The sources and transport of iron in the North Pacific and its impact on marine ecosystems

WANG Yuntao①, ZHANG Haoran②③, CHEN Huanhuan②③ and CHAI Fei②③

① State Key Laboratory of Satellite Ocean Environment Dynamics, Second Institute of Oceanography, Hangzhou, China; ② College of Oceanography, Hohai University, Nanjing, China; ③ School of Marine Sciences, University of Maine, Orono, ME, USA

ABSTRACT
The limitation of iron (Fe) makes the North Pacific a typically high-nitrate, low-chlorophyll (HNLC) region in comparison with other oceanic regions of the world. Iron inputs from land via river discharge and atmospheric dust deposition are the primary processes introducing Fe into the ocean. Also, subsequent physical processes are crucial in transporting biologically available Fe into the upper ocean. As anthropogenic dust increases, the Fe from anthropogenic activities is expected to become more important in terms of impacting marine ecosystems. To investigate the Fe cycle and its impact on ecosystems, a project entitled ‘The sources and transport of Fe in the North Pacific and its impact on marine ecosystems’ has been funded by the National Natural Science Foundation of China. The project will focus on three major scientific questions: (1) What are the major sources of Fe in the North Pacific? (2) What is the influence of the Fe-binding ligand cycle on marine ecosystems? (3) What is the likely influence of global change in the future? The distribution of Fe and its corresponding impact on the marine ecosystem in current and future environmental conditions will be investigated. The results of the project are expected to improve our understanding of the marine ecosystem in the North Pacific.

1. Introduction
The North Pacific is one of the three major high-nitrate (NO₃) low-chlorophyll (HNLC) regions in the world. In these areas, the rates of specific NO₃ uptake, whether normalized to particulate organic nitrogen (N) or chlorophyll, are lower than those in coastal upwelling regions, though their nutrient concentrations are comparable (Dugdale and Wilkerson 1991). The formation of HNLC regions, as explained by the Martin hypothesis, is due to the development of the ecosystem, e.g., phytoplankton and higher trophic levels, being restricted by iron (Fe) limitation (Martin and Fitzwater 1988; Martin 1990; Martin et al. 1994). This hypothesis has been supported by numerous observations (Coale et al. 2004; Boyd et al. 2007). Wells (1989) also showed that Fe availability, which can be characterized by measurements of chemical lability, may regulate primary production. Biologically available Fe supplementation can greatly promote the growth of phytoplankton in HNLC regions and accelerate the transport of carbon (C) from the surface to the deep ocean.

The Fe cycle in the ocean, e.g., sources and transports, is summarized in Figure 1. The Fe concentration in continental shelf water, which is mainly influenced by Fe input from fresh water, is one or two orders of magnitude higher than that in the open ocean (Nishioka et al. 2001). For the open ocean, majority of the Fe in surface water is originated from
land, and atmospheric dust deposition is the primary process transporting Fe from land into the ocean (Martin et al. 1994). Globally, the atmospheric deposition of Fe is roughly equal to or greater than the riverine input for the surface ocean (Duce and Tindale 1991). There is also some evidence of the influence of atmospheric deposition on marine ecosystems. For example, the dust deposition in the North Pacific increased the assimilation rates of C and N in the ocean by 37% and 25%, respectively, and the new production increased by four times (Bishop, Davis, and Sherman 2002). Krishnamurthy et al. (2009) showed that primary production, sinking particulate organic C export, and atmospheric carbon dioxide (CO₂) uptake were the highest when Fe and N were added into the ocean simultaneously. In addition, some observations have revealed that the Fe solubility in aerosols originating from anthropogenic sources is significantly higher than that of aerosols originating from sand-dust sources (Zhu et al. 2016). As anthropogenic dust will reach a larger proportion of total dust in the future, the Fe from atmospheric dust deposition will become more influential on the marine ecosystems. Therefore, biologically available Fe in the ocean is expected to increase, and the corresponding process needs to be quantified.

