

and metals by marine biota in different oceanic regions? What is the prognosis for the future?

There were seven live presentations, five recorded oral presentations, and fifteen electronic poster presentations during the session. An active discussion took place about the understanding of atmospheric iron (Fe) and nutrient deposition to the ocean and its influence on ocean biogeochemistry in the Pacific Ocean. A wide range of results were reported, such as atmospheric-ocean material cycles, atmospheric nutrient supply, atmospheric aerosol Fe from coal combustion and its deposition to China adjacent seas, phytoplankton community response to trace metals deposition, controlling physical and chemical mechanism for biological production, dynamics of organic ligands in the Pacific water which is the key to trace metals dynamics, and air pollution and future forecasting for nitrate (NO_3^-) deposition to Pacific ocean. Among them, the subject of aeolian Fe and nitrogen (N) deposition, and the importance of anthropogenic aerosols and their solubility and impacts on the ecosystem was thoroughly discussed. However, it is worth pointing out that these presentations were limited to discussing the impacts on the waters near Asia adjacent sea, and a remaining issue was to quantitatively estimate the impacts on a wider area of the Pacific Ocean in the future.

The future directions of the SOLAS Theme 3, Atmospheric deposition and ocean biogeochemistry Implementation Plan will be extracted from this session. The following issues should be further investigated in order to clarify the impacts of the atmosphere-derived nutrient supplies on biological production in a wider area of the Pacific Ocean.

- To estimate the impacts of atmospheric Fe supply on oceanic phytoplankton growth, quantitatively, and the contribution of anthropogenic aerosol Fe will be the key issue. It is clear that more work is needed to reveal the anthropogenic aerosol Fe transport scale, frequency, deposition area, residence time in surface water

and dissolution rate, and the fraction of bioavailable Fe under natural conditions.

- There are still important gaps in quantitative understanding along with a coherent explanation of the biological response in the High Nutrient Low Chlorophyll (HNLC) waters and the subtropical Low Nutrient Low Chlorophyll (LNLC) waters in the North Pacific. It was frequently suggested that this must be achieved by integrating both, the knowledge of atmospheric Fe supplies and the oceanic Fe supplies. Modelling studies, which incorporate atmospheric nutrients (NO_3^- and Fe) deposition processes with accurate oceanic nutrient dynamics, and its validation by observational data, should be constructed for understanding real biological production and forecasting the future changes in the North Pacific Ocean.

In order to discuss these remaining issues, many participants agreed that we should organise a follow-up SOLAS session at the 2021 PICES annual meeting.

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Atmospheric aerosol iron from coal combustion

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Atmospheric iron (Fe) deposition alters biogeochemical cycles in the global ocean, possibly affecting the marine carbon budget and consequently the climate (e.g. Jickells *et al.*, 2005). Modelling studies suggest that atmospheric deposition of soluble (and, thus potentially available) Fe has doubled since the preindustrial era due to air pollution (e.g. Ito and Shi, 2016). In particular, the uptake of acidic gases during long-range transport is a key factor enhancing the Fe solubility in specific aerosol sources (e.g. Li *et al.*, 2017). Mineral dust accounts for around 95% of the total Fe emissions (e.g. Ito *et al.*, 2018), but the solubility of Fe in mineral dust is generally below 0.5% (e.g. Shi *et al.*, 2011). The Fe solubility in anthropogenic aerosol sources, including for example solid fuel combustion, biomass burning and liquid fuel combustion, is significantly different (up to around two orders of magnitude) depending on the sources (e.g. Oakes *et al.*, 2012).

Here, we investigated the Fe dissolution kinetic of anthropogenic aerosol sources (e.g. coal fly ash) in acidic aqueous solutions, which simulate chemical processes in the atmosphere. Coal fly ash

samples were collected from the electrostatic precipitator of three coal-fired power stations at different locations: United Kingdom, Poland, and China. Samples were aerosolised to separate the fractions of the Particulate Matter with a diameter of 10 microns or less (PM₁₀). The PM₁₀ fractions were then exposed to sulphuric acid (H₂SO₄) solutions at low pH of 1, 2 or 3, in presence of oxalic acid (H₂C₂O₄) and/or ammonium sulphate ((NH₄)₂SO₄) to simulate aerosol conditions. The pH of the leaching media was calculated using the Extended Aerosol Inorganics Model (E-AIM) III for aqueous solutions, considering the buffer capacity of carbonates in the samples. A mineral dust sample from Libya was used for comparison.

