Atmospheric chemistry in East Asia determines the iron solubility of aerosol particles supplied to the North Pacific Ocean

Kohei Sakata[1,a*], Shotaro Takano[2], Atsushi Matsuki[3], Yasuo Takeichi[4], Hiroshi Tanimoto[1,5], Aya Sakaguchi[6], Minako Kurisu[7,b], and Yoshio Takahashi[8,9]

[1]Earth System Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan.

[2]Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan.

[3]Institute of Nature and Environmental Technology, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192, Japan.

[4]Department of Applied Physics, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.

[5]Graduate School of Environmental Studies, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

[6]Institute of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan.

[7]Submarine Resources Research Center, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15, Natsushima-cho, Yokosuka, Kanagawa, 237-0061, Japan.

[8]Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

[9]Institute of Materials Structure Science, High-Energy Accelerator Research Organization Tsukuba, Ibaraki 305-0801, Japan.

[a]now at: Institute of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan.

[b]now at: Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8564, Japan.

*Corresponding author: Kohei Sakata.

Email: kohei.sakata.33@outlook.jp

ORCID: 0000-0002-0103-9631

Abstract.

The deposition of dissolveddissolve iron (d-Fe) from East Asian aerosols to the North Pacific Ocean modulates primary productivity in surface waters seawaters, facilitating the uptake of atmospheric carbon dioxide by the ocean, thereby impacting affecting the global climate. Since the Given that microorganisms in the surface seawater utilize d-Fe as a micronutrient, the bioavailability of aerosol Fe depends on its fractional solubility (Fe_{sol}%). Although Fe_{sol}% is influenced by both emission sources and atmospheric processing, influence Fe_{sol}%, their effects on Fe_{sol}% are not fully incompletely understood. We assessed the factors controlling Fe_{sol}% in size-fractionated aerosol particles collected along the coast of the Sea of Japan coast for over one year (July 2019–June 2020). Approximately 70% of d-Fe in East Asian aerosols was present in fine aerosol particles (<1.3 µm), with Fe_{sol}% ranging from 4.1% to 94.9%. Anthro-Fe accounted for about approximately 50% of d-Fe in fine aerosol particles during periods outside the pre- and post-lockdown of COVID-19 lockdown, but its contribution was negligible during the COVID-19 lockdown. The period. Fe_{sol}% in fine aerosol particles was correlated with the abundance of water-soluble Fe species (Fe(II, III)- sulfates and Fe(III)- oxalate). These water-soluble Fe species were detected in both mineral dust and anthropogenic aerosols in fine aerosol particles. Dissolution models optimized for Fe in mineral dust and anthropogenic aerosols showed demonstrated that Fe in both aerosol types aerosols dissolved by through proton-promoted dissolution under acidic conditions (pH < 2.0). Subsequently, d-Fe dissolved from aerosols was stabilized by the formation of Fe(III)-oxalate in the aqueous phase. Thus, Therefore, a comprehensive understandings understanding of the chemical alteration processes of East Asian aerosols are is essential for accurately quantifying their Fe_{sol}% upon transport to the North Pacific.

1. Introduction

Primary production in high nutrient-–low chlorophyll (HNLC) regions is limited by the depletion of dissolved ironFe (d-Fe, Martin et al., 1994; Jickells et al., 2005; Boyd et al., 2007). Ocean iron (Fe) fertilization can modulate primary production in the euphotic zone, thereby increasing the uptake of carbon dioxide and potentially exerting a significantremarkable influence on the global climate system. (Martin, 1990; Martin et al., 1994; Falkowski et al., 2000; Jickells et al., 2005; Boyd et al., 2007). AtmosphericThe atmospheric deposition of aerosol Fe is a dominant source of d-Fe in surface seawater in the North Pacific surface seawater. Given that microorganisms in surface seawater utilize d-Fe as a nutrient (Moore et al., 2013), the bioavailability of aerosol Fe is highly dependent on fractional Fe solubility (Fe_{sol}% %), which is calculated as Fe_{sol}% = (d-Fe/total Fe) × 100) (Sholkovitz et al., 2012; Mahowald et al., 2018). The values Although the Fe_{sol}% of Fe_{sol}% in aerosol particles varyvaries considerably (0.1–%–90%), but the factors controlling the Fe_{sol}% have not been fullyremain incompletely understood (Sholkovitz et al., 2012; Mahowald et al., 2018).

One of the factors controlling Fe_{sol}% in aerosol particles is theThe difference inbetween the Fe_{sol}% betweenof Fe in mineral dust and anthropogenic aerosols emitted through high-temperature combustion is a potential factor controlling Fe_{sol}% in aerosol particles (Sholkovitz et al., 2012; Mahowald et al., 2018; Ito et al., 2021). Although the annual emission of anthropogenic Fe (anthro-Fe) was aboutis approximately an order of magnitude smaller than that of Fe in mineral dust Fe (mineral-Fe), anthro-Fe is a possible source of d-Fe in surface water because it exhibits a higher Fe_{sol}% (up to 80%) than mineral-Fe (Fe_{sol}% < 1%; Myriokefalitakis et al., 2018; Hamilton et al., 2019; Ito et al., 2021). Indeed, the high Fe_{sol}% associated with anthro-Fe has been observed fromin East AsiaAsian aerosols, especially in the fine aerosol particles that they contain (Kurisu et al., 2016, 2021, 2024; L. Liu et al., 2022; Hsieh et al., 2022; Sakata et al., 2023). However, the contribution of anthro-Fe to d-Fe in aerosol particles has not been wellpoorly evaluated quantitatively through field observations. Furthermore, during atmospheric transport, mineral-Fe and anthro-Fe undergo atmospheric processes, including proton-promoted, ligand-promoted, and photoreductive dissolutions, during atmospheric transport, whichthat elevate their Fe_{sol}% (Journet et al., 2008; Shi et al., 2011a, 2015; Paris et al., 2011; Chen and Grassian, 2013; Ito and Shi, 2016; Li et al., 2017; Sakata et al., 2022). Single-particle analyses have shown that mineral-Fe and anthro-Fe in fine aerosol particles are internally mixed with sulfate, nitrate, and organic matter, including oxalate (Li et al., 2017; Sakata et al., 2022; Zhang et al., 2019; Zhou et al., 2020; Y. Zhu et al., 2020, 2022; Xu et al., 2023; Ueda et al., 2023). These internally mixed particles provide evidence of the chemical alteration of Fe-containing aerosols in the atmosphere, but; however, determining the Fe_{sol}% through single-particle analysis remains a challenging task (Ueda et al., 2023). Therefore, the net effect of the atmospheric processes of Fe-containing particles mixed with acidic species and organic mattersmatter on Fe_{sol}% remains poorly understood.

It is well-known that East Asia is one of the world's largest sources of mineral-Fe and anthro-Fe transported to the North Pacific Ocean, which is one of thean HNLC regionsregion (Myriokefalitakis et al., 2018; Hamilton et al., 2019; Ito et al., 2021). Additionally, East Asia continues to grapple with air pollution problems, and it has been reported that anthropogenic SO_2sulfate and other pollutants are causinghave been reported to cause the chemical alteration of mineral-Fe and anthro-Fe in the atmosphere over urban areas in East Asia (Li et al., 2017: Y. Zhu et al., 2020, 2022; Xu et al., 2023). Given that the Fe_{sol}%

~~in~~of aerosol particles supplied to the North Pacific is mainly controlled by processes occurring during transport between East Asia and Japan (Buck et al., 2013; Sakata et al., 2022), long-term observations in Japan, which is located ~~at~~on the eastern edge of East Asia, are crucial for providing insights into these controlling factors. Therefore, in this study, we performed monthly ~~collected~~collections of seven size-fractionated aerosol particles at the Noto Ground-based Research Observatory (NOTOGRO) along the coast of the Sea of Japan ~~coast~~ from July 2019 to June 2020. NOTOGRO is a suitable location for collecting long-range-transported aerosols that are minimally influenced by local emissions (Fig. 1, Sakata et al., 2021). ~~The~~In this study, the sampling period encompassed the COVID-19 lockdown period in China ~~when~~(from the end of January 2020 to February 2020) when the anthro-Fe concentration in China ~~was~~ considerably decreased (~~from the end of January to February 2020;~~ Liu et al., 2021; Li et al., 2021; Zheng et al., 2020; Xu et al., 2022). ~~Considerable~~The considerable reduction in anthro-Fe concentration ~~reduction~~ due to ~~this contingency provided us~~the COVID-19 lockdown provides opportunities to assess the effect of anthropogenic activities on Fe_{sol}% in aerosol particles in East Asia. ~~Using these samples, this study~~We conducted various analyses related to estimating Fe sources and alteration processes to understand ~~factor~~the factors controlling Fe_{sol}% in the East Asia region. Atmospheric concentrations of total and dissolved metals were determined ~~using~~through high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). The contributions of mineral-Fe and anthro-Fe to d-Fe were estimated ~~by~~on the basis of (i) positive matrix factorization (PMF, Norris et al., 2014) and (ii) the molar ratio of d-Fe relative to that of dissolved Al ([d-Fe]/[d-Al]) as a new indicator for the sources and dissolution processes of d-Fe in aerosol particles (Fig. S1. Sakata et al., 2023). ~~To identify d-Fe species in aerosol particles, representative~~Representative Fe species were determined by using macroscopic X-ray absorption near-edge structure (XANES) spectroscopy to identify d-Fe species in aerosol particles, and ~~then~~the relationship between Fe_{sol}% and Fe species ~~were~~was then investigated. Furthermore, the spot analyses of Fe species in mineral dust and anthropogenic aerosols were performed ~~by~~through microfocused XANES combined with X-ray fluorescence mapping (μ-XRF-XANES) to assess the alteration processes of Fe. Finally, dissolution kinetic models optimized for Fe in mineral dust and anthropogenic aerosols were used to identify the effect of pH on ~~the~~ Fe dissolution from these aerosols. ~~From these results, the~~The influence of the Fe source (mineral-Fe or anthro-Fe) on Fe_{sol}% in aerosol particles transported to the North Pacific was evaluated independently from the results.

2. Material and Methods

2.1. Aerosol sampling.

NOTOGRO is located in Suzu City in the coastal region of the Sea of Japan ~~in Suzu City~~, Japan (37.4513°N, 137.3589°E; Fig. 1). The city lacks industrial or other anthropogenic emission sources. Size-fractionated aerosol samples were collected ~~using~~by employing a high-volume air sampler (Model-120, Kimoto, Japan) equipped with a Sierra-type cascade impactor (TE-236, Tisch Environmental Inc., the USA). The air sampler was installed on ~~the~~a rooftop 10 m above ground level. Aerosol particles were collected separately in seven ~~stages~~fractions (>10.2, 4.2–10.2, 2.1–4.2, 1.3–2.1, 0.69–1.3, 0.39–0.69, and <0.39 μm) with a flow rate of 0.566 m^3 min^{-1}. Custom-made polytetrafluoroethylene (PTFE) membrane filters ~~were used as the~~

~~sampling filter for all stages (PTFE, ~~(PF050, Advantech, Japan, Sakata et al., 2018, 2021~~). The PTFE ~~) were used as the sampling filters ~~were ~~for all fractions. PTFE filters are not properly wetted by cleaning solutions because they are hydrophobic. This situation has the potential to reduce cleaning efficiency. Therefore, the filters were hydrophilized with ethanol (99.5%, Wako First Class, Wako, Japan). ~~Subsequently, the ~~The hydrophilized PTFE filters were soaked in 1 mol~~/~~ L^{-1} hydrochloric acid (EL grade, Kanto Chemical Co. Inc., Japan) and heated at 180 °C for one day. ~~After that~~Subsequently, the filters were placed in ultrapure water and heated at 180 °C for one day. The rinsed filters were then air-dried in a clean booth. ~~The~~Air drying restored the hydrophobicity of the PTFE filters ~~restored by air drying due to~~as a result of the complete removal of ethanol from the filters. The rinsed and dried PTFE filters were stored in polyethylene bags. The blank Fe concentration in the PTFE ~~filter~~filters was 0.438~~±~~ ± 0.713 ng cm^{-2} for acid digestion and 0.044~~±~~ ± 0.040 ng ~~cm^{2}~~ cm^{-2} for ultrapure water extraction. These blank concentrations were at least an order of magnitude lower than the blank Fe concentration in cellulose filters (Morton et al., 2013; Sakata et al., 2018). The filter blanks for Fe at the average sampling flow in this study (approximately 5000 m^3) was less than 0.1 pg m^{-3} and had ~~little~~a negligible effect on the Fe concentration in the aerosol samples.

Aerosol samples were collected monthly from July 2019 to June 2020 (Table S1). ~~The filters with ~~On the basis of backward and forward trajectory analyses, this study categorized aerosol samples into two groups (Figs. S2 and S3). The first group included samples collected during the Japanese air mass (JPN) period (July–October 2019 and May–June 2020). Air masses arriving at the sampling site (NOTOGRO) during the JPN period originated from the domestic region of Japan and its marginal sea (Fig. S2a). In addition, forward trajectory analyses indicated that these air masses were not transported to the North Pacific Ocean (Fig. S3a). The second group included the samples collected during the East Asian outflow (EAout) period (November 2019–April 2020; seasons: winter and spring). During the EAout period, air masses arriving at the sampling site originated from East Asia and were subsequently transported to the Pacific Ocean (Figs. S2b and S3b).

The aerosol filters were folded in half~~,~~ immediately after sampling. The folded filters were then placed in polyethylene bags~~,~~ and ~~then ~~stored in a desiccator ~~(~~with RH ~~<~~below 20~~%). Since~~% until analysis. In China, the COVID-19 lockdown ~~in China run~~was imposed from January 23 to February 19, 2020 (Liu et al., 2021; Li et al., 2021; Zheng et al., 2020; Xu et al., 2022~~),~~). Therefore, the aerosol samples collected in January and February were considered as having been collected during and after the ~~lockdown (Table S1). The status of ~~COVID-19 lockdown ~~for other samples is shown in ~~period, respectively (Table S1~~.~~).

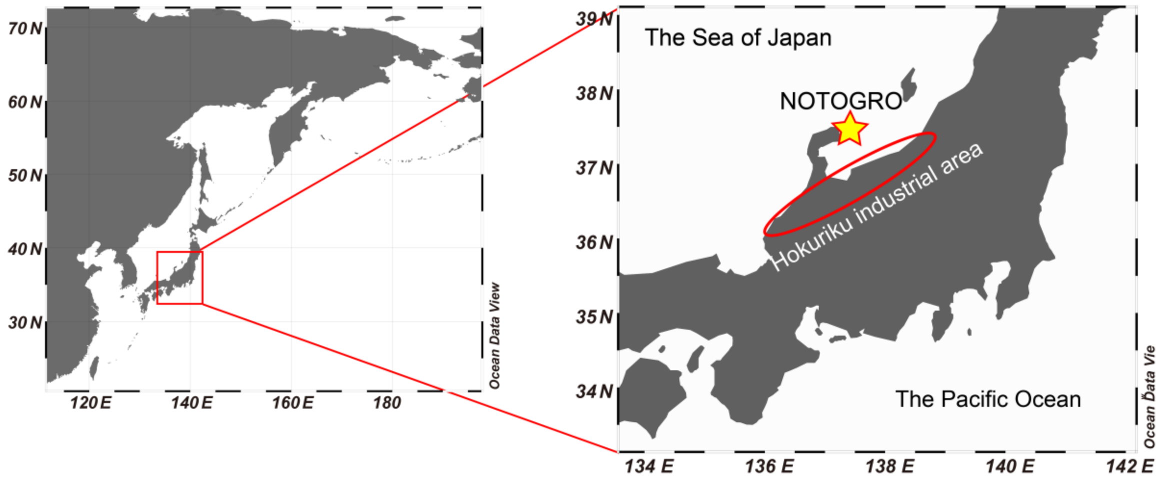


Figure 1. ~~The sampling~~Sampling site (NOTOGRO) ~~of~~for size-fractionated ~~aerosol sampling.~~ aerosols. The figure was described using Ocean Data View (Schlitzer, 2023).

~~2.1.1.~~2.2. Determinations of total and dissolved metal concentrations

~~In this study, the~~The Fe concentration measured after the complete acid digestion of aerosol particles is denoted as T-Fe (= d-Fe + insoluble Fe). ~~About~~Approximately one-fifth of the collected aerosol sample in each ~~stage~~size fraction was decomposed by ~~a mixed~~using an acid mixture (2 mL of 15.5 mol L^{-1} HNO_3, 2 mL of 11.3 mol L^{-1} HCl, and 1 mL of 28 mol L^{-1} HF, ultrapure AA 100, Kanto Chemical, Co., Inc., Japan) in perfluoroalkoxy alkane ~~(PFA)~~ vials by heating at 150 °C for one day. The mixed acid was evaporated to dryness, and ~~then~~ the evaporated residue was redissolved in 2% ~~of~~ HNO_3. The solutions were filtrated by using a syringe filter made of hydrophilic polyethersulfone ~~filter~~ (PES ~~filter;~~, Millex, ϕ: 0.45 µm, Merck, Germany). ~~D~~

Dissolved Fe in aerosol particles was extracted ~~by~~with 2–4 mL of ultrapure water in a polypropylene centrifuge ~~tubing with~~tube and horizontal shaking for one day. ~~The extracted~~ After being subjected to water extraction, the PTFE filter was removed from the vial, and the solution was ~~then~~ filtered through ~~the~~a PES syringe filter. ~~After the evaporation~~The filtrated solutions were evaporated to dryness~~, the~~. The evaporated residue was then redissolved in 2% HNO_3. Elemental concentrations were determined by using an HR-ICP-MS (Elemental II, Germany). The precision and accuracy of ~~quantifications~~the quantification of target elements were confirmed ~~by~~through the repetitive analysis of the reference material of urban ~~aerosol~~aerosols (Table S2, NIES CRM 28. Urban aerosol, Mori et al., 2008). All sample treatments described above were performed in a clean room (class 1000).