Additionally, physical processes are crucial in transporting biologically available Fe into the upper ocean. Misumi et al. (2014) found that physical processes can provide roughly 70% of the total Fe in the eastern equatorial Pacific and the Southern Ocean. For the Northeast Pacific, the Fe supplied by physical processes accounts for approximately 50% of the total available Fe (Xiu et al. 2011). Spatially, the concentration of Fe is significantly higher in the Northwest Pacific than in the Northeast Pacific, because a large amount of biologically available Fe is transported from the Okhotsk Sea to the Northwest Pacific deep ocean via the North Pacific intermediate water (Nishioka et al. 2007). In the Gulf of Alaska, Haida Eddy, which traps the continental shelf water that contains a high concentration of Fe, is a major Fe source to the HNLC waters in the central basin (Johnson et al. 2005; Xiu et al. 2011). In addition, a prominent zonal gradient of chlorophyll concentration has been observed in the surface layer of the North Pacific during summer (Shiomoto and Hashimoto 2000), which further indicates the difference in Fe limitation for phytoplankton between the Northeast and Northwest Pacific (Fujii et al. 2005). Therefore, it is also important to quantify the transport of Fe by physical processes and the corresponding differences in the Northeast and Northwest Pacific.

The impact of global warming and ocean acidification on ocean ecosystems has received much attention in recent years. For example, increased surface temperatures may increase stratification, weaken vertical mixing, and reduce the vertical flux of nutrients in the open ocean (Boyce, Lewis, and Worm 2010). Ocean acidification can impact ligand activities in the water (Breitbarth et al. 2009). Some modeling (Stockdale...
et al. 2016) and observational (Gledhill et al. 2015) studies have shown a lower pH will result in more biologically available Fe. Therefore, our hypothesis is that both global warming and ocean acidification will weaken Fe limitation in the North Pacific, but their impacts on the ecosystem will occur through different processes.

With a better understanding of the influence of Fe on marine ecosystems, many ecosystem models have started to incorporate the Fe cycle (Tagliabue et al. 2016). However, various models present large uncertainties when simulating the Fe cycle. For instance, results from 13 global models were compared with GEOTRACES observations, and large errors were found in the model simulations, such as spatial discrepancies and temporal differences (Tagliabue et al. 2016). Therefore, the accuracy for predicting future ecosystems in HNLC regions by using these models lacks credibility. In fact, the Fe cycle varies substantially in different ocean areas, indicating the need for a well-designed regional physical–biogeochemical model that can accurately simulate the Fe cycle process in the North Pacific. The leading Principal Investigator of the project, Dr. Fei CHAI, developed a physical–biogeochemical model, ROMS + CoSiNE, which had been used in the North Pacific Ocean for more than 10 years (Chai et al. 2002; Xiu and Chai 2012). The hydrodynamic component is based on ROMS, while the biological model is using CoSiNE, which stands for ‘Carbon, Silicate, Nitrogen Ecosystem’. Also, the coupled model works very well in simulating the marine environment in the North Pacific (Xiu and Chai 2013). By incorporating the Fe cycle into the current model, it is expected we can further improve the accuracy for describing the corresponding biogeochemical processes.

To investigate the Fe cycle and its impact on ecosystems, a project entitled ‘The sources and transport of Fe in the North Pacific and its impact on marine ecosystems’ has been funded by the National Natural Science Foundation of China (2018–22). The first project meeting was hosted by the Second Institute of Oceanography of the State Oceanic Administration at Hangzhou on 11–12 March 2018. More than 10 experts working on the marine Fe cycle and its impact on ecosystems attended the meeting to discuss the implementation plan. This integral project will focus on investigating the impact of Fe on the marine ecosystem at the surface of the ocean and predicting future changes by simulating the current temporal and spatial distribution of Fe in the North Pacific. The results of the study will improve our understanding of marine ecosystem development in the North Pacific, promote China’s international status in the field of Fe cycle research, and provide models to study marine ecosystems in other areas.