Fe dissolution kinetic primarily depends on the pH of the leaching media. As the pH decreases, the enhanced protonation favours Fe dissolution (Cornell and Schwertmann, 2003). Also, oxalate forms bidentate complex with Fe on the particle surface enhancing dissolution (Chen *et al.*, 2012). Our results indicate that increasing the salt concentration in solution, the Fe dissolution process is controlled by the concentration of protons, as

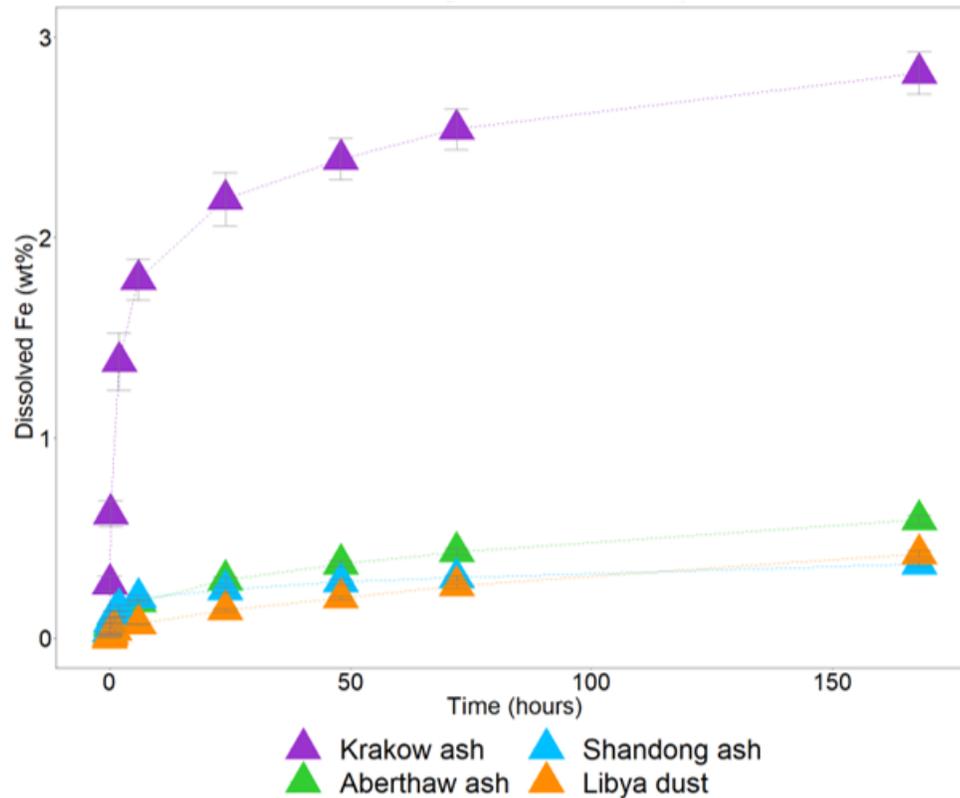


Figure 1: Fe dissolution kinetics of coal fly ash samples from UK (Aberthaw ash), Poland (Krakow ash), and China (Shandong ash), and of Saharan dust (Libya dust) in oxalic acid (H_2SO_4) solutions at pH 2 with 0.01 M sulphuric acid ($\text{H}_2\text{C}_2\text{O}_4$) and 1 M ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$).

the activity of protons and ligands in solution is suppressed at high ionic strength. Our coal fly ash samples exhibited different dissolution behaviours depending on their physicochemical properties (Figure 1). A key factor may be the Fe speciation, which varied significantly in different types of coal fly ash. Overall, coal fly ash showed higher amorphous Fe and magnetite content compared to the Saharan dust. The next step is to develop an Fe release scheme for coal fly ash to be applied in global atmospheric chemistry modelling to estimate the atmospheric concentration and deposition flux of soluble Fe.

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Haoyu Jin obtained a bachelor's degree in Environmental Science in 2016. He then conducted master studies in 2017 and started pursuing a doctoral degree in Environmental Science in Ocean University of China, Qingdao, China in 2019. As a PhD candidate, Haoyu is currently investigating the impact of atmospheric deposition on marine primary production.