~~To evaluate emission sources of Fe, the~~The enrichment factor of Fe ($EF_{T\text{-}Fe}$) normalized by the ~~Fe/Al~~mass ratio of Fe relative to that of Al in the upper continental crust (UCC) was calculated ~~by~~to evaluate the emission sources of Fe. The following equation was used for the calculation:

$$EF_{\mathrm{T-Fe}} = \frac{(\mathrm{T-Fe/T-Al})_{aerosol}}{(\mathrm{Fe/Al})_{UCC}} \quad (\text{eq.} \; \frac{(\mathrm{T-Fe/T-Al})_{aerosol}}{(\mathrm{T-Fe/T-Al})_{UCC}}, \quad (\text{Eq. } 1)$$

where (T-Fe/T-Al)$_{aerosol}$ represents the mass concentration of total Fe (= insoluble Fe + d-Fe in aerosol particles relative to the total Al). In this study, consideringin consideration of the variation of in the T-Fe/T-Al ratio in the UCC, the average value from five sources in the literature sources (=0.52 ± 0.12) was used (Turkian and Wedepohl, 1961; Taylor, 1964; Wedepohl, 1995; Taylor and McLennan, 1995; Rudnick and Gao, 2003). The contribution of anthropogenic anthro-Fe has traditionally been considered significantremarkable when EF$_{\mathrm{T-Fe}}$ exceeds 10. However, recent studies have indicated a narrow range of T-Fe/T-Al ratios infor Asian dust (X. T-Fe/T-Al: 0.56 ± 0.17, X. Liu et al., 2022; Sakata et al., 2023). Consequently, this study adopts a more conservative threshold, recognizing anthro-Fe contributionssignificant contribution of anthro-F) to T-Fe in aerosol particles was identified when EF$_{\mathrm{T-Fe}}$ is greater thanexceeds 2.0 (T-Fe/T-Al > 1.04; Sakata et al., 2023). In addition to EF$_{\mathrm{T-Fe}}$, T-Fe concentrations associated with mineral dust and anthro-Fe were estimated by using the following equations:

$$Mineral\ Fe = Aerosol\ Al \times (Fe/Al)_{crustl} \quad (\text{eq.} \quad (T - Fe/T - Al)_{crust}, \quad (\text{Eq. } 2)$$

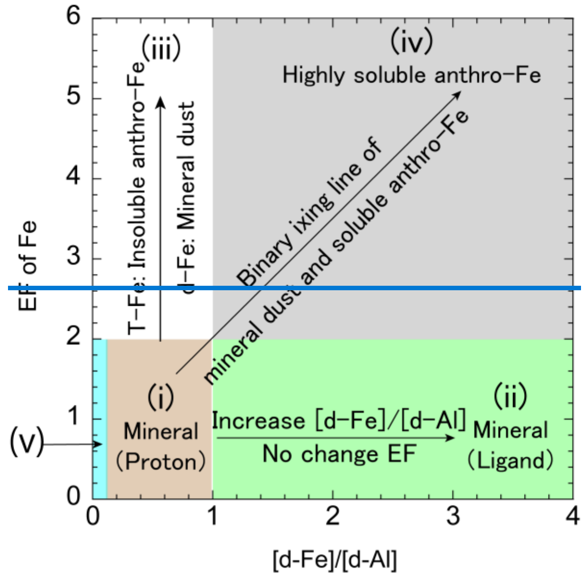
$$Anthropogenic\ Fe = Aerosol\ Fe - Mineral\ Fe \quad (\text{eq}, \quad (\text{Eq. } 3)$$

2.3. The sourceSource apportionment of T-Fe and d-Fe by a diagram

2.2.2.3.1. Diagram between EF of EF$_{\mathrm{T-Fe}}$ and [d-Fe]/[d-Al]

The diagramsA diagram of [d-Fe]/[d-Al] ratios combined with EF$_{\mathrm{T-Fe}}$ is aare useful tooltools for evaluating the sources and dissolution processes of d-Fe in aerosol particles because the Fe$_{sol}$% values of the aerosol particles vary depending on the dominant sources of T-Fe and d-Fe (Sakata et al., 2023). The T-Fe and d-Fe sources can be categorized into the following five groups (Fig. 2). In the first group,2): T-Fe is primarily associated with in groups (i) and (ii) originate from mineral dust (with EF$_{\mathrm{T-Fe}}$ < 2.0). Under conditions of proton-promoted . The [d-Fe]/[d-Al] ratio varies depending on the different dissolution, the [d-Fe]/[d-Al] ratios of aluminosilicate minerals (*e.g.*, biotite, illite, and chlorite) were ranged from 0.14 to1.03 (Kodama and Schnitzer, 1973; Lowson et al., 2005; Bibi et al., 2011; Bray et al., 2015). Furthermore, the [d-Fe]/[d-Al] ratio of Asian dust was 0.24 ± 0.20 (Duvall et al., 2008). From these reported values, the range of [d-Fe]/[d-Al] ratio of proton-promoted dissolution processes of mineral dust was defined from 0.10 to 1.00 (brown area in Fig. 2). The T-Fe in the second group is also derived from mineral dust, but the d-Fe in this group is mainly dissolved by (i.e., proton- and ligand-promoted dissolution processes). The [d-Fe]/[d-Al] ratio for ligand-promoted dissolution. The [([d-Fe]/[d-Al] > 1.0) is higher than that for proton-promoted dissolution ([d-Fe]/[d-Al] ratio in the group exceeds]: 0.1.00 owing to the preferential complexation of iron by 1.0) because Fe is preferentially dissolved by organic ligands over Al (green area. T-Fe in Fig. 2, Kodamagroups (iii) and Schnitzer, 1973; Bray et al., 2015).

Third group represent a binary mixing of mineral dust and insoluble (iv) is derived from anthro-Fe, which is characterized by with EF$_{\mathrm{T-Fe}}$ > 2.0 and a [d-Fe]/[d-Al] ratio <1.00 (white area in Fig. 2). Here, anthro-Fe refers to anthropogenic Fe-rich particles that can increase EF_{T-Fe}, including Fe-oxide nanoparticles, which emits from not only high-temperature combustion processes (*e.g.*, steel industry, coal combustion; Ito et al., 2021) but also non-combustion sources such as debris from automobile brake pads (Li et al., . In group (iii), T-Fe is mainly derived from anthro-Fe, whereas d-Fe is derived from mineral dust because2022; Fu et al., 2023). The anthro-Fe is present in this group exhibits low solubility and thus makes a negligible contribution to the increase in the [d-Fe]/[d-Al] ratio observed in the aerosols. Therefore, it is inferred that the d-Fe primarily reflects the values characteristic of mineral particles with which the insoluble the form of insoluble Fe, which cannot affect the [d-Fe]/[d-Al] ratio of aerosol particles. By contrast, the anthro-Fe in group (iv) is associated. Unlike third group, the [d-Fe]/[d-Al] ratio in the fourth group is greater than 1.0 because of thehighly soluble, and its high T-Fe/T-Al ratio (i.e., high EF_{T-Fe}) is retained upon dissolution, as reflected by its [d-Fe]/[d-Al] ratio. Consequently, aerosols in group (iv) exhibit high EF_{T-Fe} and [d-Fe]/[d-Al]. However, distinguishing between proton- and ligand-promoted dissolutions is difficult because highly soluble anthro-Fe exhibits high [d-Fe]/[d-Al] ratios in both processes. Herein, anthro-Fe refers to anthropogenic Fe-rich particles that can increase the EF_{T-Fe} emitted from not only high-temperature combustion (e.g., steel industry and coal combustion; Kajino et al., 2020; Ito et al., 2021), but also non-combusted anthro-Fe (e.g., non-exhaust vehicle particles, such as brake ring and tire wear debris; Sanderson et al., 2016; Li et al., 2022; Fu et al., 2023). Fe_{sol}% of anthro-Fe. As a result, the fourth group is characterized by aerosols where both T-Fe and d-Fe are influenced by anthro-Fe. (grey area in Fig. Finally, group (v) consists of aluminosilicate 2). Finally, final group is aluminosilicate glasses emitted from high-temperature combustionscombustion, including coal combustions. It is known that aluminosilicate glasses were emitted from high-temperature combustions, which can be characterized low EF_{T-Fe} (< 2.0) and [d-Fe]/[d-Al] ratio (<0.10), which are totally different those for anthropogenic Fe-rich particles. Thus, one of the key advantages of this method lies in its capacity to discriminate between anthropogenic Fe-richcombustion and municipal solid waste incineration. These particles and aluminosilicate glasses produced by high-temperature combustion processes.are characterized by low EF_{T-Fe} values (<2.0) and [d-Fe]/[d-Al] ratios (<0.1). A detailed description of these five classifications is presented in S.1.1 in Supplemental Information.



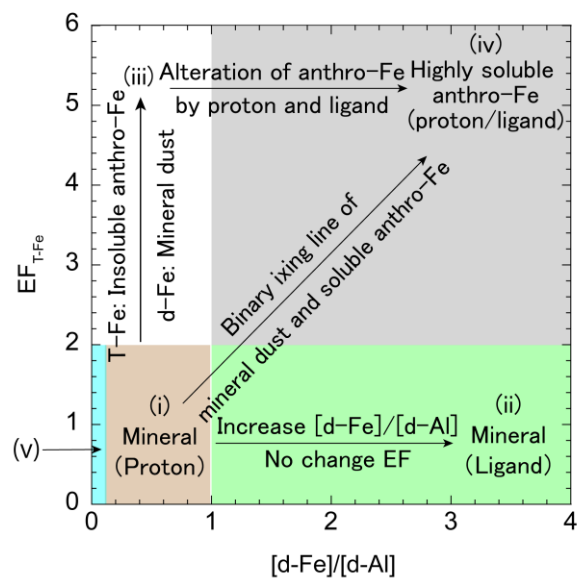


Figure 2. ~~The diagram~~Diagram of $EF_{T\text{-}Fe}$ and the [d-Fe]/[d-Al] ratio for evaluating the T-Fe and d-Fe sources of aerosol particles.

As detailed in Section 3.3.2, the d-Fe in fine aerosol particles was composed of a binary ~~mixing~~mixture of d-Fe dissolved ~~by~~through the proton-promoted dissolution of mineral dust and highly soluble anthro-Fe. ~~Here~~Herein, the contribution of anthro-Fe to d-Fe (F_{anthro}) in fine aerosol particles was estimated on the basis of a two-component mixing model by using the following equations (Sakata et al., 2023):

$$F_{mineral} + F_{anthro} = 1, \text{(Eq. 4)}$$

$$\left(\frac{[d-Fe]}{[d-Al]}\right)_{aerosol} = \left(\frac{[d-Fe]}{[d-Al]}\right)_{mineral} \times F_{mineral} + \left(\frac{[d-Fe]}{[d-Al]}\right)_{anthro} \times F_{anthro} \text{ ~~(eq,~~ (Eq. 5)}$$

The average [d-Fe]/[d-Al] ratio of coarse aerosol particles (=0.28) was the representative value of ~~the~~ ([d-Fe]/[d-Al])$_{mineral}$. The representative [d-Fe]/[d-Al] ratio of anthro-Fe was 2.18, which was the average [d-Fe]/[d-Al] ratio of fine aerosol particles with a value higher than 1.50 (Sakata et al., 2023). ~~Then, concentrations~~Concentrations of d-Fe associated with mineral dust and anthro-Fe were calculated by employing the following equations:

$$\text{Mineral d} - \text{Fe} = \text{d} - \text{Fe} \times F_{mineral} \text{ ~~(eq,~~ (Eq. 6)}$$

$$\text{Anthropogenic d} - \text{Fe} = \text{d} - \text{Fe} \times F_{anthro} \text{ ~~(eq,~~ (Eq. 7)}$$

Subsequently, the Fe$_{sol}$% of mineral dust (mineral-Fe$_{sol}$%) was calculated by dividing mineral d-Fe by ~~the~~ mineral Fe~~, using~~ through the same approach as that employed for ~~anthropogenic~~ the calculation of anthro-Fe (anthro-Fe$_{sol}$%).

~~**2.3. Positive matrix factorization**~~

2.3.2. ~~Source apportionment of~~ PMF

T-Fe and d-Fe sources in fine aerosol particles were ~~performed by positive matrix factorization~~ also evaluated through PMF (EPA PMF version 5.0, Norris et al., 2014). ~~The~~ PMF analyses were performed separately for the entire sampling period (JPN+EAout~~),~~) and the JPN~~,~~ and EAout periods. The PMF analysis for the JPN+EAout period was conducted to evaluate the monthly trend of the normalized contribution of each factor, with the average of all contributions for each factor normalized to 1. ~~In~~By contrast, PMF analyses were performed separately for the JPN and EAout periods to evaluate the average EF$_{T\text{-}Fe}$, Fe$_{sol}$%, and [d-Fe]/[d-Al] ratios of each factor. These analyses used fine aerosol particles collected during the respective periods. ~~Input data for PMF analysis are~~The concentrations of Na, Mg, Al, d-Al, K, Ca, Ti, V, Cr, Mn, Fe, anthro-Fe, d-Fe, Co, Ni, Cu, Zn, Sr, Cd, Ba, Pb, and SO_4^{2-} in the ~~fraction of~~ <0.39, 0.39–0.69, and 0.69–1.3 µm~~). The~~ fractions were used as the input ~~file~~data for PMF analysis ~~was concentrations of target species and their uncertainties. Uncertainties of each element were evaluated by the following equations:~~. A detailed descriptions of PMF method are described in S.1.2 in Supplemental Information.

~~$$Uncertainty = \frac{5}{6} \times MDL \quad \text{(eq. 8)}$$~~

~~$$Uncertainty = \sqrt{(Error\ fraction \times concentraion)^2 + (0.5 \times MDL)^2} \quad \text{(eq. 9)}$$~~

~~where MDL is the method detection limit, defined as three times the standard deviation of the filter blank concentration. Equations 8 and 9 were used when target species concentrations were lower and higher than MDL, respectively. The PMF analysis allows for three categories: “Strong”, “Weak”, and “Bad”. These categories were typically chosen based on the signal-to-noise (S/N) ratio. The “Weak” category is selected when the S/N is between 0.5 and 1.0, and the “Bad” category is used if the S/N ratio is lower than 0.5. Species classified as "Weak" had their associated uncertainties tripled, and species classified as "Bad" were excluded from further analysis. Initially, PMF analysis was performed with all elemental categories set to~~

~~"Strong" because the S/N for all species was higher than 7.0. Consequently, the coefficient of determination (r^2) between the observed and modeled concentrations of the input species was greater than 0.60, with the exception of Cr in the EAout period (Tables S3 and S4). The PMF analysis for the EAout period was then rerun with the Cr category set to "Weak," but the results did not change significantly. Therefore, this study employed the PMF results with all species categories set to "Strong," based on the conventional use of the S/N ratio for category determination.~~

2.4. Macroscopic and micro-focused ~~XAFS~~XANES.

~~The Fe K-edge XANES spectra of the aerosol samples (7050–7300 eV) were recorded at BL-9A and BL-12C, Photon Factory (PF),~~As the macroscopic and microscopic XANES techniques applied herein are consistent with those reported by Sakata et al. (2022) and Sakata et al. (2021), their description will be kept brief. The experiments for macroscopic (beamline: BL-9A and BL-12C) and semi-microscopic XANES (beamline: BL-15A) were performed at Photon Factory, High Energy Acceleration Research Organization~~ (KEK),~~, Ibaraki, Japan. ~~The synchrotron radiation generated by the bending magnet was monochromatized by a double-crystal monochromator of Si(111). The XANES experiment were performed in ambient air at room temperature. Approximately one-tenth of~~The details of the optics and experimental set-up for the macroscopic and semi-microscopic experiments are described in the Supplemental Information. The aerosol samples, initially collected ~~aerosol particles~~ on PTFE filters, were transferred ~~to a double-face~~onto carbon tape~~. The aerosol samples were oriented~~, then mounted at a 45° angle relative to the ~~incident~~incoming X-ray beam. ~~The incident X-ray energy was calibrated with the peak top of the pre-edge peak of the nonderivative Fe K-edge XANES spectrum for hematite aligned to 7112 eV. All XANES spectra of aerosol samples were recorded in fluorescence yield mode. Fluorescence X-ray from the aerosol sample was detected with a seven-element~~In microscopic and semi-microscopic analyses, XANES spectra were acquired via the fluorescence yield technique, with a silicon drift detector ~~equipped with a Soller slit to reduce elastic X-ray around the beam pass. The front face of the Soller slit was covered with a 0.2 mm-thick PTFE filter to remove~~used to detect fluorescence X-rays ~~of coexisted elements (*e.g.*, Ca and Mn) and argon in the ambient air. Linear combination fitting of the XANES spectra of aerosol samples using reference materials was performed with REX2000 software. The fitting was performed over the energy range of 7100–7200 eV. The goodness of fit was evaluated by the following equation:~~

$$\Sigma R = \frac{\Sigma[I_{obs}(E) - I_{cal}(E)]^2}{\Sigma[I_{obs}(E)]^2} \quad \text{(eq. 10)}$$

