

Phosphorus in the aerosols over oceans transported offshore from China to the Arctic Ocean: Speciation, spatial distribution, and potential sources

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Abstract Atmospheric aerosol samples were collected from July to September 2008 onboard a round-trip cruise over the Eastern China Sea, Japan Sea, Western North Pacific Ocean, and the Arctic Ocean (31.1°N–85.18°N, 122.48°E–146.18°W). Total phosphorus (TP) and total inorganic phosphorus (TIP) were analyzed. The organic phosphorus (OP) was calculated by subtracting TIP from TP. Average concentrations of TP in the East Asia, Western North Pacific and Arctic Ocean were 7.90 ± 6.45 , 6.87 ± 6.66 and 7.13 ± 6.76 ng·m⁻³, while TIP levels were 6.67 ± 5.02 , 6.07 ± 6.58 , and 6.23 ± 5.96 along the three regions. TP and TIP levels varied considerably both spatially and temporally over the study extent. TIP was found to be the dominant species in most samples, accounting for 86.6% of TP on average. OP was also a significant fraction of TP due to the primary biogenic aerosol (PBA) contribution. The phosphorus in the atmospheric aerosol over the Arctic Ocean had a higher concentration than previous model simulations. Source apportionment analysis indicates that dust is an important phosphorus source which can be globally transported, and thus dust aerosol may be an important nutrient source in some remote regions.

Keywords phosphorus aerosol, spatial distribution, speciation, sources, Arctic Ocean

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1 Introduction

Phosphorus (P) is an essential nutrient in terrestrial and marine ecosystems^[1]. At geologic timescales, ocean ecosystems are considered to be limited by phosphorus^[2]. Phosphorus also influences ecosystems on significantly shorter timescales by limiting primary production and the abundance of bacteria^[3-6]. Although many efforts have been devoted to the study of phosphorus cycle, studies of P in aerosols are still rare, particularly those that are related to the behavior of the P in the marine boundary layer. Unlike

carbon and nitrogen, P does not have a stable gaseous phase within the Earth's atmosphere. Most atmospheric phosphorus is in the form of aerosols^[7].

To estimate the impact of atmospheric phosphorus on the ocean ecosystem, the characteristics of aerosol phase phosphorus are needed, such as concentration range, geographical distribution, emission sources, source strength, and atmospheric transformation. In marine aerosols, phosphorus could come from five sources: mineral aerosol, anthropogenic aerosols, volcanic aerosols, primary biogenic aerosols, and sea salt aerosols^[8]. Some of the different aerosol sources can be generally represented by characteristic elements which have fixed mass concentration ratios to phosphorus^[9].

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Since the pioneer work in the late 1970s^[7], phosphorus composition in atmospheric aerosols has still been poorly characterized^[8]. There have been only a few measurements of the total phosphorus (TP) concentration over the open ocean regions. In order to fill this research gap, we collected and analyzed aerosol samples onboard the Chinese R/V *XUE LONG* icebreaker as it travelled over the Western and Northern Pacific Ocean as well as the Arctic Ocean (July–September 2008). The purpose of the current study is to provide the geographical distribution of TP and total inorganic phosphorus (TIP) in the East Asia Sea, Western North Pacific (WNP), and Arctic Oceans. Three tracer elements are used to estimate the relative contribution of different phosphorus sources to the TP via mathematical analysis.

2 Methods

2.1 Sampling

During the R/V *XUE LONG* icebreaker cruise, a total of 24 valid particulate samples and 4 field blanks were collected from July to September 2008 over the Western and Northern Pacific Ocean as well as the Arctic Ocean (31.1°N–85.18°N, 122.48°E–146.18°W). The sampling instrument was installed on the top of the ship which is approximately 15 m above sea level. A meteorological station on the ship supplied temperature, wind speed, and wind direction data. Total particulate aerosol samples were collected by standard glass fiber filters (Whatman EPM 2000, Maidstone, UK, 20 × 25 cm²). The filters were oven-dried at 350°C for 24 h before use. The flow rate was set at 1.05 m³·min⁻¹ and the total sampling time was 24 h which achieved a total sampling air volume of about 1400 m³. After sampling, the filters were packed in separate, sealed plastic bags and stored in the freezer at -24°C before further analysis.