Atmospheric deposition promotes the utilisation of dissolved organic phosphorus by phytoplankton in China coastal seas

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Phosphorus (P) is indispensable for phytoplankton growth and plays a crucial role in ocean primary production. However, the concentration of dissolved inorganic phosphorus (DIP), the preferred P nutrient for phytoplankton, is often at low degree (Moore *et al.*, 2013). In the case of DIP deficiency, dissolved organic phosphorus (DOP) can

be utilised through DOP hydrolases, predominantly the alkaline phosphatase (AP). Atmospheric deposition, an imperative source of nutrients and various trace metals to the ocean, can stimulate DOP utilisation to alleviate the P limitation. However, such an adaptive mechanism is generally observed in oligotrophic regions, while

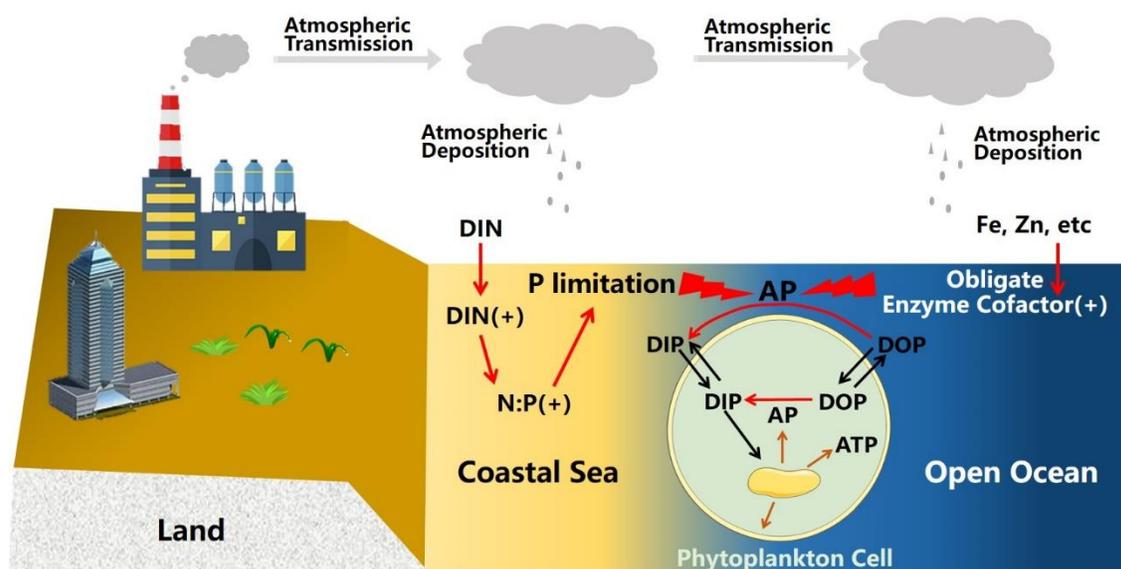


Figure 2: Dissolved organic phosphorus (DOP) utilisation by phytoplankton and its response to atmospheric deposition. N: nitrogen, P: phosphorus, Fe: iron, Zn: zinc, DIP: dissolved inorganic phosphorus, DOP: dissolved organic phosphorus, DIN: dissolved inorganic nitrogen, AP: alkaline phosphatase, ATP: adenosine triphosphate.