~~where $I_{obs}(E)$ and $I_{cal}(E)$ are X-ray absorption of the normalized X-ray absorptions of the samples and the calculated values at each energy.~~

~~The μ-XRF-XANES analyses were performed at BL-15A1 in PF. Aerosol samples with sizes of 0.39–0.69 μm and 2.1–4.2 μm, collected in September 2019, were used for the μ-XRF-XANES analyses. The beam size at the sampling position (20×20 μm^2) is larger than the aerodynamic diameter of the target samples. Although these experiments were not single-particle analyses, spot analysis combined with~~from samples. Specifically for semi-microscopic experiments, XRF mapping ~~allows for the identification of chemical species of target elements from different emission sources (*e.g.*, mineral and non-~~

~~mineral materials). Aerosol particles on the carbon tape were mounted on an acrylic sample holder and oriented at 45° to the direction of the incident X-ray beam. XRF maps of the 3d transition metals (Mn, Fe, Ni, Cu, and Zn) and light elements (Ti, Ca, K, Cl, and S) were acquired using a raster scan of the sample stage irradiated with 14 and 5.1 keV incident X-rays, respectively. Measurement spots for Fe species were selected based on the XRF maps of the target elements normalized by the incident X-ray intensity. Iron K-edge XANES spectra of~~ was performed first, and then Fe K-edge XANES spectra at the regions of interest were ~~recorded in quick-scan mode with a scan time of 180 sec. The~~ obtained. The linear combination fitting of the samples was conducted against the same ~~spectral analysis procedure used for macroscopic XANES was applied to the micro-focused XANES data~~standards reported by Sakata et al. (2022). A detailed descriptions of PMF method are described in S.1.3 in Supplemental Information.

2.5. Estimation of dissolution pH of mineral dust and anthro-Fe

2.5.1. Dissolution pH ~~for~~of mineral dust

Aerosol particles are repeatedly incorporated into and re-emitted from cloud water in the atmosphere (aerosol~~-~~–cloud cycles), with Fe dissolution primarily occurring in highly acidic aerosol phases (Spokes et al., 1994; Shi et al., 2015; Maters et al., 2016). Given that the dissolution of Fe in mineral dust occurs in the aerosol phase (pH < 3.0), Fe dissolution from mineral dust was simulated by using the three~~-~~-Fe~~-pools~~ pool model (Shi et al., 2011a; Sakata et al., ~~2023~~2022). The fast Fe ~~pool~~ (ferrihydrite and poorly crystalline Fe oxides), ~~the~~ intermediate Fe ~~pool~~ (Fe oxide nanoparticles), and ~~the~~ slow Fe ~~pool~~ (crystalline Fe oxides and aluminosilicates) pools represent three Fe pools with different dissolution rates (k, Table 1). Shi et al. (~~2011~~2011a) reported that the dissolution rate of the slow Fe~~-~~ pool is similar to that of illite. However, biotite is more abundant than illite in the aerosol samples collected ~~for this study~~in our present and ~~our~~ previous ~~work~~works (Sakata et al., ~~2022), biotite is more abundant than illite.~~2022). Given that the dissolution rate of biotite is approximately one order of magnitude higher than that of illite (Bibi et al., 2011; Bray et al., 2015), ~~we set~~ the dissolution rate of the slow Fe~~-~~ pool ~~one order of magnitude higher than in the original model. Therefore, in this study, the dissolution rate of the slow Fe-pool is set~~was set to be one order of magnitude higher than that ~~of~~in the original model. ~~Assuming~~Under the assumption of a first-order reaction, the molar concentration at a certain time (t) ([d-Fe(t)]) is described in the following equation:

$$[\mathrm{d-Fe}]_{mineral}\ (\mu mol\ g^{-1}) = [\mathrm{d-Fe}]_{\mathrm{fast}} + [\mathrm{d-Fe}]_{\mathrm{intermediate}} + [\mathrm{d-Fe}]_{\mathrm{slow}}$$ ~~(eq. 11~~, (Eq. 8)

$$[\mathrm{d-Fe}(t)]_{\mathrm{fast}}\ \sout{(\mu mol\ g^{-1}) = [\mathrm{d-Fe}]_{mineral}}(\mu mol\ g^{-1}) = [\mathrm{d-Fe}]_{mineral} \times \sout{[\%\mathrm{FeT}]_{\mathrm{fast}}}[\%\mathrm{FeT}]_{\mathrm{fast}}\ \sout{\times (1-e^{-kt})}$$ ~~(eq. 12~~ $\times\ (1-e^{-kt})$, (Eq. 9)

where $[\mathrm{d\text{-}Fe}]_{\mathrm{mineral}}$ refers to the d-Fe concentration in mineral dust calculated by using ~~eq~~Eq. 6~~, and the unit conversion from ng m^{-3} to μmol g^{-1} for d-Fe concentration are provided in the S1.1 in Supplementary Information. The~~. [%FeT] denotes the maximum percentage of Fe that can be solubilized, and k represents the rate constant (h^{-1}). The pH dependence of these parameters is presented in Table 1. The reaction time~~,~~ t~~,~~ was set to 54 ~~hours~~h, taking into account atmospheric transport and ~~the~~ aerosol~~-~~–cloud cycles (Sakata et al., 2023). Finally, the pH value for which the sum of d-Fe concentrations across all pools ~~equalled~~equaled [d-Fe]$_{aerosol}$ was determined.

Table 1 pH dependence of parameters for the three~~-~~-Fe~~-~~ pool model

Fe pool	~~%~~[%FeT] (%)	Dissolution rate (h^{-1})
Fast	pH 1.0~~-~~–2.0: Fixed at 0.9% pH 2.0~~-~~–3.0: ~~%~~[%FeT~~=~~] = –0.4 × pH +1.7	log k_{fast} = ~~-~~–0.50 × pH + 1.87
Intermediate	pH 1.0~~-~~–2.0: Fixed at 3.0% pH 2.0~~-~~–3.0: ~~%~~[%FeT~~=~~] = –2.0 × pH + 7.0	log $k_{intermediate}$ = ~~-~~–0.66 × pH + 0.36
Slow	pH 1.0~~-~~–3.0: ~~%~~[%FeT~~=~~] = –15.2 × pH + 58.4	log k_{slow} = ~~-~~–0.44 × pH – 0.76

2.5.2. Dissolution pH for anthro-Fe

~~Using~~By using hematite nanoparticles as a proxy for anthro-Fe, the dissolution pH of anthro-Fe was estimated under the assumption that anthro-Fe dissolution ~~was~~is solely driven by proton-promoted dissolutions. ~~Based on~~Under the assumption that the ~~S/L~~solid-to-liquid ratio ~~for~~of anthro-Fe is 0.06 g~~/~~ L^{-1}, which ~~was~~is comparable to that of mineral dust, the aerosol liquid water (ALW) content associated with hematite nanoparticles was quantified by using the following equation~~.~~:

$$ALW\ (L\ m^{-3}) = \frac{Anthro-Fe\ concentration/0.699}{0.06\ (=\frac{S}{L} ratio)}\ (\text{~~eq. 13~~, Eq. 10})$$

where 0.699 is the mass fraction of Fe in hematite nanoparticles, and anthro-Fe concentrations were estimated by ~~eq~~using Eq. 3. The pH dependence of ~~the~~ anthro-Fe$_{sol}$% in ALW under the equilibrium state was estimated ~~based~~ on the basis of the solubility product of hematite ~~nanoparticle~~nanoparticles (Bonneville et al., 2004). The proton-promoted dissolution of hematite nanoparticles and the solubility product ($^*K_{so}$ = 0.52) of this reaction are described as~~ the followings~~:

$$\frac{1}{2}Fe_2O_3 + 3H^+_{(aq)} \leftrightarrow Fe^{3+}_{(aq)} + \frac{3}{2}H_2O\ (\text{~~eq. 14~~, Eq. 11})$$

$$log\ ^*K_{SO} = log[a_{Fe^{3+}}] + npH\ (\text{~~eq. 15~~, Eq. 12})$$

where n is the reaction order determined ~~by~~in a previous study (n: 2.85, Bonneville et al., 2004). The $[a_{Fe^{3+}}]$ represents the activity of Fe^{3+} in the ALW. To simplify the calculations, the activity coefficient is 1, which means that the $[a_{Fe^{3+}}]$ is considered to be equal to the Fe concentration in the solution (nmol L^{-1}). The $[a_{Fe^{3+}}]$ in ALW at each pH was calculated by substituting pH values into Equation ~~15~~12. Subsequently, the anthro-Fe$_{sol}$% at equilibrium was calculated for various pH values using the following equation.

$$Equilibrium\ anthro-Fe_{sol}\% = \frac{ALW\ (L\ m^{-3}) \times [a_{Fe^{3+}}]\ (nmol\ L^{-1})}{anthropogenic\ Fe\ (ng\ m^{-3})} \times 100\ (\text{~~eq. 16~~, Eq. 13})$$

The pH at which the equilibrium anthro-Fe_{sol}% matched the actual anthro-Fe_{sol}% was determined and defined as the ~~pH exhibited during the leaching~~dissolution pH of anthro-Fe.

3. Results and Discussion

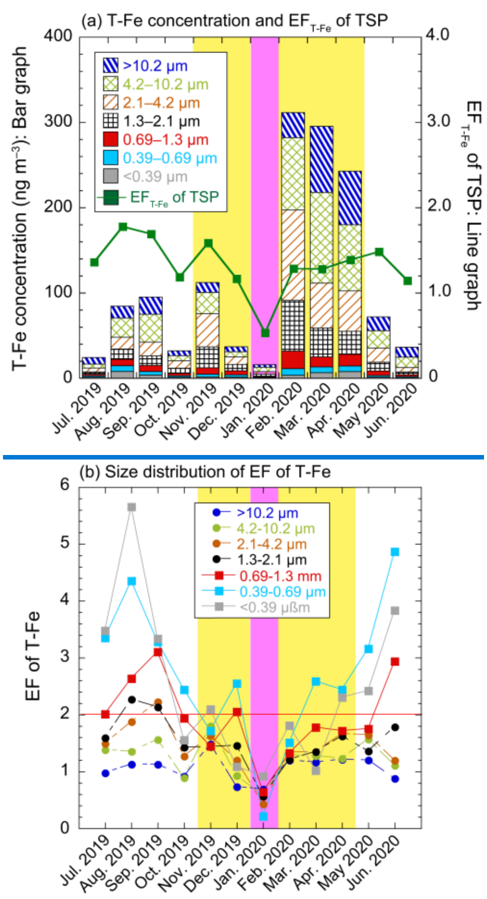
~~3.1. Backward and forward trajectories~~

~~This study categorized aerosol samples into two groups based on backward and forward trajectory analyses (Figs. S2 and S3). The first group was defined as the Japanese air mass (JPN period: July–October 2019 and May–June 2020). Air masses arriving at the sampling site (NOTOGRO) during the JPN period originated from the domestic region of Japan and its marginal sea (Fig. S2a). In addition, forward trajectory analyses indicated that these air masses were not transported to the North Pacific Ocean (Fig. S3a). The second group was defined as the East Asian outflow period (EAout period: November 2019–April 2020; seasons: winter and spring). During the EAout period, air masses arriving at the sampling site originated from East Asia and were subsequently transported to the Pacific Ocean (Figs. S2b and S3b).~~

~~3.2.~~3.1. Monthly variation and size distributions of T-Fe and $EF_{T\text{-}Fe}$

~~Atmospheric~~The atmospheric T-Fe concentration ~~in~~of total suspended particulates (TSPs: sum of the all~~-~~ size fractions) ranged from 15.6 ng m^{-3} to 312 ng m^{-3} (Fig. 3a, average ± standard deviation ~~(~~[avg ± 1σ: 113 ± 108 ng m^{-3}~~).~~]). Coarse aerosol particles (>1.3 μm) accounted for 84.8% ± 5.6% of the T-Fe ~~in~~concentration of TSPs (Fig. 3a). ~~Concentrations~~The concentrations of T-Fe and typical mineral elements (i.e., Al, Ti, and non-sea-salt Ca^{2+}) were higher ~~from~~in February~~ to~~–April than in other seasons due to the long-range transportation of Asian dust (Figs. 3a and S4, Uematsu et al., 1983; Zhu et al., 2020; Kawai et al., 2021). The annual average of $EF_{T\text{-}Fe}$ ~~in~~of TSP samples was 1.3 ± 0.3 (Fig. 3a), which was identical to that ~~for~~of coarse aerosol particles ($EF_{T\text{-}Fe}$: 1.3 ± 0.4, Fig. ~~2b~~3b). This result indicated that T-Fe in ~~TSP~~TSPs and coarse aerosol particles ~~were~~was mainly derived from mineral dust.

The T-Fe concentrations ~~in~~of fine aerosol particles (sum of the <0.39~~ μm~~, 0.39–0.69~~ μm~~, and 0.~~60~~69–1.3 μm fractions) varied from 4.1 ng m^{-3} to 31.7 ng m^{-3} (avg ± 1σ: 14.0 ± 10.2 ng m^{-3}, Fig. 3a). The annual average of $EF_{T\text{-}Fe}$ was 2.2 ± 1.0, indicating that anthro-Fe was ~~one of the sources~~a source of T-Fe in fine aerosol particles (Fig. 3b). ~~The~~The highest $EF_{T\text{-}Fe}$ was usually found in the 0.39–0.69 μm size fraction, indicating that the relative contribution of anthro-Fe to T-Fe in fine aerosol particles was the largest ~~in the 0.39–0.69 μm size fraction, owing to the high $EF_{T\text{-}Fe}$ (Fig.~~(Fig. 3b). This result ~~is consistent~~agreed with the findings of previous studies ~~using~~that used the Fe isotope ratio (Kurisu et al., 2016). The $EF_{T\text{-}Fe}$ ~~in~~of the fine aerosol particles showed distinct seasonal variations, with higher values during the JPN period (2.9 ± 0.8) than during the EAout period (1.5 ± 0.5; Fig. 3b). This result indicated that the relative abundance of anthro-Fe to that of T-Fe in fine aerosol particles was higher during the JPN period than during the EAout period~~,~~ likely due to the greater contribution of Asian dust in spring than that in other seasons (Fig. 3a). However, ~~this~~the lower relative abundance of anthro-Fe to that of T-Fe did not necessarily indicate a ~~lower~~low absolute concentration of anthro-Fe. Indeed, the absolute anthro-Fe concentration ~~in~~of fine aerosol particles during the JPN period (avg ± 1σ: 6.6 ± 5.6 ng m^{-3}, range: 2.8–16.4 ng m^{-3}) was slightly lower than the anthro-Fe concentration during the EAout period, excluding the lockdown period (avg ± 1~~σ:~~ σ: 8.2 ± 4.1 ng m^{-3} ~~ng m~~$^{-3}$, range: 0–14.0 ng m^{-3}). The reduction in anthro-Fe concentration by the limitation of human activities during the COVID-19 lockdown period highlighted the importance of anthro-Fe as ~~the~~a source of Fe in fine aerosol particles. The $EF_{T\text{-}Fe}$ of the fine aerosol particles ~~in~~during the ~~lockdown~~COVID-19lockdown period (January 2019, $EF_{T\text{-}Fe}$: 0.~~45) were~~5) was lower than those ~~in~~during the periods of pre-lockdown (December 2019, $EF_{T\text{-}Fe}$: 1.9) and post-lockdown (February 2020, $EF_{T\text{-}Fe}$: 1.4, Fig. 3b~~) periods.~~). Similarly, in Hangzhou, China, the $EF_{T\text{-}Fe}$ ~~in~~of $PM_{2.5}$ during the COVID-19 lockdown ~~in Hangzhou, China~~period ($EF_{T\text{-}Fe}$: 1.6) was ~~much~~considerably lower than ~~$EF_{T\text{-}Fe}$ in~~those during the periods of pre-lockdown ($EF_{T\text{-}Fe}$: 13.3) and post-lockdown ($EF_{T\text{-}Fe}$: 6.6, Liu et al., 2021~~) periods.~~). The decrease in $EF_{T\text{-}Fe}$ was attributed to the decrease in the emission of Fe-rich particles ~~emitted~~ from non-exhaust vehicle sources (Li et al., 2022), which, in turn, were emitted from the abrasion processes of brake rings and tire ~~ware~~wear. Furthermore, the Fe concentrations in $PM_{2.5}$ collected in Tangshan and Wuhan decreased because of the reduction in anthropogenic emissions, including those from the steel industry (Zheng et al., 2020; Xu et al., 2022). ~~Thus~~Therefore, anthro-Fe was ~~one of the~~a dominant ~~sources~~source of Fe in fine aerosol particles in East Asia under normal conditions.



