We greatly value the careful reading and the detailed comments provided by the referees. The responses to the comments of the referees in our direct reply (shown below) and within the revised manuscript (see marked copy) are provided below. The pages and lines indicated below correspond to those in the marked copy.

Response to Referee 1 (Referees' comments are italicized)

1. Referee comment: "*Line 174-178: After sonication, how were insoluble materials separated from the aqueous extracts? Was it achieved by high speed vortexing? Filtration is usually used by many studies, with filter pore-size clearly stated. More information should be provided here.*"

Author response: Both high speed vortexting and filtration were used for aqueous extraction. Filtration was performed using 0.22 µm pore size nylon filters (Jinteng Instrument Co., Tianjin, China). This information has been included in the revised manuscript:

Page 6 line 167: "One of the four pieces was extracted in purified deionized water via sonication (1 hour), followed by high speed vortexing at 3000 rpm (15 minutes). The resulting aqueous extract was filtered using 0.22 µm pore size nylon filters (Jinteng Instrument Co., Tianjin, China) before it was analyzed by a Total Organic Carbon (TOC) analyzer (TOC-VCSH, Shimadzu, Japan) to determine the concentration of water-soluble organic carbon (WSOC)."

Page 6 line 172: "The second filter piece was similarly extracted in purified deionized water via sonication and high speed vortexing at 3000 rpm, and filtered using 0.22 µm pore size nylon filters before it was analyzed by an ion chromatography (IC) system (Dionex ICS-1100, ThermoFisher Scientific, USA) using an isocratic method to determine the concentrations of water-soluble anions (NO_3^-, SO_4^{2-}, Cl^-, and $C_2O_4^{2-}$) and cations (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+})."

Page 6 line 189: "One filter piece was extracted with purified deionized water in metal-free centrifuge tubes via sonication (1 hour), followed by high speed vortexing at 3000 rpm (15 minutes). The resulting aqueous extract was filtered using 0.22 µm pore size nylon filters, and acidified with 2 % HNO_3 prior to storage at 4 °C before chemical analysis of water-soluble metals."

Page 7 line 218: "The resulting solution was filtered using 0.22 µm pore size nylon filters, and then stored at 4 °C before chemical analysis of total metals."

2. Referee comment: "*Line 250-259: Can the authors show and discuss correlations between Al and other metals? This may give further insights (in addition to size distribution) to their sources.*"

Author response: As requested, we have added a figure and a discussion about the correlations between Al and other metals to the revised manuscript:

Page 10 line 291: "The mass concentrations of the two most abundant metals, Fe and Al,

were usually higher than 10 ng m^{-3} in both fine and coarse aerosols. Fe, Al, and Cu had substantially higher mass concentrations in coarse aerosols than in fine aerosols. The positive correlations between the mass concentrations of Al with the mass concentrations of Fe and Cu were the strongest among the nine metals ($R = 0.62$ and $R = 0.52$, respectively) and statistically significant (Figure S3), which could be explained by large mass concentrations of Al, Fe, and Cu originating from similar sources. These three metals are known to originate mainly from dust sources (e.g., mineral dust and road dust) (Hopke et al., 1980; Garg et al., 2000; Adachi and Tainosho, 2004; Lough et al., 2005; Chow et al., 2022). This is consistent with results from our PMF source apportionment analysis, which showed that the "dust" factor had large mass contributions from Al, Fe, and Cu (Figures S4 and S5). Mn, Ni, V, and Cd had higher mass concentrations in fine aerosols than in coarse aerosols. These four metals are known to be consistently found in aerosols from anthropogenic sources such as vehicle and ship emissions, combustion and industrial processes (Chow et al., 2022). Pb, Cr, and Co had mostly similar concentrations in the fine and coarse aerosols. Interestingly, the mass concentrations of Mn and Cr were positively correlated with the mass concentration of Al ($R = 0.42$ and $R = 0.33$, respectively), and these correlations were statistically significant (Figure S3). Our PMF analysis apportioned Al to two factors, "dust" and "industrial factor 1", though the Al contribution to "industrial factor 1" was substantially smaller compared to "dust" (Figures S4 and S5). The "dust" factor had a significant Mn contribution, which could explain the strong correlation between the mass concentrations of Al and Mn. Cr was apportioned primarily to "industrial factor 1", which could explain the strong correlation between the mass concentrations of Al and Cr. The mass concentrations of Ni, V, Cd, Pb, and Co showed weak correlations with the mass concentration of Al (Figure S3)."

