. Generally, 8L samples were filtered onto pre-combusted (450 °C, 5 hours) Whatman QMA filters (25 mm, 1 μm) at pressure of 0.3 atm. The filter was dried overnight at 50 °C and firstly used for the measurements of ^{234}Th. Prior to analysis, POC samples will be placed overnight in a desiccator saturated with HCl fumes. The filters will then be dried again at 50 °C and packed in tin-foil film. POC will be analyzed on a vario EL cube CHNS Elemental Analyzer following the guidelines provided by the manufacturer as dried, acidified samples of particulate matter is combusted at 960 °C and release CO_2 converted from organic carbon and N_2 subsequently reduced from nitrogen oxides. Both gases are measured by thermal conductivity.

4.1.3.11. Dissolved Barium (DBa) and its isotopes ($\delta^{138}Ba_{DBa}$)

Seawater samples for the concentrations and isotopic compositions of DBa were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. Samples were stored in 250 mL polyethylene bottles immediately after sampling and subsequently acidified to pH~2 with 0.1% (v/v) distilled concentrated HCl and stored at room temperature in the dark until analysis in the laboratory. DBa

concentrations in seawater will be analyzed using an isotope dilution method (Klinkhammer and Chan, 1990; Freydier et al., 1995) on an Agilent 7500 quadrupole-ICP-MS, and $\delta^{138}Ba_{DBa}$ will be determined using double spike technique (Rudge et al., 2009) in the static mode on a Nu Plasma HR MC-ICP-MS.

References

Klinkhammer, G.P., and L. H. Chan. 1990. Determination of barium in marine waters by isotope dilution inductively coupled plasma mass spectrometry. Anal. Chim. Acta 232: 323-329.

Freydier, R., B. Dupre, and M. Polve. 1995. Analyses by inductively coupled plasma mass spectrometry of Ba concentrations in water and rock samples. Comparison between isotope dilution and external calibration with or without internal standard. Eur. Mass Spectrom. 1: 283-291.

Rudge, J. F., B. C. Reynolds, and B. Bourdon. 2009. The double spike toolbox. Chem. Geol. 265: 420-431.

4.1.3.12. Particulate Barium (PBa) and its isotopes ($\delta^{138}Ba_{PBa}$)

Samples for the concentrations and isotopic compositions of PBa were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. About 8 L of seawater was filtered through 0.4 μm polycarbonate membranes, which were then dried at 50°C overnight and stored in polycarbonate dishes until analysis in the laboratory. The suspended particle samples will be dissolved completely using the digestion method developed by Cardinal et al. (2001) and the resultant digested solution will be dried down and re-dissolved in small amounts of 1 mol L^{-1} HCl. Both Ba and Al will be measured using a quadrupole-ICP-MS (Agilent 7500) and PBa concentrations can be calculated by the excess above the lithogenic Ba/Al ratios (Jacquet et al., 2008). $\delta^{138}Ba_{PBa}$ will be determined using double spike technique (Rudge et al., 2009) in the static mode on a Nu Plasma HR MC-ICP-MS.

References

Jacquet S. H. M., F. Dehairs, N. Savoye, I. Obernosterer, U. Christaki, C. Monnin and D. Cardinal. 2008. Mesopelagic organic carbon mineralization in the Kerguelen Plateau region tracked by biogenic particulate Ba. Deep-Sea Res. II 55: 868-879.

Rudge, J. F., B. C. Reynolds, and B. Bourdon. 2009. The double spike toolbox. Chem. Geol. 265: 420-431.

4.1.3.13. Dissolved silicon isotopes ($\delta^{30}Si_{Si(OH)4}$)

Seawater samples for dissolved silicon isotopes were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. Samples were stored in 250 mL polyethylene bottles immediately after sampling and subsequently acidified to pH~2 with 0.1% (v/v) distilled concentrated HCl and stored at room temperature in the dark until analysis in the laboratory. $Si(OH)_4$ will be separated from the major matrix elements using a two-step brucite co-precipitation technique adapted from the MAGIC method (Karl and Tien, 1992). The precipitates will be further purified using cation-exchange chromatography (Georg et al., 2006). $\delta^{30}Si_{Si(OH)4}$ will be determined in the pseudo high-resolution mode on a Nu Plasma HR MC-ICP-MS.

References

Georg, R.B., B. C. Reynolds, M. Frank, and A. N. Halliday. 2006. New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS. Chem. Geol. 235: 95–104.

Karl, D.M., and G. Tien. 1992. MAGIC: a sensitive and precise method for measuring dissolved phosphorus in aquatic environments. Limnol. Oceanogr. 37: 105–116.

4.1.3.14. Particulate biogenic silicon (BSi) and its isotopes ($\delta^{30}Si_{BSi}$)

Samples for the concentrations and isotopic compositions of particulate biogenic silicon were collected with 12-liter Niskin bottles mounted onto a Rosette sampling assembly,

equipped with a CTD recorder (Sea-Bird SBE911 plus), at all stations with full depth profiles. About 10 L of seawater was filtered through 0.4 μm polycarbonate membranes, which were then dried at 50°C overnight and stored in polycarbonate dishes until analysis in the laboratory. The suspended particle samples will be dissolved using the double wet-alkaline digestion method (Rgueneau et al., 2005). BSi concentrations will be analyzed with a Technicon AA3 Auto-Analyzer (Bran+Luebbe GmbH) following classical colorimetric methods, and $\delta^{30}Si_{BSi}$ will be determined in the pseudo high-resolution mode on a Nu Plasma HR MC-ICP-MS.

References

Ragueneau, O., N. Savoye, Y. Del Amo, J. Cotten, B. Tardiveau, and A. Leynaert. 2005. A new method for the measurement of biogenic silica in suspended matter of coastal waters: using Si:Al ratios to correct for the mineral interference. Cont. Shelf Res. 25: 697-710.

4.1.3.15. $^{15}NO_3^-$

Samples for seawater $^{15}NO_3^-$ were collected at all clean stations with full depth profiles. The $^{15}NO_3^-$ will be analyzed following the denitrifier method on an IR-MS (Casciotti et al., 2002; McIlvin and Casciotti, 2011; Sigman et al., 2001).

References

Casciotti, K. L., D. M. Sigman, M. G. Hastings, J. K. Böhlke, and A. Hilkert. 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. Analytical Chemistry, 74(19): 4905-4912.

McIlvin, M. R., and K. L. Casciotti. 2011. Technical updates to the bacterial method for nitrate isotopic analyses. Analytical Chemistry, 83(5): 1850-1856.

Sigman, D. M., K. L. Casciotti, M. Andreani, C. Barford, M. B. J. K. Galanter, and J. K. Böhlke. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Analytical chemistry, 73(17): 4145-4153.

4.1.4. Nd isotopes (By Qian Liu, Jing Zhang, Siteng Zhu)

The dissolved Nd isotope ratio ($^{143}Nd/^{144}Nd$, expressed as εNd) of seawater is widely used as water mass tracer in the different ocean basins. In our study, sources of macro- and micro-nutrients to the North Pacific Subtropical Gyre from terrestrial input (e.g. island), water mass transport, and hydrothermal vent etc. will be examined using εNd. During this cruise, seawater samples of Nd isotopes from surface to bottom were taken from 12 L Niskin bottles mounted on a Rosette sampler equipped with a calibrated CTD recorder. Upon sampling, 10 L or 20 L of seawater were filtered on board in a clean bench with 0.45 μm Polyethersulfone membrane filter into pre-cleaned LDPE cubitainers. The filtrate was acidified to a pH of ~2 with ultra-clean 6 N HCl (self-distilled or Fisher Scientific optima grade). Nd isotope will be analyzed using MC-ICP-MS in the laboratory on land.

Seawater samples were taken from hydro CTD at Stations K1, K2, K3, K4, K5, K6, K7, K8, K9, K10, K11, K12, K13, and K14 from surface to bottom. The detailed information is presented in table below.

Table 5 The detailed sampling information of Nd isotopes

Station	Latitude (ºN)	Longitude (ºE)	Cast Number	Bottle Number	Depth (m)
K1	21	121.25	8	1	3630
K1	21	121.25	8	2	3630
K1	21	121.25	8	3	2500
K1	21	121.25	8	4	1600
K1	21	121.25	8	5	1600
K1	21	121.25	8	6	1000
K1	21	121.25	8	7	1000
K1	21	121.25	8	8	700
K1	21	121.25	8	9	700
K1	21	121.25	8	10	400
K1	21	121.25	8	11	400
K1	21	121.25	8	12	300
K1	21	121.25	8	13	270
K1	21	121.25	8	14	250
K1	21	121.25	8	15	250

K1	21	121.25	8	16	240
K1	21	121.25	8	17	200
K1	21	121.25	8	18	180
K1	21	121.25	8	19	180
K1	21	121.25	8	20	110
K1	21	121.25	8	21	70
K1	21	121.25	8	22	70
K1	21	121.25	8	23	20
K1	21	121.25	8	24	20
K2	20	125.8333	5	2	5000
K2	20	125.8333	5	4	3000
K2	20	125.8333	5	6	2000
K2	20	125.8333	5	8	1500
K2	20	125.8333	5	10	1000
K2	20	125.8333	5	12	800
K2	20	125.8333	5	14	620
K2	20	125.8333	5	16	400
K2	20	125.8333	5	18	210
K2	20	125.8333	5	20	100
K2	20	125.8333	5	22	50
K2	20	125.8333	5	23	20
K3	18.6	130.4167	3	4	400
K3	18.6	130.4167	3	8	200
K3	18.6	130.4167	3	14	100
K3	18.6	130.4167	3	18	50
K3	18.6	130.4167	3	22	20
K3	18.6	130.4167	4	2	5000
K3	18.6	130.4167	4	8	3000
K3	18.6	130.4167	4	12	2000
K3	18.6	130.4167	4	15	1500
K3	18.6	130.4167	4	19	1000
K3	18.6	130.4167	4	21	800
K3	18.6	130.4167	4	23	600
K4	17.2	135	2	4	400
K4	17.2	135	2	8	200
K4	17.2	135	2	14	100
K4	17.2	135	2	18	50
K4	17.2	135	2	22	20
K4	17.2	135	4	2	4380
K4	17.2	135	4	7	3000
K4	17.2	135	4	12	2000
K4	17.2	135	4	15	1500
K4	17.2	135	4	19	1000

K4	17.2	135	4	21	800
K4	17.2	135	4	23	600
K5	17.2	140	2	2	4430
K5	17.2	140	2	8	3000
K5	17.2	140	2	12	2000
K5	17.2	140	2	15	1500
K5	17.2	140	2	19	1000
K5	17.2	140	2	21	800
K5	17.2	140	2	23	600
K5	17.2	140	4	4	400
K5	17.2	140	4	8	200
K5	17.2	140	4	14	100
K5	17.2	140	4	18	50
K5	17.2	140	4	22	20
K6	17.2	145	2	2	3415
K6	17.2	145	2	4	3000
K6	17.2	145	2	7	2500
K6	17.2	145	2	10	2000
K6	17.2	145	2	13	1500
K6	17.2	145	2	18	1000
K6	17.2	145	5	1	800
K6	17.2	145	5	6	600
K6	17.2	145	5	8	400
K6	17.2	145	5	10	200
K6	17.2	145	5	15	100
K6	17.2	145	5	17	70
K6	17.2	145	5	19	50
K6	17.2	145	5	21	30
K6	17.2	145	5	23	10
K7	14.1	150	2	4	400
K7	14.1	150	2	8	200
K7	14.1	150	2	14	100
K7	14.1	150	2	18	50
K7	14.1	150	2	22	20
K7	14.1	150	4	2	5000
K7	14.1	150	4	8	3000
K7	14.1	150	4	12	2000
K7	14.1	150	4	15	1500
K7	14.1	150	4	19	1000
K7	14.1	150	4	21	800
K7	14.1	150	4	23	600
K8	11	155	6	9	5605
K8	11	155	6	12	5605