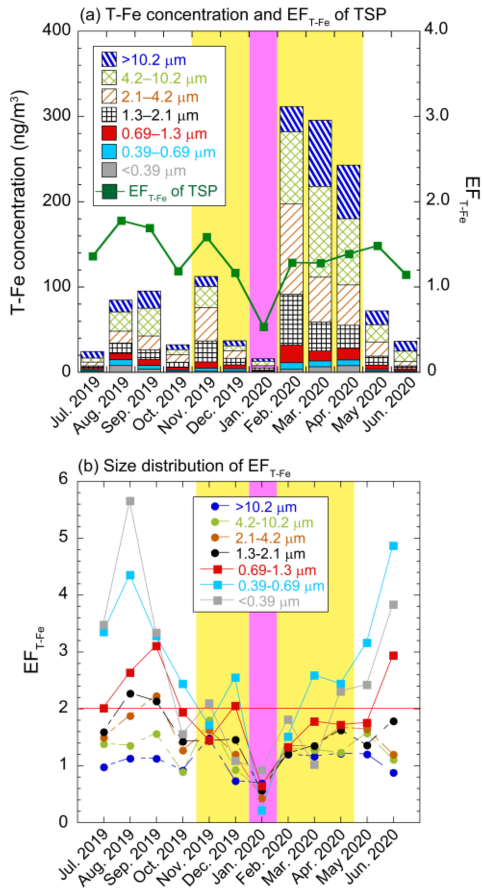


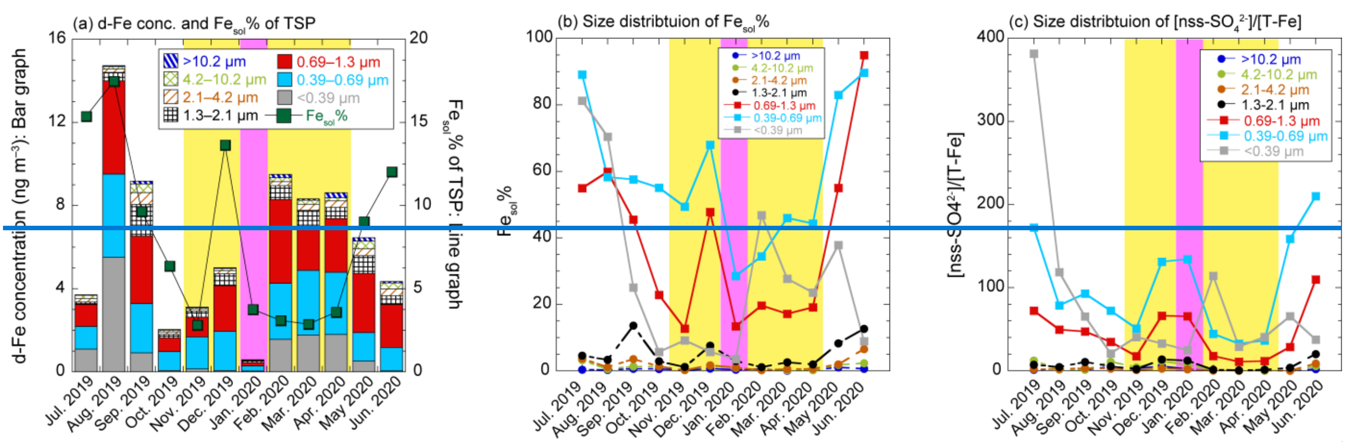
Figure 3. (a) Monthly variations in T-Fe concentration and EF$_{T-Fe}$ in TSPs and (b) size distributions of ~~(a) T-Fe concentration in TSP, (b)~~ EF$_{T-Fe}$ (red line: EF$_{T-Fe}$ ~~is~~= 2.0). The data of coarse aerosol particles are shown in dashed boxes or lines, ~~while the data~~whereas those of fine aerosol particles are described in solid boxes or lines. Yellow and pink shaded regions show the EAout and COVID-19 lockdown periods, respectively.

~~3.3.~~3.2. Monthly ~~variation~~variations and size distributions of d-Fe, Fe$_{sol}$%, and [d-Fe]/[d-Al] ratio

~~3.3.1.~~3.2.1. Coarse aerosol particles

The d-Fe concentrations and Fe$_{sol}$% ~~in~~of TSPs varied from 0.6 ng m^{-3} to 14.7 ng m^{-3} (avg ± 1σ: 6.3 ± 4.0 ng m^{-3}) and ~~from~~ 2.8% to 17.4% (avg ± 1σ: 8.3% ± 5.3%), respectively (Fig. 4a). The seasonal average Fe$_{sol}$% of ~~TSP~~TSPs for the EAout ~~periods~~period (avg ± 1σ: 4.9% ± 4.3%) were lower than those for the JPN period (avg ± 1σ: 11.6% ± 4.2%). ~~The~~ Consistent with those of the TSP samples collected during the EAout period, the Fe$_{sol}$% ~~values in~~of TSPs collected over the Pacific Ocean were typically 1.0–%–10~~%, consistent with those in our TSP samples collected during the EAout period~~% (Table S3). In line with previous observations in Japan (Sakata et al., 2023, Takahashi et al., 2013~~The d-Fe~~), the d-Fe concentration ~~in~~of the TSPs decreased from August ~~2019 ~~to January~~ 2020 and~~, then increased from January to June ~~2020, consistent with previous observations in Japan (~~(Fig. 4a~~;)~~.~~Sakata et al., 2023, Takahashi et al., 2013).~~ The d-Fe concentration ~~in TSP~~of TSPs from July 2019 to January 2020 was controlled by factors that ~~affect~~affected Fe_{sol}% (e.g., emission sources and chemical ~~alteration~~alterations of Fe-bearing particles) ~~because monthly variations were similar between~~ considering that d-Fe concentration and Fe_{sol}% ~~in the~~ showed monthly variations during this period (Fig. 4a). ~~In~~By contrast, the d-Fe concentrations ~~in~~of TSPs collected from February to April were considerably higher than those of the ~~d-Fe concentration~~samples collected in ~~the~~ January~~ sample, but~~, whereas the Fe_{sol}% ~~values in~~of TSPs collected from February to April were almost the same as that of the samples collected in January ~~sample~~ (Fig. 4a). In this case, the atmospheric concentration of d-Fe increased because of the large ~~loading of~~ mineral dust load in the atmosphere.

The Fe_{sol}% of coarse aerosol particles (avg ± 1σ: 2.2% ± 3.0%, range: 0.1%–13.6%) was slightly higher than that of typical mineral dust (<1%, Fig. 4b). The [d-Fe]/[d-Al] ratio ~~in~~of coarse aerosol particles (avg ± 1σ: 0.28 ± 0.12, range: 0.13–0.82) was ~~consistent~~in line with that of d-Fe dissolved from Asian dust ~~by~~through proton-promoted dissolution (0.24 ± 0.20, Figs. 5a and 5b~~). This result indicates~~), indicating that d-Fe in coarse aerosol particles mainly originated from the proton-promoted dissolution of mineral dust. Indeed, the ~~correlation of~~ Fe_{sol}% ~~with [nss-SO_4^{2-}]/[T-Fe], further supports the contribution of proton-promoted dissolution to Fesol% in~~of coarse aerosol particles was correlated with the [nss-SO_4^{2-}]/[T-Fe] ratio as an indicator of the acidity of Fe-bearing particles (Fig. ~~S5a).~~S5a; Zhu et al., 2020, 2022; Liu et al., 2022). Furthermore, the Fe_{sol}% ~~in the~~of coarse aerosol particles increased with decreasing aerosol diameter because of ~~increasing~~ the increase in specific surface area, which is ~~one of the factors~~a factor controlling aerosol reactivity (Fig. 4b). A similar result was obtained by ~~the~~an observational study at Higashi-Hiroshima, Japan (Sakata et al., 2023). Therefore, Fe % in coarse aerosol particles collected at NOTOGRO is mainly governed by proton-promoted dissolutions.



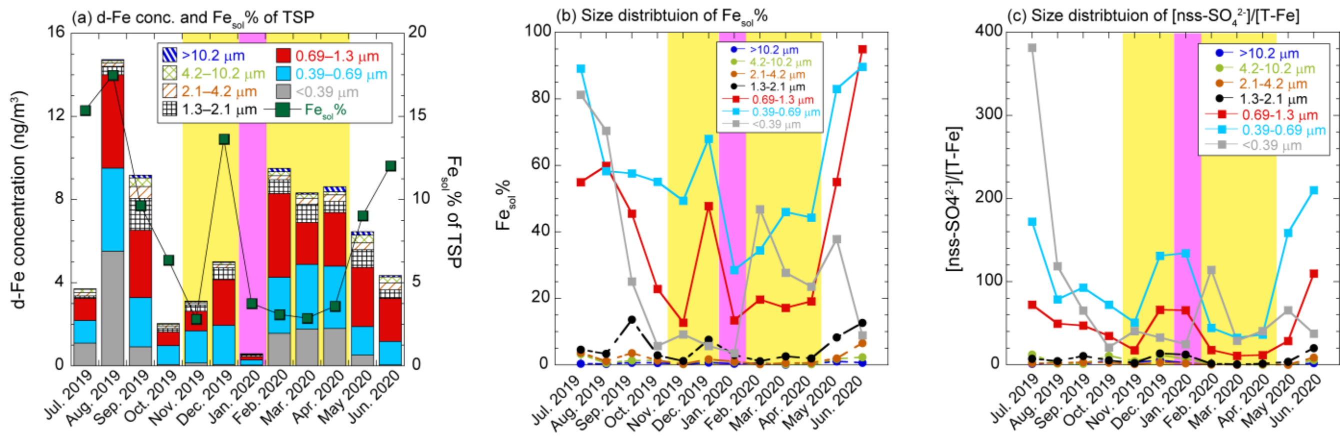
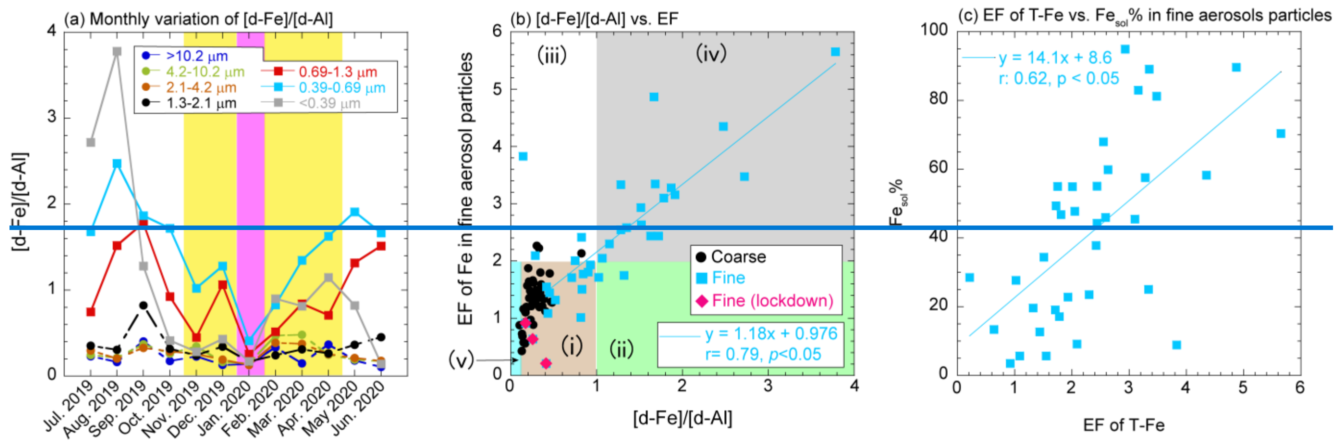


Figure 4. (a) d-Fe concentration and Fe$_{sol}$% ~~in TSP~~of TSPs; (b) Fe$_{sol}$~~%,~~%; and (c) the [nss-SO^{4}$_{2-}$~~]/[~~-]/[T-Fe~~].~~] ratio. The data of coarse aerosol particles are shown in dashed boxes or lines, ~~while the data~~whereas those of fine aerosol particles are ~~described~~presented in solid boxes or lines. Yellow and pink ~~shaded regions show~~areas indicate the EAout and COVID-19 lockdown periods, respectively.

~~3.3.2.~~3.2.2. Fine aerosol particles

The summation of d-Fe in fine aerosol particles varied from 0.5 ng m^{-3} to 14.0 ng m^{-3} (avg ± 1σ: 5.3 ± 3.7 ng m^{-3}), accounting for 71.1–%–94.8% (avg ± 1σ: 81.7% ± 7.0%) of d-Fe in ~~the~~ TSPs (Fig. 4a). The Fe$_{sol}$% ~~in~~of each size fraction of fine aerosol particles (avg ± 1σ: 42.1% ± 25.6%, range: 4.1–%–94.9%) was an order of magnitude higher than ~~those in~~that of coarse aerosol particles (Fig. 4b). As mentioned above, the Fe$_{sol}$% ~~in~~of our TSP samples ~~were~~was identical to ~~those in~~that of Pacific aerosol (Table S3), and the size distribution of the Fe$_{sol}$% of our samples ~~was consistent~~agreed with that reported by previous observational studies conducted in East Asia and the Pacific Ocean (Sakata et al., 2022, 2023; Kurisu et al., 2024). ~~Thus~~Therefore, fine aerosol particles transported from East Asia play an essential role in the supply of d-Fe to the North Pacific Ocean. Chemical alterations, including aerosol acidification, was ~~one of the factors~~a factor increasing the Fe$_{sol}$% ~~in~~of fine aerosol particles because the Fe$_{sol}$% of fine aerosol was correlated with the molar ratio of non-sea-salt sulfate to that of T-Fe ([nss-SO$_4^{2-}$]/[T-Fe]; Fig. S5b). ~~Iron~~Fe-bearing particles in fine aerosol particles were more acidified than those in coarse aerosol particles ~~because~~considering that the annual average of the [nss-SO$_4^{2-}$]/[T-Fe] ~~in~~ratio of fine aerosol particles (avg ± 1σ: 75 ± 71, range: 11–381) was higher than that ~~in~~of coarse aerosol particles (avg ± 1σ: 4 ± 5, Fig. 4c). The average [nss-SO$_4^{2-}$]/[T-Fe] ratio for the JPN period (avg ± 1σ: 101 ± 87) was higher than that for the EAout period (avg ± 1σ: 50 ± 39; Fig. 4c). This result indicated that consistent with the higher Fe$_{sol}$% in the JPN period than that in the EAout period, the fine aerosol particles collected ~~for~~during the JPN period were more acidified than those ~~for the EAout period, consistent with higher Fe$_{sol}$% in the JPN period than in~~collected during the EAout period.

The [d-Fe]/[d-Al] ratio in fine aerosol particles ranged from 0.14 to 3.78 (avg ± 1σ: 1.18 ± 0.77, Fig. 5a~~). Ligand~~), with these values being higher than those in coarse aerosol particles (Fig. 5b). Factors potentially contributing to an increased [d-Fe]/[d-Al] ratio in aerosols include ligand-promoted Fe dissolution ~~of~~from mineral dust ~~can increase [d-Fe]/[d-Al] ratio in aerosol particles, but this process~~and the contribution of anthro-Fe to d-Fe. However, considering the absence of aerosol samples in area (iv) as illustrated in Fig. 5b, ligand-promoted dissolution was not the primary cause of the high [d-Fe]/[d-Al] ratio ~~because of the absence of aerosol samples in the area (iv) in Fig. 5b. Although~~in fine aerosol particles. Therefore, the elevated [d-Fe]/[d-Al] ratio in fine aerosol particles ~~was higher than coarse aerosol particles because of~~is primarily attributed to the influence of anthro-Fe ~~with high [d-Fe]/[d-Al] ratio (Fig. 5b), the ratio reflected the values characteristic of mineral dust only during the COVID-19 period (pink diamonds in Fig. 5b). This result indicates that anthro-Fe is a dominant source of d-Fe under normal conditions. Furthermore~~. Indeed, the data for fine aerosol particles plotted along the mixing line between proton-promoted dissolution of mineral dust and highly soluble anthro-Fe (Fig. 5b) indicate that these two processes are ~~the~~ dominant sources of d-Fe ~~in fine aerosol particles (Fig. 5b).~~. The significant contribution of d-Fe from highly soluble anthro-Fe was further supported by the correlation between $EF_{T\text{-}Fe}$ and $Fe_{sol}\%$ ~~in fine aerosol particles (Fig. 5c).~~ of fine aerosol particles (Fig. 5c). Furthermore, observations during the COVID-19 lockdown period provide crucial insights into the importance of anthro-Fe as a source of d-Fe under normal conditions. This is because the [d-Fe]/[d-Al] ratio in fine aerosol particles collected during the lockdown period was similar to that of mineral dust (pink diamonds in Fig. 5b), suggesting a reduced influence of anthropogenic sources on d-Fe during the lockdown.