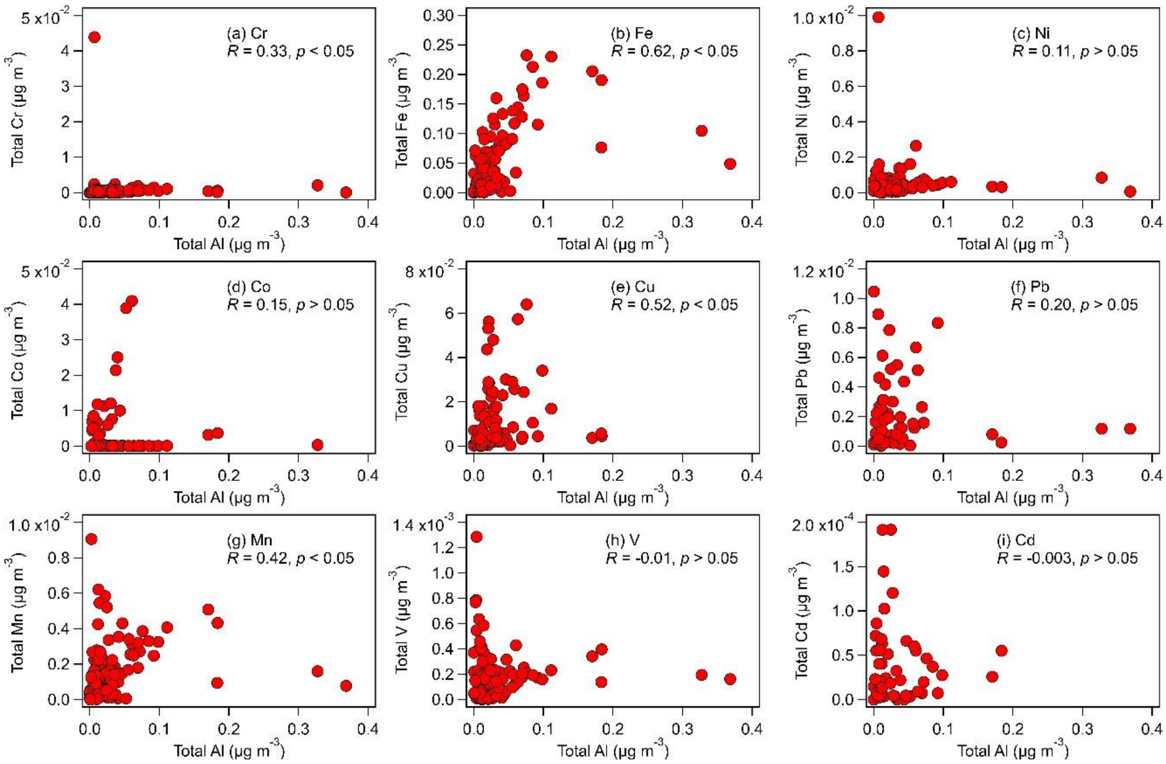

Figure S3: Relationships between the mass concentrations of total Al and the other total metals in coarse and fine aerosols. Only data with non-zero total metal concentrations were used in the figures. Also shown are the spearman correlation coefficients for each relationship.

3. Referee comment: "*Line 352-353: Several previous studies, including our work (Zhang et al., 2022) and references therein, also found that Fe solubility (as also other metals) was higher in fine particles than coarse particles. The authors may consider discussing these studies.*"

Author response: We thank the referee for bringing these previous studies to our attention. We have added the references to our revised manuscript.

