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#### **Key Points:**

- Steel plant emission dominate anthropogenic iron deposition in East Asia
- Coal-burning fly ash dominates soluble iron deposition
- Strong seasonal variation in both dust and fly ash iron deposition

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## Atmospheric iron deposition in the northwestern Pacific Ocean and its adjacent marginal seas: The importance of coal burning

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**Abstract** This study applied a regional air quality model, incorporated with an emission module, to quantitatively differentiate the atmospheric iron sources originating from lithogenic dusts or coal-burning fly ashes deposited in the Northwestern Pacific Ocean and its marginal seas. Particular attention was paid to the high iron content of fly ashes emitted from steel and iron plants burning coals. Using the year 2007 as an example, the modeling results exhibit large seasonal variations in iron deposition, with highest deposition fluxes occurred during spring and autumn, which are comparable to the seasonal fluctuation of chlorophyll *a* concentrations estimated by satellite images in the oceanic regions. Fly ash from coal burning accounted for 7.2% of the total iron deposited over the northwestern Pacific Ocean and 15% of that over the northern South China Sea. After considering the difference of iron solubility in the aerosols, anthropogenic aerosol associated with coal burning would be the major bioavailable iron source in the surface water of the oceanic regions.

## 1. Introduction

Iron (Fe) supply to the surface water of the ocean is an important factor in controlling marine biological pump, which may regulate global carbon cycling and climate change [Martin and Fitzwater, 1988; Martin, 1990; Martin et al., 1994; Jickells et al., 2005]. Atmospheric deposition is known to be the major pathway to transport Fe to the surface waters. It is believed that most of the iron deposited on the surface ocean originates from lithogenic dust of major upwind deserts [Moore et al., 1984; Duce, 1986; Jickells et al., 2005]. However, the solubility of the iron in mineral dust is relatively low so that most of the Fe in the deposited dust is not bioavailable to marine phytoplankton [Journet et al., 2008]. Some studies suggest that the iron in mineral dust may become increasingly soluble after mixing with acidic pollutants or after photochemical reactions during long-distance transporting process [Zhuang et al., 1992b; Fan et al., 2006]. However, laboratory experiments showed that the Fe solubility only slightly increases up to 4% at most among different mineral forms [Journet et al., 2008]. Some studies have suggested that the aerosols generated from coal combustion may be an important source of bioavailable iron in marine environment due to the high Fe content in the fly ash and the high Fe solubility in the ashes generated through high temperature combustion process [Zhuang et al., 1992a; Jickells et al., 2005; Sedwick et al., 2007; Sholkovitz et al., 2009, 2012; Chen et al., 2012]. It still remains unclear whether the high-solubility Fe observed in long-distance transported aerosols mainly originates from lithogenic dust or anthropogenic aerosols.

Coal is the most widely used form of fuel globally [*Luo et al.*, 2008]. In 2011, two thirds of the world's coal was consumed in East Asia, with China accounting for more than 60% of the world's coal consumption according to the statistics of the International Energy Agency (IEA) (http://www.iea.org/statistics). Marginal seas surrounding East Asia are located downwind of these emissions during winter monsoon, which also transport lithogenic dusts from the deserts in northern China and Mongolia to the oceans. In this paper, we investigate the potential impact of this combination of natural and anthropogenic aerosols on the biogeochemistry of the South China Sea (SCS), East China Sea (ECS), and the northwestern Pacific Ocean (NWPO).

Indeed, both satellite images and field studies have revealed the importance of anthropogenic aerosols in the surface water of the oceanic regions [*Lin et al.*, 2007; *Zhang et al.*, 2007]. Data obtained from the Moderate Resolution Imaging Spectroradiometer (MODIS) and the Quick Scatterometer indicate that most of the fine aerosols that reaching the ECS, SCS, and NWPO during the northeastern monsoon period are anthropogenic, witnessed by the strong correlation between the concentrated aerosols with the densely populated and



**Figure 1.** Domain of model simulation (light blue shading) and the area of the ocean that was analyzed (dotted rectangles). Red dots indicate the location of observation sites. D: Dongsha Island; S: South East Asia Time Series Station; P: Pengjia Islet; C: Cape Fuguei; W: Wanli; X: Xiaomen Islet; and M: Magong.

industrialized regions in eastern and southern China [*Lin et al.*, 2007]. Further field study in the SCS demonstrates that anthropogenic aerosols, rather than lithogenic aerosols, are the primary source of many biologically active trace metals in the ocean [*Ho et al.*, 2010]. In addition, although *Luo et al.* [2008] showed that mineral dust represents the main source of overall iron deposition in the ocean, they also indicated that aerosols from combustion sources could be more important than mineral dust in the oceanic regions adjacent to combustion sources, and the importance of anthropogenic aerosols may be more pronounced if the solubility factor is taken into account.

The quantitative estimate of anthropogenic iron emission is still lacking for the East Asia region, although some estimates have been derived from the variation in the iron mass fraction of particles from several combustion sources [*Luo et al.*, 2008; *lto*, 2013]. It should be noted that most studies applied emission factors for combustion iron derived from North America, which are not necessarily appropriate for the East Asia region. In addition, the iron content of fly ash produced in steel and iron refineries, which are the most important coal consumption and iron emission sector in China, have been significantly underestimated in the past due to inadequate knowledge in the composition of fly ash from steel plants. This study developed a novel approach to estimate the emission of iron produced through combustion and applied a regional model to quantitatively differentiate the relative contribution of atmospheric iron sources originated from lithogenic dust or coal-burning fly ash deposited in the northern SCS (NSCS) and NWPO. Their seasonal variation patterns will also be revealed.

## 2. Methodology

This study applied the regional air quality model, the Community Multi-scale Air Quality Modeling System (CMAQ), to estimate the contribution of atmospheric iron deposition from mineral dust and fly ash particles. This model has been shown to perform well in air quality simulations [e.g., *Binkowski and Roselle*, 2003; *Mebust et al.*, 2003; *Byun and Schere*, 2006]. We included detailed emission inventories of iron in mineral dust and fly ash particles into the CMAQ. We then calculated the dry and wet deposition rates of these particles, taking into account the particle size spectrum using an advanced modal aerosol parameterization scheme.

## 2.1. Numerical Models

CMAQ considers the chemistry, transport, and deposition processes associated with trace gases and aerosol particles. In the model, transport through atmospheric circulation is driven by meteorological fields simulated using the Fifth-Generation Penn State/National Center for Atmospheric Research Mesoscale Model (MM5) [*Grell et al.*, 1994], with the final analysis data provided by National Centers for Environmental Prediction (NCEP) as the initial and boundary conditions. The physical schemes used in the MM5 include a simple ice moisture scheme, Kain-Fritsch cumulus scheme, Medium Range Forecast planetary boundary layer scheme, and Noah land surface multilayer soil temperature model. The simulation covered continental East Asia and the NWPO and NSCS (Figure 1), with 85 and 67 grids of 81 km by 81 km resolution in the latitudinal and longitudinal directions, respectively. A total of 31 layers was applied in the vertical direction

using the sigma coordinate [*Arakawa and Suarez*, 1983], with 9 grids below the 0.8 sigma level (roughly the height of the planetary boundary layer) and 10 grids above the 0.2 sigma level (roughly the height of the tropopause). We employed the inventory of *Zhang et al.* [2009] for the emission rates of natural and anthropogenic gases. This inventory includes the emission rates of aerosol particles such as elementary carbon and organic carbon; however, it lacks emission data related directly to dust and fly ash, which are the main focus of this study. The methods used to estimate the emissions of dust and fly ash are discussed in section 2.2.

The ability to describe particle size distribution with a high degree of precision is crucial to the calculation of wet and dry deposition rates. We substituted the aerosol scheme in CMAQ with the accurate and computationally efficient Statistical-Numerical Aerosol Parameterization (SNAP) scheme developed by *Chen et al.* [2013]. The SNAP scheme uses several lognormal modes to represent particle size distribution and takes three moments of size distribution (i.e., number, surface area and mass concentrations) as prognostic variables for each mode. In this study, mineral dust and fly ash particles were assumed to exist in two modes—fine and coarse. They were assumed to mix externally (i.e., exist in the same air parcel but not the same particle) with other aerosol species.