K8	11	155	6	15	4500
K8	11	155	6	18	4500
K8	11	155	6	21	3500
K8	11	155	6	24	3500
K8	11	155	7	3	2500
K8	11	155	7	4	2500
K8	11	155	7	10	1500
K8	11	155	7	13	1500
K8	11	155	7	17	1000
K8	11	155	7	20	1000
K8	11	155	11	1	500
K8	11	155	11	2	500
K8	11	155	11	4	300
K8	11	155	11	6	300
K8	11	155	11	8	200
K8	11	155	11	9	200
K8	11	155	11	13	100
K8	11	155	11	14	100
K8	11	155	11	17	50
K8	11	155	11	18	50
K8	11	155	11	20	25
K8	11	155	11	22	10
K9	11	150	2	4	400
K9	11	150	2	8	200
K9	11	150	2	14	100
K9	11	150	2	18	50
K9	11	150	2	22	20
K9	11	150	4	2	5000
K9	11	150	4	8	3000
K9	11	150	4	12	2000
K9	11	150	4	15	1500
K9	11	150	4	19	1000
K9	11	150	4	22	800
K9	11	150	4	23	600
K10	11	145	4	1	2100
K10	11	145	4	3	1500
K10	11	145	4	5	1000
K10	11	145	4	7	800
K10	11	145	4	9	600
K10	11	145	4	11	500
K10	11	145	4	13	400
K10	11	145	4	15	300
K10	11	145	4	17	200

K10	11	145	4	19	100
K10	11	145	4	21	50
K10	11	145	4	23	10
K11	11	140	3	4	400
K11	11	140	3	8	200
K11	11	140	3	14	100
K11	11	140	3	18	50
K11	11	140	3	22	10
K11	11	140	5	2	4700
K11	11	140	5	8	3000
K11	11	140	5	12	2000
K11	11	140	5	15	1500
K11	11	140	5	19	1000
K11	11	140	5	21	800
K11	11	140	5	23	600
K12	11	135	3	2	400
K12	11	135	3	7	200
K12	11	135	3	14	100
K12	11	135	3	18	50
K12	11	135	3	22	10
K12	11	135	4	2	3100
K12	11	135	4	6	3000
K12	11	135	4	10	2000
K12	11	135	4	12	1500
K12	11	135	4	17	1000
K12	11	135	4	19	800
K12	11	135	4	22	600
K13	11	130	2	4	400
K13	11	130	2	8	200
K13	11	130	2	14	100
K13	11	130	2	18	50
K13	11	130	2	22	10
K13	11	130	4	2	5000
K13	11	130	4	8	3000
K13	11	130	4	12	2000
K13	11	130	4	16	1500
K13	11	130	4	19	1000
K13	11	130	4	21	800
K13	11	130	4	23	600
K14	15.5	127.9167	4	4	260
K14	15.5	127.9167	4	8	170
K14	15.5	127.9167	4	12	100
K14	15.5	127.9167	4	18	40

K14	15.5	127.9167	4	22	15
K14	15.5	127.9167	5	2	3000
K14	15.5	127.9167	5	4	2000
K14	15.5	127.9167	5	6	1500
K14	15.5	127.9167	5	8	1000
K14	15.5	127.9167	5	12	800
K14	15.5	127.9167	5	16	600
K14	15.5	127.9167	5	22	360

4.1.5. Isotopic compositions of oxygen, hydrogen, dissolved inorganic carbon (By Na Qian, Yongrui An, Liping Zhou)

Seawater samples were collected to determine the distributions of $\delta^{13}C$ and $\Delta^{14}C$ in DIC, $\delta^{18}O$ and $\delta^{2}H$ in seawater, DIC and TA throughout the full depth of the water, and to understand the marine biogeochemical cycle and hydrological processes in the wNP.

Analytical Methods:

(1) AMS $\Delta^{14}C$ measurement

DIC in water samples will be extracted by the Headspace-Extraction Method and reduced to graphite with the Sealed Tube Zinc Reduction Method. The prepared graphite targets will then be measured by the accelerator mass spectrometry (AMS) at the Institute of Heavy Ion Physics, Peking University, China.

(2) IRMS $\delta^{13}C$ measurement

DIC in water samples will be converted to CO_2 by H_3PO_4 acidification and then be measured by a continuous flow Delta V plus IRMS coupled with a Thermo Gas Bench II, at Peking University, China.

(3) Picarro L2130-i $\delta^{18}O$, $\delta^{2}H$ measurement

$\delta^{18}O$ and $\delta^{2}H$ in seawater will be measured directly with a Picarro L2130-i WS-CRDS water isotope analyzer at Peking University, China.

(4) Apollo Sci Tech Analyzer DIC and TA measurements

DIC in seawater samples will be converted to CO_2 by H_3PO_4 acidification and the subsequent quantification of CO_2 will be done on an Apollo Sci Tech Analyzer with a

Li-Cor 7000 IR detector at Peking University, China. TA will be determined by Gran titration calibrated by the Certified Reference Material from A. Dickson of the Scripps Institution of Oceanography.

Sampling Information

Seawater samples were collected at different depths from surface to ~6000m at 15 stations (K1-K14a) using a normal Rosette sampling system equipped with 24 12 L Niskin bottles on board *R/V Tan Kah Kee.*

Samples for DIC/TA, $\Delta^{14}C$ and $\delta^{13}C$ analyses were respectively stored in 100 ml and 20 ml well-sealed glass bottles and poisoned by adding saturated solution of mercury chloride ($HgCl_2$) to inhibit biological activities. Samples for seawater $\delta^{18}O$ and $\delta^{2}H$ were preserved in 2 ml glass bottles and kept in a 4°C refrigerator to prevent evaporation before measurements.

4.1.6. ^{210}Po-^{210}Pb (By Xin Wang, Yihua Cai)

^{210}Po-^{210}Pb disequilibrium in the wNP will be obtained to investigate the particle dynamics in the oligotrophic mesopelagic and deep waters and to determine the export fluxes of biogenic particles out of the euphotic zone.

Analytical Methods:

Dissolved ^{210}Po-^{210}Pb: For operationally defined dissolved Po and Pb, the water samples are filtered through the PC membrane with a pore size of 0.4 μm and acidified immediately to pH<2 with reagent grade 6M HCl after sampling onboard. ^{209}Po spike, stable Pb ($PbCl_2$) and $FeCl_3$ will be added into the filtrate after returning to the onshore laboratory. Pb and Po will be simultaneously co-precipitated with $Fe(OH)_3$. The $Fe(OH)_3$ precipitate will be collected and redissolved in HCl, then ^{210}Po and ^{209}Po will be spontaneously deposited onto silver plates for alpha spectrometry analysis.

Particulate ^{210}Po-^{210}Pb: The particulate samples retained on the PC membrane will be

dried in an oven and weighed to estimate the concentration of total suspended matter. After adding ^{209}Po spike, the filters will be digested by mixed concentrated HNO_3/HCl/$HClO_4$ solution. ^{210}Po and ^{209}Po will be deposited onto silver plates and counted following the same procedures as dissolved phases.

Sampling Information:

10-liter seawater samples for particulate and dissolved ^{210}Po-^{210}Pb are collected from each layer. 12 layers were sampled at all 12 clean stations above 1000m and 24 layers in 2 mega stations through the whole water column.

4.1.7. ^{230}Th, ^{231}Pa, ^{232}Th (By Xin Wang, Yihua Cai)

^{230}Th, ^{231}Pa, ^{232}Th in seawater will be determined to investigate the particle dynamics, to quantify the lithogenic dust deposition flux, and to help obtaining the residence times of biogenic TEIs in the wNP.

Analytical Methods:

The water samples were filtered in-line with capsule filters (0.8 μm/0.45 μm Acropak® 500 filters) and acidified immediately with optima HCl to pH<2 after the sample collection. After weighting, spiking and preconcentration with Mg hydroxide, ^{230}Th, ^{232}Th, and ^{231}Pa will be separated and purified with AG1×8 resin and then measured with Element XR HR-ICP-MS.

Sampling information:

Sampling strategy and depth of seawater ^{230}Th, ^{231}Pa, ^{232}Th samples are consistent with samples for ^{210}Po-^{210}Pb.

4.2. Clean CTD (By Liping Ye, Yihua Cai, Ruifeng Zhang, Yanbin Li)

4.2.1. Instrument information

The Clean CTD Sampling System includes clean sampling bottles (OTE C-FREE or GO Niskin-X), a SBE 911plus CTD attached to a 32G-24P sampling carousel, a clean sampling van, a clean analysis van, and a clean CTD winch with electrical control container. Table 6 shows the detailed information of the clean CTD sampling system.

Table 6 Instrument information

Instrument	**Specification**	**Manufacturer**
Clean sampling Bottle	C-FREE 114, 12L	Ocean Test Equipment
	Niskin-X, 12L	General Oceanics
CTD and sampling carousel	CTD: SBE 911Plus; Carousel: 32G-24P, 24-position for use with 12-liter sampling bottles, Integrated with 2 sets of temperature-conductivity sensors, SBE43 dissolved oxygen sensor, WET Labs C-Star, WET Labs ECO-FLrtd, and VA-500 altimeter	SeaBird
Clean CTD winch	2550*2350*1950mm; contain 8000m Vectran conducting cable	Kleyfrance
Winch electrical control container	3000*2450*2850mm; Contain portable control console	Kleyfrance
Sampling van	Custom, 606*244*259cm, Class1000	GeOceanTech Co., Ltd.
Analysis van	Custom, 606*244*259cm, Class1000	GeOceanTech Co., Ltd.

4.2.2. Parameters

Parameters obtained with Clean CTD sampling system include nutrient concentrations and trace element concentrations and isotopic compositions:

1) Nutrient concentrations: NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, SiO_3^{2-}

2) Trace metal concentrations: REE, Fe (FIA), Fe (ICP-MS), Cu, Zn, Cd, Ni, Pb, Co, Mn (FIA), Mn (ICP-MS), Al, THg, MeHg, Mo, V
3) Trace metal isotopes: $\delta^{56/54}$Fe, $\delta^{66/64}$Zn, $\delta^{114/110}$Cd, $^{206/207}$Pb, $^{208/207}$Pb, $^{206/204}$Pb, δ^{65}Cu

4.2.3. Objectives

To investigate the distribution of TEIs in the wNP and to improve the understanding of biogeochemical cycles of TEIs.

4.2.4. Analytical Methods

1) Nutrients

Nutrient concentrations will be analyzed onboard with a Four-channel Continuous Flow Technicon AA3 Auto-Analyzer (Bran-Lube, GmbH) according to classic colorimetric methods. Nanomolar level NO_3^- is determined on a continuous flow analysis system combined with a liquid waveguide capillary flow cell. SRP at nanomolar level is determined using a flow injection system onboard within 1 day of sampling. Detailed information was described in section 4.1.6.

2) Trace metal concentration and their isotopes

The dissolved Fe(FIA) concentration will be analyzed following a modified flow injection-based luminol chemiluminescence method with a detection limit of 0.026 nM. Fe(III) in seawater samples will be reduced to Fe(II) by sodium sulfite before preconcentration. A mini column packed with PA1 resin (Hitachi) will be used for on-line preconcentration of iron from seawater matrix at pH 6.2. After preconcentration, iron will be eluted from the PA1 column by 0.08 mol/L HCl solution and then merged with luminol solution at a reaction pH of 10.1 to produce chemiluminescence for the detection.

The concentrations of dissolved Al(FIA) and Mn(FIA) will be analyzed by the flow

injection analysis methods with on-line preconcentration following the protocol described in Brown and Bruland (2008) and Aguilar-Islas and Bruland (2006). The detection limits are 0.18 nM and 0.2 nM for Al and Mn, respectively.