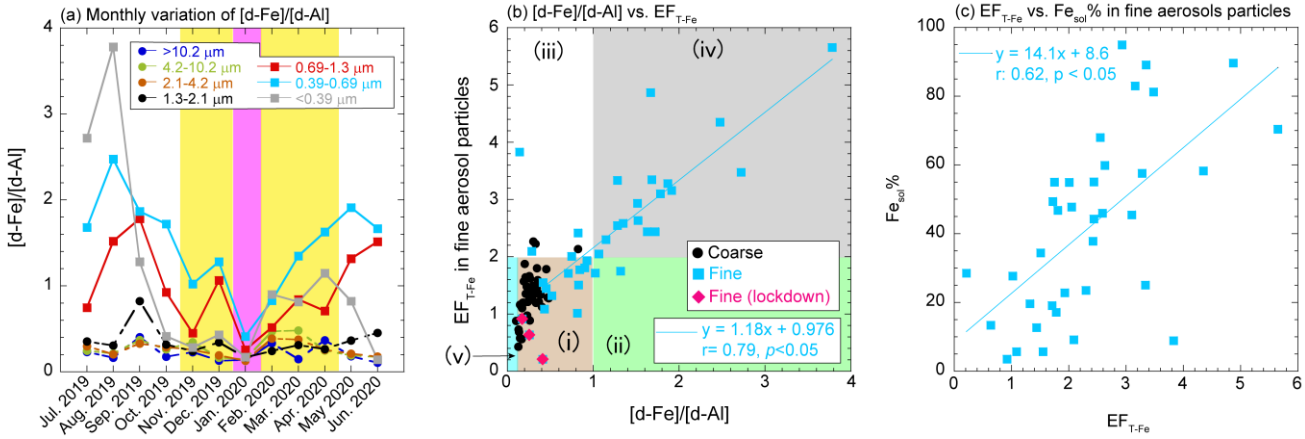


Figure 5. (a) ~~A size~~Size distribution of the [d-Fe]/[d-Al] ratio. ~~The yellow~~Yellow and pink areas ~~are shown in~~indicate the ~~JPN~~EAout and COVID-19 lockdown periods~~.~~, respectively. (b) relationships of $EF_{T\text{-}Fe}$ and the [d-Fe]/[d-Al] ratio. The background color indicates the emission sources of T-Fe and d-Fe, which are detailed in Fig. 2. (c) ~~a correlation~~Correlation between $EF_{T\text{-}Fe}$ and Fe_{sol}%.

The annual average ~~of~~ F_{anthro} ~~in~~of fine aerosol particles was 46.2% ± 26.3% (range: 1.4~~–~~%–100%) and was higher during the JPN period than during the EAout period (Fig. ~~6a). The F_{anthro} was most often the highest in the 0.39–0.69 µm fraction (Fig. 6a), consistent~~6a). Consistent with the results from previous studies using ~~the~~ [d-Fe]/[d-Al] and Fe isotope ratios (Kurisu et al., 2016; Sakata et al., 2023~~). In TSPs, the~~), T-Fe in the 0.39–0.69 µm fraction was most influenced by anthro-Fe due to the highest F_{anthro} (Fig. 6a). The seasonal average ~~of~~ F_{anthro} values ~~for~~ of TSPs collected during the JPN and EAout periods were 33.7% ± 20.9% and 16.6% ± 9.6%, respectively. The lower F_{anthro} ~~in~~of TSPs than of fine aerosol particles was attributed to the large contribution of mineral dust in coarse aerosol particles, especially during the EAout period. A similar result has been reported by a previous study performed in Higashi-Hiroshima, Japan, in 2013 (range: 1.~~48–~~5%–80.7%, JPN: 29.4% ± 25.8%, EAout: 13.5% ± 10.6%, Sakata et al., 2023). Although annual anthro-Fe emissions in China are an order of magnitude higher than those in Japan (Kajino et al., 2020), the lower F_{anthro} in the EAout period compared with that in the JPN period can be ~~attributed~~ascribed to the ~~large~~extensive emission of mineral-Fe, especially in spring. ~~Thus,~~Therefore, although mineral dust was the most dominant source of d-Fe in TSPs collected at the eastern end of East Asia, ~~but~~ the contribution of anthro-Fe to d-Fe ~~cannot be~~was not negligible.

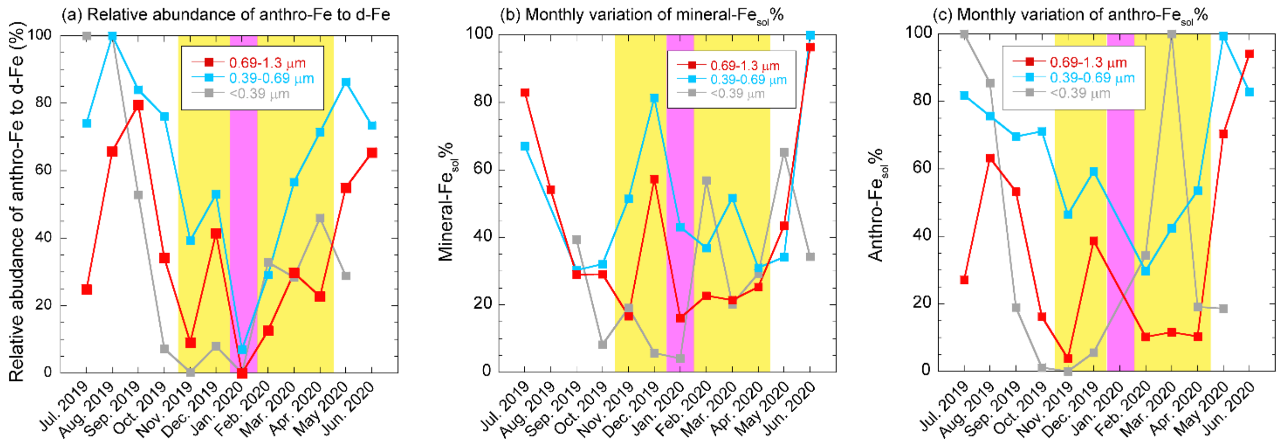


Figure 6. ~~(a) A size distribution of [d-Fe]/[d-Al] ratio. (b) relationships of EF$_{T-Fe}$ and [d-Fe]/[d-Al] ratio. Background color indicates the major sources of T-Fe and d-Fe in aerosols. The (c) a correlation between EF$_{T-Fe}$ and Fe$_{sol}$%. (d–f) monthly~~Monthly trends of the relative ~~abundance~~abundances of anthro-Fe to those of (a) d-Fe, (b) mineral-Fe$_{sol}$%, and (c) anthro-Fe$_{sol}$% in fine aerosol particles~~, respectively. The yellow~~. Yellow and pink ~~areas are shown in~~shaded regions show the ~~JPN~~EAout and COVID-19 lockdown periods, respectively. The plots of anthro-Fe$_{sol}$% in panel (c) are missing because either or both anthro-Fe or anthro-dFe concentrations were 0 due to the remarkable but small contributions of anthro-Fe during the COVID-19 lockdown period.

~~3.4.~~3.3. Fe$_{sol}$% of mineral dust and anthropogenic aerosols

The annual average of mineral-Fe$_{sol}$% (40.5% ± 24.8%) was ~~much~~considerably higher than the Fe$_{sol}$% of coarse aerosol particles (Fig. 6b). ~~Considering~~Given that the Fe$_{sol}$% of mineral dust at ~~the~~ emission is typically ~~lower~~less than 1% regardless of aerosol diameter (Shi et al., 2011b), the high mineral-Fe$_{sol}$% values ~~observed in~~of fine aerosol particles were caused by the severe chemical alteration, including proton-promoted dissolution, of mineral dust. Indeed, mineral-Fe$_{sol}$% was correlated with [nss-SO_4^{2-}]/[T-Fe~~],~~] ratios, which were plotted on an extension of the approximate line for coarse aerosol particles (Fig. S6a). This result indicated that similar to that in coarse aerosol particles, mineral dust in fine aerosol particles underwent ~~similar~~ alteration processes~~ to those in coarse aerosol particles, but~~. However, the extent of ~~chemical alteration~~aerosol acidification differed between coarse and fine aerosol particles. ~~Despite~~Although mineral dust in fine aerosol particles exhibited high Fe$_{sol}$%, the annual average mineral-Fe$_{sol}$% ~~in TSP is~~of TSPs was only 4.4% ± 2.3% (range: 1.9–%–9.5%) owing to the low Fe$_{sol}$% of mineral dust in coarse aerosol particles. This finding ~~emphasizes~~emphasized the importance of the ~~chemical alterations~~proton-promoted dissolution of mineral dust in fine aerosol particles for the d-Fe supply via mineral dust deposition. Notably, ligand-promoted dissolution is considered a process that increases the Fe$_{sol}$% of mineral dust. However, the contribution of ligand-promoted Fe dissolution was likely small because there were almost no plots of aerosol particles in region (ii) of Fig. 5b, a region where this process is a major contributor to mineral dust.

The annual average of anthro-Fe_{sol}% was 46.7% ± 32.9~~%, which~~% and was higher in the JPN period than in the EAout period (Fig. 6c). ~~The anthro~~Anthro-Fe_{sol}% can be enhanced not only by the chemical alteration of anthropogenic aerosols but also by the direct emission of highly soluble anthro-Fe emitted from liquid fuel ~~combustions~~combustion, including fuel oil and gasoline (Fe_{sol}%: up to 80%, Sedwick et al., 2007; Sholkovitz et al., 2009; Schroth et al., 2009; Oakes et al., 2012). However, the contribution of anthro-Fe from liquid fuel combustion to T-Fe and d-Fe in our samples was not ~~significant~~remarkable, as described in the following section (Fig. 7). Therefore, the seasonal ~~fluctuation~~variation in anthro-Fe_{sol}% is primarily controlled by the extent of the chemical alterations of anthro-Fe~~.~~, including aerosol acidification. This finding is supported by the strong correlation between anthro-Fe_{sol}% and the [nss-$SO4^{2-}$]/[T-Fe] ratio (Fig. S6b). Notably, anthro-Fe_{sol}% tended to be higher than mineral-Fe_{sol}% during the JPN period~~,~~ (summer), whereas the opposite was true during the EAout period~~,~~ (winter), with mineral-Fe_{sol}% exceeding anthro-Fe_{sol}% (Figs. S6c–S6e). This shift is likely attributable to the differing sensitivities of mineral-Fe_{sol}% and anthro-Fe_{sol}% to changes in aerosol acidity (further details are discussed in Section 3.~~8).~~7).

~~3.5.~~3.4. ~~Sources~~Source apportionment of Fe in fine aerosol particles by PMF

~~3.5.1.~~3.4.1. Sources of T-Fe and anthro-Fe

Six factors were identified as sources of fine aerosol particles during the JPN+EAout period: (~~1~~i) sea spray aerosol and ~~less-aged~~fresh mineral dust (hereafter ~~and~~ referred to as fresh dust~~), (2~~; Fig. S7a), (ii) aged mineral and road dust (hereafter referred to as aged dust~~), (3~~; Fig. S7b), (iii) the steel industry~~, (4~~ (Fig. S7c), (iv) heavy oil combustion~~, (5~~ (Fig. S7d), (v) the non-steel industry~~,~~ (Fig. S7e), and (~~6~~vi) secondary sulfate aerosol and dissolved metals formed through aerosol acidification (hereafter referred to as secondary aerosol~~.~~; Fig. ~~S7). Here,~~S7f). Fresh and aged dust ~~includes~~factors (factors i and ii) included mineral-Fe and anthro-Fe, such as non-exhaust vehicle particles in road dust. The primary sources of the precursors of secondary sulfate aerosols (factor iv) and metal elements were mainly derived from coal combustion, as indicated by the large contributions of K, Zn, Cd, and Pb as the tracer elements of its emission. Detailed classification methods, including the tracer elements used for each factor, are described in the Supplemental Information. ~~It should be noted that several~~Several factors grouped into multiple emission sources ~~due to the~~ because of their similar emission processes and/or physicochemical properties. For instance, sea spray aerosols and ~~less-aged mineral~~fresh dust ~~in~~grouped into factor ~~1, both of which~~(i). Both are ~~wind~~ blown by the wind from their sources~~,~~ and are likely to exhibit covarying atmospheric concentrations. Consequently, the PMF model may have limitations in resolving covariant sources (Pindado and Perez, 2011).

Next, PMF analyses were performed individually by using fine aerosol particles collected during the JPN and EAout periods to evaluate the seasonal average contribution of each factor to T-Fe, anthro-Fe, and d-Fe (~~Fig~~Figs. 7 and S7). Moreover, the $EF_{T\text{-}Fe}$, Fe_{sol}%, and [d-Fe]/[d-Al] ratio of each factor were ~~also~~ estimated by PMF for each period (Tables S4 and S5). The same factors were identified as the dominant sources of fine aerosol particles during the JPN period (Fig. S8). While heavy oil combustion was not identified as a ~~significant~~major source of fine ~~saerosol~~aerosol particles during the EAout period, the other five emission sources remained important contributors to the source of fine aerosol particles in this period~~.~~ (Fig. S9). These results are reasonable because the PMF analysis of the JPN+EAout period ~~showed~~revealed a small contribution to~~ the~~ heavy oil combustion during the EAout period (Fig. S7d). T-Fe in fine aerosol particles during the JPN and EAout periods were mainly derived from the steel industry ~~followed by~~, then from aged dust, fresh dust, and secondary aerosol (Figs. 7a and 7d). Anthro-Fe in fine aerosol particles collected during the JPN period originated from the steel industry (36.8%) and secondary aerosols associated with high-temperature combustion (27.1%, Fig. 7b). Given that ~~sulfur dioxide~~SO_2, a precursor of sulfate aerosols in East Asia, was mainly emitted from coal ~~combustions~~combustion (Wang et al., 2014; Kurokawa and Ohara, 2020), ~~the~~ anthro-Fe in the secondary aerosol factor was also emitted from coal combustion. Non-exhaust vehicle particles in aged and fresh ~~dusts~~dust contributed ~~an~~to anthro-Fe sources (28.5%, Fig. 7b). ~~Thus~~Therefore, anthro-Fe in fine aerosol particles originated from high-temperature ~~combustions~~combustion and non-combusted anthro-Fe. This result is consistent with the anthro-Fe ~~source~~sources in Japanese $PM_{2.5}$ estimated by a ~~semi-bottom~~semibottom-up model (Kajino et al., 2020): the steel industry (20–%–50%), brake pad debris (20–%–40%, main components of non-exhaust vehicle particles), and coal-fired power plants (10–%–20%). During the EAout period, approximately 80% and 20% of anthro-Fe originated from the steel industry and non-exhaust vehicle particles in aged dust + fresh dust factors, respectively (Fig. 7e). This result ~~is consistent~~was in line with ~~the results of previous studies~~previously reported findings because approximately 90% and 60% of anthropogenic nanoparticles (mainly composed of magnetite) and anthro-Fe were emitted from the steel industry in China, respectively (Li et al., 2021; Chen et al., ~~2021). The importance of the steel industry as the source of anthro-Fe was emphasized by the reduction of human activities by the COVID-19 lockdown because the normalized contribution of the steel industry in the lockdown period was considerably low compared with that in pre- and post-lockdown periods (Fig. S7c).~~ 2021).

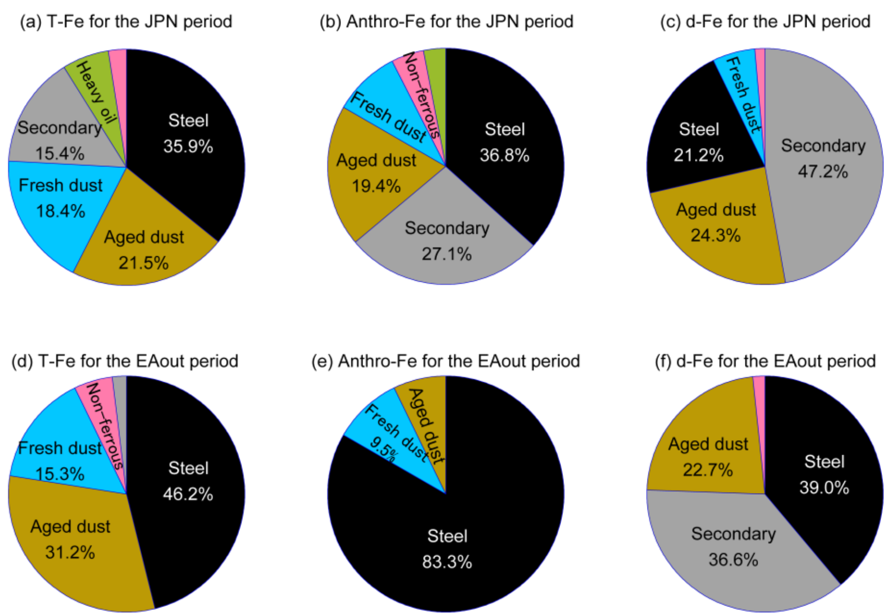


Figure 7. ~~The~~ Panels (a-c) show average ~~contribution of the emission sources~~contributions to ~~(a)~~ T-Fe, ~~(b)~~ anthro-Fe, and ~~(c)~~ d-Fe ~~in fine aerosol particles collected~~ , respectively, for the JPN period. Panels (d-f) ~~the same figures during the~~ show contributions to T-Fe, anthro-Fe, and d-Fe, respectively, for the EAout period.