2.2 Chemical analysis

When the expedition returned, samples were taken to the laboratory and each filter was cut into pieces (3 cm²) for different analyses. The separated pieces were then prepared via three methods (Figure 1). The first subsample (Sample A)

was extracted overnight with 12 mL of HNO₃ and 4 mL of HCl and was then digested at 180°C with a microwave oven. Sample A was used for analyzing the total P and trace metals. The second subsample (Sample B) was extracted by 20 mL of 1 N HCl^[10–11] and was classified as TIP. The organic P (OP) content was then calculated as the difference between TP and TIP. The third subsample (Sample C) was extracted via deionized water assisted by ultrasound. Sample C was used for the analysis of water soluble phosphorus (WSP) and ionic species.

The molybdenum blue (MB) method was employed to determine different forms of phosphorus concentration (TP, TIP, and WSP). Details of the MB method have been described in the literature^[12–13]. The detection limit of the MB method (defined as three times the standard deviation of blank measurements) was approximately 0.05 μM of phosphorus, which corresponds to approximately 0.17 ng·m⁻³ of phosphorus when aerosols were fully sampled for 24 h. The TP concentration was high enough to analyze via inductively-coupled plasma atomic emission spectrometry (ICP-AES). By comparing the concentrations of total phosphorus determined by the two different analytical methods, we found a linear relationship (close to 1:1) which supports the quality of our phosphorus analysis.

3 Results and discussions

3.1 The distributions of P during the round-trip cruise

The geographical course of the entire cruise is shown in Figure 2. The cruise was divided into three ocean regions which are generally related to the location and hydrology state: East Asia Sea, Western North Pacific, and Arctic Ocean. Geographical distributions of TP are shown in Figure 2. The height of each bar represents aerosol-phase elemental concentration in each sampling period. The minimum concentrations of TP were measured in the Arctic Ocean, and the maximum values appeared in the East Asia Sea (Table 1). The mean values were found to be similar in the three regions. Figure 3 shows the measured concentrations of TP, TIP, OP, and WSP.

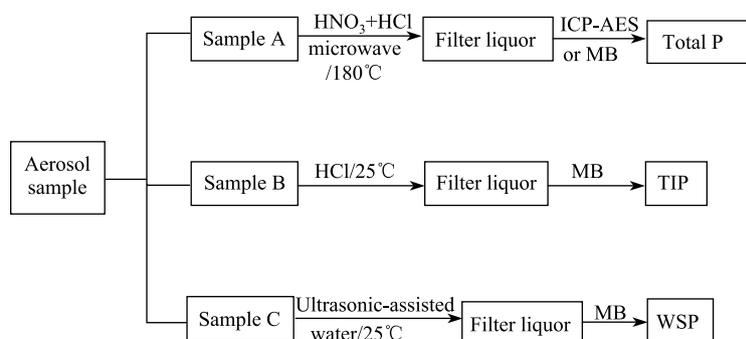


Figure 1 Chemical analytical method for different forms of P in particulate aerosols.

