

The origin of water soluble particulate iron in the Asian atmospheric outflow

P. Y. Chuang,¹ R. M. Duvall,² M. M. Shafer,² and J. J. Schauer²

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[1] Iron, and in particular water soluble iron, is an important trace nutrient in the surface ocean, and therefore an important component in the global carbon cycle. Deposition of Asian aerosol is thought to be a primary source of water soluble iron in the northern Pacific. Analysis of aerosol samples obtained during the Aerosol Characterization Experiment (ACE)-Asia field campaign from Jeju Island, Korea, which intercepts the outflow from the Asian continent, shows that water soluble iron is not dominated by mineral dust sources even during large dust storms. Instead, our analysis indicates that particulate soluble iron and elemental carbon concentrations are correlated. This leads to the conclusion that soluble iron in this region is strongly connected to anthropogenic activity and not connected to mineral dust emissions, especially if the budget averaged over annual time scales is considered. **Citation:** Chuang, P. Y., R. M. Duvall, M. M. Shafer, and J. J. Schauer (2005), The origin of water soluble particulate iron in the Asian atmospheric outflow, *Geophys. Res. Lett.*, 32, L07813, doi:10.1029/2004GL021946.

1. Introduction

[2] Laboratory and field scale experiments demonstrate that primary production in the high nutrient, low chlorophyll (HNLC) regions of the Pacific (near the equator and the subarctic), may be limited by the availability of *soluble* iron or silica [Coale *et al.*, 2004; Buesseler *et al.*, 2004]. By influencing pCO₂ in the atmosphere, carbon fixation in the oceans may affect the radiative balance of the planet [Martin, 1990]. Models [Sigman and Boyle, 2000] and ice core data [Petit *et al.*, 1999] suggest that variations in the atmospheric flux of iron to the HNLC Pacific have regulated marine production over the past four glacial cycles. Biological primary production has been predicted to be very sensitive to the fraction iron that is soluble when deposited into the surface ocean [Fung *et al.*, 2000].

[3] The transport and deposition of atmospheric aerosol, and in particular mineral dust, has been identified as a major source of iron to the open ocean, although the origin of soluble Fe is less clear [Duce and Tindale, 1991; Jickells and Spokes, 2001]. Recently, Meskhidze *et al.* [2003] show measurements that support the existence of low pH aqueous aerosol in association with dust in the East Asian region, and hypothesize that this environment can significantly

increase the soluble Fe fraction. Briefly, their hypothesis is that Fe can be mobilized when exposed to aqueous sulfuric acid of pH < 2 for a duration of 3 to 5 days. In this paper, we examine the sources of soluble Fe in the Asian outflow further north using data collected during the ACE-Asia field project (March to May 2001). The air masses sampled during the project include two prominent dust storms (April 10 to 13 and 24 to 25), as well as pollution events from China, Korea and Japan.

2. Method

[4] The ACE-Asia Gosan (Kosan) Supersite (Figure 1) was a heavily instrumented ground-based field site on the western tip of Jeju (Cheju) Island, Korea. Details about the entire measurement suite at this site are available elsewhere [Huebert *et al.*, 2003]. Relevant to this study, samples of total suspended particulates (TSP, which has an upper size limit of 60 μm) were collected daily between March 31 and May 2, 2001. The collected aerosol was analyzed for elemental carbon (EC) and organic carbon (OC) using the standard ACE-Asia technique [Schauer *et al.*, 2003]. Total Fe (soluble and insoluble), along with other metals, were measured for the TSP aerosol samples (which includes both fine and coarse aerosol modes) using inductively coupled plasma optical emission spectrometry (ICP) and inductively coupled plasma mass spectrometry (ICP-MS) from acid digests of the aerosol samples. Soluble Fe was measured in Milli-Q water extracts using ICP, and is assumed to be primarily ferrous rather than the much less soluble ferric iron. The use of unbuffered Milli-Q water instead of seawater to infer soluble Fe could lead to differences in the absolute amounts of soluble Fe. However, the results reported here rely on the relative amounts of soluble Fe. Previous studies suggest that the use of seawater would enhance soluble Fe from anthropogenic sources of Fe relative to crustal Fe, and therefore, if anything, these results are biased towards increasing the contribution of crustal Fe [Jickells and Spokes, 2001]. Details of the iron analysis methods and further discussion of this issue are presented in the auxiliary materials¹.

[5] In addition to Gosan data, measurements of aerosol (TSP and PM₅ fractions) mass and chemical composition were obtained from a site in Dunhuang (Figure 1) using methods identical to those used on Gosan samples. Dunhuang is located within one of the important source regions for the Yellow Sand events [Huebert *et al.*, 2003], and is used to characterize recently resuspended aeolian dust. Based on back trajectory analyses, the air masses

¹Department of Earth Sciences, University of California, Santa Cruz, California, USA.

²Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, Wisconsin, USA.

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2004GL021946>.

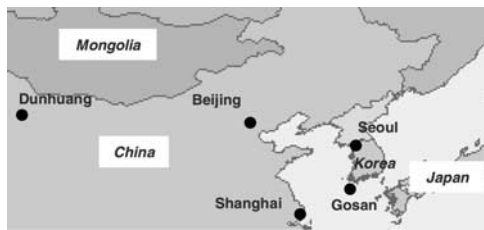


Figure 1. Map of the ACE-Asia experimental region with the Gosan (Kosan) and Dunhuang sites identified. See color version of this figure in the HTML.

sampled at Gosan during the dust events passed within a few hundred kilometers of Dunhuang, therefore it is reasonable to consider that the dust at Dunhuang is fairly representative of the source region of the Gosan dust aerosol.

[6] Data from 27 days of the sampling period are used in this paper; the data from the remaining six days are incomplete due to instrument problems. Of these 27 days, 6 days (April 2, 11, 13, 19, 21, and 25) have total Fe concentrations greater than $4 \mu\text{g Fe m}^{-3}$, which we denote as the dust-dominated days. Similarly high Al and Ca concentrations, along with HYSPLIT isentropic back trajectory calculations that show that these air masses originate from N and W China, support the assertion that the aerosol is primarily dust. Of these six days, three appear to have low mixing between pollution and dust based on the low fraction of EC present in the coarse aerosol fraction. On these three days, April 19, 11, and 21 (“clean dust days”), the fraction of total EC that was in the coarse aerosol fraction was 7, 12 and 14% respectively. On the other three dust event days, April 25, 2, and 13 (“polluted dust days”), the dust appears to have a greater pollution component with 28%, 40% and 45% of the total EC in the coarse fraction, respectively. Absolute EC concentrations (rather than fractions) in the coarse particle phase show the same trends. Since EC is dominated by combustion sources, and emitted as primary fine particles, the likely mechanism for the presence of EC in the coarse particle phase at this location is coagulation with dust during transport.

3. Results and Discussion

3.1. Is Dust the Main Source of Soluble Fe?

[7] The question of whether or not dust-derived Fe was a dominant source of soluble Fe is examined. We first examine data from the Dunhuang sampling site, which is in the source region for aeolian dust. Soluble iron data from this site shows that dissolved iron fractions are between 0.05 and 1%. This gives us an indication as to the soluble Fe levels and variability in freshly resuspended dust in this dust source region. During the six dust days, the data at the downwind Gosan site do not show any evidence for enhanced soluble Fe relative to Dunhuang. This is the first indicator that suggests that acid processing to form soluble Fe was not observed at Gosan anytime during the project.

[8] Figure 2 shows the relationship between soluble and insoluble Fe at Gosan. If acid attack of Fe-containing aerosol (dust or otherwise) was the primary route to form soluble iron, then there should be a significant correlation between the insoluble and soluble Fe (although such a

relationship would also be influenced by other factors, such as the amount of processing that occurred in transit). Figure 2 shows that there is no such correlation, suggesting that processing is not significant, and that some other source is responsible for the soluble Fe sampled at Gosan. In fact, the days with high dust concentrations exhibit low to average soluble Fe concentrations. On the dust days, the soluble Fe fraction was 0.12, 0.33, and 0.58% for the clean dust cases, and 0.10, 0.57, and 0.91% for the polluted dust cases. Also, there is no clear evidence that the polluted dust cases exhibit enhanced soluble Fe fractions relative to clean dust days, further strengthening the conclusion that processing of dust is not a significant control of soluble Fe. The same conclusion is reached when examining the data in absolute mass concentration terms. The six dust-dominated days exhibit mean soluble Fe concentrations less than that for the non-dust days (with 99% confidence level using t-test). Average soluble Fe concentration for all 27 days is $32 \pm 19 \text{ ng Fe m}^{-3}$, whereas for the 6 dust days, the average is $24 \pm 10 \text{ ng m}^{-3}$, with only one day (April 25 with 37 ng m^{-3}) exceeding the project average. Again, these data reinforce the hypothesis that total Fe is not controlling soluble Fe during dust events.