As mentioned previously, the contribution of anthro-Fe to T-Fe in fine aerosol particles collected during the COVID-19 lockdown was almost 0 because EF_{T-Fe} in these samples was less than 1.0 (Fig. 3b). The normalized factor contribution of the steel industry during the COVID-19 lockdown period was significantly lower than those during the pre-lockdown and post-lockdown periods (Fig. S7c). This result indicated that the steel industry was the dominant source of anthro-Fe. The importance of the steel industry as the source of anthro-Fe was emphasized by the reduction in human activities caused by the COVID-19 lockdown considering that the normalized contribution of the steel industry during the lockdown period was considerably lower than that during the pre- and post-lockdown periods.

~~3.5.2.~~3.4.2. Sources of d-Fe

PMF analysis indicated that d-Fe in the fine aerosol particles collected during the JPN and EAout periods originated from three primary sources: the steel industry, aged dust, and secondary aerosol formation (Figs. 7c and 7f). The steel industry factor can be characterized by the highest EF_{T-Fe} (JPN: 3.9, EAout: 4.9). Given that non-atmospherically aged Fe-rich particles collected from the steel plants are likely insoluble (Li et al., 2017), the Fe-rich particle unlikely contributed to increasing the [d-Fe]/[d-Al] ratio without chemical alteration in the atmosphere (Fig. 2). However, the [d-Fe]/[d-Al] ratio in the steel industry factor (JPN: 5.67, EAout: 1.20) is higher than 1.0 and their Fe_{sol}% showed high water solubility (JPN: 31.8%, EAout: 22.4%). Therefore, insoluble Fe-rich particles released from steel plants are thought to transform into d-Fe in the atmosphere. This is supported by the high [nss-SO_4^{2-}]/[T-Fe] ratio of the steel industry factor, despite Fe-rich particles collected at the plants lacking sulfur (Li et al., 2017; Zhu et al., 2020, 2022). This indicates atmospheric reactions with H_2SO_4, leading to an increased Fe_{sol}% for the steel industry factor.

Moreover, the Fe_{sol}% exhibited by aged dust (JPN: 60.6%, EAout: 19.3%) was considerably higher than that shown by fresh mineral dust (typically less than 1.0%; Shi et al., 2011b), indicating that Fe in the aged dust factor also dissolved through chemical alterations in the atmosphere. The fresh dust factor had a [nss-SO_4^{2-}]/[T-Fe] ratio of 0, whereas the aged dust factor had a high [nss-SO_4^{2-}]/[T-Fe] ratio, indicating that aged dust was subjected to the effects of aerosol acidification by H_2SO_4 (Tables S4 and S5). The [d-Fe]/[d-Al] ratio of the aged dust factor (JPN: 0.92, EAout: 0.69) was within that of mineral dust originating from proton-promoted dissolution but was higher than the average ratio of coarse aerosol particles minimally influenced by aerosol acidification (0.28 ± 0.12). As mentioned above, the aged dust fraction contained non-exhaust vehicle emissions (e.g., brake rings and tire wear debris), which were mainly present in the form of Fe-rich particles, such as Fe oxides (Sanderson et al., 2016; Li et al., 2022; Fu et al., 2023). Given that the Fe_{sol}% values of brake ring and tire wear debris were less than 0.01% in the absence of chemical alterations, including proton- and ligand-promoted dissolutions (Shupert et al., 2013; Halle et al., 2021), the increase in the [d-Fe]/[d-Al] ratio of the aged dust factor may have been caused by the dissolution of Fe from these materials during chemical alterations in the atmosphere. Previous research suggests that tire wear acts as an emission source of d-Fe in $PM_{2.5}$ (Fang et al., 2015), which can be dissolved by SO_2 emitted from coal combustion (Wong et al., 2020). Although further research is needed, our findings indicate that NEV particles, such as brake ring particles, can also be a source of d-Fe via aerosol acidification in the atmosphere.

The considerable contribution of the secondary aerosol factor to d-Fe highlights the importance of aerosol acidification in the dissolution of Fe from fine aerosol particles. As mentioned previously, the secondary aerosol factor is ~~significantly~~markedly influenced by coal combustion, a primary source of SO_2, and ~~this~~ can be a source of d-Fe in ~~aerosols.~~aerosol particles. However, d-Fe in the ~~factors~~above factor likely originated from not only coal ~~combustions~~combustion but also ~~d-Fe~~ dissolved from other factors (e.g., aged dust and the steel industry) because the d-Fe concentrations within the secondary aerosol factor exceeded T-Fe concentrations (Tables S4 and S5). ~~The reason is that~~ PMF methods ~~is~~were unable to distinguish between direct d-Fe emissions from coal combustion and d-Fe dissolution from ~~aerosols~~aerosol particles acidified by SO_2 emitted from coal combustion due to the covariance of d-Fe concentration with the nss-SO_4^{2-} concentration, a limitation that has also been observed in previous studies (Zhu et al., 2022; Gao et al., 2024; Sun et al., 2024). The contribution of d-Fe ~~in~~to the secondary aerosol factor in this study was higher than those reported for fine aerosol particles collected in urban areas in China ~~because~~as a result of the further chemical alterations of Fe-bearing particles during transport from China to Japan (Zhu et al., 2022; Gao et al., 2024; Sun et al., 2024). ~~Furthermore, the Fe_{sol}% of aged dust (JPN: 60.6%, EAout: 19.3%) and steel industry (JPN: 31.8%, EAout: 22.4%) were higher than those at the emissions (Ito et al., 2021; Li et al., 2017) because a part of d-Fe dissolved by the chemical alteration of Fe was included in these factors. Thus~~Therefore, PMF analysis showed that ~~atmospheric processes~~the aerosol acidification of mineral dust and anthro-Fe ~~play~~plays an important role in the source of d-Fe in fine aerosol particles.

~~The PMF-estimated [d-Fe]/[d-Al] ratios for the steel industry were 5.67 and 1.20 for the JPN and EAout periods, respectively. This result indicated that the high [d-Fe]/[d-Al] ratio in fine aerosol particles was mainly attributed to the d-Fe dissolved from anthro-Fe emitted from the steel industry. By contrast, the [d-Fe]/[d-Al] ratio in the factor of aged dust (JPN: 0.92, EAout: 0.69) was within the range of mineral dust of proton-promoted dissolution, but the ratio was higher than the average ratio for coarse aerosol particles less influenced by aerosol acidification (= 0.28 ± 0.12). As mentioned above, the aged dust fraction contained non-exhaust vehicle emissions (e.g., brake rings and tire wear debris). Given that the Fe_{sol}% values of brake ring and tire wear debris were less than 0.01% without chemical alterations (Shupert et al., 2013; Halle et al., 2021), the increase in [d-Fe]/[d-Al] ratio in the factor may have been caused by Fe dissolution from these materials during chemical alterations in the atmosphere. Thus, anthro-Fe emitted from high-temperature combustions and non-vehicle exhaust particles (*i.e.*, non-combusted anthro-Fe) contributed as a source of d-Fe in the fine aerosol particles.~~

~~3.6.~~3.5. Monthly variation and size distributions of Fe species

The abundances of Fe species in size-fractionated aerosol particles were estimated through the linear combination fitting of the XANES spectra of aerosol samples with those of reference materials (Fig. S10). Representative Fe species in coarse aerosol particles were ferrihydrite and Fe in crystalline aluminosilicates (e.g., illite, biotite, and smectite; Figs. S10 and S11), which were similar to the species in mineral dust (Jeong and Achterberg, 2014; Jeong, 2020). ~~Spot~~The spot analyses of Fe species in coarse aerosol particles revealed that the Fe species in most measurement spots were ~~consistent~~in accord with ~~Fe species~~those in coarse aerosol particles detected through macroscopic XANES spectroscopy (Fig. S12a). The ~~sulfur~~S intensity of these measurement spots was ~~not intense~~weak (white circle in Fig. S12d), indicating that ~~less-aged~~fresh mineral dust ~~was dominant~~dominated in the spots. By contrast, Fe(II~~) sulfate and Fe(~~, III)-~~sulfate~~sulfates coexisted with aluminosilicate and Fe-(hydr)oxides in spots with high ~~sulfur~~S intensity (green circle in Figs. S12b–S12d). This result indicated that Fe(II~~)- and Fe(~~, III)-sulfates were present in severely aged mineral dust in ~~the~~ coarse aerosol particles. Fe(II~~)- and Fe(~~, III)-sulfates are water-soluble Fe species~~, which~~ that can enhance Fe_{sol}% in aerosol particles. However, ~~the~~their effects ~~of Fe(II)- and Fe(III)-sulfate~~ on Fe_{sol}% in coarse aerosol particles were not substantial because the abundance of Fe~~-~~ sulfates to that of T-Fe was below the detection limit for macroscopic XANES (Fe-sulfates~~/~~: T-Fe <10%), ~~consistent~~in line with the low Fe_{sol}% in coarse aerosol particles.

Fe(II~~) sulfate, Fe(~~, III)-~~sulfate,~~sulfates and Fe(III)-oxalate were ~~found as~~identified to be representative Fe species in fine aerosol particles (Fig. 8a). ~~Iron~~Fe(III)-oxalate is also known as a water-soluble Fe species. The ~~most important result is that~~correlation of the abundance of these water-soluble Fe species ~~is correlated~~ with the Fe_{sol}% in fine aerosol particles was the most important result (Fig. 8b). ~~To confirm whether these water-soluble Fe species were readily dissolved in water, the~~The Fe species in the residue of ultrapure water extraction (i.e., insoluble Fe species) were determined~~. As a result, crystalline~~ to confirm whether these water-soluble Fe species readily dissolved in water. Crystalline aluminosilicates and Fe oxides (hematite and magnetite) were ~~found~~identified as insoluble Fe species in the residues, whereas Fe(II~~) sulfate, Fe(~~, III)-~~sulfate,~~sulfates and Fe(III)-oxalate were not detected (Fig. S13). ~~Thus, the Fe_{sol}%~~ The water-soluble Fe species in fine aerosol particles ~~were strongly related to the abundance of water-soluble Fe species. These water-soluble Fe species were derived from either or both direct emissions from high-temperature combustion and secondary formation in the atmosphere. Although Fe(II)- and Fe(~~likely formed through the chemical alterations of insoluble Fe, rather than directly emitted from primary sources. Although Fe(II, III)-sulfates are directly emitted from liquid fuel combustion~~ (Schroth et al., 2009; Oakes et al., 2012), these emissions were not identified by the~~ , PMF analysis did not identify these emissions as the dominant source of Fe in fine aerosol particles ~~(Figs. 7e and 7f). Furthermore~~. Similarly, Fe(III)-oxalate ~~has~~was not ~~been~~ detected ~~from~~in the emission source samples of anthro-Fe. ~~Therefore, these water-soluble Fe species were likely formed by the chemical alterations of the Fe in the~~ PMF results indicated that the total Fe in fine aerosol particles~~.~~ mainly originated from fresh and aged dust and the steel industry, with the dominant Fe species being primarily aluminosilicates and Fe-oxide nanoparticles. These Fe species were consistent with the insoluble Fe species identified in fine aerosol particles through XAFS spectroscopy. These primary sources, mineral dust, and steel industry–derived anthro-Fe typically exhibit low Fe_{sol}% without atmospheric chemical alterations. However, PMF analysis also revealed that aged dust and steel industry factors had a high Fe_{sol}%, highlighting the importance of the chemical alterations of Fe in mineral dust and anthro-Fe as key processes enhancing the water solubility of Fe in fine aerosol particles.

Aerosol samples in the 0.39–0.69 and 0.69–1.3 μm fractions contained at least one~~ of the~~ water-soluble Fe species throughout the sampling campaign, whereas the finest fraction did not always contain ~~these~~ water-soluble Fe species (Fig.

5a8a). These results indicated that the degree and process of chemical alterations differs betweendiffered among the finest fraction and the 0.39–0.69 and 0.69–1.3 µm fractions. Previous studies showedhave shown that baredbare Fe-rich particles (= (uncoated with sulfate and oxalate) were mainly present in particles finer than 0.4 µm, which was; these particles are expected to be lessminimally aged by atmospheric processes (Zhu et al., 2020; 2022, Xu et al., 2023). By contrast, Fe-rich particles coated with sulfate and oxalate were approximately 0.6 µm in diameter (Zhang et al., 20192017; Zhou et al., 2020; Zhu et al., 2020, 2022; Xu et al., 2023). Sulfate and oxalate, mainly formed through chemical reactions in cloud water, arewere abundant in fine aerosol particles aroundapproximately 0.7 ± 0.2 µm in diameter (John et al., 1990; Meng and Seinfeld, 1994; Yu et al., 2005; Zhang et al., 2017). This diameter was consistent with those of Fe-bearing particles mixed internally with sulfate and oxalate, which were one of theare components of cloud interstitial particles with a typical diameter of 0.5–1.0 µm (Zhang et al., 2017; Li et al., 2013; Liu et al., 2018). ThusTherefore, the internal mixing of Fe-bearing particles with sulfateSO_4 and oxalate was promoted in the cloud water and interstitial cloud particles.

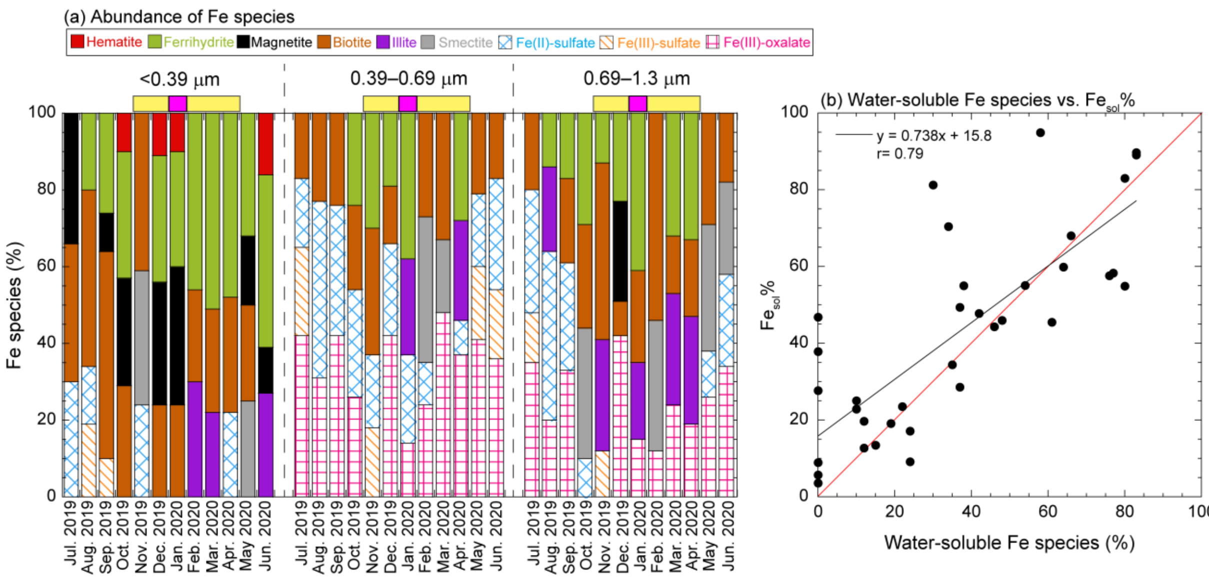


Figure 8. (a) Representative Fe species and their abundances in fine aerosol particles. Water-soluble Fe species (Fe(II)-sulfate, Fe(III)-sulfate, and Fe(III)-oxalate) wereare shown with lattice patterns. Yellow and pink bars above the panels showindicate the period of Asian outflowEAout and the COVID-19 lockdown periods, respectively. (b) A scatterScatter plot between the abundanceabundances of water-soluble Fe species and Fesol% in fine aerosol particles.