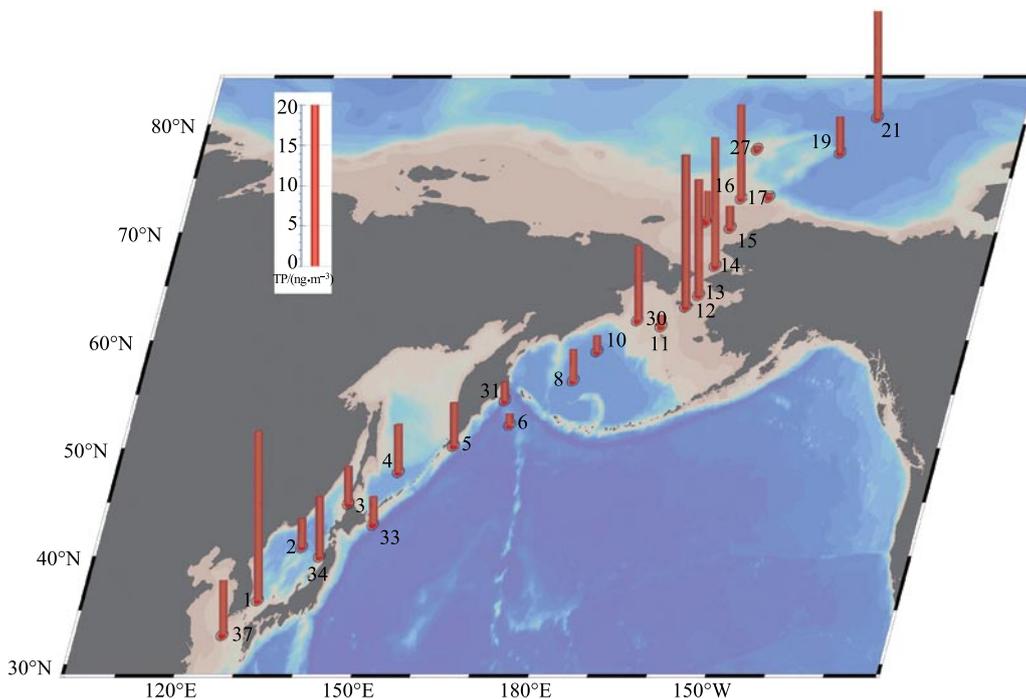


Figure 2 Ship tracks and geographical distributions of aerosol-phase concentrations of total phosphorus (TP) in $\text{ng}\cdot\text{m}^{-3}$ observed during round-trip cruise in the East Asia, Western North Pacific (WNP) and Arctic Ocean.

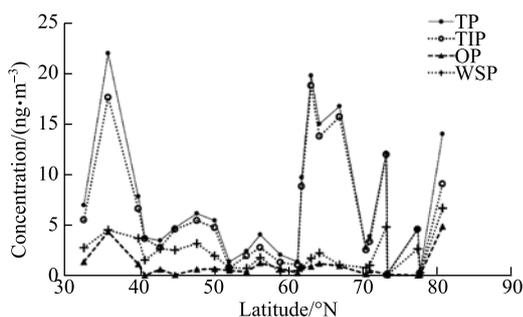


Figure 3 Spatial variations of TP, TIP, OP and WSP during the sampling period of this study.

Table 1 Concentrations of phosphorus in total suspended particles

	Minimum	Maximum	Median	Mean	Standard deviation
East Asia	3.53	22.05	6.20	7.90	6.45
Western North Pacific	1.41	19.85	4.12	6.87	6.66
Arctic Ocean	0.34	16.79	4.88	7.13	6.76

Note: Phosphorus species concentration expressed as $\text{ng}\cdot\text{m}^{-3}$.

Table 2 lists the average concentrations of particulate TP measured in the three transects as well as several previous observations taken in the North Pacific region. The values obtained for atmospheric phosphorus in the Western North Pacific by this study are similar to those previously observed^[14]. The measured geographical distribution of the TP concentrations in the East Asia Sea and the WNP were within the range of those simulated by a global model of atmospheric phosphorus^[8]. It shows the concentration of TP is high in close

vicinity to East Asia and sharply decreases away from the land. But the trends of geographical distribution of TP in our results have a large discrepancy with the model. One should keep in mind that our research was conducted in June, August, and September, while the modeled concentration represents an annual average. There is another discrepancy found in the Arctic Ocean. Although the minimum appeared in this region, the average measured concentration of TP in this area was about one order of magnitude higher than modeled. Such high concentration of TP may be an important source of nutrients for the Arctic Ocean.

Table 2 Comparison of concentrations of TP measured during CHINARE2008 with previous data

Region/Location	Season	Mean	Std.	<i>n</i>	Reference
East Asia	Jun–Sep 2008	7.9	6.4	7	this study
Western North Pacific	Jun–Sep 2008	6.9	6.6	9	this study
Arctic Ocean	Jun–Sep 2008	7.0	6.8	8	this study
Central North Pacific	Aug–Sep 2005	2.5	1.2	28	[14]
Western North Pacific	Jun 2006	7.3	4.3	34	[14]
Tropical and subtropical North Pacific	May–Jun 1975	0.4	0.57	21	[7]
Taiwan, China	Sep 2003–Dec 2004	20–70	–	12	[23]
Cheju Island, Korea	Jan–Jun 2002	22	20	–	[24]

Note: Concentrations of TP expressed as $\text{ng}\cdot\text{m}^{-3}$.

Obviously, TIP is the dominant species in most of the samples. The average proportion of TIP in TP over the entire course is 86.6%. The value is much higher in some samples with concentrations reaching up to $10 \text{ ng}\cdot\text{m}^{-3}$. The total average proportion of OP is 16%. The values of OP for the WNP Ocean are especially high and reached up to 20%, indicating that OP is also a significant fraction of total phosphorus.