2. Plans and goals

2.1. The major sources of Fe in the North Pacific

A quantitative description of the sources of Fe in the ocean is fundamentally important for understanding the marine biogeochemical processes. The sources of Fe can be traced back using isotopes. Zhang et al. (2015) used Fe stable isotopes (δ56Fe) to constrain glacial fluxes of dissolved Fe in the ocean and found that glacial meltwater is a significant potential source of biologically available Fe to the oceans. Recently, Ye and Völker (2017) used a global ocean model to find that dust particles play an important role in Fe sources and sinks in the marine Fe cycle.

With the development of numerical simulation, ocean modeling is becoming increasingly important to help in our understanding and quantifying of ocean processes. A physical–biogeochemical model (ROMS+COSiNE) has been built to investigate the spatial and temporal variability in nutrients, phytoplankton and chlorophyll in the North Pacific (Xiu and Chai 2012, 2013). In this project, a comprehensive physical–biogeochemical model, ROMS+CoSiNE+Iron, will be developed and optimized. The fully coupled model will be used to investigate the major sources of Fe in the North Pacific.

After incorporating the Fe cycle into the model, the corresponding parameters will be optimized using the observational data obtained from cruise observations in the western North Pacific (Nishioka et al. 2007, 2011). The model can quantify how the solubility of atmospheric deposits influences the spatial distribution and temporal variability of Fe in the surface layer of the North Pacific. The spatial distribution and temporal variability of Fe, impacted by atmospheric deposition and physical processes, will be subsequently described.

2.2. The influence of the Fe-binding ligands cycle on marine ecosystems

Natural Fe-binding ligands, such as dissolved organic matter, have been found in terrestrial and aquatic environments (Sorichetti, Creed, and Trick 2013). Dissolved Fe in the ocean is overwhelmingly complexed by strong organic ligands, which may control the uptake rate of Fe by microbiota (Macrellis et al. 2001). Their results also provided further insight into the characteristics of the Fe-binding ligands that are important in controlling the biological availability of Fe in the ocean. In HNLC waters, Wells, Perry, and Trick (2008) showed that the relative availability of Fe, which is bound to weak or strong classes of ligands, varies among different phytoplankton groups. In addition, the differences can significantly influence the evolution of the phytoplankton community.
Accordingly, we plan to study the spatial distribution and temporal variability of Fe-binding ligands and their relationships with the evolution of the phytoplankton community and with primary production. With the newly developed physical–biogeochemical Fe model, the next step is to study the influence of the spatial distribution and properties of Fe-binding ligands on primary production and the phytoplankton community. First, the model will incorporate the information about the distribution of Fe-binding ligands. Next, the phytoplankton biomass, community structure, and photosynthesis efficiency will be measured in typical regions (Fe-limited or unlimited) by field observation and the data will be used to optimize the model. Lastly, the influence of Fe limitation with Fe-binding impacts will be investigated using the model outputs.

2.3. The influence of global change in the future

The response of the Fe cycle to future changes in oceanic and atmospheric conditions, such as ocean acidification and warming, is one of the major foci of the project. First, we will investigate the influence of pH and sea temperature change on the Fe cycle. Recent studies have shown that lowered pH may decrease the Fe uptake rate of diatoms (Shi et al. 2010). However, Stockdale et al. (2016) predicted with the IPCC model that ocean acidification could lead to an increase in biologically available Fe. Laboratory experiments will be conducted to test the change in biologically available Fe in areas that are either Fe limited or not. Second, changes in phytoplankton primary production will be studied under different pH and sea temperature conditions. In addition, for phytoplankton, ocean acidification can enhance the growth rate of larger diatoms and may selectively increase the growth rates of larger phytoplankton species in the ocean (Wu et al. 2014).

Boyce, Lewis, and Worm (2010) indicated that ocean warming may reduce primary production because higher surface temperatures could increase ocean stratification and weaken vertical mixing, which could affect vertical nutrient transport. Indeed, we will make a prediction about the ecosystem in the North Pacific and investigate the changing ecosystem processes in the western and eastern North Pacific with the physical–biogeochemical Fe model.

