Solubility of Iron in the Aerosol Collected during Kosa (Asian Dust) Events in Japan

Ikuko Mori¹, Masataka Nishikawa¹, Atsushi Shimizu¹, Masamitsu Hayasaki², and Takumi Takasuga³

¹National Institute for Environmental Studies, Tsukuba, Japan
²Center for Environmental Remote Sensing, Chiba University, Chiba, Japan
³Shimadzu Techno-Research, Kyoto, Japan

Abstract

The main contributor of aerosol particulate soluble iron to Japan and the Pacific Ocean has been investigated using data obtained during the research campaign entitled “A Study on Dust and Sand Storms” conducted by the Ministry of the Environment, Japan. The concentration of particulate soluble iron was not correlated to total iron concentration. Particulate iron solubility ranged from less than 1% to 6%. It was low when the air mass was dominated by kosa aerosols, and high when the air mass was dominated by pollutants. Durations for the kosa and pollution events over Jeju Island, Matsue, and the Pacific Ocean in April and May 2007 were estimated using a Chemical Weather Forecasting System (CFORS). The estimated durations of the pollution events at Jeju and Matsue were slightly shorter than those of the kosa events. The calculated duration of the pollution event over the Pacific Ocean was only three hours, much shorter than that of the kosa event. Kosa aerosols are the main contributor of soluble iron to the Pacific Ocean; however anthropogenic aerosols should not be discounted as contributors of soluble iron to an area off the coast of the Asian continent.

1. Introduction

Iron is essential for the growth of organisms and may limit phytoplankton primary production, especially in the remote ocean, and several studies on the solubility of atmospheric particulate iron have been conducted (Zhuang et al. 1992; Spokes et al. 1994; Fan et al. 2006). Previous studies considered the solubility of aerosol iron mainly from two aspects; differences in leaching processes and differences in the source of the iron. Laboratory studies suggested that iron solubility should be predictable in terms of the pH/solubility relationship (Spokes et al. 1994) and demonstrated that acidification by gaseous nitric acid led to an increase in water-soluble iron (Duvall et al. 2008). Meskhidze et al. (2003) predicted that the pH estimated by using the observed nitrate ion and gaseous nitric acid concentrations was low enough to facilitate iron mobilisation in mineral dust from East Asia. On the other hand, the laboratory study conducted by Schroth et al. (2009) showed that the solubility of iron in an aerosol could vary depending on its source; the measured solubility of iron in arid soils was less than 1%, that in glacially produced soils was 2–3%, whereas in oil combustion products it was 77–81%. Acid processing of insoluble iron was not significant in authentic aerosol samples (Chuang et al. 2005; Baker et al. 2006). Aguilar-Islas et al. (2010) concluded, based on the result of leaching experiments and using data from the literature, that more variability in aerosol iron solubility resulted from differences in aerosol type than from different leaching protocols.

The main contributing source of soluble iron, especially to the remote ocean, is still a matter of controversy. Chuang et al. (2005) concluded, based on the results of chemical analysis, that the iron released by fuel combustion was the main contributor of the soluble iron in aerosols collected in Jeju, Korea. Sedwick et al. (2007) agreed with this conclusion following chemical analysis of aerosols collected from the Sargasso Sea. A model calculation suggested that anthropogenic emissions contributed approximately 70% and 85% of the annual dry deposition of soluble iron to the surface ocean near Bermuda and Ireland, respectively (Sholkovitz et al. 2009). Another model calculation suggested that iron from combustion processes can represent up to 50% of the total iron deposited, but over open ocean regions it usually contributes less than 5% of the total iron, with the highest values (< 30%) close to the East Asian continent in the North Pacific (Luo et al. 2008).

In this paper, the main contributor of soluble iron to Japan and the Pacific Ocean was investigated using data obtained during the research initiative entitled “A study on Dust and Sand Storms” conducted by the Ministry of the Environment, Japan.