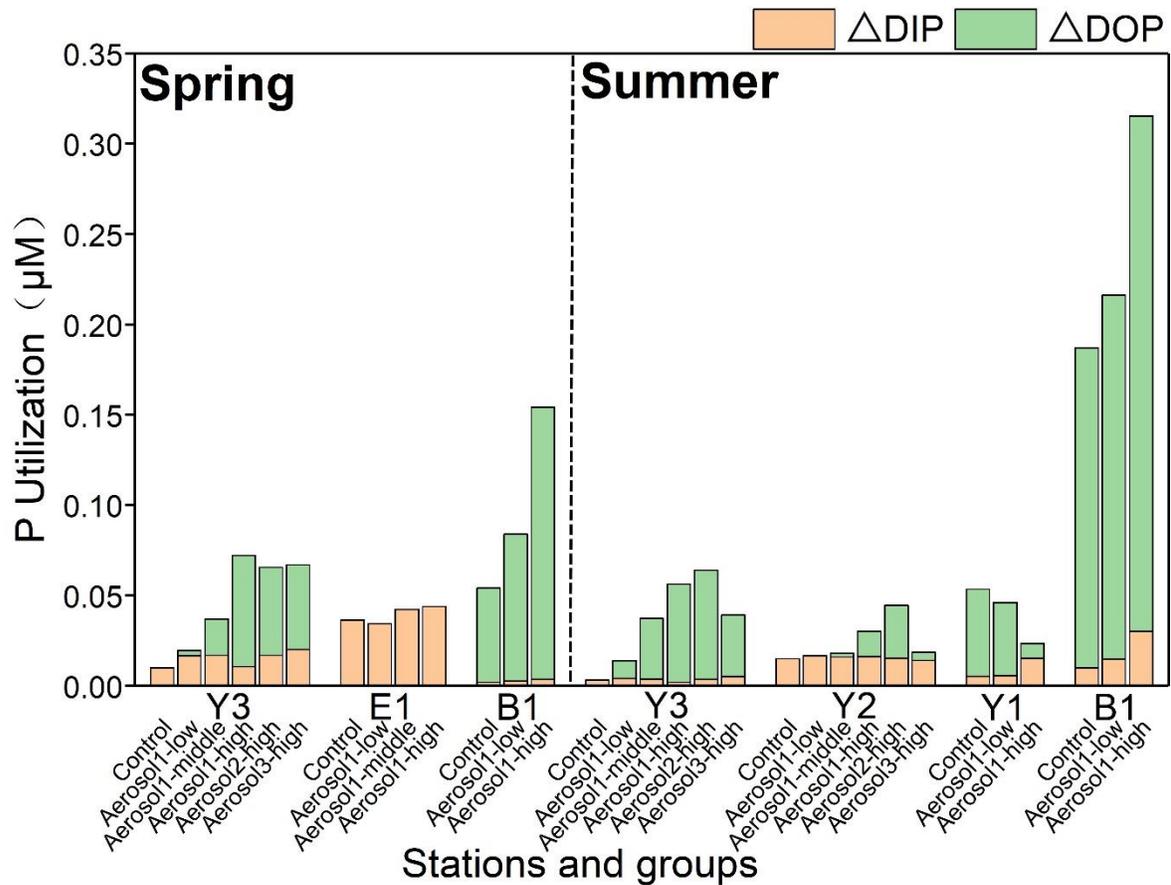


Figure 3: Utilisation of dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP) during microcosm experiments in the Yellow Sea (Y1, Y2, Y3), the Bohai Sea (B1), and the East China Sea (E1). Δ DIP is the consumption of DIP during incubation, Δ DOP ($=\Delta$ DIN/16- Δ DIP) is the estimated DOP consumption based on a nitrogen (N): phosphate (P) uptake ratio of 16:1 by phytoplankton (Browning *et al.*, 2017).

poorly understood in other P limited regions with higher trophic states (Mahaffey *et al.*, 2014). In recent years, atmospheric deposition with high nitrogen (N):P ratio has input loads of dissolved inorganic nitrogen (DIN) to China coastal seas, and leads to increasing P limitation there (Sharples *et al.*, 2017).

To investigate the impact of atmospheric deposition on DOP utilisation in eutrophic coastal seas, seven on-board microcosm experiments amended with atmospheric aerosols and nutrients were implemented in China coastal seas during the spring and summer of 2018 and 2019.

The results showed that atmospheric deposition can promote DOP utilisation by enhancing the AP activity (APA) in the coastal seas, and therefore

promote the phytoplankton growth under N, P, and N+P limited conditions. However, the promotion mechanism in the coastal seas is dissimilar from that of the open ocean. In the open ocean, atmospheric deposition promotes DOP utilisation by phytoplankton mainly through the input of obligate enzyme cofactors such as Fe and zinc (Zn) (Mahaffey *et al.*, 2014; Browning *et al.*, 2017). However, in the coastal seas, it is the large amount of N from atmospheric deposition that plays a key role in promoting DOP utilisation. The N provided by atmospheric aerosols raised the N:P ratio in the coastal seawaters, leading to serious P limitation, thus facilitating DOP utilisation (Figure 2). In this study, the APA surged when the DIP concentrations were below 0.015 μ M in the Yellow Sea. The booming APA was also found in the Bohai Sea when the DIP concentrations were

below 0.004 μM in spring and 0.026 μM in summer, respectively. Under the impact of atmospheric deposition, the DOP consumption increased significantly and even became a main P nutrient (Figure 3). In summary, promoting DOP utilisation is a prominent mechanism for atmospheric deposition to alleviate P limitation and of great significance for primary production in the coastal seas.