3. Summary

The ocean Fe cycle is an international frontier scientific focus. Especially in the North Pacific, which is an HNLC region, Fe plays an important role in determining marine ecosystem dynamics. Increased exogenous Fe, such as that from dust caused by human activities, can promote phytoplankton primary production and uptake of CO₂. The changes in these processes are closely related to the ocean C cycle and global climate change. Furthermore, a change in primary production will also have a significant influence on dissolved oxygen, which can affect marine fishery resources.

Through this study, we hope to gain a better understanding of the Fe distribution in the ocean and achieve the following goals: an understanding of the influence of the spatial and temporal variation in Fe solubility from atmospheric deposits on biologically available Fe in the North Pacific; quantification of the transport of biologically available Fe though physical processes, such as advection and mixing; and improvement in our understanding of the effect of ocean acidification on the Fe uptake rate by phytoplankton. Moreover, we intend to answer the following question: Under the influence of ocean acidification and stratification, how will the North Pacific upper marine ecosystem respond in future?

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work is supported by the National Natural Science Foundation of China (NSFC) [grant number 41730536].

References

Bishop, J. K., R. E. Davis, and J. T. Sherman. 2002. “Robotic Observations of Dust Storm Enhancement of Carbon Biomass in the North Pacific.” Science 298 (5594): 817–821. doi:10.1126/science.1074961.

Boyce, D. G., M. R. Lewis, and B. Worm. 2010. “Global Phytoplankton Decline over the past Century.” Nature 466 (7306): 591–596. doi:10.1038/nature09268.

Boyd, P. W., T. Jickells, C. S. Law, S. Blain, E. A. Boyle, K. O. Buesseler, K. H. Coale, et al. 2007. “Mesoscale Iron Enrichment Experiments 1993–2005: Synthesis and Future Directions.” Science 315 (5812): 612–617. doi:10.1126/science.1131669.

Breitbarth, E., E. P. Achterber, M. V. Ardelan, A. R. Baker, E. Bucciarelli, F. Chever, P. L. Croot, et al. 2009. “Iron Biogeochemistry across Marine Systems at Changing Times-Conclusions.” Paper Presented at the Workshop for the Biogeosciences Discussions 6 (4): 6635–6694.

Chai, F., R. C. Dugdale, T. H. Peng, F. P. Wilkerson, and R. T. Barber. 2002. “One-Dimensional Ecosystem Model of the Equatorial Pacific Upwelling System. Part I: Model Development and Silicon and Nitrogen Cycle.” Deep Sea Research Part II: Topical Studies in Oceanography 49 (13–14): 2713–2745. doi:10.1016/S0967-0645(02)00055-3.

Coale, K. H., K. S. Johnson, F. P. Chavez, K. O. Buesseler, R. T. Barber, M. A. Brzezinski, W. P. Cochlan, et al. 2004. “Southern Ocean Iron Enrichment Experiment: Carbon
Cycling in High- and low-Si Waters.” *Science* 304:408–414. doi:10.1126/science.1089778.

Duce, R. A., and N. W. Tindale. 1991. “Atmospheric Transport of Iron and its Deposition in the Ocean.” *Limnology and Oceanography* 36 (8): 1715–1726. doi:10.4319/lo.1991.36.8.1715.

Dugdale, R. C., and F. P. Wilkerson. 1991. “Low Specific Nitrate Uptake Rate: A Common Feature of High-Nutrient, Low-Chlorophyll Marine Ecosystems.” *Limnology and Oceanography* 36 (8): 1678–1688. doi:10.4319/lo.1991.36.8.1678.

Fujii, M., N. Yoshie, Y. Yamanaka, and F. Chai. 2005. “Simulated Biogeochemical Responses to Iron Enrichments in Three High Nutrient, Low Chlorophyll (HNLC) Regions.” *Progress in Oceanography* 64 (2): 307–324. doi:10.1016/j.pocean.2005.02.017.