[9] The conclusion that dust is not a major source of soluble Fe is supported by other observations during ACE-Asia. To further address the question of sulfuric acid attack of dust, we examine measured aerosol sulfate concentrations. Of the days that we label “high dust”, two exhibited particularly high SO_4 concentrations (ranked 1 and 4 among all samples). The soluble Fe concentrations on these days were not notably high; the first was slightly above average, the other considerably below average. Looking at the data as a whole, SO_4 exhibits very little correlation with soluble Fe (data not shown; correlation coefficient R^2 is 0.007). This suggests that acid attack from sulfuric acid is not a strong factor in determining soluble Fe concentrations. This

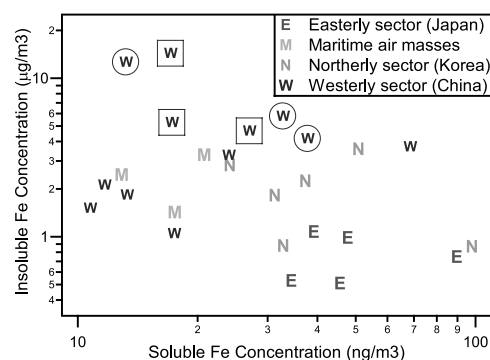


Figure 2. Relationship between insoluble and soluble iron concentration at Gosan, Korea, including region of air mass origin. The dust-dominated days are the six days with insoluble Fe $> 4 \mu\text{g Fe m}^{-3}$ (points with boxes are the clean dust days and with circles \circ are polluted dust days). The figure shows a possible relationship between the air mass origin and soluble Fe content, with E and N air masses tending to have higher soluble Fe concentrations as compared with W and M air masses. More data would be needed to more carefully explore this preliminary result. See color version of this figure in the HTML.

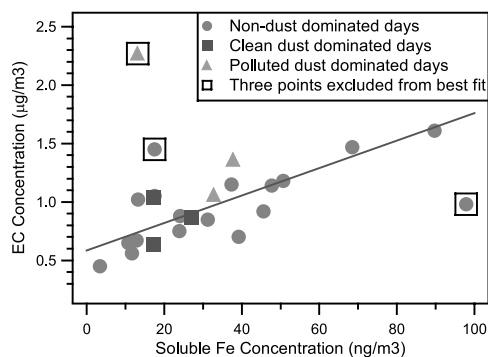


Figure 3. Relationship between soluble Fe and EC concentrations at Gosan, Korea. See text for discussion. See color version of this figure in the HTML.

is not a perfect method, since the presence of SO_4 does not conclusively demonstrate the presence of sulfuric acid, although it is reasonable to deduce that low SO_4 concentrations in the dust imply very little possibility of sulfuric acid processing.

[10] These observations are in agreement with one study of the dust storm of April 9 to 12. *Tang et al.* [2004] compared model results to aircraft observations of this storm in the Yellow Sea region, a location closer to continental Asia than Gosan, and concluded that all the nitrate and sulfate existed as salts of Ca, Mg, Na, and NH_4^+ , i.e. there did not seem to be any evidence of the presence of excess acid in the east Asian outflow. The explanation they offer is that the nitric and sulfuric acids were neutralized by the alkalinity of the dust, and strong emissions of ammonia from east Asia.

3.2. What Controls Soluble Fe?

[11] If total Fe is not controlling soluble Fe, then what is? Somewhat surprisingly, we observe that there is a good correlation ($R^2 = 0.7$) between soluble Fe and EC concentrations, as shown in Figure 3 for 24 of the 27 days. (Of the three points that were excluded from this fit the point at the top left is a dust day that appears clearly anomalous for reasons we have not yet identified. The other two days have in common that back trajectories show that they have spent most of the past 96 hours in the marine environment, which means that they are less representative of the Asian outflow that we seek to study here.) This significant correlation holds true despite the fact that Gosan receives a wide variety of air masses. Combustion of various fuels for energy production is the dominant source of EC, accounting for over 90% of EC emissions in China (with similar if not higher values expected for Japan and Korea), although the source strength depends on, among other factors, the fuel and combustion method used [*Bond et al.*, 2004]. Biomass burning accounts for most of the remainder of the EC inventory. No correlation between EC and water soluble potassium was found during this study (results not shown), suggesting that biomass burning was not a primary source of EC.

[12] Previous studies have found that coal fly ash contains significant amounts of iron, ca. 1% by mass [*Smith*, 1980] as does particulate matter emitted by diesel and gasoline motor vehicles [*Hildemann et al.*, 1991]. The

solubility of iron in particle samples is not well established, but appears to vary between nearly insoluble to highly (35% of total Fe) soluble, with typical values $\sim 1\%$ [*Desboeufs et al.*, 2005], which is consistent with our data.

[13] There are two reasonable scenarios for which a correlation between soluble Fe and EC may exist:

[14] (A) EC and soluble iron are co-emitted as primary pollutants from the same sources.