3.2 Backward trajectories and statistical analysis

Air Mass Back Trajectories (AMBTs) were calculated from the National Oceanic and Atmospheric Administration (NOAA) FNL database using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) model. The 15th of each month was selected to represent typical trajectories. AMBTs were performed at 10, 500, and 1000 m height levels above the ground level to represent the airflow trajectories at the surface, middle altitudes, and high altitudes, respectively.

Figure 2 shows that the TP concentrations vary considerably. There were no geographical gradients. Values varied greatly even for samples that were collected over adjacent regions. A possible cause of this phenomenon may be due to the influence of the air mass transportation. For example, the samples numbered 16, 17, and 27 were collected in adjacent regions in the Arctic Ocean at different times. The measured concentrations of sample 16 are approximately 20 times higher than sample 17 and 27. The AMBTs of the three samples show that sample 16 was influenced by an air mass that had passed over Siberia and Alaska (Figure 4a), while sample 17 and 27 were collected at a time when winds were coming from the remote center of the Arctic Ocean (Figures 4b and 4c). The air mass from the continent may have a higher concentration of phosphorus aerosol. The AMBTs of other samples were also calculated. Results show that the winds from the mainland will increase the measured TP in aerosols, implying that the continental sources may be important contributors.

3.3 Sources analysis of TP

Mineral aerosols, anthropogenic aerosols, sea salt aerosols, volcanoes, and primary biogenic particles are significant sources of atmospheric aerosol. Unlike other sources, volcanoes are usually point emission sources. Thus, volcanoes should create large geographical gradients in TP which were not found in our research. With similar formation pathways^[15-16], the concentration of primary biogenic aerosols (PBA) in the marine boundary layer is much lower than the sea salt aerosols^[17].

The characteristic chemical composition of different aerosols allows us to estimate the contribution of different sources to TP^[18]. Fe, Zn, and Cl are selected to conduct a source apportionment analysis for TP since these elements and their ionic forms generally represent different aerosol sources (Fe: crustal, Zn: anthropogenic, and Cl: oceanic)^[19-20].

Using the concentrations of the tracers, phosphorus from the different sources can be estimated as:

$$\text{TP}_{\text{aerosol}} \approx \text{Fe}_{\text{aerosol}} \times \left(\frac{\text{P}}{\text{Fe}}\right)_{\text{crustal}} + \text{Zn}_{\text{aerosol}} \times \left(\frac{\text{P}}{\text{Zn}}\right)_{\text{anthro}} + \text{Cl}_{\text{aerosol}} \times \left(\frac{\text{P}}{\text{Cl}}\right)_{\text{seawater}}$$

The individual terms take the form of $(\text{P}/\text{Z})x$ where x = crustal, anthropogenic, or oceanic) and Z = Fe, Zn, and Cl. Thus, these terms represent the characteristic ratio of mass concentrations of phosphorus and compound Z in source x , which we assume to be constant for each source. The product of Z_{aerosol} and $(\text{P}/\text{Z})x$ is the estimated phosphorus concentration from source x . There should be some additional phosphorus from other sources, however, actual estimates of the amount of TP emitted from other sources are extremely low^[21]. As these tracer elements are mutually exclusive, spatially explicit TP emissions from each source were calculated using the multiple linear regressive model (Table 3). SPSS 18.0 (SPSS Inc., Chicago, IL, USA) was used to analyze the experimental results.

By creating a multiple linear regressions model, we calculated the contributions of each source for every sample. Table 4 shows the average contributions of different sources in East Asia, the WNP, and the Arctic Ocean. The range in values presented in the results simply represents a range of contributions based on different sources. Mineral aerosols or crustal aerosols were found to be the most important source of phosphorus in aerosol. High levels of TP concentrations due to the contribution of mineral aerosols were observed even in the remote sea regions, implying that the aerosol particles containing phosphorus can be transported over long distances and thereby influence the global phosphorus cycle.