In calculating the rates of dry deposition of aerosol particles, we took into account mechanisms associated with aerodynamic resistance, quasi-laminar resistance and gravitational sedimentation [Wesely, 1989]. Gravitational sedimentation has been parameterized as a function of the particle size spectrum and ambient conditions in SNAP. In CMAQ, the calculations used to determine the rates of wet deposition are performed in two steps for each of the two types of precipitation specified in the meteorological model: subgrid convective precipitation and grid point (nonconvective) precipitation. The cumulus parameterization scheme used to calculate subgrid precipitation indicates rain intensity only at the surface, with no information with regard to rain in the air or the size of raindrops. Thus, wet deposition rates can only be calculated to a rough approximation using an empirical formula [Pruppacher and Klett, 1978; Wang et al., 2000], which is directly proportional to precipitation rate and particle mass concentration. A lack of information on airborne precipitation particles prevent us from calculating in-cloud scavenging, so we only calculated below-cloud scavenging due to convective precipitation. However, the explicit microphysical scheme used to calculate grid point precipitation provides information on airborne precipitation particles. This made it possible to treat wet scavenging in greater detail using the SNAP scheme with consideration of wet scavenging due to Brownian diffusion, phoretic forces, and gravitational impaction. We also keep track of aerosols collected by raindrops such that in-cloud scavenging can be calculated.

## 2.2. Dispersion of Iron

Our model deals with two types of airborne iron: iron from mineral dust deflation and from the anthropogenic burning of coal. Estimating iron dispersion requires information related to the overall mass flux and particle chemical composition.

#### 2.2.1. Iron in Airborne Dust

To model the dispersion of iron in mineral dust, this study adopted the dust deflation module developed by *Wang et al.* [2000], which provided accurate results when incorporated into the Taiwan Air Quality Model (TAQM) by *Chen et al.* [2004] and into CMAQ by *Chen et al.* [2013]. Calculating the size distribution of dust particles in TAQM involves applying 12 size bins. However, *Chen et al.* [2013] demonstrated that the SNAP scheme, which applies two lognormal modes with three moments each, can provide essentially the same results as the binned approach, with significantly less computation time. Thus, we adopted the SNAP scheme in the CMAQ to describe the processes associated with airborne mineral dust.

In accordance with the approach of *Wang et al.* [2000], the intensity of dust deflation was described as a function of relative humidity (a surrogate for soil moisture), friction velocity, and the characteristics of the land. The types of land that provide dust most readily are deserts and semiarid areas, as well as nondesert areas such as cropland and grassland, in accordance with the MODIS classification [*Hall et al.*, 2002]. The size distribution of deflated dust varies with land type according to the specification outlined by *Wang et al.* [2000] (Table 1). It should be noted that *Luo et al.* [2008] included dust from desert and desertified areas; however, they disregarded dust emissions from nondesert areas. This study accounted for the effects of snow cover on the dispersion of dust by linearly reducing dust emission according to the MODIS snow cover fraction.

	Fine Mode		Coarse Mode		
Land Type	Modal Size	Spectral Width	Modal Size	Spectral Width	
Desert	0.07	1.80	1.19	2.31	
Loess Plateau	0.07	1.78	0.83	2.52	
Urban	0.07	1.80	1.00	1.80	
Others <sup>b</sup>	0.07	1.79	1.16	2.38	

**Table 1.** Modal Size (μm) and Spectral Width of Dust Size Distribution Used in the Model<sup>a</sup>

Spectral width is defined as the standard deviation of the lognormal distribution. <sup>b</sup>Others include forest, cropland, and grasslands, etc.

Iron content in mineral dust was estimated according to the mass fraction of iron in various source materials (Figure 2). The iron content in the dust originating in the deserts of Asia is relatively constant compared to other species shown in Figure 2, with a mass fraction ranging from 1.2 to 5.9%. This study applied a median value of 4.00%, in accordance with that used by Zhang et al. [2003]. The values for agricultural and other types of soil are in a similar range, with a mean value of 4.05%. Figure 2 also listed the aluminum (AI) content which we use to help identify the lithogenic iron sources as suggested by Ho et al. [2010].

## 2.2.2. Iron in Fly Ash

Most previous studies dealing with atmospheric iron deposition into the oceans have failed to consider the contribution of fly ash produced by coal burning. Luo et al. [2008] and Ito and Feng [2010] simulated iron emissions associated with coal burning using a global model that assumed fixed fractions of fine-mode and coarse-mode particulate matter (PM) in the emissions. Their PM emissions data were obtained from Bond



Figure 2. Mass fractions of Fe and Al in various types of dust and soil particles, coal, and combustion ashes. Red circles and black dots enclosed by red circle represent typical fly ash [Yuan et al., 1998; Liu et al., 2004; Koukouzas et al., 2006; Liu et al., 2007; Cao et al., 2008; Wang et al., 2008; Vassilev and Vassileva, 2009; Zhang et al., 2010; Tang et al., 2012; Zhang et al., 2012] and bottom ash [Liu et al., 2004; Wang et al., 2008], respectively; red dots represent fly ash from steel plant [Prati et al., 2000; Geagea et al., 2007; Tsai et al., 2007]; green dots with red circles represent fly ash from biomass burning [Gaudichet et al., 1995; Yamasoe et al., 2000]; black squares represents coal [Querol et al., 1997; Liu et al., 2001; Zhang et al., 2004; Dai et al., 2005b, 2005a; Dai et al., 2006a, 2006b; Yang, 2006; Song et al., 2007; Wang et al., 2008; Yang, 2008; Sun et al., 2010; Zhou et al., 2010; Li et al., 2012]; orange, blue, green and purple diamonds represent desert dust [Li et al., 1984; Ishizaka, 1991; Tian et al., 1993; Mori et al., 2003; Zhang et al., 2003], river dust [Li et al., 1984; Tan et al., 2006; Lin, 2010], agriculture and topsoil dust [Su et al., 2007; Li et al., 2009; Yanai et al., 2012], and urban dust [Dong et al., 1984], respectively. The blue-shaded area represents the range (i.e., 1.3 to 2.7) of Fe to Al ratios in particles collected in seawater from the SEATS 2007 observations [Ho et al., 2010]. Sources pertaining to the data points are listed in Table A2 and below.

et al. [1998] and Streets et al. [2001], while the proportion of fine-mode particles in the total PM was obtained from the U.S. Environmental Protection Agency [Streets et al., 2001]. However, North America data are not necessarily applicable to the East Asian region. Zhang et al. [2009] implemented a series of improved methodologies to gain a better understanding of pollutant emissions from China and other Asian countries. They provided important anthropogenic data for SO<sub>2</sub>, NO<sub>x</sub>, BC, CO, and PM but excluded emissions from biomass burning.

Luo et al. [2008] have estimated Fe emissions as a fraction of PM emissions. Because the fraction is not well known for East Asia, we use an alternative approach that estimates Fe emission from SO<sub>2</sub> emissions and the chemical analysis of coal and coal fly ash from Chinese data (Appendix A). We then use the reported  $SO_2$ emissions in China, which generally have uncertainties within 14% [Streets et al., 2003; Zhao et al., 2011], to establish the relationship between S and Fe emissions associated with coal burning and steel smelting (Figure 3). This approach assumes that **AGU** Global Biogeochemical Cycles



**Figure 3.** Mass fractions of S and Fe in various types of coal and combustion ashes. Red circles represent fly ash, dark dots with red circles represent bottom ash, and black squares represent coal. The black line is the geometric mean of S:Fe (0.62) for coal, and the red line is the geometric mean of fly ash (0.086); the line for the geometric mean of bottom ash (0.088) overlaps with the red line. Sources of the data points are listed in Tables A1–A3.

other anthropogenic sources of aerosol Fe are negligible.