[15] (B) Some component emitted from the EC source is critical to forming soluble Fe during atmospheric processing.

[16] Obviously, if scenario A is true, then there would be a good correlation between EC and soluble Fe. The remaining variability in soluble Fe concentration could be explained by, for example, differing EC to soluble Fe emission ratios for different sources, which would lead to different slopes in Figure 3. The mixing of aerosols from multiple EC sources would then lead to some scatter in Figure 3.

[17] Scenario B encompasses a wide variety of possible mechanisms. We have shown that during dust-dominated days, there is no evidence of enhanced soluble Fe in comparison with the initially resuspended dust, and that the amount of pollution mixed with the dust does not appear to be a factor. However, we cannot rule out the possibility that a subset of insoluble Fe (e.g. Fe of a particular oxidation state, mineral form, or morphology) is processed during transit by some species that is emitted simultaneously with EC. The lack of correlation between soluble and total insoluble Fe mass concentration does not necessarily exclude processing as a mechanism. We leave elucidation of the mechanism that connects soluble Fe and EC as a subject of future research. In either case, the main conclusion is that anthropogenic emissions, as traced by EC, appear to be strongly connected to particulate soluble Fe.

[18] The intermittency of dust storms, which occur predominantly during late winter and spring, also makes dust a less important source of soluble Fe than that derived from anthropogenic combustion, which occurs year round. To estimate the relative importance of dust versus non-dust events to soluble Fe, we obtained historical dust storm records from Kwangju, Korea provided by the Korean Meteorological Administration. For the period from 1961 to 2000, the average number of dust storm days per year is 4.5 days with a standard deviation of 3.6 days (range is 0 to 14 days). If we compare the contribution of, say, 10 dust days with Gosan dust day average of 24 ng Fe m^{-3} over the course of a year to the remaining 355 non-dust days with the Gosan overall project average soluble Fe concentration of 32 ng Fe m^{-3} , clearly non-dust soluble Fe dominates, contributing over 98% of soluble Fe. Given the strong correlation of soluble Fe with EC, we conclude that, annually averaged, anthropogenic activity is a key factor influencing the annual outflow of soluble particulate Fe from Asia, whereas dust storm activity is not a significant factor.

3.3. Uncertainties

[19] A number of uncertainties are associated with this analysis. We do not deny that acid processing of these aerosol can lead to enhancements in soluble Fe concentration, and perhaps this was not observed because the necessary conditions were not satisfied. However, we sampled two major dust events, and neither showed any evidence of enhanced soluble Fe via this mechanism. We

therefore question the importance of acid processing of dust to the soluble Fe budget on an annual time scale if the conditions are not commonly met. It is also possible that further downwind of the Asian outflow, continued processing of dust by pollution could occur and enhance dust-derived soluble Fe over that found at Gosan. Contact time of dust with pollution has been estimated to range up to 3 days prior to arrival at Gosan [Chuang *et al.*, 2003], which may not be sufficient contact time for significant processing. The layered structure of unmixed pollution and dust typically (but not always) measured during ACE-Asia [e.g., Bahreini *et al.*, 2003] suggest that acid-processing of dust may not play a significant role downwind. Note that as discussed above, Tang *et al.* [2004] concluded that during the dust storm of April 9 to 13, aerosol sulfate and nitrate was neutralized either by dust or ammonia and therefore not present as acids. In such a situation, acid processing cannot occur downwind. However, our data cannot definitively rule out this mechanism and we therefore leave this issue as a subject for further study.

4. Summary

[20] Analysis of aerosol data from Gosan, Korea during ACE-Asia leads to a number of conclusions relevant to particulate iron in the Asian outflow:

[21] 1. Dust storms do not exhibit enhanced soluble Fe levels relative to their source region, or relative to non-dust days. Also, soluble Fe is not correlated with insoluble Fe. These two observations leads to the conclusion that processing of insoluble Fe during dust storms is not a significant contributor to soluble Fe at Gosan.

[22] 2. The observed correlation between soluble Fe and EC is surprisingly strong given that a number of other variables are expected to influence this relationship. This leads us to conclude that anthropogenic activity is a key factor in particulate soluble Fe concentrations. We believe that the most likely mechanism is the emission of soluble Fe from combustion sources, but our data do not permit testing of this hypothesis.

[23] 3. Annually averaged, soluble Fe from dust storms is a minimal contributor, while anthropogenic activity appears to be a primary contributor in the Asian outflow.

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P. Y. Chuang, Department of Earth Sciences, University of California, Santa Cruz, Santa Cruz, CA 95064, USA. (pchuang@es.ucsc.edu)

R. M. Duvall, J. J. Schauer, and M. M. Shafer, Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI 53706, USA.