Table 3 Multiple linear regression analysis of the concentrations of total phosphorus

	Regression model	R^2	n
East Asia	$0.617 + 12.615X_{\text{Fe}} + 6.5195X_{\text{Zn}} + 0.069X_{\text{Cl}}$	0.882	7
Western North Pacific	$0.809 + 17.507X_{\text{Fe}} + 27.079X_{\text{Zn}} + 0.162X_{\text{Cl}}$	0.967	9
Arctic Ocean	$0.209 + 18.825X_{\text{Fe}} + 27.899X_{\text{Zn}} + 0.131X_{\text{Cl}}$	0.981	8

Note: ^a X_Z (Z = Fe, Zn, Cl) – concentrations of Fe, Zn, Cl in aerosols

Table 4 Average contributions to total phosphorus from each sources in regressive model

	Mineral aerosols ^a	Anthropogenic aerosols ^a	Marine aerosols ^a
East Asia	58.42	22.59	4.12
Western North Pacific	66.62	3.09	9.96
Arctic Ocean	70.87	1.48	18.39 ^b

Notes: ^a Contributions to total phosphorus and expressed as %.

^b A particular samples were found which considered 99% originating from sea salt because of the low concentrations of Fe and Zn. The mean would be 7.86% by excluding it.

The ratio of Fe and P is different in the variation sea areas. The ratio for the WNP is higher than for the East Asia Sea but slightly lower than values from the Arctic Ocean. This ratio varies in different region could be simply due to the contribution of dust source from different regions. Bulk chemical compositions of sands and silty soils in Chinese dust

sources soils have been extensively studied. Some research indicates that the $(P/Fe)_{\text{crustal}}$ from silty soils is lower than those from sandy soils^[22]. In addition, the chemical compositions of anthropogenic aerosols are more complex and irregular which hinders further discussion.