The concentrations of dissolved REE, Fe(ICP-MS), Cu, Zn, Cd, Ni, Pb, Co, Mo, V will be pre-concentrated and analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo ICAP-Q/Element XR) using isotopic dilution or standard addition method.

For the THg concentration analysis, samples will be oxidized with 0.05% bromine monochloride (BrCl) solution or equivalent for at least 1 hour. Then excess halogens will be removed by mixing with 0.05% v/v hydroxylamine hydrochloride (NH_2OH•HCl) solution for at least 5 minutes, and final reduction will be conducted with 0.05% v/v stannous chloride ($SnCl_2$) solution. Hg^0 in solution will be purged and trapped on gold or gold-coated sand (or the equivalent). Purging should proceed at a volumetric flow rate of no more than 1 L min^{-1} (we recommend 0.5 L min^{-1}) until a volume of gas of at least 15 times the volume of liquid has been sparged. For MeHg analysis, HCl (conc.) is added to 250 ml seawater sample to form a final concentration of 0.5% and the samples are stored at -20 ºC before analysis. Upon arrival at the laboratory, 250 ml seawater sample is digested at 2% H_2SO_4 for > 12h. After that, the sample is first neutralized with 7.5 mL of 50% KOH, and then buffered to pH=5 with 3.75 mL of 2 M Na-Acetate/Acetic buffer, the pH should be checked and adjusted as necessary with small additions of strong acid (H_2SO_4) or strong base (KOH). 0.18 mL of 1% NaTEB will be added to the buffered 250 ml sample, allowing each sample to react for at least 15 minutes, and then sparging the formed MeHgEt from the sample to a Tenax trap. MeHgEt on the trap will then be detected by a packed column GC (OV-3)-AFS.

$\delta^{56/54}$Fe, $\delta^{66/64}$Zn, $\delta^{114/110}$Cd will be analyzed using double spike method followed by the batch resin extraction. $^{206/207}$Pb, $^{208/207}$Pb, $^{206/204}$Pb will be purified using column chemistry method. δ^{65}Cu will be analyzed using standard bracketing method after batch resin extraction. All of these isotopes will be measured on a multiple collector ICP-MS (Conway et al., 2013).

4.2.5. Sampling Information

Samples for trace elements were collected by 12-liter Niskin-X bottles mounted onto a clean rosette sampling assembly, equipped with a CTD recorder (Sea-Bird SBE911Plus, see 4.2.1 for detailed information).

Unfiltered and filtered seawater samples were subsampled for each depth. Detailed sampling information is given in Table 7. To obtain filtered samples, seawater was filtered in-line from Niskin-X bottles in the clean van through AcroPak 1000 cartridges (pore size of 0.8/0.45 mm) into pre-cleaned LDPE/HDPE bottles. The filtrate was acidified to a pH of ~2 with ultra-clean 6 N HCl (Fisher Scientific optima grade) in a 100-class clean van onboard and stored for more than one month before analysis.

Table 7 Sampling information for each TEIs clean cast

Bottle number	Unfiltered				Filtered						
	TEs	Hg	Low N&P	Nutrient	REEs	Al/Mn	V	Fe (FIA)	Fe/Zn/Cd isotopes	Fe (ICP-MS) /Cu/Zn/Cd/Ni/Co	Pb and Pb isotopes
1	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
2	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
3	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
4	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
5	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
6	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
7	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
8	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
9	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
10	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
11	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
12	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
13	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
14	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
15	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
16	0.5	0.5		0.125	0.5	0.25	0.25	0.125	2	4	1
17	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1
18	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1
19	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1
20	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1

21	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1
22	0.5	0.5	0.5	0.125	0.5	0.25	0.25	2.125	1	3	1
23	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1
24	0.5	0.5	0.5	0.125	0.5	0.25	0.25	0.125	2	4	1

References

Brown, M. T., and K. W. Bruland. 2008. An improved flow-injection analysis method for the determination of dissolved aluminum in seawater. Limnology and Oceanography: Methods, 6(1): 87-95.

Aguilar-Islas A. M., and K. W. Bruland. 2006. Dissolved manganese and silicic acid in the Columbia River plume: a major source to the California current and coastal waters off Washington and Oregon. Marine chemistry, 101(3-4): 233-247.

Conway T. M., A. D. Rosenberg, J. F. Adkins, et al. 2013. A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. Analytica Chimica Acta, 793: 44-52.

4.3. In-situ Pump (Kuanbo Zhou, Kan Zhang, Zixiang Yang, Yating Li, Junhui Chen)

4.3.1. Objectives:

1. To determine the particulate concentrations and isotopes of the major elements, e.g. POC, PN and biogenic silica.

2. To determine the particulate concentrations and isotopes of the trace elements, e.g. Fe, Zn, Cd, Co, Cu, Ni and REE.

3. To determine the particulate activities of the natural occurring radionuclides, e.g. ^{234}Th.

4. To evaluate the size-fractionated information and particle dynamics of the trace elements.

5. To estimate the downward fluxes of the trace elements.

4.3.2. Sample strategy and collection

We re-designed the configuration of the two pump heads in situ pump system based on the GEOTRACES cookbook in order to satisfy the trace metal sampling requirements for the GEOTRACES cruise (See Figure 7). Briefly, for one pump head, seawater will sequentially pass through a 51μm Nitex (acid cleaned) and 0.8 μm PES membrane (acid cleaned) for trace metal analysis. For the other pump head, seawater will also pass a 51μm Nitex (acid cleaned) and 1.0 μm QMA filter (400 ºC combusted) for major element (or natural radionuclides) analysis. We use a one-way valve to prevent the back flow of the seawater to the pump heads, which will potentially induce trace metal contamination.

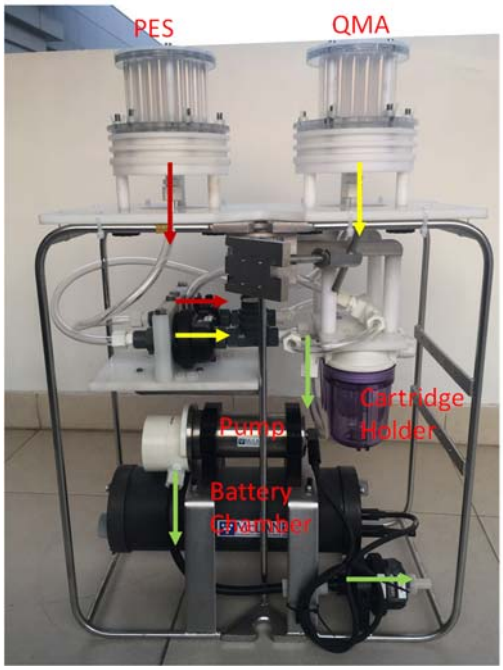


Figure 7. The new design of in-situ pump water transfer system with two pump heads

4.3.3. Sample processing:

1. 1/2 51μm Nitex filter from QMA pump head and one punch of 23 mm diameter QMA filter are used for POC, PN and particulate ^{234}Th analysis. The Nitex filter samples will be first washed onto a 25 mm diameter 1.0m QMA filter. Both QMA

filters will be mounted on plastic discs with a layer of aluminum foil and mylar cover, and beta counted onboard with a low-level beta counter.

2. 1/4 51μm Nitex samples from QMA pump head are washed onto a 25 mm 0.4μm polycarbonate membrane, and dried under 50 ºC in an oven for biogenic silica analysis.

3. 1/2 QMA filter is preserved under -20 ºC for particulate amino acids (PAA) analysis.

4. The whole 51μm Nitex samples from PES pump head are washed with clean filtered seawater onto a 25mm 0.8μm PES membrane, and dried under room temperature in a clean flow bench (Class 100) for further analysis of trace elements.

4.3.4. Sampling information:

Table 8 The deployment depth and pumping volumes of two pump heads

Station	Cast	Depth[a]	QMA-V[b] [L]	PES-V[b] [L]	Total-V [L]
K1	1	30	57.7	45.8	105
K1	1	60	442.6	645.2	1124.1
K1	1	90	92.4	173.5	323.8
K1	1	120	156.5	293.5	464.5
K1	1	200	587.7	791.1	1378.5
K1	1	300	436.2	1004.8	1446
K1	1	500	343.7	1089.4	1438.3
K1	2	1000	440.9	465.4	897
K1	2	1300	486.6	756	1248.7
K1	2	1500	367.1	779	1150.7
K1	2	1700	264.5	642	1162.5
K1	2	2000	364.8	500.4	869.5
K1	2	2500	313.6	552.3	870

K1	2	3000	268.1	1143.5	1396.7
K2	1	30	54.3	59.2	113
K2	1	60	288.9	535.3	866.7
K2	1	100	325.4	567.1	897
K2	1	130	289.5	611.5	1207
K2	1	250	551.6	803.7	1356
K2	1	400	472.1	764.5	1243
K2	1	700	264.2	1139.6	1392.9
K3	1	30	213.7	277.9	490
K3	1	80	319.7	562.8	910
K3	1	120	394.7	556.2	955.5
K3	1	200	371	670.5	1280.5
K3	1	300	550.2	734.1	1285
K3	1	420	439.2	564.8	1010
K3	1	700	326.1	1069.2	1385.3
K4	1	40	206.2	368.2	611
K4	1	80	319.4	431.9	754
K4	1	120	321.5	447.9	774.4
K4	1	170	308.6	625.4	936.6
K4	1	260	362	462	1019
K4	1	390	524.5	573.8	1099
K4	1	520	688.4	498.6	1188
K4	1	650	458.1	538.9	1048
K5	1	40	208.3	191.5	1667
K5	1	80	285	494.6	784
K5	1	120	300	707.6	1016.9
K5	1	170	419.4	941.5	1365.7
K5	1	260	527	572	1358

K5	1	390	576.9	782.1	1359
K5	1	520	484.4	713.6	1204
K5	1	650	358.2	506.2	912
K6	1	30	271.5	514.6	798
K6	1	80	392.9	479.8	877
K6	1	170	517.7	656.5	1212.9
K6	1	270	460.2	1101.9	1564.8
K6	1	410	573	565	1125
K6	1	550	453.8	591.4	1048
K6	1	690	476.1	425.1	903
K6	1	830	234	393.3	660
K7	1	30	263.2	500.1	771
K7	1	70	341.2	525.6	872
K7	1	110	475.3	692	1202.1
K7	1	190	592.2	1189.9	1785.9
K7	1	240	774	679	1432
K7	1	360	525.6	741.7	1268
K7	1	480	499.2	602.5	1109
K7	1	600	344.5	571.3	968
K8	1	40	396.8	608.9	1021
K8	1	80	405.2	886.2	1294
K8	1	130	362.4	630.2	1018.3
K8	1	210	396.1	714.5	1168
K8	1	280	617	872	1467
K8	1	420	486.5	715	1198
K8	1	560	554.2	991	1551
K8	1	700	612.7	673.9	1291.8
K8	2	700	358	455.2	842

K8	2	820	498.1	580.8	1086
K8	2	940	425.4	869.1	1424
K8	2	1200	254.2	416.7	704
K8	2	1750	403	574	968
K8	2	2300	393.6	533.5	929
K8	2	2900	621.4	624	1253
K8	2	3500	491	1359.8	1860
K9	1	50	326	543	889
K9	1	100	359.6	584.7	949
K9	1	140	13.6	32.1	34.2
K9	1	220	392.9	660.6	1112
K9	1	320	712	706	1394
K9	1	480	544.5	733.6	1279
K9	1	640	622.9	657.7	1284
K9	1	800	380.6	1548.4	1939.7
K11	1	80	368.1	530.8	931
K11	1	120	364.3	508.4	879
K11	1	180	406.9	737	1176.9
K11	1	250	589.6	673.5	1328
K11	1	300	648	669	1297
K11	1	400	510.2	715.1	1202
K11	1	600	570.6	576.1	1150
K11	1	1000	475	1429.4	1914.7
K12	1	60	376.8	543.5	929
K12	1	120	335.7	504.6	845
K12	1	200	416.9	574.7	1020.1
K12	1	250	541.7	461.5	1052
K12	1	400	505	477	966

K12	1	600	323.7	439.6	767
K12	1	800	516.5	522.6	1045
K12	1	1000	379.1	1453.2	1841.8
K13	1	60	338.5	487.5	832
K13	1	120	217.6	412	635
K13	1	200	347.2	575.1	938
K13	1	400	505.3	554.1	1112
K13	1	520	377	438	803
K13	1	600	678	560	1239
K13	1	800	542.8	484.9	1031
K13	1	1000	318.1	1173.3	1500.7
K14	1	60	193.2	309.2	505
K14	1	120	215.1	353.6	588
K14	1	180	390.2	498.6	903.6
K14	1	240	347.6	434.6	784
K14	1	400	359	407	754
K14	1	600	298.4	441.4	743
K14	1	800	380.7	370.7	754
K14	1	1000	249.3	852.5	1107.6

a: this depth information is determined from the length of winch cable.

b：QMA-V and PES-V refer to the pumping volumes for the QMA and PES pump heads, respectively.