4. Referee comment: "*Line 392-405: As this work did not manage to detect oxalate in aerosol particles, I feel this paragraph is tedious and not very relevant. The authors may consider making it more concise.*"

Author response: As requested, we have made this paragraph more concise in the revised manuscript:

Page 17 line 484: "To investigate whether organic ligands influenced aerosol metal solubilities in this study, we attempted to measure oxalate in the size-fractionated aerosol samples using IC. However, we could not detect oxalate, which indicated that the concentrations of oxalate (if present) were below the detection limits of our IC instrument. It should be noted that although a recent study reported the copresence of Fe and oxalate in individual aerosol particles at a suburban site in Hong Kong using single particle mass spectrometry (Zhou et al., 2020), organic ligand-promoted metal dissolution is a slow process, and it plays a minor role in metal dissolution under low pH conditions (Zhu et al., 1993). The fine aerosols collected in this study were mostly acidic, with about 60 % of the calculated pH values being less than 3. This suggested that organic ligand-promoted dissolution may have played a minor role in enhancing aerosol metal solubilities in this study due to the acidic nature of the aerosols."

5. Referee comment: "*Line 67-69: The first sentence only mentioned "many atmospheric processes", but the second and third sentences mainly discussed ocean biogeochemistry. The authors may need to modify the first sentence to make it more appropriate.*"

Author response: The following changes have been made to the revised manuscript:

Page 3 line 77: "Water-soluble metals also play important roles in ocean biogeochemistry and atmospheric processes."

6. Referee comment: "*Line 203-204: would it be enough to use only one unit (ng/L) here?*"

Author response: We have made the requested changes in the revised manuscript.

7. Referee comment: "*Line 239: It may be better to use particle diameter for x-axis in Figure 1.*"

Author response: As requested, the x axes in Figures 1 and 3 has been changed in the revised manuscript. To make the colors in Figures 1 and 3 more discernible to readers with color vision deficiencies, we also changed the color scheme for these two figures. It should be noted that the incorrect set of data was plotted for Cu in Figure 3 of the original manuscript (we previously accidentally plotted the Co data instead of the Cu data in panel 3f). This has been corrected in the revised manuscript. The corrected figure does not change the conclusions drawn in this study. The following changes have been made to the revised manuscript:

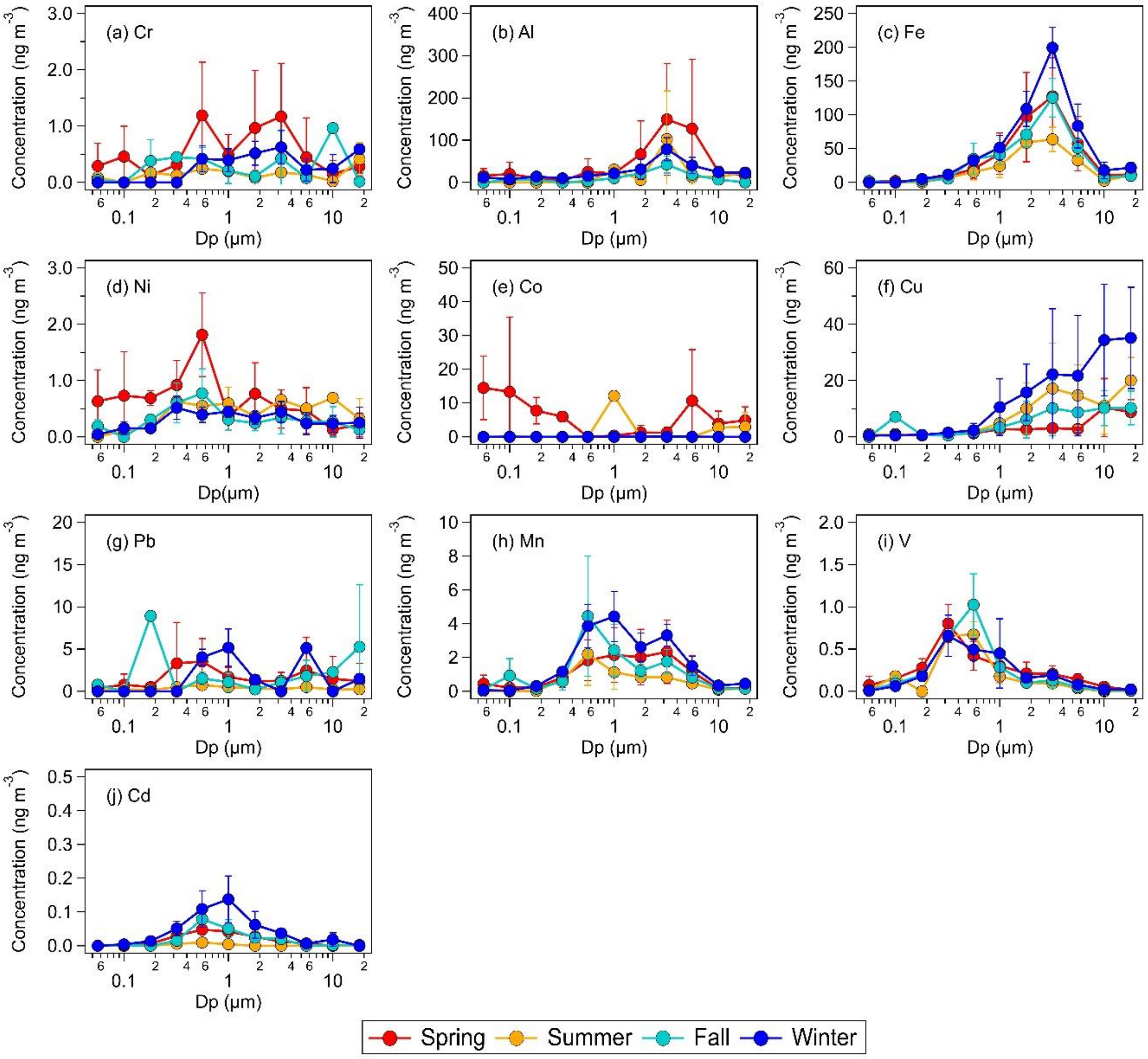

Figure 1: Seasonal average concentrations of total elemental metals in size-fractionated aerosols sampled by the MOUDI with the following nominal cut points (Dp): 0.056 µm (size fraction 1), 0.1 µm (size fraction 2), 0.18 µm (size fraction 3), 0.32 µm (size fraction 4), 0.56 µm (size fraction 5), 1.0 µm (size fraction 6), 1.8 µm (size fraction 7), 3.2 µm (size fraction 8), 5.6 µm (size fraction 9), 10 µm (size fraction 10), and 18 µm (size fraction 11). The error bars represent one standard deviation of the seasonal average value.