3.7.3.6. Alteration processes and dissolution pH of mineral dust

To assess the alteration process of mineral Fe and anthro-Fe in fine aerosol particles, we determined the The Fe species ofin mineral dust and anthropogenic aerosol collected in September 2019 were determined through µ-XRF–XANES. The technique to assess the alteration in mineral-Fe and anthro-Fe in fine aerosol particles. μ-XRF–XANES is suitable for the source identification of metal elements in aerosol particles through the determination of elemental compositions and chemical species in regions of interest (Sakata et al., 2017, 2021). TheIn the present study, the regions of interest for this study were Fe-poor spots (M1–M10) and Fe-rich spots (A1–A12, Figs. 9a and S14). The Fe-poor spots contained Ca but did not containlacked anthropogenic metals (e.g., Mn, Ni, Cu, Zn, and Pb, Figs. 9a and S14), indicating that Fe in these spots was associated with mineral dust. The M1 spot contained less aged mineral dust because (i) the XRF spectrum of the spot did not yield an intense S peakspots exhibited low S intensity, and (ii)their Fe species in the spot were similar to those in mineral dust (aluminosilicates and hematite) were similar to mineral dust (Fe-(hydr)oxides; Figs. 9a and 9b). By contrast, Fe(II)- and Fe(III)-sulfates coexistedThese findings were in accord with the μ-XAFS results for coarse aerosol particles. Furthermore, the SEM–EDX of aluminosilicates in coarse aerosol particles collected at the same observation point revealed low amounts of S (Sakata et al., 2021). M2–M10 spots, and As mentioned previously, PMF analyses indicated that fresh mineral dust was characterized by the [nss-SO_4^{2-}]/[T-Fe] ratio of 0 (Tables S4 and S5). Therefore, the M1 spots in fine aerosol particles represented fresh mineral dust. By contrast, the XRF spectra yielded an intense peak of sulfur. These results of M2–M10 spots showed thatan intense S peak, and Fe-containing aluminosilicates were found to coexist with Fe(II, III)-sulfates, suggesting that these Fe-sulfates formed through the chemical alterations of Fe in mineral dust by H_2SO_4. This finding is supported by the PMF analysis, wherein the aged mineral dust factor included nss-SO_4^{2-}. Therefore, the internal mixing of Fe-bearing aluminosilicates with sulfateH_2SO_4 is important toa dominant process for the secondary formation of Fe(II)- and Fe(III)-sulfates in the atmosphere.with high Fe_{sol}%. The average abundance of water-soluble Fe species in the Fe-poor spot (avg ± 1σ: 46 (i.e., Fe(II, III)-sulfates and Fe(III)-oxalate) in M1–M10 was 46% ± 25%)%, which was higher than that in mineral-Fe_{sol}% estimated by Eq. 3 (20.3%). This result is partly due to the small number of measurements of Fe species at points of low S intensity, such as the M1 spot.

Given that Fe(III)-oxalate was detected in mineral dust in fine aerosol particles (Fig. 9a9b), ligand-promoted dissolution appearsappeared to contribute to Fethe dissolution of Fe from mineral dust. Previous research has shown that oxalate plays two key roles in controlling Fe_{sol}% in aerosols, depending on the aerosoltheir acidity (Myriokefalitakis et al., 2015; Tao and Murphy, 2019; Sakata et al., 2022; Zhang et al., 2024). The first role of oxalate in Fethe dissolution of Fe from mineral dust is to stabilize d-Fe in the aqueous phase asin the form of oxalate complexes after proton-promoted dissolution under highly acidic conditions (pH < 3.0). InUnder such a pH conditions, oxalate does not significantlymarkedly contribute to Fe release from mineral dust because the dissolution rate of Fe from aluminosilicate mineralminerals via proton-promoted dissolution is more than an order of magnitude higher than that via ligand-promoted dissolution (Balland et al., 2010; Cappelli et al., 2020). Additionally, Fe(III)-oxalate can be stabilized underin highly acidic solutions (Sakata et al., 2022), which). This phenomenon not only stabilizes Fe in the aqueous phase but may also promote further Fe dissolution bythrough proton-promoted dissolution by reducing the saturation of inorganic Fe (Ito and Shi, 2016). ThusTherefore, oxalate assists the Fe dissolution of Fe from mineral dust via proton-promoted dissolution under highly acidic conditions. Conversely, the dissolution rate of Fe from aluminosilicate via ligand-promoted dissolution exceeds those via proton-promoted dissolutions under moderately acidic

~~conditions (pH > 3.0) because the dissolution rate of Fe from mineral dust by proton-promoted dissolution decreases markedly with increasing pH. Therefore,~~The second role of oxalate is the promotion of Fe dissolution from aluminosilicate under moderately acidic conditions~~, but its effect is not sufficient to~~ (pH > 3.0). However, ligand-promoted dissolution under moderately acidic conditions cannot dissolve as much Fe from mineral dust as proton-promoted dissolution under highly acidic conditions (Balland et al., 2010). Indeed, previous experiments on the ligand-promoted dissolution of mineral dust in simulated cloud water ~~showed~~demonstrated that organic ligands, ~~such as~~including oxalates (0–8 ~~μ~~μmol L^{-1}), ~~increased~~did not achieve a Fe_{sol}% ~~but was limited to less than 1%~~ above 10% under moderately acidic conditions (Paris et al., 2011, Paris and Desboeufs, 2013). Therefore, ~~it is considered that~~ Fe dissolution under highly acidic conditions is necessary to ~~reach~~explain high mineral-Fe_{sol}% in ~~the~~ fine aerosol particles.

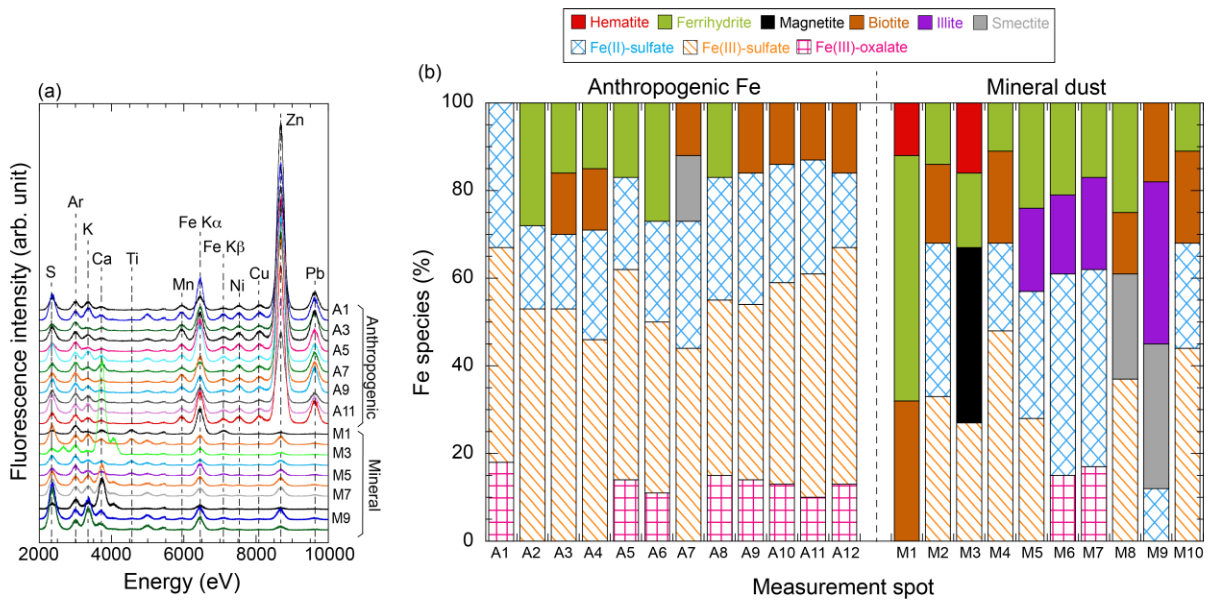
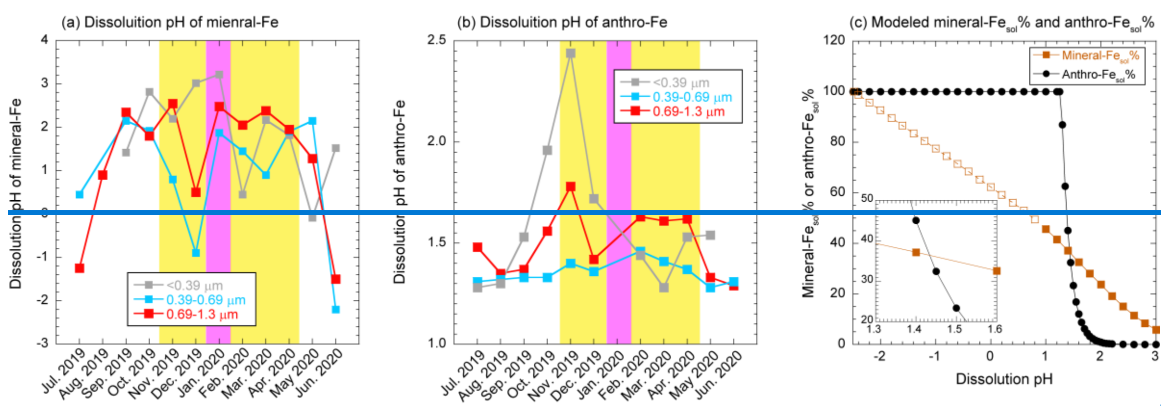


Figure 9. (a) μ-XRF ~~spectrum~~spectra of Fe-rich (anthropogenic: A1–A12) and Fe-poor (mineral: M1–M9) spots in 0.39–0.69 μm aerosol particles collected in September 2019. (b) ~~Abundance~~Abundances of Fe species in each measurement spot.

~~To assess whether mineral dust has undergone highly acidic conditions in the atmosphere, we~~We estimated the aerosol pH of mineral dust ($pH_{mineral}$) needed to reach the observed mineral-Fe_{sol}% in ~~the~~ fine aerosol particles~~, assuming~~ under the assumption that only proton-promoted dissolution~~. As a result, the~~ occurred to assess whether mineral dust had undergone highly acidic conditions in the atmosphere. The examples for dissolution curve of mineral dust were shown in Figure S15. The average $pH_{mineral}$ during the JPN~~-~~ period (0.60) was lower than that during the EAout~~-~~ period (average $pH_{mineral}$: 1.78; Fig. 10a). The decrease in aerosol pH during summer, as also indicated by aerosol pH estimation using thermodynamic models, can be attributed largely to the enhanced proton activity resulting from ~~higher~~high temperatures (Pye et al., 2020; Song and Osada, 2020). ~~Thus~~Hence, the seasonal variation in $pH_{mineral}$ is likely to be synchronized with the overall changes in aerosol pH. One potential issue is the mitigation of the decrease in the $pH_{mineral}$ of mineral dust in fine aerosol particles due to the buffering capacity of alkaline minerals, including ~~calcium carbonate (~~$CaCO_3$~~)~~. Previous studies have shown that the buffering capacity of alkaline mineral species in fine aerosol particles is almost completely consumed by chemical reactions with H_2SO_4, leading to the formation of $CaSO_4 \cdot 2H_2O$ during transport from East Asia to Japan (Takahashi et al., 2008; Miyamoto et al., 2020). ~~Aadditionally~~Additionally, the thermodynamic model predicted that the pH of mineral dust would reach 0.0–1.0 after ~~overwhelming~~ the buffer capacity of $CaCO_3$ is overwhelmed (Meskhidze et al., 2003, 2005). Therefore, ~~it is reasonable to infer that~~ the mineral dust in ~~the~~ fine aerosol particles ~~underwent significant~~can be inferred to have undergone considerable acidification (pH < 2.0). ~~From~~As inferred from these results, Fe(III)-oxalate ~~was~~ formed as a result of the stabilization of d-Fe in the aqueous phase following proton-promoted dissolution. This finding ~~is~~was supported by the ~~lack~~absence of a correlation ~~of~~between mineral-Fe_{sol}% ~~with~~and the abundance of Fe(III)-oxalate (Fig. 11a). The importance of ~~the~~ proton-promoted dissolution for the ~~Fe~~ dissolution of Fe from mineral dust in fine aerosol particles ~~is~~found in our present work was consistent with that observed in our previous studies because Fe in mineral dust collected above the North Pacific Ocean ([d-Fe]/[d-Al]: 0.~~255~~26–0.~~567) was~~5) dissolved ~~by~~through proton-promoted dissolution under highly acidic conditions, even though organic Fe complexes with humic-like substances ~~(Fe(III)-HULIS)~~ are dominant Fe species in fine aerosol particles (Sakata et al., 2022, 2023).



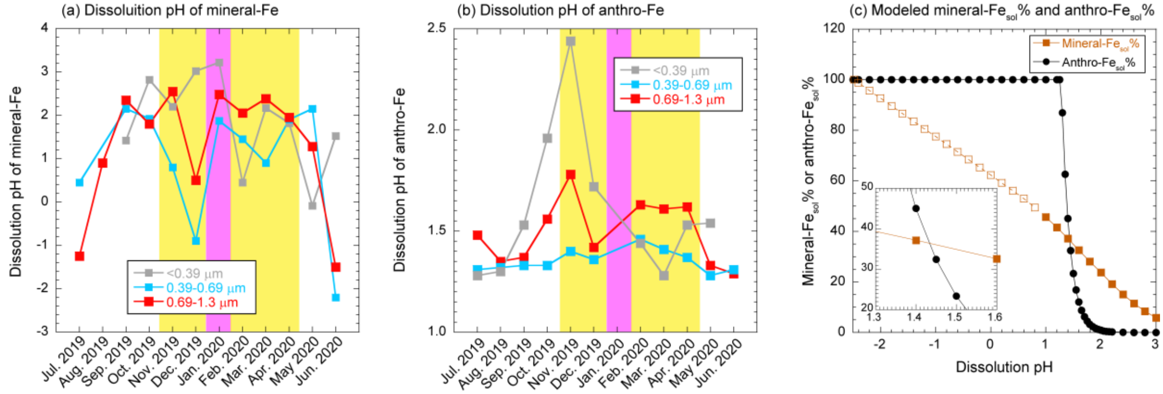


Figure 10. Monthly ~~variation of~~variations in (a) mineral-Fe$_{sol}$% and (b) anthro-Fe$_{sol}$% in fine aerosol particles. Yellow and pink shaded areas show the EAout and COVID-19 lockdown ~~period~~periods, respectively. (c) pH dependences of modeled mineral-Fe$_{sol}$% and anthro-Fe$_{sol}$%. Mineral-Fe$_{sol}$% plotted with closed symbols was estimated by using the kinetic data shown in ~~Fig. S15a~~Table 1. Mineral-Fe$_{sol}$% plotted with open ~~symbol~~symbols was calculated by extrapolating the kinetic equation for pH 1–2 ~~shown~~presented in ~~Fig. S15a~~Table 1.

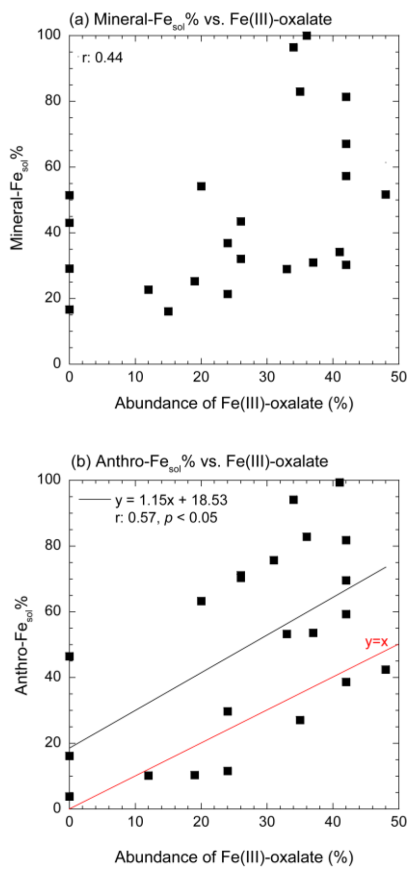


Figure 11. Scatter plots of ~~abundance~~the abundances of Fe(III)-oxalate with (a) mineral-Fe_{sol}% and (b) anthro-Fe_{sol}% in fine aerosol particles (0.39–0.69 and 0.69–1.3 μm). The ~~back~~black and red lines in ~~a panel~~panels in (b) show the regression line and y = x, respectively.

~~3.8.~~3.7. Alteration processes of anthro-Fe

Aerosol particles in Fe-rich spots primarily originated from anthropogenic emissions with high-temperature combustion ~~because~~considering that anthropogenic elements, including Mn, Ni, Cu, Zn, and Pb, were abundant in the spots (A1–A12 in Figs. 9a and S14). Furthermore, Fe intensities ~~was much~~in Fe-rich spots were considerably higher than those in Fe-poor spots containing mineral dust. This result ~~suggests~~suggested that ~~the~~ Fe in these spots originated from anthropogenic emissions with high $EF_{T\text{-}Fe}$, including emissions from the steel industry (~~Table S3~~Tables S4 and ~~S4). The high sulfur intensity of Fe-rich spots indicated~~S5). A previous study has demonstrated that ~~the anthro-~~Fe ~~in~~-rich particles (mainly Fe-oxides) collected directly from steel plants did not contain S but instead acquired a thick sulfate coating over one or two days of transport (Li et al., 2017). Given that the Fe-rich spots exhibited an intense S peak (Fig. 9a), these ~~spots was significantly~~particles were markedly aged by SO_2 and/or H_2SO_4 in the atmosphere ~~(Figs. 6a and S14a). As evidence~~. Consequently, more than half of the Fe in these spots existed ~~as~~in the form of water-soluble Fe species, including Fe(II)-sulfate, Fe(III)-sulfate, and Fe(III)-oxalate (Fig. 9b). The average abundance of water-soluble Fe species in Fe-rich spots (avg ± 1~~σ: ~~σ: 81% ± 9%) was ~~consistent~~in agreement with ~~the~~that of anthro-Fe_{sol}% in the sample estimated by Eq. 4 (74.0%), indicating that the representative anthro-Fe species in this sample can be determined. Furthermore, ~~the~~this consistency ~~supports~~supported the reliability of estimating anthro-Fe_{sol}% ~~based~~ on the basis of the [d-Fe]/[d-Al] ratio ~~can provide~~in providing reasonable results.