During this cruise we deployed the in-situ pumping system at 11 clean stations and 2 mega stations. Generally, 7-8 in situ pumps were deployed in the upper 500 m in the clean stations while 16 depths were sampled in the upper 3500 m in the mega stations. The total pumping volume for all 13 stations summed to 123490.9 liters, which equals 428 CTD deployments (24 12-L Niskins bottles). For the PES pump head, 46739.1 liters seawater was pumped and 73023.2 liters seawater was pumped through QMA pump head.

4.3.5. Conclusion

This is the first Chinese GEOTRACES cruise with particulate trace element sampling that used the re-designed two-pump-head in-situ pump systems. Based on the pumping information onboard, the systems functioned well and satisfied the trace metal sampling. Further work after cruise will focus on the analysis of the samples collected from this cruise.

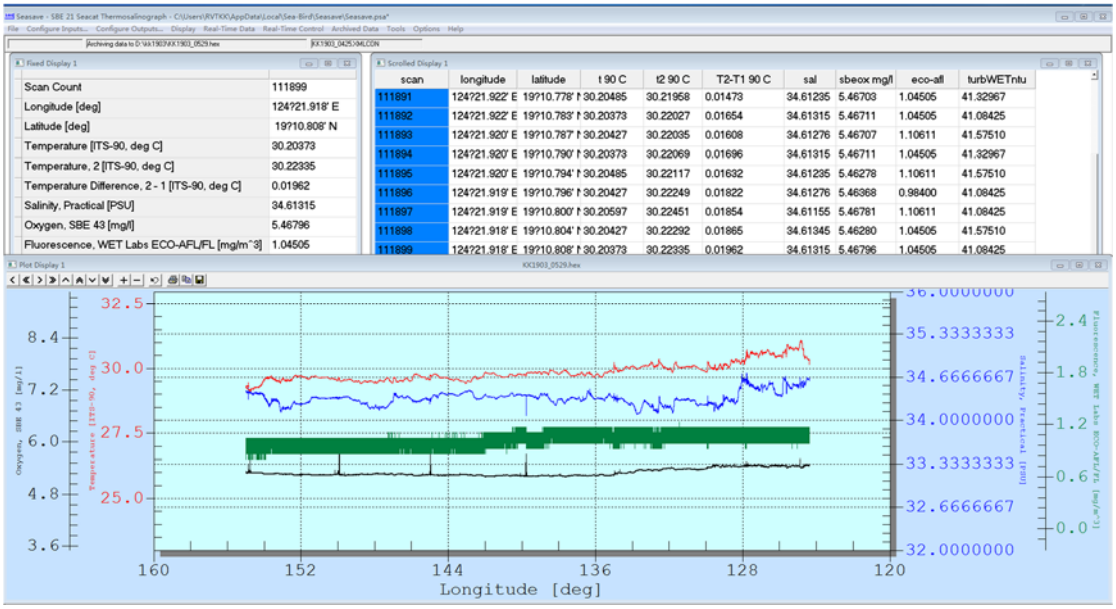
4.4. Underway Sampling

4.4.1. Underway CTD information (By Xirong Chen)

Table 9 Underway CTD information

Instrument	Parameters	Start Time	End Time
SBE 21	Temperature	Leg Ⅰ:2019 04 25 Leg Ⅱ:2019 05 15	Leg Ⅰ:2019 05 08 Leg Ⅱ:2019 06 13
	Conductivity/Salinity		
	Oxygen		
	Fluorescence		
	Turbidity		
OS-38K ADCP	Depth	Leg Ⅰ:2019 04 25 Leg Ⅱ:2019 05 15	Leg Ⅰ:2019 05 08 Leg Ⅱ:2019 06 13
	Seawater Speed/Direction		
WHM-300K ADCP	Depth	Leg Ⅰ:2019 04 25 Leg Ⅱ:2019 05 15	Leg Ⅰ:2019 05 08 Leg Ⅱ:2019 06 13
	Seawater Speed/Direction		
Vaisala (Maritime Observation Console)	Wind Speed/Direction	2019 04 25	2019 06 13
	Air Temperature		
	Air Humidity		
	Air Pressure		
	Dew Point		
	Precipitation		
	Solar Radiation		

An Example of data of SBE 21, ADCP and meteorological parameters is shown below.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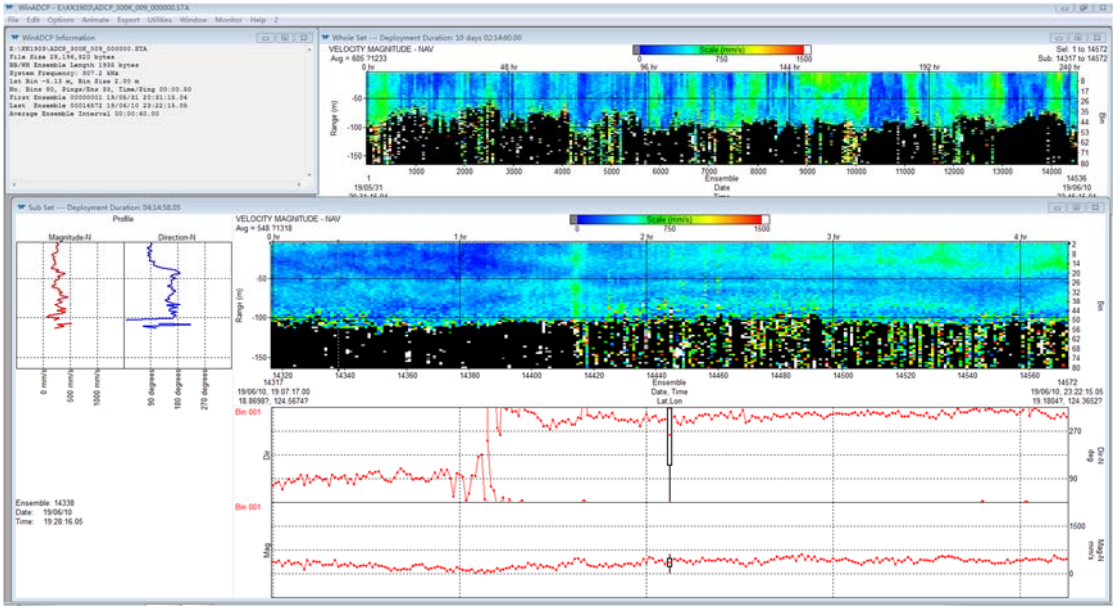
Scan Count 111899
Longitude [deg] 124?21.918' E
Latitude [deg] 19?10.808' N
Temperature [ITS-90, deg C] 30.20373
Temperature, 2 [ITS-90, deg C] 30.22335
Temperature Difference, 2 - 1 [ITS-90, deg C] 0.01962
Salinity, Practical [PSU] 34.61315
Oxygen, SBE 43 [mg/l] 5.46796
Fluorescence, WET Labs ECO-AFL/FL [mg/m^3] 1.04505
Scrolled Display 1
scan | longitude | latitude | t 90 C | t2 90 C | T2-T1 90 C | sal | sbeox mg/l | eco-afl | turbWETntu
111891 | 124?21.922' E | 19?10.778' N | 30.20485 | 30.21958 | 0.01473 | 34.61235 | 5.46703 | 1.04505 | 41.32967
111892 | 124?21.922' E | 19?10.783' N | 30.20373 | 30.22027 | 0.01654 | 34.61315 | 5.46711 | 1.04505 | 41.08425
111893 | 124?21.920' E | 19?10.787' N | 30.20427 | 30.22035 | 0.01608 | 34.61276 | 5.46707 | 1.10611 | 41.57510
111894 | 124?21.920' E | 19?10.790' N | 30.20373 | 30.22069 | 0.01696 | 34.61315 | 5.46711 | 1.04505 | 41.32967
111895 | 124?21.920' E | 19?10.794' N | 30.20485 | 30.22117 | 0.01632 | 34.61235 | 5.46278 | 1.10611 | 41.57510
111896 | 124?21.919' E | 19?10.796' N | 30.20427 | 30.22249 | 0.01822 | 34.61276 | 5.46368 | 0.98400 | 41.08425
111897 | 124?21.919' E | 19?10.800' N | 30.20597 | 30.22451 | 0.01854 | 34.61155 | 5.46781 | 1.10611 | 41.08425
111898 | 124?21.918' E | 19?10.804' N | 30.20427 | 30.22292 | 0.01865 | 34.61345 | 5.46280 | 1.04505 | 41.57510
111899 | 124?21.918' E | 19?10.808' N | 30.20373 | 30.22335 | 0.01962 | 34.61315 | 5.46796 | 1.04505 | 41.08425
Plot Display 1
Longitude [deg]
160
152
144
136
128
120

(a)


WinADCP Information
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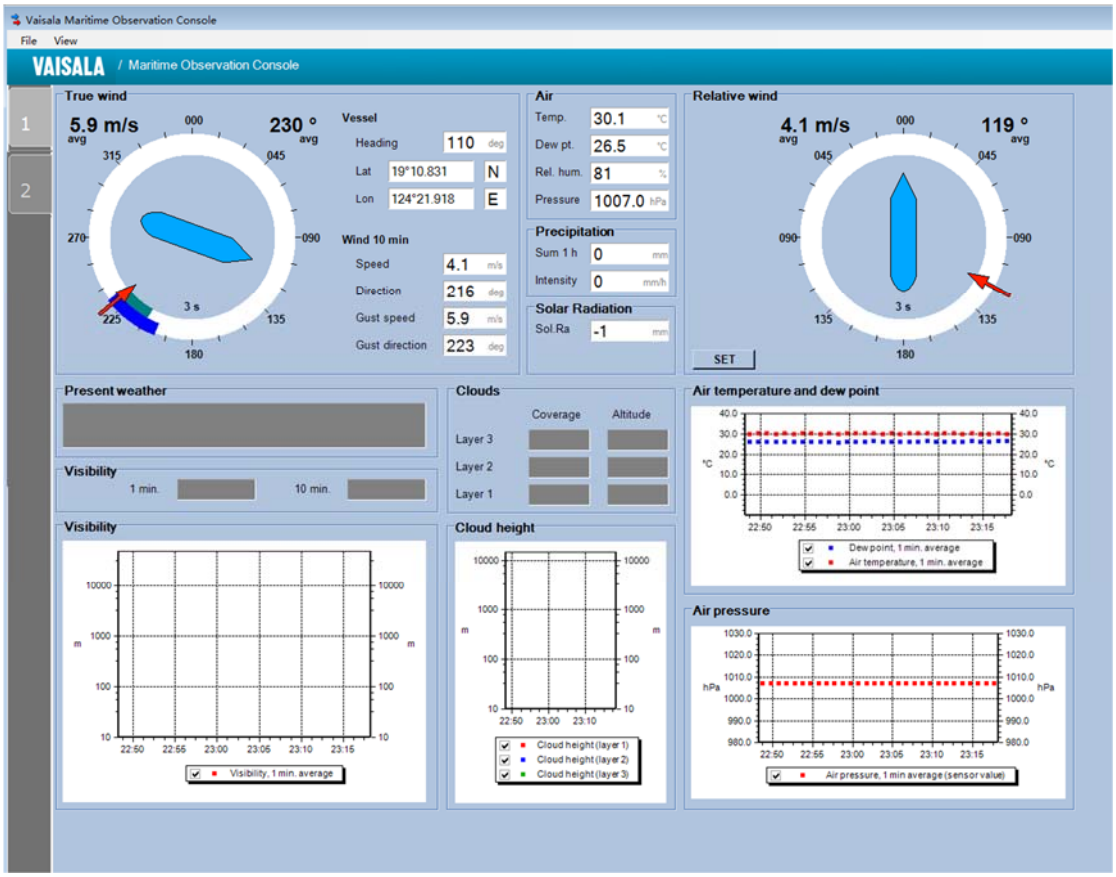
VELOCITY MAGNITUDE - NAV
Sub Set --- Deployment Duration: 04:14:58.05
Profile
Magnitude-N
Direction-N
VELOCITY MAGNITUDE - NAV
Ensemble
Date, Time
Lat,Lon