In accordance with the mass balance principle, the sulfur contained in coal (S<sub>c</sub>) is converted to gaseous SO<sub>2</sub> (S<sub>g</sub>), sulfur in fly ash (S<sub>f</sub>), and sulfur in bottom ash (S<sub>b</sub>) via the process of burning. Similarly, iron in coal (Fe<sub>c</sub>) is converted to iron in fly ash (Fe<sub>f</sub>), and iron in bottom ash (Fe<sub>b</sub>). These mass balances can be written as follows:

$$S_c = S_f + S_b + S_g \tag{1}$$

$$Fe_c = Fe_f + Fe_b \tag{2}$$

The ratio of iron in fly ash to  $SO_2$  generated from coal burning, which we call the composition factor, can then be derived as follows:

$$\frac{\mathsf{Fe}_f}{\mathsf{S}_g} \equiv \alpha = \frac{1}{\frac{\mathsf{S}_c}{\mathsf{Fe}_c}(1+q) - \frac{\mathsf{S}_f}{\mathsf{Fe}_f} - \frac{\mathsf{S}_b}{\mathsf{Fe}_b}q} \quad (3)$$

where *q* is the ratio of bottom ash to fly ash, under the assumption that the iron fraction in fly ash and in bottom ash is the same.

Information on the *q* value is difficult to obtain, particularly with regard to the East Asian region. Only one report was available, which is for the power plants in Taiwan [*Yen*, 2011], with a *q* value of 0.25, which is the same as that reported in *Kim et al.* [2005] for North America. By adopting this *q* value and data shown in Figure 3 and Tables A1–A3, we estimated the composition factor  $\alpha$  to be about 1.5 (for details see Appendix A).

However, the above derivation fails to consider the recovery of sulfur or fly ash, which is widely applied in power plant operations and a number of industries to reduce air pollution. Equation (3) therefore must be modified by adding the following coefficient:

$$\beta = \frac{(1 - r_f)}{(1 - r_s)} \tag{4}$$

where  $r_f$  and  $r_s$  are the recovery ratios of fly ash and SO<sub>2</sub>, respectively. We call  $\beta$  the "recovery factor." The net emission flux of iron (in the form of fly ash) can then be written as follows:

$$F_{\rm Fe} = \alpha \cdot \beta \cdot F_{\rm S} \tag{5}$$

where  $F_{\rm S}$  is the emission flux of sulfur (in the form of SO<sub>2</sub>). The parameters  $\alpha$  and  $\beta$  have very little data to constrain them, since they depend on the deployment of desulphurization technologies in coal-burning power plants. Values used for  $\beta$  in the model are 0.033, 0.2, and 1.0 for power plants, industry, and residential sources, respectively (for details see Appendix A).

An important factor that was not considered in the estimates of Fe emissions by *Luo et al.* [2008] and *Ito and Feng* [2010] is the Fe enrichment during steel manufacturing. This issue is particularly important in East Asia, because iron and steel industries are among the most energy-intensive industries worldwide, and China produced 35% of the world's steel in 2007 and 47% in 2010 (IEA statistics). Particles emitted from iron and steel plants are known to be rich in iron. Iron mass fraction in steel plant fly ash is variously reported as 26.0% [*Tsai et al.*, 2007], 27.6% [*Geagea et al.*, 2007], or 35.0% [*Prati et al.*, 2000], giving a geometric mean of 29.3%. These values are substantially higher than the 4.0%, 2.0%, and 4.8% of mineral dust, coal, and coal-burning fly ash, respectively (the latter two values are averages of data provided in Tables A1 and A2). Due to a lack of other information, this study applied the 29.3% value mentioned above for calculating the Fe emission from steel plants. Evaluating the degree of the iron enrichment requires information

related to the amount of coal used in the steel industry, but this information is not available in the regional emission inventory that we used. So, this study estimated the proportion of coal used in the iron and steel industry according to the energy consumption data from IEA (for details see Appendix A). For this calculation we used data for China due to its dominance in the East Asia steel industry. We found that the iron and steel industry accounted for approximately 46% of the total coal consumption in the industry sector in 2007.

Additional details required for estimating anthropogenic iron deposition include the total mass of emissions and the size distribution of fly ash particles. The mass fraction of iron in fly ash was 4.82% (Table A2), from which the mass of fly ash emissions was calculated using equation (5). *Zhang et al.* [2005] provided size spectra of fly ash for Chinese power plants. Their data show that freshly emitted fly ash particles have a size range exceeding that of ambient aerosols; however, very large particles fall out quickly and thus are of little consequence to long-range transport. The upper size limit for fly ash particles that can effectively enter the atmosphere is ~20  $\mu$ m [*McElroy et al.*, 1982]. Applying this upper limit to the size distribution provided by *Zhang et al.* [2005] led us estimate that only 20% of the mass of fly ash calculated from SO<sub>2</sub> emissions should be counted as effective emissions.

It was also necessary to determine the size distribution of fly ash particles, which is generally not provided in emission inventories. In accordance with *Luo et al.* [2008] and *Ito and Feng* [2010], we assumed that the particle size distribution of fly ash has two modes—fine mode and coarse mode—and that each mode can be represented by a lognormal function [cf. *Chen et al.*, 2013]. We used the parameters for fly ash size distribution provided by *McElroy et al.* [1982] and set the modal diameter at 0.11  $\mu$ m and standard deviation of the size distribution at 1.4 for the fine mode. For the coarse mode, these parameters were set at 2.2  $\mu$ m and 1.8. We assigned 1.5% of the fly ash mass to the fine mode and the remainder to the coarse mode according to that outlined by *McElroy et al.* [1982]. It should be note that the removal efficiency of fly ash for the facilities reported by *McElroy et al.* [1982] is 99.7%, similar to the present-day efficiency. This may be an indication of the maturity of the removal technology and justify our use of somewhat dated data. The bimodal size distribution constructed using the above parameters is relatively consistent with those reported by *Yi et al.* [2006] for fly ash emissions from power plants in China.

## 2.3. Measurement Data

Observational verification of the simulation results is somewhat limited, particularly in terms of particle composition. This study obtained aerosol measurements at two stations (locations shown in Figure 1), which were suitable for model verification. The Magong station (23°34′09″N, 119°33′58″E) is on the Pescadores Islands, in the Taiwan Strait. These islands are relatively remote (approximately 45 km and 130 km from Taiwan and Mainland China, respectively), sparsely populated (population just under 100,000), and without major pollution sources. The Magong station can therefore be regarded as a regional background station. The Wanli station (25°10′46.8″N, 121°41′23.57″E) is located in a small town (population ~ 22,000) on the northern coast of Taiwan, where a northerly wind prevails for most of the year except during summer. The Wanli station is therefore also representative of regional background situations during the winter monsoon.

Both stations are equipped with standard air pollution instruments operated by the Environmental Protection Administration of Taiwan (TEPA). This study used data on the mass concentration of PM smaller than 10  $\mu$ m (PM<sub>10</sub>), as measured using tapered element oscillating microbalance samplers. Near the two TEPA stations are also located two Taiwan Aerosol Observation Network (TAON) aerosol measurement sites, operated by the Research Center for Environmental Changes, Academia Sinica [cf. *Chou et al.*, 2010]. The Cape Fuguei site (25°17′53.8″N, 121°32′11.4″E.) is at the northern tip of Taiwan, about 20 km northwest of Wanli, and the Xiaomen Islet site (23°39′7.4″N, 119°31′7.1″E) is about 10 km northwest of the Magong site. These sites measure PM<sub>10</sub> and PM<sub>2.5</sub> mass concentrations and chemical composition by collecting samples on filters. Analysis of chemical composition includes soluble ions and metal elements, as well as organic and elemental carbon. Fractions of the measured PM<sub>10</sub> composition contributed specifically by mineral dust and fly ash were unavailable. Mineral dust and fly ash are generally considered insoluble in water; therefore, we can calculate their mass concentration by subtracting the soluble species (such as sulfate, nitrate, sea salt, and soluble organic carbon) and other main insoluble species (elementary carbon and insoluble organic carbon) from the PM<sub>10</sub> values. Volcanic ash is another common insoluble aerosol; however, it is probably rare in this area in 2007.



**Figure 4.** Simulated mean emission flux (in mg  $m^{-2} d^{-1}$ ) of (top) mineral dust and (bottom) fly ash over East Asia in 2007. Note the difference in color scales.