Gledhill, M., E. P. Achterberg, K. Li, K. N. Mohamed, and M. J. A. Rijkenberg. 2015. “Impact of Ocean Acidification on the Complexation of Iron and Copper by Organic Ligands in Estuarine Waters.” *Marine Chemistry* 177 (13): 421–433. doi:10.1016/j.marchem.2015.03.016.

Johnson, W. K., L. A. Miller, N. E. Sutherland, and C. S. Wong. 2005. “Iron Transport by Mesoscale Haida Eddies in the Gulf of Alaska.” *Deep-Sea Research Part II* 52 (7): 933–953. doi:10.1016/j.dsr2.2004.08.017.

Krishnamurthy, A., J. K. Moore, N. Mahowald, C. Luo, S. C. Doney, K. Lindsay, and C. S. Zender. 2009. “Impacts of Increasing Anthropogenic Soluble Iron and Nitrogen Deposition on Ocean Biogeochemistry.” *Global Biogeochemical Cycles* 23 (3): GB3016. doi:10.1029/2008GB003440.

Macrellis, H., C. G. Trick, E. L. Rue, G. Smith, and K. W. Bruland. 2001. “Collection and Detection of Natural Iron-Binding Ligands from Seawater.” *Marine Chemistry* 76 (3): 175–187. doi:10.1016/S0304-4203(01)00061-5.

Martin, J. H. 1990. “Glacial-Interglacial CO₂ Change: The Iron Hypothesis.” *Paleoceanography* 5: 1–13. doi:10.1029/PA005i001p00001.

Martin, J. H., K. H. Coale, K. S. Johnson, S. E. Fitzwater, R. M. Gordon, S. J. Tanner, C. N. Hunter, et al. 1994. “Testing the Iron Hypothesis in Ecosystems of the Equatorial Pacific Ocean.” *Nature* 371 (6493): 123–129. https://www.nature.com/articles/371123a0.

Martin, J. H., and S. E. Fitzwater. 1988. “Iron Deficiency Limits Phytoplankton Growth in the North-East Pacific Subarctic.” *Nature* 331: 341–343. doi:10.1038/331341a0.

Misumi, K., K. Lindsay, J. K. Moore, S. C. Doney, F. O. Bryan, D. Tsumune, and Y. Yoshida. 2014. “The Iron Budget in Ocean Surface Waters in the 20th and 21st Centuries: Projections by the Community Earth System Model Version 1.” *Biogeoosciences Discussions* 10 (5): 8505–8559. doi:10.5194/bgd-11-33-2014.

Nishioka, J., T. Ono, H. Saito, T. Nakatsuka, S. Takeda, T. Yoshimura, K. Suzuki, et al. 2007. ”Iron Supply to the Western Subarctic Pacific: Importance of Iron Export from the Sea of Okhotsk.” *Journal of Geophysical Research Oceans* 112:C10012. doi:10.1029/2006JC004055.

Nishioka, J., T. Ono, H. Saito, K. Sakaoka, and T. Yoshimura. 2011. “Oceanic Iron Supply Mechanisms Which Support the Spring Diatom Bloom in the Oyashio Region, Western Subarctic Pacific.” *Journal of Geophysical Research Oceans* 116: C02021. doi:10.1029/2010JC006321.

Nishioka, J., S. Takeda, C. S. Wong, and W. K. Johnson. 2001. “Size-Fractionated Iron Concentrations in the Northeast Pacific Ocean: Distribution of Soluble and Small Colloidal Iron.” *Marine Chemistry* 74 (2): 157–179. doi:10.1016/S0304-4203(01)00013-5.

Shi, D., Y. Xu, B. M. Hopkinson, and F. M. Morel. 2010. “Effect of Ocean Acidification on Iron Availability to Marine Phytoplankton.” *Science* 327 (5966): 676–679. doi:10.1126/science.1183517.

