

Seasonal changes in Iron species and soluble Iron concentration in the atmosphere in the Northwest Pacific region based on the analysis of aerosols collected in Tsukuba, Japan

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Atmospheric iron (Fe) can be a significant source of nutrition for phytoplankton inhabiting remote oceans, which in turn has a large influence on the Earth's climate. The bioavailability of Fe in aerosols depends mainly on the fraction of soluble Fe ($=[\text{Fe}_{\text{Sol}}]/[\text{Fe}_{\text{Total}}]$, where $[\text{Fe}_{\text{Sol}}]$ and $[\text{Fe}_{\text{Total}}]$ are the atmospheric concentrations of soluble and total Fe, respectively). However, the numerous factors affecting the soluble Fe fraction have not been fully understood. In this study, the Fe species, chemical composition, and soluble Fe concentrations in aerosols collected in Tsukuba, Japan were investigated over a year (nine samples from December 2002 to October 2003) to identify the factors affecting the amount of soluble Fe supplied into the ocean. In this study, we used X-ray absorption fine structure (XAFS), which is a powerful analytical tool to identify chemical species of Fe and other elements in aerosols to speciate Fe in aerosols. Identifying the Fe species in aerosol can improve understanding of the factors controlling $[\text{Fe}_{\text{Sol}}]/[\text{Fe}_{\text{Total}}]$, because this ratio is strongly related to the Fe species. We also conducted leaching experiments to study the relationship between the $[\text{Fe}_{\text{Sol}}]/[\text{Fe}_{\text{Total}}]$ ratio and Fe species. By combining atmospheric Fe concentration, XAFS analysis, and leaching experiments, we revealed important factors controlling the supply of soluble Fe into the ocean [1].

X-ray absorption fine structure (XAFS) spectroscopy was performed in this study to identify the Fe species in aerosols. Hence, iron K-edge XAFS was performed at beamlines BL-12C and BL-9A at the Photon Factory, details of the procedures of XAFS analyses were described by Takahashi et al. [2]. Combining the results of both XANES and EXAFS can make our speciation analysis more reliable [3]. In addition, simulated seawater [0.70 M NaCl and pH 8 with 0.10 mM ethylenediaminetetraacetic acid (EDTA) as an analogue of ligands in seawater] was used to determine the fraction of Fe that can be dissolved into the ocean.

The soluble Fe concentration in aerosols is correlated with those of sulfate and oxalate originated from anthropogenic sources, suggesting that soluble Fe is mainly derived from anthropogenic sources. Moreover, the soluble Fe concentration is also correlated with the

enrichment factors of vanadium and nickel emitted by fossil fuel combustion. These results suggest that the degree of Fe dissolution is influenced by the magnitude of anthropogenic activity, such as fossil fuel combustion.

The fitting of XAFS spectra coupled with micro X-ray fluorescence analysis (XRF) determined the main Fe species in aerosols in Tsukuba to be illite, ferrihydrite, hornblende, and Fe(III) sulfate. Moreover, the soluble Fe fraction in each sample measured by leaching experiments is closely correlated with the Fe(III) sulfate fraction determined by the XAFS spectrum fitting, suggesting that Fe(III) sulfate is the main soluble Fe in the ocean. Another possible factor that can control the amount of soluble Fe supplied into the ocean is the total Fe(III) concentration in the atmosphere, which was high in spring due to the high mineral dust concentrations during spring in East Asia. However, this factor does not contribute to the amount of soluble Fe to a larger degree than the effect of Fe speciation, or more strictly speaking the presence of Fe(III) sulfate. Therefore, based on these results, the most significant factor influencing the amount of soluble Fe in the North Pacific region is the concentration of anthropogenic Fe species such as Fe(III) sulfate that can be emitted from megacities in Eastern Asia. Generally speaking, anthropogenic aerosol is rich in fine particles, thus, anthropogenic Fe(III) sulfate can be transported over relatively long distances and can have a great impact on phytoplankton activity in the open ocean. Fe in mineral dusts, especially in the dust storm season, is possibly an important Fe source in the North Pacific, but the contribution of Fe(III) sulfate from megacities in Eastern Asia must not be disregarded.

References

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