(b)



(c)

Figure 8. Data of SBE 21 (a), ADCP (b) and meteorological parameters (c).

4.4.2. Partial pressure of carbon dioxide (pCO_2) (By Yi Xu, Minhan Dai)

The surface seawater partial pressure of carbon dioxide was continuously measured onboard with a cavity ring-down analyzer (Picarro G2301) integrated into an underway automated flowing pCO_2 system (Model 8050, General Oceanic Inc. USA). The schematic diagram of the underway pCO_2 system is shown in Fig. 9. The system is highly compact and operates by directing seawater to flow through a chamber (the equilibrator) where the CO_2 contained in the seawater equilibrates with the gas in the chamber (the headspace gas). The equilibrated gas in the headspace is pumped into a cavity ring-down analyzer (Picarro G2301) to measure its CO_2 mole fraction (xCO_2) instantaneously, and then returned to the equilibrator, forming a closed loop. Periodically, atmospheric air is also pumped through the analyzer to measure its CO_2

mole fraction. The analyzer is calibrated with four CO_2 standard gases at regular intervals. Meanwhile, temperature and salinity of flowing seawater are measured by temperature and salinity sensors (Seabird SBE 45), respectively, and dissolved oxygen is measured by oxygen sensor (Aanderaa 4330) throughout the system for analytical, troubleshooting, and quality control purposes.

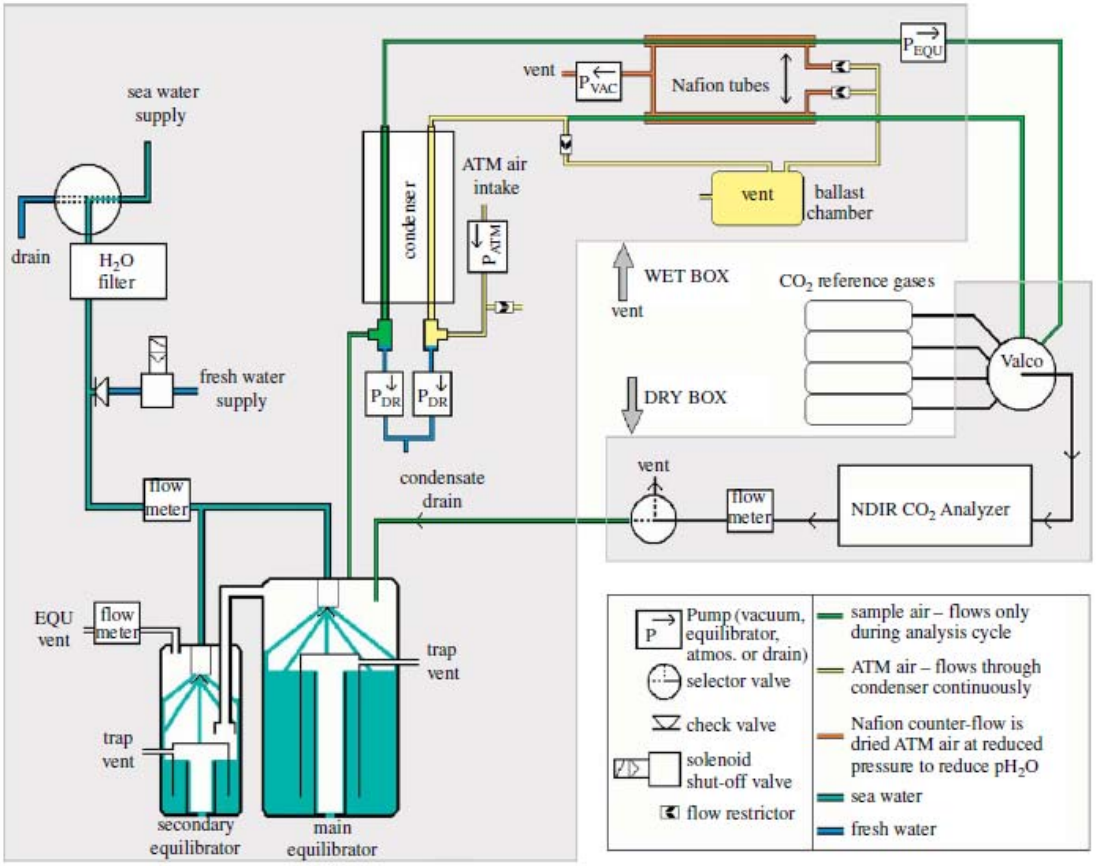


Figure 9. Schematic diagram of the underway pCO_2 system

4.4.3. Towed fish (By Jing Liu, Yaojing Chen, Qian Liu, Ruifeng Zhang, Yihua Cai)

4.4.3.1. Objectives

The aim of the towed fish sampling in this cruise was to obtain the high spatial resolution biogeochemical information along the cruise track in the wNP. The main objective of the GEOTRACES program was to describe the high-resolution trace

element distributions in the global ocean. While the trace metal clean rosette sampling allows us to obtain the high resolution vertical distributions of TEIs, the towed fish sampling allows us to observe a high resolution surface distribution for the trace substances in the ocean. Based on the information from the fish sampling, we can depict the distribution patterns of a lot more detailed biogeochemical parameters along the cruise track, and are able to link the detailed physical, biological, and chemical processes at surface. The fish also provided an opportunity to collect trace metal clean surface seawater for the incubation experiments.

4.4.3.2.Parameters

Underway samples were collected at a high spatial resolution (~50 km) by a towed fish while the ship was steaming. Parameters from the towed fish sampling include phosphorus, NO_3^-+NO_2^-, silicate, trace metals (e.g. Fe, Zn, Cd, Al, Mn, REEs), trace metal isotopes (e.g. δ^{56}Fe, δ^{66}Zn, δ^{114}Cd), dissolved organic carbon (DOC), dissolved organic nitrogen (DON), dissolved organic phosphorous (DOP), and chlorophyll *a*.

4.4.3.3.Analytical Methods

The analytical methods for each parameter are described at Sections 4.1.2, 4.1.3., and 4.2.4, respectively.

4.4.3.4.Sampling information

A towed fish was deployed to obtain high resolution surface seawater samples. The configuration of the fish system was upgraded from the combination of the previous designs, e.g. Bruland et al, (2005), Vink et al., (2000) and Zhang et al., (2019). A 6-m long boom kept the fish distanced from the ship when towed at sea (Figure 10). Low density polyethylene tubing was used to collect surface samples from the sea surface directly into a trace metal clean van on the vessel. Our fish system allowed collection of trace metal clean seawater at a depths between 0.5-1.5 m while the ship speed was at 10-13 knots during the whole cruise. The samples were either collected unfiltered, or

filtered by a 0.8/0.2 μm capsule filter (Millipore).

A total of 146 surface towed fish samples were obtained by the towed fish system. The Fish system was first deployed at 18:29, 4/30/2019 in the oligotrophic Luzon Strait, and recovered at 12:30, 6/12/2019 in the coastal ocean of Taiwan Strait.

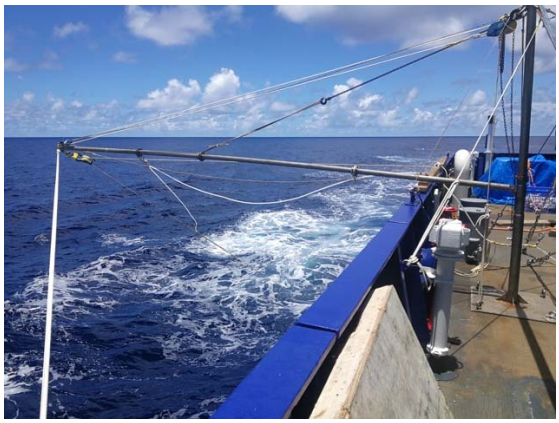


Figure 10. Towing Fish at sea

Table 10 The information of 146 surface towed fish samples

Sample ID	Date (Beijing time)	Time (Beijing time)
GP09-TF-0001	4/30/19	18:29
GP09-TF-0002	4/30/19	21:10
GP09-TF-0003	5/1/19	0:00
GP09-TF-0004	5/1/19	3:24
GP09-TF-0005	5/1/19	5:55
GP09-TF-0006	5/1/19	9:00
GP09-TF-0007	5/1/19	12:15
GP09-TF-0008	5/1/19	14:58
GP09-TF-0009	5/2/19	22:00
GP09-TF-0010	5/3/19	2:10
GP09-TF-0011	5/3/19	13:05
GP09-TF-0012	5/3/19	16:15
GP09-TF-0013	5/3/19	19:30
GP09-TF-0014	5/16/19	9:00
GP09-TF-0015	5/16/19	10:00
GP09-TF-0016	5/16/19	11:00
GP09-TF-0017	5/16/19	12:00
GP09-TF-0018	5/16/19	13:00
GP09-TF-0019	5/16/19	14:00

GP09-TF-0020	5/16/19	15:00
GP09-TF-0021	5/16/19	16:00
GP09-TF-0022	5/16/19	17:00
GP09-TF-0023	5/16/19	18:00
GP09-TF-0024	5/16/19	19:00
GP09-TF-0025	5/16/19	20:00
GP09-TF-0026	5/16/19	21:00
GP09-TF-0027	5/16/19	23:55
GP09-TF-0028	5/17/19	3:00
GP09-TF-0029	5/17/19	6:00
GP09-TF-0030	5/17/19	9:00
GP09-TF-0031	5/17/19	12:00
GP09-TF-0032	5/17/19	15:00
GP09-TF-0033	5/17/19	17:58
GP09-TF-0034	5/17/19	21:03
GP09-TF-0035	5/18/19	0:00
GP09-TF-0036	5/18/19	2:58
GP09-TF-0037	5/18/19	5:59
GP09-TF-0038	5/18/19	8:58
GP09-TF-0039	5/18/19	12:00
GP09-TF-0040	5/18/19	15:03
GP09-TF-0041	5/18/19	17:55
GP09-TF-0042	5/18/19	21:03
GP09-TF-0043	5/19/19	0:02
GP09-TF-0044	5/19/19	2:55
GP09-TF-0045	5/19/19	5:57
GP09-TF-0046	5/19/19	9:00
GP09-TF-0047	5/19/19	12:00
GP09-TF-0048	5/19/19	15:00
GP09-TF-0049	5/19/19	17:58
GP09-TF-0050	5/19/19	21:00
GP09-TF-0051	5/20/19	23:03
GP09-TF-0052	5/21/19	1:56
GP09-TF-0053	5/21/19	5:00
GP09-TF-0054	5/21/19	8:03
GP09-TF-0055	5/21/19	10:58
GP09-TF-0056	5/21/19	13:56
GP09-TF-0057	5/21/19	17:00
GP09-TF-0058	5/21/19	19:58
GP09-TF-0059	5/22/19	20:00
GP09-TF-0060	5/22/19	23:02