## **3. Simulation Results**

We estimated the annual atmospheric input of iron into the ocean based on conditions in 2007. This year was selected partly due to the availability of emissions data and concurrent observational data, and partly because no strong climate anomalies occurred in the region during that year, and it could therefore be considered representative of recent climate conditions. One noticeable climate anomaly that did occur in 2007 was a weak-to-moderate La Niña in the latter part of the year. Note that the strength of the El Niño or La Niña events are defined as sea surface temperature anomalies (positive or negative) for the region 5°N-5°S, 120°W-170°W, reaching the following thresholds for five consecutive months: weak: 0.5 to 0.9, moderate: 1.0 to 1.4, and strong  $\geq$  1.5 (see http://www.esrl.noaa. gov/psd/enso/mei/). This was also the first year in which China's demand for coal exceeded its domestic supply, according to statistics presented by the World Coal Association for 2009 (http://www.worldcoal.org/resources/ coal-statistics/). In the same year,

China's SO<sub>2</sub> emissions peaked with declines in the following years occurring mainly in the energy sector, rather than the industry sector [*Klimont et al.,* 2013].

## 3.1. Meteorological Aspects

The transport of aerosols from the East Asia continent to the marginal seas is largely controlled by the Asian monsoon system which exhibits significant seasonal variations. Northerly winds, which generally originate in populated lands, dominate the marginal sea regions in autumn and winter; while southerly winds, which originate mostly from the oceans and thus tend to be cleaner, prevail in summer. The precipitation fields show a SSE to NNW (i.e., open sea to inland) gradient in all seasons, with maximums and minimums occurring in summer and winter, respectively. Winds and precipitation in the simulations were compared with the NCEP Reanalysis II data (representing observations). From a statistical analysis on the 5 day average data over the entire domain, the space and time correlation coefficient reached 0.89 for winds and 0.78 for precipitation. These high correlations indicate good model performance. Model bias was shown to be relatively small in the case of winds but more significant with regard to precipitation. Precipitation bias was the highest in spring (+24%) and lowest in winter (-2%), and the annual mean was overestimated by 11%. More details of the meteorological aspects are provided in Appendix C.

## 3.2. Simulated Aerosol Emission and Concentration

Emissions and transport of mineral dust and fly ash were simulated using the CMAQ model, according to meteorological conditions generated from MM5 (Figure 4). As discussed earlier, we used iron mass fractions of 4.00% and 4.82% to convert dust and ash emissions to iron emissions. Most (89%) of the dust iron in East Asia originates in the desert areas of northern China and Mongolia, with the remainder (11%) from nondesert areas including agricultural lands. Total iron emissions in this region are 26.0 Tg yr<sup>-1</sup> from mineral dust and 7.2 Tg yr<sup>-1</sup> from fly ash. Industrial coal-burning accounts for 64% of total fly ash iron emissions, while residential use and



**Figure 5.** Simulated seasonal mean concentration (in  $\mu$ g m<sup>-3</sup>) of near-surface mineral dust in 2007.

power plants contribute 27% and 9%, respectively. The large fraction originating from residential sources appears anomalous, as only a minor fraction of total coal consumption is for residential use (less than 14%, according to IEA 2007 statistics). This anomaly reflects the fact that recovery devices are seldom used in the residential coal burning.

The emission and transport of mineral dust are controlled primarily by meteorological factors. The East Asian monsoon system, in particular, determines the emission strength and low-altitude transport, whereas the high-altitude westerlies facilitate long-range transport in the free troposphere. Our goal was to evaluate the deposition of atmospheric nutrient into the oceans, so we focused on the NWPO and NSCS and excluded iron deposition on land. Figure 5 presents simulations of seasonal variations in the near-surface mass concentration of mineral dust (all sizes) in spring (March-May), summer (June-August), autumn (September–November), and winter (December–February). Due to their short lifetimes, aerosols tend not to move very far from their geographically fixed sources. As a result, the general patterns in the four seasons seem to be similar at a first glance. More obvious seasonal differences tend to be observed when focusing on more distant areas, such as over open oceans. Over the desert regions, airborne dust concentrations are generally greater in spring than in winter, due partly to stronger synoptic activity and partly to the reduced snow cover. Over the NWPO, particularly the ECS, the highest dust concentrations occurred during spring. Over the NSCS, the highest dust concentrations occurred during winter. This reflects the characteristics of the continental cold-air outflow, which results in stronger southward transport in winter and stronger eastward transport in spring. Dust concentrations tend to be the lowest during summer over the land as well as the ocean, because seaward transport of land pollutants tends to be limited under the southerly summer monsoon winds. Average dust concentrations over the NWPO during the winter and the spring are approximately 30 times higher than those during the summer, whereas over the NSCS, winter concentrations exceed summer concentrations by more than 2 orders of magnitude.

Unlike mineral dust, fly ash emissions tend not to be very sensitive to seasonal variations in the weather. As a result, seasonal variations in the concentration of fly ash tend to be less pronounced, despite similarities in atmospheric transport and removal conditions (Figure 6). Summertime concentrations over the NSCS and the NWPO are good examples of this. Over the NWPO, fly ash concentrations are highest in the spring and smallest in the summer, with seasonal contrast within a factor of 3. Over the NSCS, fly ash seasonal concentrations are highest in the fall and winter, which are approximately 10 times higher than those in the summer.



Figure 6. Simulated seasonal mean concentration (in  $\mu$ g m<sup>-3</sup>) of near-surface fly ash in 2007.

We evaluated the simulation results by comparing them with observational data. Figure 7 shows the monthly mean  $PM_{10}$  concentrations at the Magong and Wanli stations. In simulations, aerosols were divided into mineral dust, fly ash, and others (including sulfates, nitrates, and sea salt). The fraction of mineral dust and fly ash in the atmosphere was also estimated based on composition analysis obtained through direct observation. Monthly variations in simulated  $PM_{10}$  resembled the seasonal trend observed at the testing stations, with maximum values occurred in the winter and minimum in the summer. A secondary peak occurred in spring, which was probably due to the occurrence of dust storms in East Asia. Our simulations indicate that mineral dust contributes a large fraction of  $PM_{10}$  in East Asia during the winter and spring, while the contribution of fly ash was relatively small. However, the simulated summertime concentrations of fly ash at Magong were comparable to those of mineral dust.

The absolute values of simulated  $PM_{10}$  at Magong were in good agreement with the observational data. The largest difference between simulation and observations results (less than 45%) was obtained for August and September. In contrast, the simulations at Wanli showed significant underestimation during the autumn, with a deficit of up to 67%. These large discrepancies are likely due to inaccuracies in data related to local emissions, specifically surf zone sea salt and secondary organic aerosols, which are significantly lower than those reported by *Chou et al.* [2008, 2010]. Simulated mineral dust concentrations are in strong agreement with observed dust concentrations, particularly at the Cape Fuguei station. Values at the Xiaomen station were generally on par, except during summer and early autumn when the model tend to underestimate the amount of dust. One likely cause of this underestimation is the fact that local dust emissions from the Pescadores Islands or main island of Taiwan were not accounted for in the simulation due to the coarse resolution of the model. Comparison of simulated daily mean  $PM_{10}$  with measurements in 2007 had overall high correlations (0.89 for Xiaomen Islet, 0.70 for Magong; 0.61 for Wanli, and 0.72 for Cape Fuguei; see Appendix B), indicating that the model is overall simulating aerosol deposition in the region well.

## 3.3. Deposition of Iron Into the Oceans

The seasonal deposition patterns of dust iron were similar to their mass loading in the air, but with significantly greater spatial inhomogeneity (Figure 8). This is likely due to nonuniform precipitation (see Figure C1 in Appendix C) resulting in wet deposition patterns. Over the NWPO, the most pronounced dust iron



**Figure 7.** Monthly mean mass concentration of particulate matters observed and simulated at the (left) Magong and (right) Wanli stations in 2007. Black lines (TEPA): TEPA measurement of PM<sub>10</sub>; black dashed lines (total): total simulated PM<sub>10</sub>; orange solid lines (TAON): mineral dust PM<sub>10</sub> estimated from TAON measurements; orange dashed lines (Dust): simulated PM<sub>10</sub>; mineral dust PM<sub>10</sub>; red dashed lines (FA): simulated fly ash PM<sub>10</sub>; blue dashed lines; and (other): all other simulated PM<sub>10</sub>.



Figure 8. Simulated seasonal mean dust iron deposition (in  $\mu g m^{-2} d^{-1}$ ) for the year 2007.