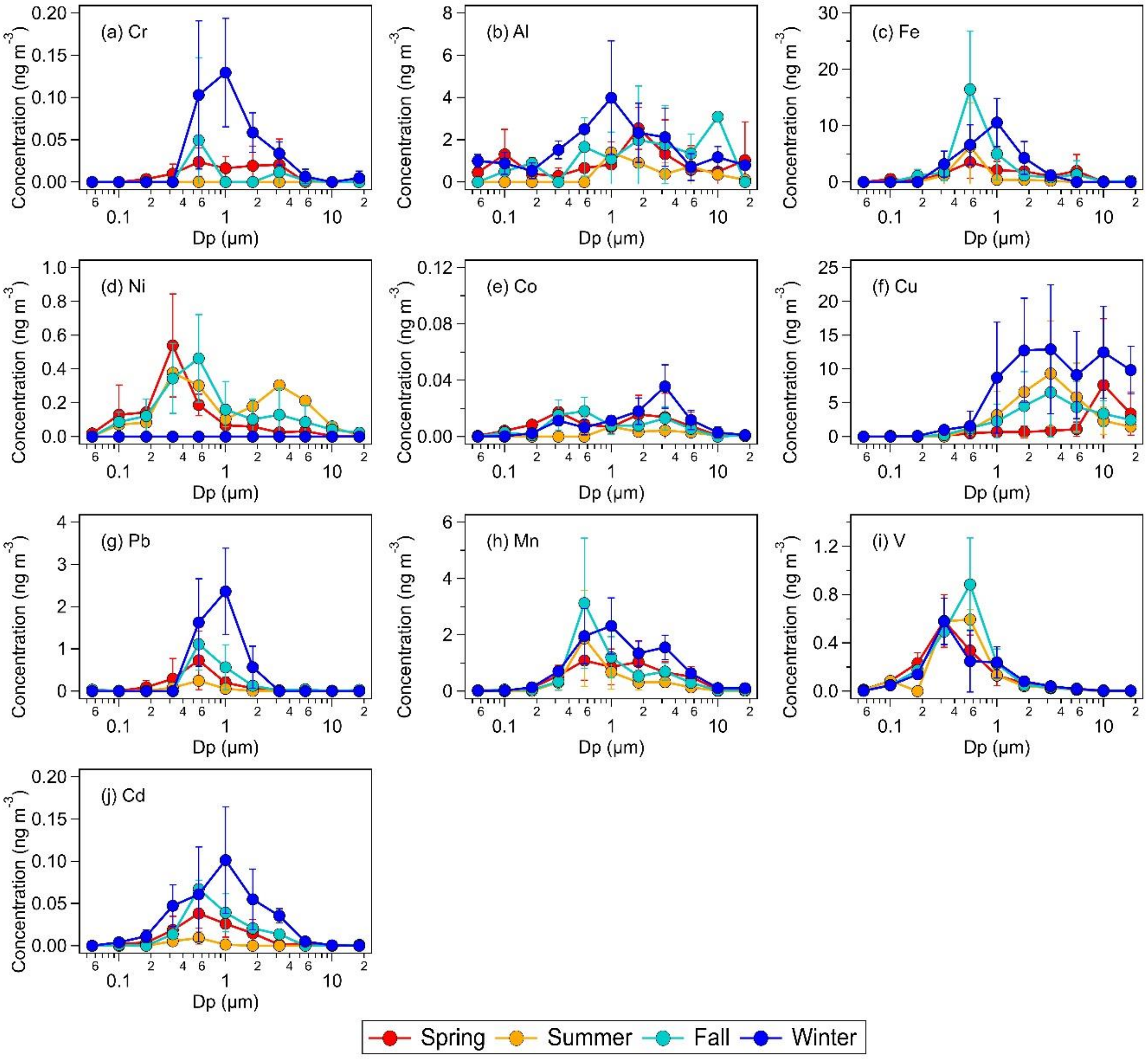

Figure 3: Seasonal average concentrations of water-soluble metals in size-fractionated aerosols sampled by the MOUDI with the following nominal cut points (Dp): 0.056 μm (size fraction 1), 0.1 μm (size fraction 2), 0.18 μm (size fraction 3), 0.32 μm (size fraction 4), 0.56 μm (size fraction 5), 1.0 μm (size fraction 6), 1.8 μm (size fraction 7), 3.2 μm (size fraction 8), 5.6 μm (size fraction 9), 10 μm (size fraction 10), and 18 μm (size fraction 11). The error bars represent one standard deviation of the seasonal average value.

Response to Referee 2 (Referees' comments are italicized)

1. Referee comment: "*L49-52, are there any references to study metal particles in HK or upwind cities such as Guangzhou. Ref: Atmospheric Environment, 41, 2, Pages 432-447; Int. J. Environment and Pollution, Vol. 36, Nos. 1/2/3, 2009; Environ. Sci. Technol., 47(16), 9124-9131;*"

Author response: We thank the referee for bringing these previous studies to our attention. We have added the references to our revised manuscript.

2. Referee comment: "*Here why did the authors did not consider the nitrates and organic acids. Does nitrates have large contribution for metal solubility? Nitrate is also acidic aerosols in the air.*"

Author response: In our study, the mass concentrations of nitrate were very low (about 18 times lower than sulfate in fine aerosols, on average), so sulfate was considered to be the main acidic species in fine aerosols, and consequently plays an important role in modulating the solubilities of metal solubilities in fine aerosols. Nevertheless, we have added a discussion on the (small) role that nitrate plays in modulating the solubilities of metal solubilities in fine aerosols in the revised manuscript. We were unable to detect any organic acids in our collected size-fractionated aerosol samples. This is now stated explicitly in our revised manuscript. The following changes have been made to the revised manuscript:

Page 19 line 521: "Sulfate was the most abundant aqueous-phase acidic species in our size-fractionated aerosol samples. The concentrations of nitrate (another aqueous-phase acidic species) were very low (about 18 times lower than sulfate, on average), while aqueous-phase organic acids were not detected. Hence, we first analyzed the relationships between the concentrations of water-soluble metals and sulfate."