GP09-TF-0061	5/23/19	2:00
GP09-TF-0062	5/23/19	5:00
GP09-TF-0063	5/23/19	8:04
GP09-TF-0064	5/23/19	10:59
GP09-TF-0065	5/23/19	14:00
GP09-TF-0066	5/24/19	16:01
GP09-TF-0067	5/24/19	19:02
GP09-TF-0068	5/24/19	21:56
GP09-TF-0069	5/25/19	0:58
GP09-TF-0070	5/25/19	4:01
GP09-TF-0071	5/25/19	7:03
GP09-TF-0072	5/25/19	9:59
GP09-TF-0073	5/25/19	13:01
GP09-TF-0074	5/25/19	16:00
GP09-TF-0075	5/25/19	19:06
GP09-TF-0076	5/26/19	19:56
GP09-TF-0077	5/26/19	23:05
GP09-TF-0078	5/27/19	2:20
GP09-TF-0079	5/27/19	5:00
GP09-TF-0080	5/27/19	8:01
GP09-TF-0081	5/27/19	10:59
GP09-TF-0082	5/27/19	13:55
GP09-TF-0083	5/27/19	17:15
GP09-TF-0084	5/27/19	20:00
GP09-TF-0085	5/27/19	22:55
GP09-TF-0086	5/28/19	2:00
GP09-TF-0087	5/30/19	9:58
GP09-TF-0088	5/30/19	13:03
GP09-TF-0089	5/30/19	16:04
GP09-TF-0090	5/30/19	19:05
GP09-TF-0091	5/30/19	22:01
GP09-TF-0092	5/31/19	0:58
GP09-TF-0093	5/31/19	3:59
GP09-TF-0094	6/1/19	8:00
GP09-TF-0095	6/1/19	11:00
GP09-TF-0096	6/1/19	14:00
GP09-TF-0097	6/1/19	17:00
GP09-TF-0098	6/1/19	20:00
GP09-TF-0099	6/1/19	23:00
GP09-TF-0100	6/2/19	2:00
GP09-TF-0101	6/2/19	19:12

GP09-TF-0102	6/2/19	21:59
GP09-TF-0103	6/3/19	1:00
GP09-TF-0104	6/3/19	4:00
GP09-TF-0105	6/3/19	6:59
GP09-TF-0106	6/3/19	10:06
GP09-TF-0107	6/3/19	12:58
GP09-TF-0108	6/4/19	14:01
GP09-TF-0109	6/4/19	17:00
GP09-TF-0110	6/4/19	19:58
GP09-TF-0111	6/4/19	23:00
GP09-TF-0112	6/5/19	1:50
GP09-TF-0113	6/5/19	5:05
GP09-TF-0114	6/5/19	8:15
GP09-TF-0115	6/6/19	6:30
GP09-TF-0116	6/6/19	8:52
GP09-TF-0117	6/6/19	12:00
GP09-TF-0118	6/6/19	15:00
GP09-TF-0119	6/6/19	18:00
GP09-TF-0120	6/6/19	21:00
GP09-TF-0121	6/6/19	23:56
GP09-TF-0122	6/8/19	2:00
GP09-TF-0123	6/8/19	5:00
GP09-TF-0124	6/8/19	8:00
GP09-TF-0125	6/8/19	11:35
GP09-TF-0126	6/8/19	14:05
GP09-TF-0127	6/8/19	16:58
GP09-TF-0128	6/8/19	20:00
GP09-TF-0129	6/9/19	22:21
GP09-TF-0130	6/10/19	0:56
GP09-TF-0131	6/10/19	4:00
GP09-TF-0132	6/10/19	7:00
GP09-TF-0133	6/10/19	10:11
GP09-TF-0134	6/10/19	13:15
GP09-TF-0135	6/10/19	16:20
GP09-TF-0136	6/11/19	6:05
GP09-TF-0137	6/11/19	9:00
GP09-TF-0138	6/11/19	12:02
GP09-TF-0139	6/11/19	15:02
GP09-TF-0140	6/11/19	19:08
GP09-TF-0141	6/11/19	21:03
GP09-TF-0142	6/12/19	0:00

GP09-TF-0143	6/12/19	3:00
GP09-TF-0144	6/12/19	6:00
GP09-TF-0145	6/12/19	9:00
GP09-TF-0146	6/12/19	11:55

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Zhang, R., X. Zhu, C. Yang, L. Ye, G. Zhang, J. Ren, Y. Wu, S. Liu, J. Zhang, and M. Zhou. 2019. Distribution of dissolved iron in the Pearl River (Zhujiang) Estuary and the northern continental slope of the South China Sea. Deep-Sea Res. II, doi: 10.1016/J.DSR2.2018.12.006.

4.5. Aerosol Sampling

4.5.1. Major ions and water soluble organic carbon (By Zixiang Yang, Xiongfeng Huang, Hongyan Bao, Shuh-Ji Kao)

Total suspended particles (TSP) were collected by using a large volume aerosol sampler on board. The aerosol sampler was placed on the top deck of the ship, and air was pumped through a filter (Whatman QMA, pre-combusted at 450 ºC for 5h) at a rate of approximately 1 m^3 min^{-1} while cruising. All samples were then stored frozen after retrieving until further analysis. To improve our understanding of the spatial distributions, the chemical properties of the major aerosol types and their contributions to the upper ocean nutrient budget, major ions and nutrients (including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, NO_2^-, NH_4^+ and SO_4^{2-}) and water soluble organic carbon (WSOC) will be measured. Major ions and nutrients will be extracted by ultrapure water, and then be determined by an ion chromatograph following the method described in Luo et al. (2016). WSOC will be extracted in the lab following the method described in Bao et al.

(2017), and determined by using a Shimadzu TOC analyzer.

References

Bao H. Y., J. Niggemann, L. Luo, T. Dittmar, and S.-J. Kao. 2017. Aerosols as a source of dissolved black carbon to the ocean. Nature Communications, 8: 510.

Luo, L., X. H. Yao, H. W. Gao, S. C. Hsu, J. W. Li, and S.-J. Kao. 2016. Nitrogen speciation in various types of aerosols in spring over the northwestern Pacific Ocean, Atmospheric Chemistry and Physics, 16(1): 325-341.

4.5.2. Amino acids (By Zixiang Yang, Tiantian Tang)

10 samples in total for amino acids were collected using a high-volume TSP air sampler (Model 2031, Laoying Co., Ltd.) with a pre-combusted (450°C) quartz filter. The sampler only operated during sailing with a flow of 1.05 m^3/min. Each sample was collected for 2-3 days. The filtered samples were stored at -20 °C before analysis. These aerosol samples will be analyzed for organic carbon, amino acids and related compounds. Total carbon (TC) concentration and the stable carbon isotopic composition ($\delta^{13}C$) of TC will be determined using an Elemental Analyzer-Isotope Ratio Mass Spectrometry (EA-IRMS). The stable carbon isotope of individual amino acids and their relative composition will be further measured using gas chromatography-mass spectrometry (GC-MS) and gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS).

4.5.3. Thorium solubility (By Xin Wang, Yihua Cai)

Aerosol samples were collected for the determination of Th solubility in the wNP. The obtained Th solubility will then be applied in the long-lived Th isotopes ($^{230}Th/^{232}Th$) approach to quantify the lithogenic dust deposition rate.

Shipboard aerosol collection was conducted using Volumetric Flow Controlled (VFC) medium volume samplers (100L/min) with Whatman 41 low ash cellulose esters

membranes. Aerosol particles on the membrane will be leached by acetic acid and/or seawater and ^{232}Th in the leachate will be measured by ICP-MS.

Three samples are collected from Xiamen to K3, K4 to K8, and K8 to K11, respectively.

4.5.4. Trace Elements and Isotopes (By Siteng Zhu, Noguchi Tadateru, Qian He, Huijun He, Jing Zhang)

Objectives:

It has been recognized that atmospheric deposition might be an important source of micro-nutrient (e.g. Fe, Mn, Cu) and macro-nutrient (N, P) to the euphotic zone of open oceans. For example, the seasonal variation of Fe concentration in the upper layer of station ALOHA (time-series station in Hawaii) had significant correlation with the variability of dust deposition. However, the observation data in the North Pacific Subtropical Gyre (NPSG) are scant. In our study, we aim to quantify the micro-nutrient (Fe etc.) input from atmospheric deposition (aerosol and rainwater) and reveal the spatial variability and their origin in the NPSG.

Parameters:

Trace elements (Al, Ti, Fe, V, Zn, Pb, Mn, Ni, Cu, Hg), REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), major anions (SO_4^{2-}, Cl^-), isotopes ($^{34/32}S$), and nutrients (NO_3^-, PO_4^{3-}).

Sampling Information:

In this cruise, 20 aerosol samples were collected using a trace atmospheric sampler. Details are presented in Table 11.

Analytical Methods:

Table 11 GP09 spring cruise-Aerosol trace metal sampling log

Sample No.	Start time	Start longitude and latitude	End time	End longitude and latitude	Sample time	Sample volume/m^3	Sample station
AERT01	4-25	N 24°18.556	4-27	N 21°0.557	29h54min	1803.6	XM-K1
TSP01	11:16	E 118°10.989	3:00	E 121°20.196			
AERT02	4-27	N 21°0.732	4-30	N 21°6.915	80h04min	4880.8	K1
TSP02	5:30	E 121°12.791	13:55	E 121°19.628			
AERT03	4-30	N 21°3.006	5-3	N 18°35.929	50h36min	3050.4	K1-K3
TSP03	16:39	E 121°42.446	21:00	E 130°25.392			
AERT04	5-4	N 18°37.726	5-7	N 21°32.697	57h52min	3489.4	K3-K1
TSP17	23:17	E 130°19.568	10:30	E 120°13.010			
AERT05	5-7	N 21°35.014	5-9	N 24°14.657	22h53min	1381.4	K1-XM
TSP15	10:57	E 120°9.124	0:12	E 118°11.215			
AERT06	5-10	N 24°27.236	5-13	N 24°27.236	69h02min	4044.8	XM01
TSP14	18:09	E 117°58.947	15:14	E 117°58.947			
AERT07	5-13	N 24°27.236	5-14	N 24°27.236	27h14min	1648.5	XM02
TSP09	15:21	E 117°58.947	18:30	E 117°58.947			
AERT08	5-14	N 24°27.236	5-15	N 24°27.236	16h01min	971.2	XM03
TSP08	18:45	E 117°58.947	11:00	E 117°58.947			
AERT09	5-15	N 24°13.989	5-16	N 21°40.409	17h26min	1067.7	Taiwan Strait
TSP10	14:03	E 118°11.055	7:30	E 120°7.992			