	Spring	Summer	Autumn	Winter	Annual
		NWPC	)		
Dust Iron	146 (77)	24 (96)	59 (80)	129 (71)	89 (77)
Fly Ash Iron	7 (15)	4 (62)	6 (24)	11 (7)	7 (21)
		NSCS	;		
Dust Iron	90 (95)	26 (92)	191 (93)	144 (73)	112 (87)
Fly Ash Iron	14 (64)	10 (78)	31 (56)	25 (24)	20 (50)

**Table 2.** Simulated Seasonal Variations in Iron Deposition (in  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>) in the NWPO and NSCS for the Year 2007<sup>a</sup>

<sup>a</sup>Values in the parentheses are the fraction (in percent) of total deposition attributable to wet deposition.

deposition occurred in the spring, reaching 146  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>; during the summer the deposition was 24  $\mu$ g m<sup>-2</sup> d<sup>-1</sup> (Table 2). In contrast, the most pronounced dust iron deposition over the NSCS occurred in the autumn. This seasonality differs from those of surface concentrations of mineral dust (Figure 5), the greatest concentration of which occurred in the winter. The relatively low deposition of dust iron over the NSCS in the winter could be attributed to low seasonal precipitation and thus weak wet deposition. Wet deposition is the primary mechanism involved in the deposition of dust over the NWPO and NSCS, accounting for 77% and 87% of the annual deposition, respectively (Table 2). Clearly, seasonal and spatial variations in precipitation add heavily to the complexity of dust iron deposition.

In contrast, the deposition of fly ash iron over the NWPO was highest in the winter (Figure 9), with a seasonal mean flux of  $10.5 \,\mu g \,m^{-2} \,d^{-1}$ , which was more than double the summer minimum flux (Table 2). The average annual flux of  $6.9 \,\mu g \,m^{-2} \,d^{-1}$  accounted for only 8% of the dust iron deposition. The proportion of iron contributed by the wet deposition of fly ash was significantly smaller than that contributed by the wet deposition of mineral dust (Table 2). This is because dust storms are generally associated with strong weather



**Figure 9.** Simulated seasonal mean fly ash iron deposition (in  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>) for the year 2007.

# **Global Biogeochemical Cycles**

Chlorophyll a

Soluble iron (4%)

Chlorophyll a

Soluble iron (40%)

Total iron



Figure 10. (a) Fraction (in %) of fly ash iron deposition in total iron deposition; (b) fraction (in %) of fly ash soluble iron deposition in total soluble iron deposition; (c) fraction (in %) of combustion iron deposition associated with steel plant emissions. All fractions were calculated for the year 2007.

activities, which carries mineral dust high into the troposphere. The deposition of such elevated dust relies heavily on precipitation scavenging. However, as reflected in the vertical profiles of our model results (not shown), fly ash particles are more likely to remain in the planetary boundary layer, making them more susceptible to dry deposition. This was particularly true during winter over the NWPO, in which more than 90% of the fly ash was removed via dry deposition. Only during summer did wet deposition exceed dry deposition in that area. Over the NSCS, autumn saw the highest fly ash iron deposition, as did for dust iron deposition. Over the NSCS, wet deposition dominated the total deposition at all times except winter. The mean annual deposition of fly ash iron over the NSCS was double that over the NWPO, partly due to the stronger regional precipitation resulting in wet deposition.

It is important to evaluate the degree of human influence on the deposition of atmospheric iron into the ocean. Figure 10a shows the fraction of combustion iron in the total amount of deposited iron. With the exception of some areas near the land, the fraction of combustion iron was generally below 20%, which tended to decrease with an increase in the distance from the Asian continent. The annual mean fraction of combustion iron was 7% and 15% over the NWPO and NSCS, respectively. The highest fraction of combustion iron was in the summer, reaching 15% over the NWPO and 28% over the NSCS (Table 3). These ratios are similar to those presented by *Luo et al.* [2008], whose global simulations estimated fractions of 5–20% over the NWPO and 10–40% over the NSCS.

These figures do not imply that the influence of humans on the amount of iron being deposited in the ocean is inconsequential. The solubility of coal iron may be enhanced during combustion or subsequent processing [cf. *Baker and Croot*, 2010]. *Luo et al.* [2008] suggested that the solubility of iron from combustion

in the NWPO and NSCS	in 2007 <sup>a</sup>				
	Spring	Summer	Autumn	Winter	Annual
		NWPO			
Total iron	153 (5)	28 (15)	65 (9)	<b>140</b> (8)	96 (7)
Soluble iron (4%)	<b>1.0</b> (31)	0.3 (60)	0.5 (47)	1.0 (42)	0.7 (41)
Soluble iron (40%)	<b>3.6</b> (82)	1.8 (94)	2.6 (90)	4.8 (88)	3.2 (87)

NSCS

49 (64)

221 (14)

2.1 (59)

13.1 (93)

241 (150)

47 (51)

36 (28)

0.5 (78)

4.1 (97)

121 (123)

**Table 3.** Simulated Seasonal Variations in Iron Deposition (in  $\mu$ g m<sup>-2</sup> d<sup>-1</sup>) and Chlorophyll *a* Concentration (in  $\mu$ g m<sup>-3</sup>) in the NWPO and NSCS in 2007<sup>a</sup>

<sup>a</sup>Total iron is the sum of dust iron and fly ash iron; "Soluble iron (4%)" and "Soluble iron (40%)" indicate fly ash iron with 4% and 40% solubility, respectively; dust iron solubility is fixed at 0.45%., Values in the parentheses are the percentage of fly ash iron in total iron or climatological (2001–2010) mean Chl *a* concentrations. The highest seasonal values are set in italics, and the second highest values are in bold font.

87 (78)

103 (13)

1.0 (58)

5.9 (93)

110 (110)

67 (71)

132 (15)

1.3 (61)

8.4 (94)

170 (135)

85 (91)

168 (15)

1.6 (60)

10.5 (94)

205 (156)

sources is approximately 4%, which is far higher than that of dust iron (0.45%). If this value was accepted, then the annual mean fraction of bioavailable iron associated with human activity would be much higher as shown in Figure 10b, with 41% over the NWPO and 61% over the NSCS (Table 3).

## 4. Discussion

This study demonstrated that large quantities of iron are being deposited in the NWPO and NSCS in the forms of fly ash and mineral dust. Industrial coal burning was the largest contributor of fly ash iron, accounting for 64% of the total emissions. Within the industrial sector, steel/iron plants represent the largest source of fly ash iron emissions, contributing more than 50% and 60% of the fly ash iron that ends up in the NWPO and NSCS, respectively. Dust iron still remains the largest contributing source of total iron deposition over the NSCS and NWPO, accounting for 85% and 92% of the total deposition, respectively.

Nonetheless, taking into account the fact that Fe in combustion aerosols is much more soluble than Fe in lithogenic dust, the relative contribution of the bioavailable iron should be further evaluated among the two different types of aerosols. It has been reported that the Fe solubility in lithogenic dusts are generally less than 1% or only a few percent after low pH solution leaching process [Zhuang et al., 1992b; Fu et al., 2012]. Using 4% as Fe solubility in anthropogenic aerosols, Luo et al. [2008] indicated that human activity would be the largest single contributor of bioavailable iron in the NSCS. It should be noted that 4% for Fe solubility in anthropogenic aerosols is indeed a conservative estimate for Fe solubility in combustion aerosols [Sholkovitz et al., 2012]. Although a couple of studies by measuring fly ash directly collected from power plants observed low Fe solubility [Crecelius, 1980; Oakes et al., 2012], it is generally believed that Fe solubility in anthropogenic remote aerosols over the ocean are extremely high. Zhuang et al. [1992a] claimed that most of the aerosols collected over the central North Pacific were anthropogenic and more than 60% of the total iron is soluble. Studies show that the solubility of iron in fly ash created through the burning of oil can actually exceed 70% [e.g., Schroth et al., 2009; Fu et al., 2012]. The Fe solubility in either anthropogenic aerosols or mineral dust would become increasingly soluble after long-distance atmospheric transport, most likely due to the acid-base and/or photochemical reactions after contacting acidic pollutants, clouds, or rainwater [Zhuang et al., 1992b; Meskhidze et al., 2003; Shi et al., 2009]. In addition, the Fe solubility in remote aerosols often exhibits an inverse relationship with the concentrations of mineral aerosol [Baker and Croot, 2010]. It is unclear whether this is due to limitations in the overall solubility of dust iron or because the solubility elevation during transport is more pronounced for anthropogenic aerosols than mineral dust. In Table 3, we reevaluated the relative contribution of bioavailable iron from anthropogenic sources based on an iron solubility of 40%, which remains a modest assumption considering the values widely suggested for combustion-derived aerosols over remote areas. The soluble or bioavailable iron from anthropogenic sources would account for 87% and 94% in the NWPO and NSCS, respectively.