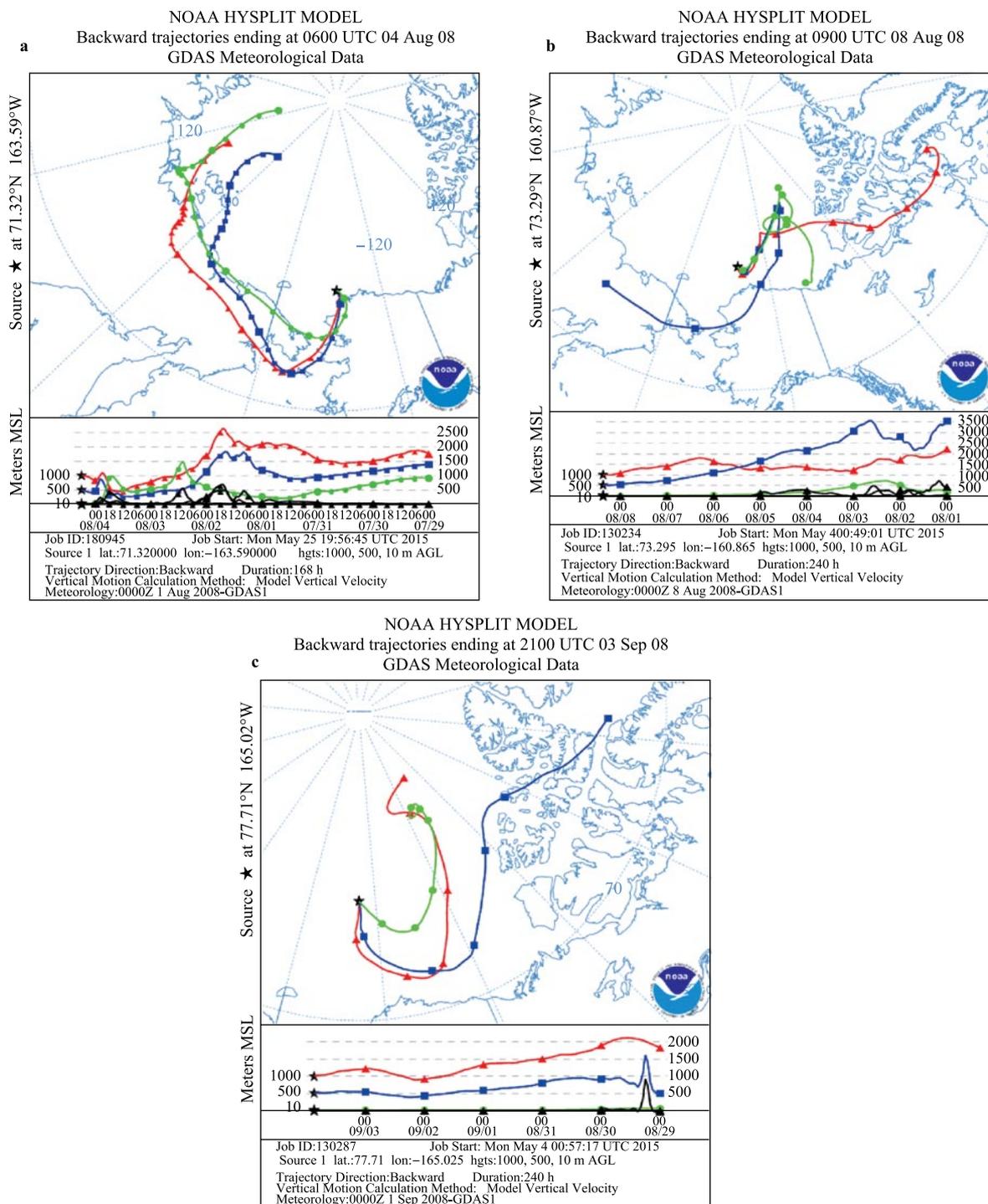


Figure 4 The 168 h (7 d) air mass back trajectories for starting altitudes of 10, 500 and 1000 m above ground level (AGL) calculated from the FNL database of the National Ocean and Atmospheric Administration (NOAA) and simulated by using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HY-SPLIT) model: **a**, sample 16; **b**, sample 17; **c**, sample 27.

The average contributions to total phosphorus from anthropogenic aerosols in East Asia are close to 28%. This contribution reached up to 30%–50% in some samples such as sample 34 and 37. However, the contributions sharply declined to 5% or lower in the WNP and the Arctic Ocean. It is likely that being away from the Chinese and Japanese coasts, which have dense populations and industry, may lead to a decrease in anthropogenic aerosols. This effect would be particularly pronounced in remote regions like the Arctic Ocean. Different from anthropogenic aerosols, the sea salt aerosols were found to be quite stable in all three regions.

A high proportion of phosphorus from crustal sources will lead to high levels of inorganic phosphorus, which is in agreement with our results. In addition, the measured inorganic phosphorus was higher than that calculated via regression of crustal sources of phosphorus, indicating that crustal sources are not the only source of inorganic phosphorus. The WSP, which is part of the inorganic P, agrees well with the values for the anthropogenic fraction. Significance tests show Zn and Cl have strong correlation with WSP ($r = 0.337$, $P = 0.66$ for Fe; $r = 0.574$, $P = 0.044$ for Zn; $r = 0.672$, $P = 0.039$ for Cl). The most significant influencing factor of WSP is sea salt aerosols. The soluble fraction from anthropogenic sources may be reduced by physical or chemical reactions over long distance transport. On the other hand, the accuracy of this analysis could also be affected by the low concentration of Zn and WSP in remote regions.

An intercept of the regression model could be derived when we assumed the contribution of those sources is zero. All the intercepts for the three ocean regions are higher than the detection limit in our measurement. Therefore, there must be another appreciable source influencing the observed TP. P_{other} is used to refer to the unaccounted portion of the TP. Given the characteristics of atmospheric activity and the assumptions we developed before, a probable source of P_{other} may be primary biogenic aerosols (PBA). The largest intercept was obtained for the Western North Pacific Ocean which corresponds with the highest proportion of OP in this region. This indicates that PBA may be an important contributor to OP.

4 Conclusions

Aerosols represent a significant source of nutrient elements to the marine environment. The TP concentrations observed in the Eastern China Sea, Japan Sea and WNP were similar to those previously observed^[14]. However, the concentrations in the Arctic Ocean were approximately one order of magnitude higher than the simulation results from a global model of atmospheric phosphorus. Inorganic phosphorus (TIP) is the dominant species in most of samples. Measurements are significantly affected by the air mass transportation. The air mass from the continent may have a higher concentration of phosphorus aerosol. Source apportionment used the tracer species (Fe, Zn, and Cl) as representatives of crustal,

anthropogenic, and seawater sources. A multiple linear regression model showed that mineral aerosols are the dominant contributor of aerosol phosphorus. However, those sources could not account for all of the TP concentrations. A possible source of the additional fraction may be primary biogenic aerosols which contribute to the organic phosphorus. The measurement of P speciation in the marine boundary provides an opportunity to better understand the global cycle of phosphorus.

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