AERT10	5-16	N 21°40.409	5-16	N 21°2.497	10h18min	631.2	Luzon Strait
TSP05	7:30	E 120°7.992	18:00	E 121°50.849			
AERT11	5-16	N 21°2.497	5-17	N 19°59.730	20h	1348.4	
TSP16	18:00	E 121°50.849	16:00	E 125°50.543			
AERT12	5-17	N 19°55.771	5-18	N 19°18.876	0h	0	Blank
TSP13	18:44	E 126°3.175	6:28	E 128°4.57			
AERT13	5-18	N 19°18.876	5-20	N 17°12.000	39h29min	2420.6	0
TSP12	6:28	E 128°4.57	0:14	E 135°0.031			
AERT14	5-20	N 17°8.846	5-23	N 17°11.902	49h59min	3029.9	K4-K6
TSP07	20:30	E 135°28.133	18:00	E 144°58.482			
AERT15	5-24	N 17°7.354	5-28	N 11°32.580	61h54min	3749	K6-K8
TSP18	12:40	E 145°4.818	0:00	E 154°7.752			
AERT16	5-28	N 10°59.385	5-30	N 10°59.385	37h24min	2264.4	K8
TSP25	9:01	E 154°55.694	12:00	E 154°55.694			
AERT17	5-30	N 10°56.615	6-3	N 10°59.691	64h36min	3911.1	K8-K11
TSP38	8:01	E 154°34.916	14:54	E 140°9.423			
AERT18	6-4	N 11°5.799	6-7	N 11°0.038	39h45min	2408.5	K11-K13
TSP34	11:30	E 139°39.835	1:30	E 130°2.069			
AERT19	6-7	N 11°15.719	6-12	N 22°18.827	76h46min	4647.5	K13-K14a
TSP39	22:50	E 129°36.742	7:30	E 119°24.231			

Aerosol samples were collected using a high-volume (1000 L/min) air sampler on the compass deck with Whatman 41 membrane filter (low ash cellulose esters, PN 1441-047) during this cruise. The samples were preserved at 4 degree Celsius on board. Half of the aerosol filters will be digested using a mixture of HNO_3 and HF with heat and/or pressure in specially designed microwaves or in sealed Teflon jars on hotplates. The aerosol digestion solutions will be determined for trace metals elements (Al, Ti, Fe, V, Zn, Pb, Mn, Ni, Cu, Hg) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) by inductively coupled plasma mass spectrometry and anion ions (SO_4^{2-}, Cl^-) by ion chromatography.

One quarter of aerosol filters will be shredded and soaked overnight in Milli-Q water. Filters will be isolated from solutions by centrifugation and the water-soluble sulfate will be precipitated from solution as $BaSO_4$ by the addition of $BaCl_2$ solution. The $BaSO_4$ precipitates will be separated from the solution by filtration and reduced to sulfide by gently boiling of a reduction solution (HI + H_3PO_2 + HCl) while purging with N_2. Sulfide will be chemically trapped as Ag_2S in a second trap filled with Milli-Q water, $AgNO_3$ and HNO_3. The solution with precipitated Ag_2S will be aged in the dark, then filtered and rinsed with Mill-Q water and NH_4OH. The Ag_2S precipitate in package will be subsequently filled with fluorine gas and heated overnight to produce sulfur hexafluoride (SF_6) and determined by MAT 253 mass spectrometer to get the ratio of $^{34/32}S$.

4.6. Turbulence and light spectrum

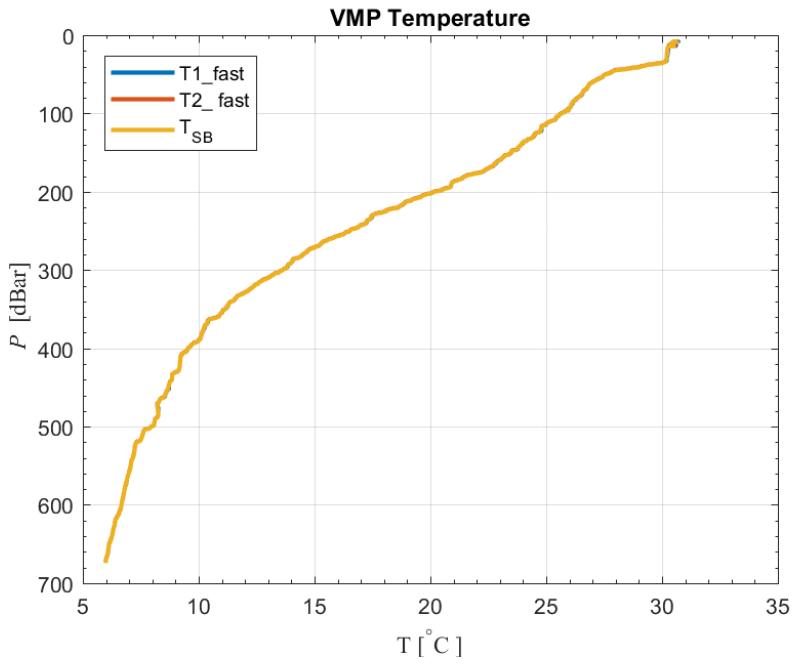
4.6.1. Turbulence (By Xirong Chen, Fangtao Zhang, Zhiyu Liu)

Table 12 VMP basic information

instrument	Parameter	station number	cast number
VMP	Temperature	14	27
	Conductivity/Salinity		
	Pressure/Depth		
	turbulent dissipation		

The main purpose of turbulence field work on this voyage is to obtain the profile data of turbulence dissipation rate using the turbulence profiler (VMP). The turbulent mixing group mainly uses a turbulence profiler to observe turbulence by measuring turbulent velocity fluctuating shear and calculating turbulent dissipation rate. The mixing intensity of the sea area is obtained by observing the turbulent dissipation rate, and the material and energy fluxes of the sea are calculated. VMP includes a fast temperature probe, a conductivity probe and shear probe, which can measure the temperature, salinity and turbulent dissipation of seawater.

VMP example is shown below:



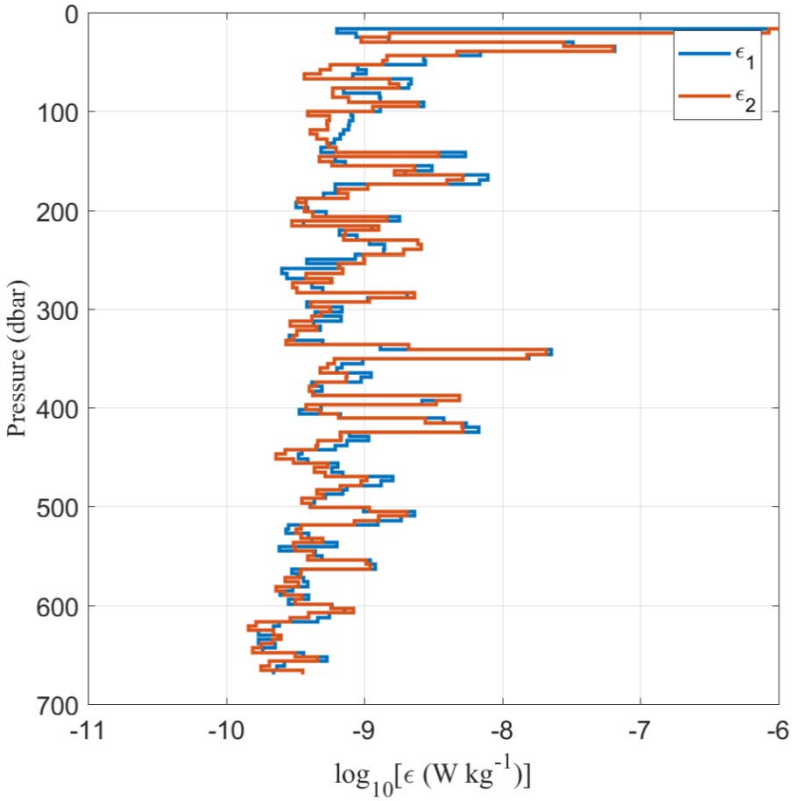


Figure 11. VMP example

4.6.2. Light spectrum measurement by Stor-X (Satlantic inc) (By Yuanli Zhu, Fei Chai)

SIO group measured the underwater light spectrum (348.2-806.5 nm, every 3.5 nm) until 200 m, to obtain the light field characteristic. This information can be further used for analyzing phytoplankton production while combining with Chl-*a*, absorption and other information.

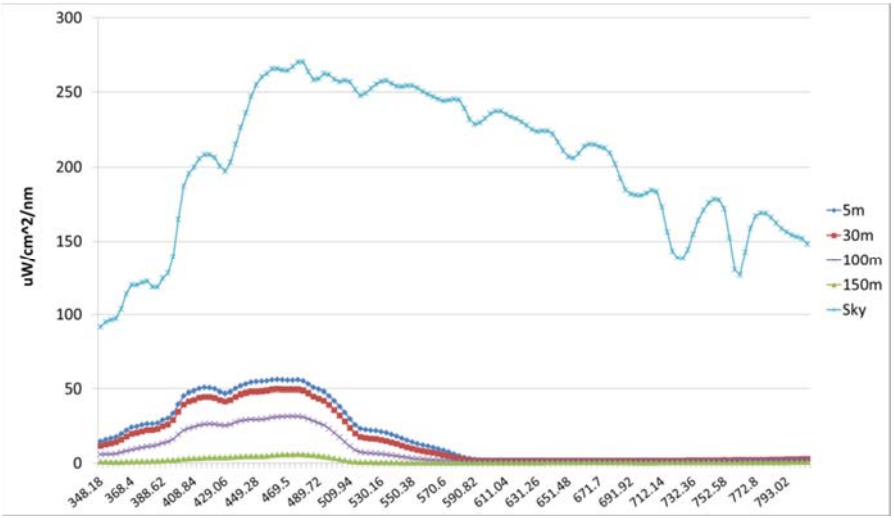


Figure 12. Light spectrum at different depths at K6

4.7. On-deck Incubation

4.7.1. N_2 fixation rate (By Zuozhu Wen, Wenfang Lin, Rongbo Dai, Dalin Shi)

The N_2 fixation is a key process which provides bioavailable nitrogen for the growth of phytoplankton that living in the euphotic zone. In some areas of the oligotrophic open ocean, such "new nitrogen" derived by the N_2-fixers can equal to the nitrogen that diffused from the deep water, which substantially supports primary production and subsequently export production. In the western North Pacific Subtropical Gyre, however, few efforts have been conducted to understand the spatial distribution of N_2 fixation and its controlling factors. For these purposes, N_2 fixation rates as well as the diazotroph composition were measured during this cruise. In addition, deck-based incubation experiments were set up by adding Fe and P alone or simultaneously to understand the limiting nutrients of N_2 fixation across the wNPSG. Sampling stations and experiments conducted in the NPSG are listed in Figure 13. 15 stations are sampled and investigated in total. At each station, seawater of 6 layers in the upper DCM are collected to measure the N_2 fixation rates, primary production, Diazotroph composition, Chl-*a* and POC/PON. Surface water was also collected at 64 stations to measure N_2

fixation rates, primary production, Diazotroph composition and POC/PON.

9 Fe and/or P addition experiments are conducted at selected stations (green triangles in Figure 13). Our purpose is to understand the nutrients limitation pattern of N_2 fixation and its spatial variation in the NPSG. Samples for N_2 fixation rates, primary production, Diazotroph composition and POC/PON were collected.