Fe is known to be a limiting factor for phytoplankton growth in most of the high-nutrient low-chlorophyll waters globally [Martin and Fitzwater, 1988; Martin et al., 1994]. In contrast, bioavailable Fe deposition is relatively high in the NSCS and the NWPO. We simply compare the simulated Fe fluxes with chlorophyll a concentrations (Chl a) among different seasons of 2007 (Table 3). We found that the seasonal fluctuation of Chl a in both NSCS and NWPO are comparable to that in iron deposition. In the NSCS, both the elevated Fe flux and Chl a occured in autumn and winter. Over the NWPO, the elevated Chl a and Fe flux were observed in winter and spring. The correlation suggests that atmospheric forcing is an important factor causing the elevated phytoplankton biomass. However, it should be noted that the relative high Fe supply is not necessary to be the controlling factor for phytoplankton growth in the NSCS. Indeed, field studies has shown that the elevated primary production in the NSCS during winter time is most likely due to the mixing process, drawing major and minor nutrients from the subsurface waters to the euphotic zone of the well-stratified tropical water tropical water during the strong monsoon season [Tseng et al., 2005]. The trace metal studies in suspended and sinking particles in the NSCS also observed elevated extracellular Fe adsorption on phytoplankton and extremely high aeolian Fe supply in the region [Ho et al., 2007, 2010]. The elevated input of Fe and other trace metals through the aeolian deposition, existing either in dissolved or particulate forms, may be transported to the North Pacific gyre with the strong western boundary current and may have further biogeochemical effects in other oceanic region. The biogeochemical effects of both major nutrients and essential trace metals originating from anthropogenic aerosols deserve future exploration in the oceanic regions.



**Figure 11.** Simulated percentage of iron deposition from fly ash in total deposition over the (top) NWPO and (bottom) NSCS with fly ash composition factor  $\alpha$  (columns) and recovery factor  $\beta$  (symbols) of different values. Columns from left to right (dark to light shading) are values calculated using  $\alpha = 6.06$  (upper 1 geometric standard deviation), 1.5 (mean), and 0.04 (lower 1 geometric standard deviation), respectively, and with  $\beta$  for the year 2007 Symbols represent values calculated using various  $\beta$  values at  $\alpha = 1.5$ : Filled triangles for  $\beta_{2001}$ , cross for  $\beta_{2007}$ , and inverted filled triangle for  $\beta_{2009}$ .

The uncertainty of the modeling Fe deposition is due to complexities involved in assessing the chemical composition and emissions of fly ash, as illustrated by the large scattering of data in Figures 2 and 3 and Tables A1–A3. The rate of deposition of fly ash iron in this study exceeds that of Luo et al. [2008], who reported a flux of 9–90  $\mu$ g m<sup>-2</sup> d<sup>-1</sup> in dust iron over the NWPO and NSCS, a flux of 0.9–9  $\mu$ g m<sup>-2</sup> d<sup>-1</sup> in combustion iron over the NWPO, and a flux of 9–18  $\mu$ g m<sup>-2</sup> d<sup>-1</sup> in combustion iron over the NSCS. These discrepancies may be due to differences in meteorological conditions, considering that their simulation was based on conditions in 2001. It may also be due to differences in dust emission schemes. Furthermore, we considered iron enrichment associated with steel plants, which accounted for more than half of the combustion iron deposited in the oceans (Figure 10c). If this factor had not been considered in our model, the deposition rate in this study would be significantly lower than that in the study by Luo et al. [2008]. Despite numerous differences with regard to the model details, most of the discrepancies are actually attributable to differences in the estimation of fly ash iron emissions. As discussed in section 2, this study applied the composition factor  $\alpha$  and

recovery factor  $\beta$  in order to link fly ash emissions to SO<sub>2</sub> emissions; however, these two factors retain a high degree of uncertainty. Here we evaluate the uncertainties in  $\alpha$  (original value 1.5) by varying it by one geometric standard deviation (e.g., 0.40 and 6.06) for the values given in Tables A1–A3. With respect to recovery factor  $\beta$ , the coefficients used for evaluation contain a high degree of uncertainty as the factor itself presents significant year-to-year variation associated with efforts to reduce pollution in China, particularly during the last two decades. To understand the possible range of variation, we estimated  $\beta$  values for the years 2001 and 2009, using coefficients estimated from data provided by *Zhang et al.* [2009] and *Guan et al.* [2011]. The original values of  $\beta$  for 2006 were 0.03 and 0.20 for power plants and industrial sources, respectively. The values are 0.93 and 0.95 for 2001 and 0.07 and 0.13 for 2009. For residential sources,  $\beta$  was fixed at 1.0, i.e., under the assumption of no recovery effort. The annual mean fraction of iron deposit by fly ash ranged from 2% at low  $\alpha$  to 28% at high  $\beta$  over the NWPO, and 4.5–46% over the NSCS (Figure 11). The sheer range of these variations is a clear indication that the uncertainty is associated with not only the coal and fly ash composition but also the yearly variations in recovery of fly ash and SO<sub>2</sub>. Mineral dust emissions also present strong interannual variability. As a result, the results derived for 2007 can only be viewed as a rough estimation of the general situation.

Some elemental compositions can vary considerably between mineral dust and fly ash. As shown in Figure 2, since the Fe:Al ratios of desert dust reside in a relatively narrow range, Fe to Al ratios may be a useful



**Figure 12.** Simulation results for Fe:Al ratio in 2007 compared with those observed at the following locations and times: the Pengjia Islet (green) in 2005 (unpublished data) and 2010 (unpublished data); East China Sea (red) in 2007 [*Hsu et al.*, 2010] and 2008 (unpublished data); Dongsha Islet (blue) in 2007 [*Ho et al.*, 2010] and 2010 (unpublished data). Also, included are the seawater samples from the SEATS station (purple) collected in 2007 [*Ho et al.*, 2010]. The square, circle, triangle, and diamond symbols represent seasonal averages in spring, summer, autumn, and winter, respectively. These seasonal averages were calculated by taking the mass-weighted geometric mean of daily data. The cross bars indicate the range of seasonal variation in both simulation and observation data at one geometric standard deviation, and line with different styles indicate observations obtained during different years. Model results were interpolated to the location of the observation sites, with the exception of shipboard measurements obtained in the East China Sea for which the corresponding model results are area averages.

parameter to provide clues to the aerosol sources and help the evaluation of model results. For example, the values out of the range in mineral dust, particularly for those larger than 1, may be regarded as none-lithogenic. The data presented in Figure 2 indicate that the Fe:Al ratio of mineral dust is generally below 1. The Fe:Al ratio in fly ash varies considerably, but generally remains below 1. However, the observed Fe:Al ratios were often greater, and sometimes substantially exceeded 1. In Figure 12 we showed the simulated Fe:Al ratios and a comparison with measurement data collected from islands and ships on NWPO and NSCS (see locations shown in Figure 1). Our model performed relatively well, particularly when compared with the shipboard measurements over the ECS. The range of Fe:Al ratio in the simulations (0.74 ~ 1.1) is quite close to the observed values of 0.65 ~ 1.1. Note that, without taking into account the high iron content in fly ash from steel plants, the simulated Fe:Al ratios would remain between 0.56 (for mineral dust) and 0.63 (for typical fly ash), indicating the importance of fly ash from steel plants. Over the Pengjia Islet, a small islet in southern ECS, the model also performed well in all cases except comparing to the 2010 summer and winter measurements. In the NSCS, the Fe:Al ratios in aerosols collected at the Dongsha atoll (in the central region of the NSCS), were 1.3 and 0.92 during summer and autumn, respectively [Ho et al., 2010]. These values are greater than the model estimations of 0.76 and 0.68, respectively. These slight discrepancies indicate that our model possibly lacked a number of other iron-rich aerosol sources which may be important in the NSCS. For example, the river dust and urban dust data shown in Figure 2 reveal relatively high Fe:Al ratios. Further field studies in the oceanic regions are needed to resolve the discrepancy.