Shiomoto, A., and S. Hashimoto. 2000. “Comparison of East and West Chlorophyll a Standing Stock and Oceanic Habitat along the Transition Domain of the North Pacific.” *Journal of Policy History* 22 (1): 444–460. doi:10.1093/plankt/22.11.1.

Sorichetti, R., I. Creed, and C. Trick. 2013. “Dissolved Organic Matter Influences Fe-Binding Ligand Availability for Cyanobacteria in Oligotrophic Ontario Lakes.” *EGU General Assembly* 15: 13280.

Stockdale, A., E. Tipping, S. Loffs, and R. J. Mortimer. 2016. “The Effect of Ocean Acidification on Organic and Inorganic Speciation of Trace Metals.” *Environmental Science and Technology* 50 (4): 1906–1913. doi:10/1021/acs.est.5b05624.

Tagliabue, A., O. Aumont, R. Death, J. P. Dunne, S. Dutkiewicz, E. Galbraith, K. Misumi, et al. 2016. “How Well Do Global Ocean Biogeochemistry Models Simulate Dissolved Iron Distributions?” *Global Biogeochemical Cycles* 30 (2): 149–174. doi:10.1002/2015GB005289.

Wells, M., M. Perry, and C. Trick. 2008. “Collaborative Research: The Effect of Iron-Complexing Ligands on Iron Availability to Phytoplankton in HNLC Waters of the Subarctic Pacific Ocean.” *University of Maine Office of Research and Sponsored Programs: Grant Reports*, 162. https://digitalcommons.library.umaine.edu/orsp_reports/162.

Wells, M. L. 1989. “The Availability of Iron in Seawater: A Perspective.” *Biological Oceanography* 6 (5–6): 463–476. doi:10.1080/096558198.10749545.

Wu, Y., D. A. Campbell, A. J. Irwin, D. J. Suggett, and Z. V. Finkel. 2014. “Ocean Acidification Enhances the Growth Rate of Larger Diatoms.” *Limnology and Oceanography* 59 (3): 1027–1034. doi:10.4319/lo.2014.59.3.1027.

Xiu, P., and F. Chai. 2012. “Spatial and Temporal Variability in Phytoplankton Carbon, Chlorophyll, and Nitrogen in the North Pacific.” *Journal of Geophysical Research Oceans* 117: C11023. doi:10.1029/2012JC008067.

Xiu, P., and F. Chai. 2013. “Variability of Oceanic Carbon Cycle in the North Pacific from Seasonal to Decadal Scales.” *Journal of Geophysical Research Oceans* 118 (9): 5270–5288. doi:10.1002/2013JC009505.

Xiu, P., A. P. Palacz, F. Chai, E. G. Roy, and M. L. Wells. 2011. “Iron Flux Induced by Haida Eddies in the Gulf of Alaska.” *Geophysical Research Letters* 38 (13): 392. doi:10.1029/2011GL047946.

Ye, Y., and C. Völker. 2017. “On the Role of Dust-Deposited Lithogenic Particles for Iron Cycling in the Tropical and Subtropical Atlantic.” *Global Biogeochemical Cycles* 31 (10): 1543–1558. doi:10.1002/2017gb005663.

Zhang, R., S. G. John, J. Zhang, J. Ren, Y. Wu, Z. Zhu, S. Liu, X. Zhu, C. M. Marsay, and W. F. Sander. 2015. “Transport and Reaction of Iron and Iron Stable Isotopes in Glacial Meltemwaters on Svalbard near Kongsfjorden: From Rivers to Estuary to Ocean.” *Earth and Planetary Science Letters* 424 (10): 201–211. doi:10.1016/j.epsl.2015.05.031.

Zhu, M., J. Shi, X. Ben, S. Qiu, H. Gao, and X. Yao. 2016. “Solubility of Trace Elements in Atmospheric Aerosols and Determination Factors in Qingdao, China.” *China Environmental Science* 36 (11): 3245–3252.