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Impacts of atmospheric deposition on phytoplankton community structure in the Yellow Sea

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Atmospheric deposition is an important source of nutrients for the upper ocean. The annual nitrogen (N) input by atmospheric deposition accounts for about half of the land source, and the iron (Fe) brought by atmospheric deposition is the main source to meet the growth requirement of phytoplankton in the euphotic zone of the ocean (Jickells *et al.*, 2005; Duce, 2008). Atmospheric deposition can stimulate phytoplankton growth by alleviating nutrient restrictions in seawater (Paytan *et al.*, 2007; Duce, 2008). The deposition of atmospheric subsidence can lead to excess N in many sea areas of the world, so that the nutrient limitation for phytoplankton growth has a tendency from N to phosphorus (P) (Kim *et al.*, 2014; Wu *et al.*, 2018). In addition to the shifts of dominant species, the expansion of the N/P ratio in seawater can also change the phytoplankton size structure (Zhang *et al.*, 2019), but the mechanism is still poorly understood.

In order to explore the competition between different species using different schemes with (system) and without (subsystem) micro-sized (20-200 μm) cells under the condition of anthropogenic aerosol

(AA) additions, we collected the surface and sub-surface seawater of the Yellow Sea to conduct a series of onboard incubation experiments.

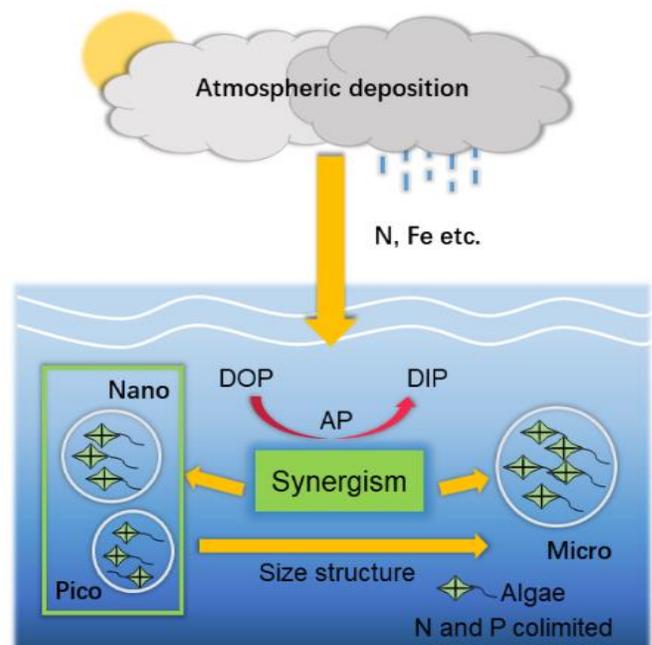


Figure 4: The way that atmospheric deposition influences phytoplankton size structure. N: nitrogen, Fe: iron, DIP: dissolved inorganic phosphorus, DOP: dissolved organic phosphorus, AP: alkaline phosphatase

We found that the micro-sized cells were not only working as nutrient competitors for small cells. In P-deficient environment, micro-sized cells promoted the growth of small cells by utilising dissolved organic phosphorus (DOP), thereby increasing the total biomass (Figure 4). Under the influence of atmospheric deposition, the structure of the community shifts to large size (Zhang *et al.*, 2019).

In low nutrient seawaters, the micro-sized cells of AA treatment groups had an advantage in growth over those of the control groups. The high and stable N concentrations as well as the depleted P concentrations in the AA treatment groups indicated that P had become a primary limiting nutrient in the incubated seawaters. The alkaline phosphatase activity (APA), which can reflect the DOP utilisation of phytoplankton, was at least 1.6 times higher in the system than those in the subsystem, indicating the micro-sized cells played an important role in utilising DOP. Therefore, the increase of bioavailable P brought by micro-sized cells might cause higher Chlorophyll a concentrations of the nano- and pico-sized cells in the system.

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