## 5. Conclusion

Due to the rapid economic development in East Asia, anthropogenic aerosols have become an important Fe source in the surrounding oceans. This study applied a regional meteorological and air quality model to simulate the deposition of atmospheric iron in the ECS, SCS, and the NWPO. The quantity of fly ash iron emission was estimated by linking them to  $SO_2$  emissions, using a composition factor based on the iron and sulfur content of coal and typical fly ash, as well as a recovery factor that takes into account the removal of fly ash and sulfur before waste gases are emitted into the atmosphere. Special consideration was given to iron emissions from steel and iron plants, in which iron content is substantially higher than in the fly ash typically encountered in coal burning.

Simulations revealed large amounts of iron being deposition in the NWPO and NSCS from both mineral dust and fly ash. The industrial coal burning was the largest source of iron associated with fly ash, among

Sample Source	S (%)	Fe (%)	S/Fe	Reference
Fuxin, Liaoning	0.356	1.51	0.236	Querol et al. [1997]
Dafang, Guizhou				
Mine No. 3	1.86	0.987	0.25	<i>Dai et al.</i> [2005b]
Mine No. 11	0.46	23.32	0.020	<i>Dai et al.</i> [2005b]
Western Guizhou	1.96	1.83	1.07	<i>Dai et al.</i> [2005a]
Puan, Guizhou	2.51	2.01	1.25	Yang [2006]
Luquan, Yunnan	5.7	5.23	1.09	Dai et al. [2006a]
Huainan, Anhui	0.5	2.17	0.230	Sun et al. [2010]
Junggar, Xinjiang				
Mine No. 6	0.73	0.651	1.12	<i>Dai et al.</i> [2006b]
Wuchaiwan	0.4	0.2	2.00	Zhou et al. [2010]
Xiheishan	0.2	0.8	0.25	Zhou et al. [2010]
Shajiuhe	0.9	1.5	0.600	<i>Li et al</i> . [2012]
Luchaogou	0.3	0.6	0.500	<i>Li et al</i> . [2012]
Zhangnandon	0.1	0.3	0.333	<i>Li et al.</i> [2012]
Dajjing	0.05	0.2	0.250	<i>Li et al</i> . [2012]
Jijihuxi	0.2	0.6	0.333	<i>Li et al.</i> [2012]
Xiaoxigou	0.2	1.1	0.182	<i>Li et al.</i> [2012]
Pingshou, Shanxi				
Mine No. 4	0.455	0.315	1.44	<i>Liu et al</i> . [2001]
Mine No.5	5.75	0.32	17.97	<i>Liu et al</i> . [2001]
Mine No. 9	1.25	2.57	0.486	<i>Liu et al</i> . [2001]
Mine No. 11	2.29	1.03	2.22	<i>Liu et al.</i> [2001]
Junggar, Inner Mogolia	0.59	0.472	1.38	Yang [2008]
Datong, Shanxi	0.663	3.93	0.169	Song et al. [2007]
Pingshou, Shanxi	2.02	0.817	2.47	Song et al. [2007]
Shendong, Shaanxi	0.238	0.768	0.310	Song et al. [2007]
Shizuishan, Ningxia	3.13	1.43	2.19	Song et al. [2007]
Baijigou, Ningxia	0.14	0.47	0.298	Song et al. [2007]
Rujigou, Ningxia	0.08	0.95	0.084	Song et al. [2007]
Shitanjing, Inner Mogolia (PP)	2.83	2.89	0.979	Song et al. [2007]
Shentou, Shanxi (PP)	1.32	0.67	1.97	Song et al. [2007]
Shangwan, Inner Mogolia (PP)	1.48	0.23	6.43	Song et al. [2007]
Daliuta, Shaanxi (PP)	0.37	0.53	0.698	Song et al. [2007]
Haibowan, Inner Mogolia (PP)	1.52	4.0	0.380	Song et al. [2007]
Shizishan, Ningxia (PP)	1.5	1.4	1.07	Song et al. [2007]
PinshouAntaibao, Shanxi (CPP)	1.57	1.0	1.57	Song et al. [2007]
Dawukou, Ningxia (CPP) <sup>I</sup>	1.91	1.4	1.36	Song et al. [2007]
Wuda, Inner Mogolia (CPP)	1.08	1.3	0.832	Song et al. [2007]
Taixi, Ningxia (CPP)	0.07	1.48	0.047	Song et al. [2007]
Shizuishan, Ningxia (PP)	1.5	3.57	0.420	Wang et al. [2008]
Geometric mean			0.618	

Table A1. Sulfur and Iron Mass Fraction in Various Types of Coal Used in China<sup>a</sup>

<sup>a</sup>PP: coal used in Power Plant, CPP: coal in Coal Preparation Plant.

which steel/iron plants were the largest contributors, accounting for more than 50% and 60% of the fly ash iron deposited in the NWPO and NSCS, respectively. Iron from mineral dust remains the main source of iron over the NSCS and NWPO, contributing 85% and 92% of the total iron input, respectively. However, when taking into account the high solubility of combustion-related iron, the proportion of bioavailable iron from anthropogenic sources may well exceed that from natural sources. Over 77% and 87% of the dust iron entered NWPO and NSCS, respectively, via wet deposition. However, dry deposition played a more important role in fly ash iron, accounting for 50% of the deposition in the NWPO and 79% in the NSCS.

Our model results indicate that seasonal variations in iron deposition over the NSCS and NWPO were mainly due to the changes in atmospheric circulation system (such as monsoon), and cloud and precipitation systems. Large seasonal variations were observed for Fe deposition fluxes and the relative contributions of fly ash and mineral dust. Over the NWPO, the highest deposition rate of dust iron occurred in the spring, whereas the highest deposition rate of fly ash iron was in the winter. Over the NSCS, the strongest deposition of dust iron as well as fly ash iron occurred in the autumn. The lowest rate of iron deposition occurred in the

Data Source	S (%)	Fe (%)	AI (%)	S/Fe	Fe/Al	References
China PP	0.228	4.82	14.77	0.0473	0.326	Yuan et al. [1998]
Hebei	1.14	11.52	9.98	0.0990	1.154	<i>Liu et al.</i> [2004]
Guangdong	0.936	8.03	10.62	0.117	0.756	<i>Liu et al.</i> [2004]
Shanghai	0.86	9.28	13.84	0.0927	12.33	<i>Liu et al.</i> [2004]
Hebei	0.004	0.37	0.030	0.0108	0.189	Koukouzas et al. [2006]
Henan	0.992	3.28	17.38	0.302	0.105	<i>Liu et al.</i> [2007]
Northern China	0.28	2.45	23.32	0.114	0.558	<i>Cao et al.</i> [2008]
Shizuishan, Ningxia	0.52	10.08	18.06	0.0516	6.440	Wang et al. [2008]
Datong, Shanxi	0.788	6.73	1.045	0.117	0.782	Vassilev and Vassileva [2009]
Zhuzhou, Hunan	2.38	10.48	13.40	0.227	0.233	<i>Zhang et al.</i> [2010]
Luohe, Anhui	0.245	3.84	16.45	0.0448	0.233	<i>Tang et al.</i> [2012]
Phnwei, Anhui	0.2	4.4	16.15	0.0455	0.272	<i>Tang et al.</i> [2012]
Huainan	1.02	5.05	17.28	0.202	0.292	Zhang et al. [2012]
Geometric mean		4.82		0.086	0.630	-
app. Devuer Dient						

Table A2. Sulfur, Iron, and Aluminum Mass Fraction in Coal-Burning Fly Ash in China<sup>a</sup>

<sup>a</sup>PP: Power Plant.

summer, and the values are 5 times lower than the maximum seasonal rates for both oceans. The influence of human activity was most pronounced in the summer, at which time contributing 14% and 28% of the total iron was deposited into the NWPO and NSCS, respectively.