2. Aerosol samples and methods

Since 2002 the Ministry of the Environment of Japan has conducted a research campaign entitled “A Study on Dust and Sand Storms” to investigate the physical and chemical characteristics of kosa (Asian dust) aerosols. During this research, total suspended particulates (TSP) were collected in nine locations throughout Japan (Fig. 1) using high volume samplers with quartz fibre filters, when kosa events were observed in China. This aerosol sampling has been conducted a few times each year. The aerosol mass concentration and the concentrations of the chemical components of the aerosols were determined by the procedure described by Mori et al. (2002). In brief, water-soluble components were extracted using ultrapure water, and bulk components were digested using a mixture of nitric, perchloric, and hydrofluoric acids. Aerosol vertical distribution was measured by lidar (Shimizu et al. 2004). The concentrations of suspended particulate matter (SPM) and sulfur dioxide (SO₂) were measured simultaneously. Five events (Table 1) were selected for discussion of the characteristics of water soluble iron in aerosols collected during heavy dust events. Results of backward trajectory analyses revealed that the air masses came to Japan from the Asian continent during these events. Details of the research campaign and the selected heavy dust events are described in MOE (2009).

3. Results and discussion

3.1 Total and water soluble iron concentrations

Concentrations of TSP, total iron (Fe), and water soluble iron in the aerosols collected during five heavy dust events over Japan were in the ranges 66–509 µg m⁻³, 1.7–20.2 µg m⁻³, < 0.01–0.13 µg m⁻³, respectively. The concentration of total iron increased with an increase in the TSP concentration. However, the concentration of water soluble iron did not increase with increases in TSP or total iron concentrations (Fig. 2). This result agreed with that from aerosol monitoring in Jeju Island, Korea (Chuang et al. 2005). The particulate soluble iron concentration is not correlated to the total iron concentration in the Asian outflow atmosphere.
3.2 Particulate iron solubility and source

The particulate iron solubility ranged from less than 1% to 6% during the five heavy dust events in Japan. This result is consistent with that reported for the Jeju aerosol (Chuang et al. 2005; Duvall et al. 2008) and with that for the aerosol collected over the Sagasso Sea (Sedwick et al. 2007).

Laboratory studies demonstrated that the solubility of iron in loess was less than 1% (Duvall et al. 2008; Schroth et al. 2009). In contrast, the solubility of iron in oil combustion products ranged from 49−100% (Henry and Knapp 1980; Schroth et al. 2009). These results derived from laboratory studies indicated that particulate iron solubility in aerosols could be controlled by the source of the aerosol.

To investigate the relationship between the solubility of particulate iron and the contribution of kosa to the aerosol, the particulate iron solubility was plotted against the ratio of the aluminium concentration to TSP (Fig. 3), which shows the particulate iron solubility decreased as the Al/TSP increased. Aluminium is often used as an indicator of mineral aerosols (Uematsu et al. 1983; Duce 1995), and therefore the higher the Al/TSP, the higher the contribution of kosa to the aerosol. That kosa was the main contributor to the aerosol was also supported by the observation that its Fe/Al value approached 0.5, very close to the Fe/Al value for Simulated Asian Mineral Dust certified reference material (0.51) (Nishikawa et al. 2000), as Al/TSP increased (Fig. 4). From these results, it could be concluded that the solubility of particulate iron was ca 1% when kosa aerosol was the predominant material in the atmosphere.

The particulate iron solubility was also plotted against the ratio of the sum of the concentrations nitrate (NO$_3^-$) and non-sea salt sulfate (nssSO$_4^{2-}$) ions (Anion) to TSP (Fig. 5) in order to investigate the relationship between iron solubility and the contribution of anthropogenic aerosol. Sulfate and nitrate ions are mainly formed from substances supplied to the atmosphere through human activity. Generally, a higher Anion/TSP value indicates a higher contribution of an anthropogenic aerosol. Figure 5 shows that the particulate iron solubility was high when the Anion/TSP was high. This result suggested that particulate iron solubility is high when anthropogenic aerosols are predominant in the atmosphere.

The dependency of particulate iron solubility on air mass type was also investigated. The air mass was categorised: 1) kosa, 2) kosa + pollutant, 3) pollutant; according to the analytical results of lidar measurements and SPM and SO$_2$ measurements (MOE...
The solubility of iron in the aerosol collected when the air mass was categorised as kosa was low, and the iron solubility when the air mass was categorised as pollutant was high (Table 2). These results were consistent with the results of the laboratory study as described above. Particulate iron solubility in the atmosphere over Japan would be controlled by the aerosol source as described by Schroth et al. (2009) and Aguilar-Islas et al. (2010).