The number of particles containing Fe(III)-oxalate appeared to be ~~greater~~higher in Fe-rich spots than in Fe-poor spots (Fig. 9b). The abundance of Fe(III)-oxalate in fine aerosol particles with diameters of 0.39–0.69 and 0.69–1.3 μm was weakly correlated with anthro-Fe_{sol}% (r~~:~~ = 0.57; Fig. 11b). Therefore, oxalate may partially contribute to the dissolution of anthro-Fe. Oxalate in fine aerosol particles ~~was~~ formed in cloud water (average pH of East Asia: 4.2, Shah et al., 2020), increasing the number of oxalate-bearing Fe-rich particles through cloud processing (Li et al., 2013; Zhang et al., 2017; Liu et al., 2018). The acquisition of an oxalate coating by anthro-Fe in cloud water promoted Fe dissolution after anthro-Fe was released ~~by~~through cloud water evaporation because the dissolution rate of oxalate-coated hematite at pH 2.4 ~~is~~was higher than that of noncoated hematite (Xu and Gao, 2008). By contrast, proton-promoted dissolution dominated Fe dissolution from hematite under highly acidic conditions (pH < 2.0, Xu and Gao, 2008). ~~Assuming~~Under the assumption that anthro-Fe dissolution occurred solely through proton-promoted dissolution, the pH range for the proton-promoted dissolution of anthro-Fe was estimated ~~based~~ on the basis of the solubility product of hematite nanoparticles. ~~As a result, the~~The predicted pH range for the proton-promoted dissolution of anthro-Fe was narrow (1.3–2.0) due to the sharp increase in anthro-Fe_{sol}% at pH levels below ~~pH~~ 2.0 (Figs. ~~11b~~10b and ~~11c~~10c). Considering that anthro-Fe ~~has underwent~~had experienced highly acidic conditions and the abundance of Fe(III)-oxalate ~~is~~was lower than that of anthro-Fe_{sol}%, ~~it is inferred that~~ proton-promoted dissolution was inferred to be the primary mechanism for the dissolution of anthro-Fe. Subsequent complexation with oxalate in the aqueous phase to form

Fe(III)-oxalate likely reduced the saturation index of inorganic Fe, potentially facilitating further proton-promoted dissolution from the solid phase (Ito and Shi, 2016).

As mentioned previously mentioned, anthro-Fe$_{sol}$% tendtended to be higher than mineral-Fe$_{sol}$% for the JPN period, whilewhereas the opposite trend was observed for the EAout period (Figs. S6c–S6e). The This difference in seasonal trends of mineral-Fe$_{sol}$% and anthro-Fe$_{sol}$% can be explainedunderstood by their examining the responsiveness of mineral-Fe and anthro-Fe to the dissolution pH, as both mineral-Fe and anthro-Fe were mainly dissolved by because proton-promoted dissolution. Anthro-Fe$_{sol}$% exhibited a rapid increase from near 0% to 100% between pH 2.2 and 1.2, whereas mineral-Fe$_{sol}$% showed a gradual increase with decreasing pH. As a result was the primary mechanism for mineral-Fe and anthro-Fe. The pH dependence of mineral-Fe$_{sol}$% and anthro-Fe$_{sol}$% is illustrated in Fig. 10c. Notably, when the pH was higher than 1.5, mineral-Fe$_{sol}$% was generally higher than anthro-Fe$_{sol}$%, whereas anthro-Fe$_{sol}$% exceeded mineral-Fe$_{sol}$% at pH levels lower than 1.5 (Fig. 10c). This contrasting behavior occurred because the Fe$_{sol}$% of hematite nanoparticles, representing anthro-Fe, increased dramatically by approximately three orders of magnitude per unit decrease in pH (Eq. 12), leading to a surge in Fe$_{sol}$% from roughly 0.1% to 100% as the pH dropped from 2.2 to 1.2. By contrast, mineral-Fe$_{sol}$% gradually increased with decreasing pH (Fig. 10c). Consequently, anthro-Fe$_{sol}$% exceeded mineral-Fe$_{sol}$% within the pH range of 1.4 to –1.5 (Fig. 11c). Indeed10c). In line with this pH-dependent behavior, the pH of samples wherewherein anthro-Fe$_{sol}$% exceeded mineral-Fe$_{sol}$% during the JPN period was significantlyconsiderably lower than 1.4 (average pH: 0.60), while whereas that of the samples with higherhigh mineral-Fe$_{sol}$% during the EAout period had a pH exceedingexceeded 1.4 (average pH: 1.78).

4. Implications

The dissolution of mineral-Fe and anthro-Fe in fine aerosol particles by atmospheric processes (*e.g.*, proton- and ligand-promoted dissolutions) during aerosol transport from East Asia to Japan plays a crucial role in supplying of d-Fe to the North Pacific. The Fe$_{sol}$% in TSP (2.8–17.4%) and PM$_{2.5}$ (8.0–29.2%) and size distributions in our samples were consistent with those of aerosol particles above the North Pacific (Table S2). In addition, the F_{anthro} of TSP collected for the EAout period (20.4–43.9%) was consistent with the contribution of anthro-Fe to d-Fe in the North Pacific surface seawater considering the influence of Asian aerosol deposition (21–59%, Pinedo-González et al., 2020). The consistencies of Fe$_{sol}$% and F_{anthro} between Japanese aerosols and North Pacific aerosols indicate that these parameters did not change drastically during transport from Japan to the North Pacific. This assumption is consistent with the results of previous studies (Buck et al., 2013; Sakata et al., 2022).). Therefore, given that mineral dust and anthro-Fe were emitted in the long-term observationform of factors controllinginsoluble Fe, the relationship between mineral-Fe$_{sol}$% and anthro-Fe$_{sol}$% in aerosol depended on the pH during reactions (Fig. 10c). This situation implied that the high Fe$_{sol}$% often seen in fine particles in the eastern endmight not always be linked to anthro-Fe, making determining the origin of East Asia leads toaerosol Fe solely on the developmentbasis of our knowledge about Fe supply to the North Pacific Ocean via aerosol depositionrelative Fe$_{sol}$% levels difficult.

Although this study focused primarily on Fe_{sol}%, changes in Fe species during transport can affect the optical properties of Fe-bearing particles. Recently, along with black carbon (BC), anthro-Fe has been recognized as light-absorbing aerosol particles (Moteki et al., 2017; Ito et al., 2018; Lamb

4. Future implications

In this study, we investigated the factors controlling Fe_{sol}% in size-fractionated aerosol samples collected in the coastal region of the Sea of Japan. Our results showed that the T-Fe and d-Fe concentrations in TSP samples peaked in spring due to the substantial loading of Asian dust into the atmosphere. Steel industry and NEV particles, which were primarily composed of insoluble Fe, were important sources of T-Fe in fine aerosol particles. During the COVID-19 lockdown, the contribution of anthro-Fe (especially from the steel industry) to T-Fe decreased sharply, highlighting that anthro-Fe emitted from combustion and non-combustion sources was a major source of T-Fe in fine aerosol particles over East Asia. Fe_{sol}% was higher in summer than spring, with high values mainly observed in fine aerosol particles, and correlated with the [nss-SO_4^{2-}]/[T-Fe] ratio, indicating that Fe in these fine particles was primarily dissolved through proton-promoted dissolution. Macroscopic and microscopic XANES spectroscopy revealed that the water-soluble Fe species in fine aerosol particles were Fe(II)-sulfate, Fe(III)-sulfate, and Fe(III)-oxalate and were also present in mineral dust and anthropogenic aerosols. Given the water insolubility of Fe species in freshly emitted mineral dust (aluminosilicates) and anthro-Fe (mainly Fe oxides), these water-soluble Fe species likely formed through aerosol acidification by H_2SO_4, a process supported by the strongly acidic conditions suggested by dissolution pH estimations. Therefore, chemical reactions, including aerosol acidification, play a critical role in the control of the Fe_{sol}% of aerosol particles in East Asia.

During the period of increased aerosol outflow from East Asia (November to April), the average Fe_{sol}% of TSPs collected at NOTOGRO (4.9%) was slightly lower than that of TSPs collected in the North Pacific. However, the Fe_{sol}% of fine aerosol particles increased substantially during transportation from East Asia to NOTOGRO, with their average Fe_{sol}% (14.3%) being comparable to that of fine aerosol particles collected in the western Pacific during a similar season (14.2%; Table S3). This finding suggests that the chemical alterations of Fe in mineral dust and anthro-Fe in fine aerosol particles mainly occurred over East Asia rather than during transport in the North Pacific. Therefore, long-term observations on the Fe_{sol}% of the fine aerosol particles collected at the rim of East Asia (i.e., entrance of the North Pacific) play an important role in understanding the controls on Fe_{sol}% supplied to the North Pacific. By contrast, the Fe_{sol}% of coarse aerosol particles were slightly higher in the western Pacific (average: 3.5%) than in NOTOGRO (average: 0.5%). This difference likely contributed to the difference in the Fe_{sol}% of TSPs between the two regions. Therefore, future research should also focus on the Fe dissolution processes in coarse aerosol particles during transport over the marine atmosphere to develop our understanding of aerosol Fe supply to the ocean surface because these differences may be a reason for the higher Fe_{sol}% of TSPs in the western Pacific than in East Asia.

et al., 2021). The contributions of anthro-Fe on direct radiative forcing (DRF) relative to that for BC are approximately 10% in the polluted region and up to 6% in a remote area, including the marine atmosphere (Moteki et al., 2017; Ito et al., 2018; Lamb et al., 2021). Surface coating (*e.g.*, sulfate) on BC and anthro-Fe can enhance light absorption by the lensing effect (Bond et al., 2006; Moteki et al., 2017; Liu et al., 2017). Unlike BC, internal mixing of anthro-Fe with sulfate or oxalate may produce less light absorbable Fe(II)-sulfate, Fe(III)-sulfate, or Fe(III)-oxalate, reducing the DRF of anthro-Fe. Indeed, a previous study has predicted that the transformation of anthro-Fe to ferrihydrite will reduce its DRF (Ito et al., 2018). Therefore, incorporating the transformation process of anthro-Fe to evaluate DRF (especially in remote areas) is necessary because of anthro-Fe in climate models. Thus, atmospheric processes on Fe-bearing particles in East Asia affect climate regulation factors associated with Fe aerosol, especially ocean Fe fertilization and DRF of Fe oxides. Therefore, Fe speciation not only in emission source regions and the marine atmosphere but also at intermediate points along the transport pathway plays essential roles in constraining the control factors of Fe_{sol}% and DRF of Fe-bearing particles.

Data Availability.

All quantitative data is approval in ERAN database at https://www.ied.tsukuba.ac.jp/database (doi: 10.34355/CRiES.U.TSUKUBA.00157). The XAFS data are available upon request.

Author Contributions. K.S, S.T., A.M., H.T., and Y.T. designed the research. K.S., A.S., and A.M. collected size-fractionated aerosol samples. S.T determined trace metal concentrations. K.S, Y.T, and M.K. performed macroscopic and micro-focused XAFS experiments. K.S and Y.T. wrote the manuscript, and all authors approved the manuscript before submission.

Competing interests.

The authors declare that they have no conflict of interest.

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Figure captions

Figure 1. The samplingSampling site (NOTOGRO) offor size-fractionated aerosol samplingaerosols.

Figure 2. The diagramDiagram of $EF_{T\text{-}Fe}$ and the [d-Fe]/[d-Al] ratio for evaluating the T-Fe and d-Fe sources of aerosol particles.

Figure 3. (a) Monthly variations and size distributions of (a) in T-Fe concentration and $EF_{T\text{-}Fe}$ in TSP,TSPs and (b) size distributions of $EF_{T\text{-}Fe}$ (red line: $EF_{T\text{-}Fe}$ is= 2.0). The data of coarse aerosol particles are shown in dashed boxes or lines, while the datawhereas those of fine aerosol particles are described in solid boxes or lines. Yellow and pink shaded regions show the EAout and COVID-19 lockdown periods, respectively.

Figure 4. Yellow and pink shaded regions show the EAout and COVID-19 lockdown periods, respectively.

Figure 4. (a) d-Fe concentration and Fe_{sol}% in TSPof TSPs; (b) Fe_{sol}%,%; and (c) the [nss-$SO^{4}{}_{2}$-]/[-]/[T-Fe].] ratio. The data of coarse aerosol particles are shown in dashed boxes or lines, while the datawhereas those of fine aerosol particles are describedpresented in solid boxes or lines. Yellow and pink shaded regions showareas indicate the EAout and COVID-19 lockdown periods, respectively.

Figure 5. (a) A sizeSize distribution of the [d-Fe]/[d-Al] ratio. The yellowYellow and pink areas are shown inindicate the JPNEAout and COVID-19 lockdown periods, respectively. (b) relationships of $EF_{T\text{-}Fe}$ and the [d-Fe]/[d-Al] ratio. The background color indicates the emission sources of T-Fe and d-Fe, which are detailed in Fig. 2. (c) a correlationCorrelation between $EF_{T\text{-}Fe}$ and Fe_{sol}%.

Figure 6. (a) A size distribution of [d-Fe]/[d-Al] ratio. (b) relationships of $EF_{T\text{-}Fe}$ and [d-Fe]/[d-Al] ratio. Background color indicates the major sources of T-Fe and d-Fe in aerosols. The (c) a correlation between $EF_{T\text{-}Fe}$ and Fe_{sol}%. (d–f) monthly Monthly trends of the relative abundanceabundances of anthro-Fe to those of (a) d-Fe, (b) mineral-Fe_{sol}%, and (c) anthro-Fe_{sol}% in fine aerosol particles, respectively. The yellow. Yellow and pink areas are shown in shaded regions show the JPNEAout and COVID-19 lockdown periods.

Figure 7., respectively. The average contributionplots of the emission sources to (a) T-Fe, (b) anthro-Fe, andFe$_{sol}$% in panel (c) d-Fe in fine aerosol particles collected for the JPN period. (d–f) the same figures for the EAoutare missing because either or both anthro-Fe or anthro-Fe concentrations were 0 due to the remarkable but small contributions of anthro-Fe during the COVID-19 lockdown period.

Figure 7. Panels (a-c) show average contributions to T-Fe, anthro-Fe, and d-Fe, respectively, for the JPN period. Panels (d-f) show contributions to T-Fe, anthro-Fe, and d-Fe, respectively, for the EAout period.

Figure 8. (a) Representative Fe species and their abundances in fine aerosol particles. Water-soluble Fe species (Fe(II)-sulfate, Fe(III)-sulfate, and Fe(III)-oxalate) wereare shown with lattice patterns. Yellow and pink bars above the panels showindicate the period of Asian outflowEAout and the COVID-19 lockdown periods, respectively.

(b) ~~A scatter~~Scatter plot between the ~~abundance~~abundances of water-soluble Fe species and Fe_{sol}% in fine aerosol particles.

Figure 9. (a) μ-XRF ~~spectrum~~spectra of Fe-rich (anthropogenic: A1–A12) and Fe-poor (mineral: M1–M9) spots in 0.39–0.69 μm aerosol particles collected in September 2019. (b) ~~Abundance~~Abundances of Fe species in each measurement spot.

Figure 10. Monthly ~~variation of~~variations in (a) mineral-Fe_{sol}% and (b) anthro-Fe_{sol}% in fine aerosol particles. Yellow and pink shaded areas show the EAout and COVID-19 lockdown ~~period~~periods, respectively. (c) pH dependences of modeled mineral-$Fe_{sol\%}$ and anthro-Fe_{sol}%. Mineral-Fe_{sol}% plotted with closed symbols was estimated by using the kinetic data shown in ~~Fig. S15a~~Table 1. Mineral-Fe_{sol}% plotted with open ~~symbol~~symbols was calculated by extrapolating the kinetic equation for pH 1–2 ~~shown~~presented in ~~Fig. S15a~~Table 1.

Figure 11. Scatter plots of ~~abundance~~the abundances of Fe(III)-oxalate with (a) mineral-Fe_{sol}% and (b) anthro-Fe_{sol}% in fine aerosol particles (0.39–0.69 and 0.69–1.3 μm). The ~~back~~black and red lines in ~~a panel~~panels in (b) show the regression line and y = x, respectively.

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