This study has demonstrated a strong contribution of iron deposition from anthropogenic sources in the Northwestern Pacific Ocean and the marginal seas of East Asia using year 2007 as an example. It would also be interesting to examine how trends in coal use and the application of emission scrubbers in surrounding countries affect the anthropogenic nutrient input. Also, the importance of the Fe input associated with anthropogenic aerosol deposition in oceanic biogeochemistry deserves further investigation.

# Appendix A: Details of the "Composition Factor" and "Recovery Factor" Estimates Given in Section 2.2

The four tables (Tables A1–A4) given in this section listed Chinese data used for the estimation of iron emission associated with coal combustion, including chemical composition of coal and fly ash from coal burning. The composition data were also used to provide the Fe:Al ratio in fly ash.

The net emission flux of iron (in the form of fly ash),  $F_{Fer}$  can be related to that of sulfur,  $F_{Sr}$ , via the relationship given in equation (5):  $F_{Fe} = \alpha \cdot \beta \cdot F_{Sr}$ , where  $\alpha$  is the composition factor in equation (3) and  $\beta$  is the recovery factor defined in equation (4). The chemical composition of coal varies according to its sources. In 2007, most of the coal used in China was produced domestically; therefore, any estimation of  $\alpha$  should be based on data related to Chinese coal. The sulfur to iron ratio  $\frac{S_c}{Fe_c}$  in  $\alpha$  can be obtained from data on coal composition from major coalfields in China, such as Xinjiang, Inner Mongolia, and Shanxi (Figure 3). The geometric mean of  $\frac{S_c}{Fe_c}$  was 0.618. For fly ash, the sulfur to iron ratio  $\frac{S_f}{Fe_f}$  can be obtained by analyzing data related to the composition of fly ash and bottom ash from several power plants in China. The data presented in Figure 3 were used to calculate the geometric mean of  $\frac{S_f}{Fe_f}$  (0.084) and of  $\frac{S_b}{Fe_b}$  (0.088). We used these ratios to estimate the composition factor  $\alpha$ , which resulted in a value of ~1.5. The values and reference sources of the composition data shown in Figure 3 are listed in Tables A1–A3.

Tabl	e A3.	Sulfur and	Iron M	lass l	Fraction	in (	Coal-Burning	Bottom /	Ash in C	hina
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Data Source	S (%)	Fe (%)	S/Fe	References
Hebei Guangdong Shanghai Shizuishan, Ningxia Goamattis maan	0.948 0.748 0.784 0.560	10.07 6.59 9.00 8.68	0.094 0.114 0.087 0.065	Liu et al. [2004] Liu et al. [2004] Liu et al. [2004] Wang et al. [2008]
Geometric mean			0.088	

Precipitator	Proportion (%) <sup>a</sup>	FA Removal Rate (%)	References
	Pov	ver Plant	
Electrostatic Precipitator	86	98	Gong and Zhang [2010]
Wet Precipitator	13	96.3	Ondov et al. [1979]
Machinery Precipitator	1	85	<i>Huang et al.</i> [2004]
	In	dustry	
Wet Precipitator	29	96.3	Ondov et al. [1979]
Machinery Precipitator	58	85	<i>Huang et al.</i> [2004]
Wet Fluidized Bed	9	96.3	Ondov et al. [1979]
No precipitator	4	0	
	Res	idential	
No precipitator	1	0	
a .			

**Table A4.** Types of Fly Ash Precipitator Used and Their Recovery Efficiency

<sup>a</sup>Tian and Qu [2009].

However, aerosols emitted from steel plants contain much higher fraction of iron than coal-burning aerosols. Evaluating the degree of the iron enrichment requires information related to the amount of coal used in the steel industry. For this calculation we used data for China due to its dominance in the East Asia steel industry. *Hasanbeigi et al.* [2011] reported that in 2006, the iron and steel industry accounted for 14% of the primary energy consumption in China, 93% of which is produced from coal. According to the IEA statistics for 2007, 47% of the energy consumption in China occurred in the industry sector, 59% of which was associated with coal burning. These ratios were similar in 2006. Using these numbers, we estimated that the iron and steel industry accounted for approximately 46% of the total coal consumption in the industry sector in 2007.

Recovery factor  $\beta$  is based on recovery ratios  $r_f$  and  $r_s$ , which depend on the type and prevalence of the recovery devices being used. In our model, sources of fly ash included power plants as well as industry and residential emissions. The recovery ratio varied significantly among the various emission sources due to differences in the removal efficiency. The average efficiency of iron recovery  $r_f$  is 0.98, 0.86, and 0.00 for power plants, industry, and residential sources, respectively (Table A4). Guan et al. [2011] reported that 76% of the power plants in China applied flue gas desulfurization (FGD) devices in 2009, 92% of which involved the use of wet limestone-gypsum, while the remaining 8% used seawater FGD or Circulating Fluid Bed FGD. In 2006 the proportion of power plants in China equipped with FGD was only 30% [Zhang et al., 2009]. In our model, we used an FGD deployment ratio of 30%; however, we employed the 92% fraction figure for wet limestone-gypsum FGD. The latter can achieve a recovery efficiency of 96%, whereas the other FGDs have an average recovery efficiency of 75% [Yang et al., 2003; Wang and Zhang, 2004]. Using these ratios, we obtained  $r_s = 0.28$  for power plant sources. Data related to sulfur recovery in China are difficult to come by. Little information is available with regard to the industrial use of FGD; however, Xiang [2003] did report sulfur removal efficiency of 80% using Wet Precipitators, while Yang et al. [2003] reported 70% efficiency for Fluid Bed Wet Precipitators. Using these values, we obtained  $r_s = 0.30$  for industrial applications, which is close to the  $r_s$  value that we obtained for power plants (0.28). We therefore used  $r_{\rm s}$  = 0.28 for both industry and power plants. No reports have been published with regard to recovery devices for residential sources of sulfur; therefore, we assumed that  $r_s = 0$ . With these factors determined, we are able to calculate the recovery factor  $\beta$  as 0.033, 0.2, and 1.0 for power plants, industry, and residential sources, respectively.

## Appendix B: Comparison of Simulated and Observed PM<sub>10</sub> Concentration at Various Sites

Complement to Figure 7, this section shows addition verification of the simulated aerosol mass concentration using daily mean PM10 measured at two locations. Fairly good correlations between simulations and observations can be seen in Figure B1.



**Figure B1.** Comparison of the simulated (ordinate) and observed (abscissa) daily mean  $PM_{10}$  (in  $\mu g m^{-3}$ ). Blue squares and red dots represent for measurements at the TEPA stations and TAON stations, respectively. (left) Observations at the Magong TEPA station (R = 0.70, p = 0.000) and Xiaomen Islet TAON station (R = 0.89, p = 0.122). (right): Observations at the Wanli TEPA station (R = 0.61, p = 0.000) and Cape Fuguei TAON station (R = 0.72, p = 0.002). The grey line shows the 1:1 ratio.

## **Appendix C: Key Meteorological Aspects From the Simulation**

The seasonal patterns of surface meteorological factors that are most relevant to the transport and deposition of dust and fly ash are shown in Figure C1. One can see significant seasonal variations illustrating the main features of the Asian monsoon system. For example, over the NWPO and NSCS, northerly winds dominate in autumn and winter, while southerly winds prevail in summer. Backtracking the streamlines one will see that such northerly winds generally originate in populated lands and therefore tend to carry aerosols (including dust and fly ash) toward marginal seas. In comparison, southerly winds originate from the oceans and therefore tend to be cleaner. The precipitation fields show a SSE to NNW (i.e., open sea to inland) gradient in all seasons, with maximums and minimums occurring in summer and winter, respectively. The NSCS, one of the focus areas in this study, is particularly weak with regard to precipitation, compared with its surroundings during the winter. Stronger precipitation leads to greater aerosol scavenging; therefore, it is reasonable to expect that wet deposition will be weak in the NSCS during the winter. In contrast, during the summer, the NSCS has ample precipitation but a reduced atmospheric transport of pollutants. It is therefore reasonable to expect NSCS to have lower total aerosol deposition in the summer but with a higher fraction of it from wet deposition.



**Figure C1.** Simulated seasonal wind fields (streamlines) and precipitation patterns (color shading; in mm  $d^{-1}$ ).

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