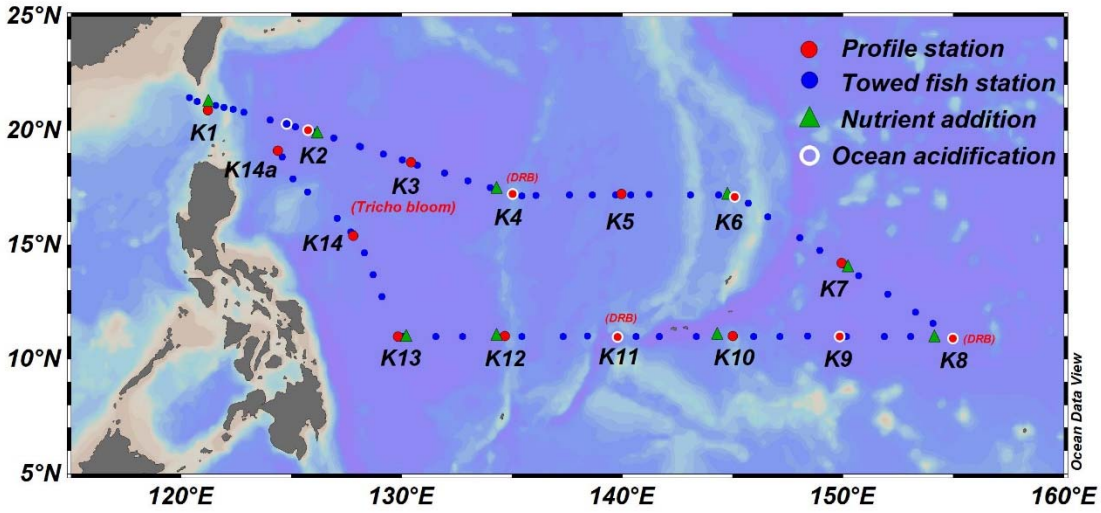


Figure 13. Sampling stations for NFR and nutrient limitation investigations

The Chla concentration at K1 to K13 profiles are shown in Figure 14.

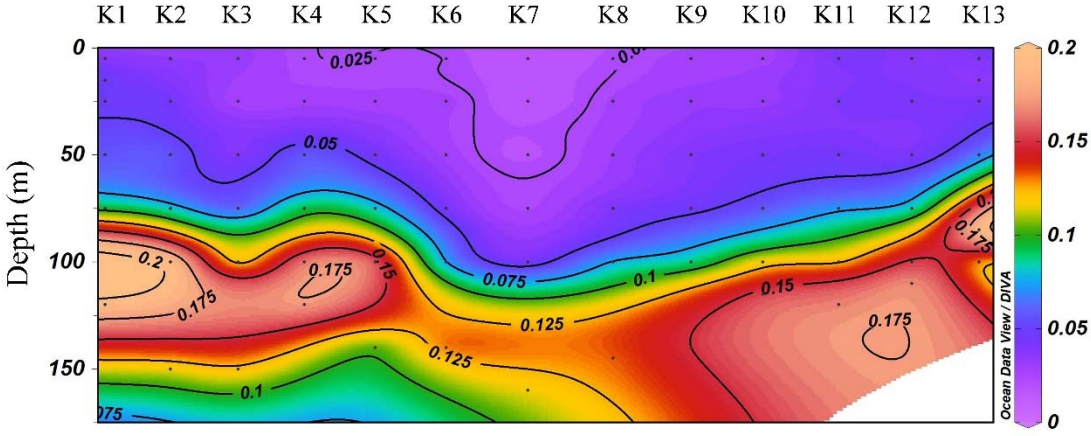


Figure 14. The Chla concentration at K1 to K13 profile stations

4.7.2. Aphotic N_2 fixation (By Siqi Wu, Shuh-Ji Kao)

Objectives:

1. To measure N_2 fixation rate profile in aphotic condition.
2. To test if amino acid addition can enhance N_2 fixation below euphotic zone.

Analytical Methods:

N_2 fixation rate will be measured following the $^{15}N_2$ gas bubble method (Montoya et al., 1996) and isotope composition of PN by alkaline persulfate oxidation method (Knapp et al., 2005).

Sampling Information:

1. N_2 fixation rate profiles in aphotic condition were conducted in K1 (12 layers), K5 (11 layers), K6 (16 layers), K7 (11 layers), K8 (13 layers), K10 (4 layers), K11 (12 layers), K13 (12 layers), and K14 (7 layers).
2. N_2 fixation with amino acid addition were conducted in K1 station (200m, 715m) and K8 station (283m, 375m).

Reference

Knapp, A. N., D. M. Sigman, and F. Lipschultz. 2005. N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site. Global Biogeochemical Cycles, 19, GB1018, doi:10.1029/2004GB002320.

Montoya, J. P., M. Voss, P. Kahler, and D. G. Capone. 1996. A Simple, High-Precision, High-Sensitivity Tracer Assay for N_2 Fixation. Appl. Environ. Microbiol., 62(3): 986-993.

4.7.3. Incubation of near-surface seawater with individual and combinations of nutrients (By Thomas Browning, Eric P. Achterberg)

Fourteen 48-hour duration on-deck nutrient addition incubation experiments were carried out in 1L trace-metal-clean Nalgene polycarbonate bottles, following protocols

described in Browning et al. (2017). Surface (~1–2 m depth) seawater for the experiments is sampled from a custom-built towed fish delivered to a container laboratory over-pressurized with HEPA-filtered air, as described previously (Section 4.4). Seawater was collected at dusk/night time. Bottle filling times were approximately 30 minutes. Bottled seawater was spiked with the following combinations of nutrients/trace metals: N (nitrate+ammonia), phosphate, Fe, (and all combinations therein), and additionally nitrate, nitrate+Fe, N+Fe+Co, N+Fe+Zn, and filters with natural aerosol collected during the cruise (Section 4.5) at some sites. Initial conditions were sampled from triplicate 1 L bottle bottles. Triplicate control bottles with no nutrients added were also collected and incubated alongside all nutrient-treated bottles. To characterize the biogeochemical setting at the seawater collection site, samples were collected for macronutrients (nitrate, phosphate, ammonia) and trace elements (0.2 µm filtered and unfiltered), either directly before or after the incubation bottle filling. Phosphate and ammonia concentrations were analysed on ship; nitrate samples were frozen at -20°C and will be analysed upon return to laboratories at Xiamen University. Samples for trace element concentration analyses are collected in acid-washed 250 mL LDPE sample bottles (Nalgene) for dissolved (0.8/0.2 µm Pall Acropak filter capsule) and total dissolvable (no filtration) fractions (metals: Fe, Zn, Mn, Mg, Cu, Co, Cd, Pb). Samples were acidified to pH 1.9 using ultrapure concentrated HCl. These samples will be returned to GEOMAR and pre-concentrated on a Sea*FAST* system (Thermo scientific) and subsequently analysed on an Element XR ICP-MS following the method of Rapp et al. (2017).

Filled and nutrient-spiked incubation bottles will be placed in on-deck (aft deck) incubators connected to the ships underway flow-through system, to continuously maintain temperatures at that of sea surface waters. Incubators were screened with Blue Lagoon screening (Lee Filters), which maintains irradiance at ~30% of that of the surface. After incubation, experiments were taken down and measurements made for: chlorophyll-a concentrations (1 replicate per treatment bottle), FRRf (1 replicate per treatment bottle), analytical flow cytometry (1 replicate per treatment bottle), and

HPLC pigments (some treatments, pooled replicates). Further details of biological sample measurements are detailed below.

- Chlorophyll-a concentrations: 250-500 mL samples were filtered onto Machery Nagel GFF filter papers and extracted for ~24 hours in 10 mL 90% HPLC-grade acetone in a -20 °C freezer in the dark before measurement on a Turner Designs fluorometer following the method of Welschmeyer (1994).
- High Performance Liquid Chromatography (HPLC): 2-5 L seawater was filtered onto Machery Nagel GFF filter papers and placed directly into a -80 °C freezer. These will be analysed following the method of e.g. Gibb et al. (2000). Chlorophyll-a concentrations determined by HPLC will be used to verify those determined by fluorimetry (above).
- Analytical flow cytometry: 1.87 mL of seawater was mixed with 0.125 mL 16% paraformaldehyde yielding a final paraformaldehyde concentration of 1%. Samples are mixed by hand and left for 10 minutes at room temperature in the dark before transfer to a -80°C freezer. Samples will be analysed on a FACSort flow cytometer (Beckton-Dickinson, UK) following the method of e.g. Davey et al. (2008), with the intention of analysing for nanophytoplankton, picophytoplankton, and total bacterial cell counts.
- Fast Repetition Rate fluorometry (FRRf): A FASTOcean fluorometer with integrated Act2 laboratory system (both Chelsea Technologies LTD., UK) was used to measure in vitro variable fluorescence of phytoplankton samples. Blank filtrates (0.2 μm) are also measured for several samples per experiment. All FRRf data will be blank-corrected and fluorescence parameters recalculated.

Water for incubation experiments was collected at the following dates/times (all Beijing time):

Table 13 The collection dates/times (all Beijing time) of incubation samples

Experiment	Date	Time
1	27/04/2019	00:05:00
2	30/04/2019	20:00:00
3	03/05/2019	03:00:00
4	18/05/2019	19:00:00
5	21/05/2019	00:15:00
6	23/05/2019	00:08:00
7	24/05/2019	23:04:00
8	26/05/2019	22:13:00
9	29/05/2019	19:04:00
10	31/05/2019	23:50:00
11	02/06/2019	21:19:00
12	04/06/2019	23:23:00
13	06/06/2019	23:15:00
14	08/06/2019	21:20:00

An example of chlorophyll-a biomass response to nutrient amendment is shown in Figure 15.

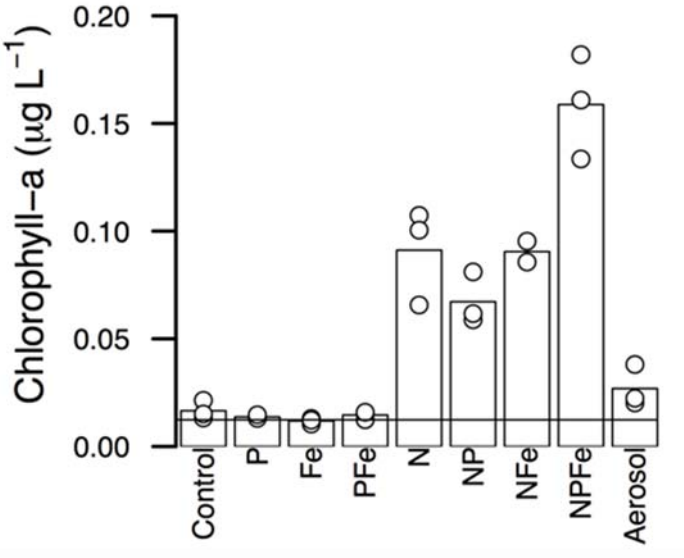


Figure 15. Example chlorophyll-a biomass response to combinations of nutrient supply in experiment 5. Bars indicate the mean responses of treatment replicates, which are themselves shown individually as circles. The horizontal line represents initial conditions. The response suggests primary limitation of the phytoplankton community by fixed nitrogen, followed by serial limitation by phosphate and iron (definitions of limitation categories are defined in Browning et al., 2017).

References:

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4.7.4. Effects of Iron and temperature on unicellular diazotrophs (By Yuanli Zhu, Qiang Hao, Yuanyuan Feng, Ruifeng Zhang, Mark Wells, Charles Trick, Fei Chai)

The SIO group conducted deck incubations for studying the effect of low and high Fe amendments on net N_2 fixation, and on the size of the dominant N fixers. We use large volumes (12 L) for the suite of analyses planned under two different temperature. In this way, the diazotroph community is maintained under semi-constant treatment conditions while the total biomass (but perhaps not cell concentrations) increases in the culture vessels. We conducted 4 culture experiments and each experiment lasted 4 days (6 for first experiment) and at the harvest day, we added a certain amount of ^{13}C and ^{15}N and cultured the samples for an additional 24 hours for measuring N/C fixation rates. Other parameters measured at harvest day included size fractionated chlorophyll a, cell abundance and speciation, photophysiology, particulate organic P, cellular metals

and DOC. This study will be helpful for answering the questions such as whether the cells that responding mainly are in the initial Fe plume at higher concentrations and how temperature would potentially affect the diazotroph growth rates we encounter in the field incubations.

Figure 16. Incubation experiments

Figure 17. Samples harvest