3.3 Primary contributor of particulate soluble iron to Japan and the Pacific Ocean

The soluble iron concentrations in the aerosols in each air mass category are summarised in Table 2. Differences in the soluble iron concentration in each air mass category were insignificant, although the differences in the iron solubility were significant. Therefore, iron solubility was not a key factor in controlling the amount of particulate soluble iron. The duration of each event (kosa, pollution or a combination of the two) would be the key factor in controlling the quantity of particulate soluble iron.

To estimate the duration of a kosa event and a pollution event, dust and sulfate concentrations throughout April and May 2007 were calculated using a chemical weather forecasting system (CFORS) (Uno et al. 2004). Three locations: 1) Jeju, Korea, 2) Matsue, Japan, 3) the Pacific Ocean (Fig. 1); were selected for this analysis. In this paper, when the calculated dust concentration near the surface exceeded 100 µg m\(^{-3}\) was categorised as the kosa event, and when the calculated sulfate concentration near the surface exceeded 10 µg m\(^{-3}\) was categorised as the pollution event. These threshold values were determined based upon CFORS results during kosa and pollution events observed in Matsue. The calculated total duration of the kosa event at Jeju and Matsue was slightly longer than that for the pollution event (Table 3). This suggested that a kosa event supplies more soluble iron to these locations than does a pollution event. This result contradicts that of Chuang et al. (2005) who concluded that soluble iron was mainly derived from anthropogenic activity with mineral dust making a negligible contribution. However, the calculated total duration of the pollution event over the Pacific Ocean was only three hours, and was much shorter than the kosa event (Table 3). This suggested that kosa aerosol is the main contributor of particulate soluble iron to the Pacific Ocean. This finding is consistent with that of Sholkovitz et al. (2009) that the annual mean dry deposition of

![Fig. 3.](image)

*Fig. 3. The relationship between particulate iron solubility and Al/TSP for the aerosols collected during heavy dust events in Japan.*

![Fig. 4.](image)

*Fig. 4. The relationship between Fe/Al and AI/TSP for the aerosols collected during heavy dust events in Japan. The dotted line represents Fe/Al for Simulated Asian Mineral Dust certified reference material (CJ-2).*

![Fig. 5.](image)

*Fig. 5. The relationship between particulate iron solubility and \((NO_3^- + nssSO_4^{2-})/TSP\) for the aerosols collected during heavy dust events in Japan.*

### Table 2. Median and range (in parentheses) of TSP, particulate total iron, particulate soluble iron, and iron solubility for the aerosols collected during high TSP events in Japan. Air mass was categorised according to the results of lidar, SPM and SO\(_2\) measurements.

<table>
<thead>
<tr>
<th>Air mass</th>
<th>TSP (µg m(^{-3}))</th>
<th>Total Fe (µg m(^{-3}))</th>
<th>Soluble Fe (µg m(^{-3}))</th>
<th>Fe Solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kosa</td>
<td>404 (149–509)</td>
<td>16.2 (5.5–20.2)</td>
<td>0.061 (0.034–0.115)</td>
<td>0.46 (0.17–1.00)</td>
</tr>
<tr>
<td>Kosa + Pollutant</td>
<td>198 (66–298)</td>
<td>7.0 (1.9–9.6)</td>
<td>0.063 (&lt;0.01–0.114)</td>
<td>0.88 (&lt;0.1–1.24)</td>
</tr>
<tr>
<td>Pollutant</td>
<td>100 (83–122)</td>
<td>2.1 (1.7–2.4)</td>
<td>0.060 (0.033–0.126)</td>
<td>2.9 (2.0–5.7)</td>
</tr>
</tbody>
</table>
soluble iron at Barbados and Izana is dominated by soil dust, even though the study location was different. It is also consistent with the conclusions based on the Saharan dust study by Baker et al. (2006). We conclude that kosa aerosols are the main contributor of soluble iron to remote ocean, such as those of the Pacific Ocean, but that anthropogenic aerosols should not be discounted as sources of soluble iron area of sea off the coast of the Asian continent.

4. Summary

The following conclusions were derived from the results of the research campaign entitled “A Study on Dust and Sand Storms” conducted by the Ministry of the Environment, Japan:

1. The particulate soluble iron concentration in the Asian outflow atmosphere is not correlated to the total iron concentration.
2. The solubility of particulate iron in the atmosphere over Japan depends upon the source of the aerosol.
3. Kosa aerosols are the main contributor of soluble iron to the remote ocean, such as the Pacific Ocean, but anthropogenic aerosols should not be discounted as a source of soluble iron to areas off the coast of the Asian continent.

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