Page 19 line 533: "To investigate the roles that sulfate and nitrate played in controlling aerosol metal solubilities, we analyzed the relationships between the metal fractional solubilities and sulfate and nitrate concentrations. In general, the correlations between the metal fractional solubilities and sulfate concentration (Table 1) were substantially higher than the correlations between the metal fractional solubilities and nitrate concentration (Table S3). This implied that sulfate likely plays a more important role than nitrate in controlling aerosol metal solubilities, which is not surprising given the low concentrations of nitrate detected (about 18 times lower than sulfate, on average)."

Table S3: Spearman rank correlations between the metal fractional solubilities and nitrate and aerosol properties[a]

Metal	Nitrate	Ammonium	RH	Temp
Cr	**0.67**	**0.51**	**-0.53**	**-0.78**
Al	-0.05	0.09	-0.07	-0.09
Fe	-0.04	**0.39**	0.01	0.06
Ni	**-0.26**	-0.05	**0.25**	**0.77**
Co	0.16	**0.33**	-0.01	0.02
Cu	**0.67**	**0.59**	0.00	0.00
Pb	**0.34**	**0.38**	-0.25	-0.12
Mn	0.14	**0.22**	0.02	-0.11
V	**-0.29**	**0.23**	0.18	0.10
Cd	-0.16	0.11	0.08	-0.17

[a] Bold: statistically significant ($p < 0.05$)"

3. Referee comment: "*If the authors discussed the metal solublization, the author firstly should consider the mixing state of metal particles. Recent, some studies nicely obtain iron associated*

with sulfate in nanoscale using nanotechniques. Adv., 3(3), e1601749, 1601741-1601746. At this stage, the authors make some discussions and then you turned into your relationship."

Author response: We thank the referee for bring this paper to our attention. The following changes have been made to the revised manuscript:

Page 18 line 507: "The acidic nature of the aerosols raises the possibility that acid processing played a major role in enhancing aerosol metal solubilities. A previous study that utilized nanoscale single-particle mass spectrometric and imaging techniques to analyze the mixing states of Fe-containing aerosols collected over the East China Sea provided insights into the mechanism of Fe dissolution by acidic species that condensed onto atmospheric aerosols (Li et al., 2017). The authors reported that Fe oxide-rich aerosols emitted from steel plants and coal combustion were coated with thick layers of acidic sulfate after 1 to 2 days of atmospheric aging. These sulfate coatings originated from the condensation of sulfuric acid, which were formed from reactions of anthropogenic SO_2. While the fresh aerosols were composed primarily of insoluble Fe oxide, the aged aerosols contained soluble Fe sulfate that were internally mixed in the sulfate coatings. Although the mechanism proposed by Li et al. (2017) focused on explaining how sulfate-driven acid processing leads to the dissolution of the water-insoluble forms Fe, this mechanism likely applies to the other aerosol metals as well."

Response to Referee 3 (Referees' comments are italicized)

1. Referee comment: "*l.53: The three references have not provided evidence for associations between water-soluble metals in aerosols and adverse human health outcomes that are significantly greater than for their water-insoluble forms. Please consider rephrasing this with relevant references.*"

Author response: As requested, the following changes have been made to the revised manuscript:

Page 2 line 58: "Compared to their water-insoluble forms, water-soluble metals have higher bioavailability, which reportedly allows them to produce adverse human health outcomes (Costa and Dreher, 1997; Heal et al., 2009; Fang et al., 2015; Gao et al., 2020; He et al., 2021)."

2. Referee comment: "*l.174: What are the advantages and disadvantages of this method to measure water-soluble metals, compared to filterable metals which include colloids, nanoparticles, and aqueous species? How did you optimize the sonication time, the vortexing speed, and its duration? Please elucidate the differences of nanoparticle size distribution in the solution extract before and after the process. How do you consider the disaggregation and detachment of nanoparticles from aerosol particles during the process? This might be associated with high solubilities at low sulfate concentrations. It is desirable for measurement report to show the differences of solubilities between the water-soluble and filterable metals using representative samples. Please elucidate the effect of the measurement technique on high*

solubilities at low sulfate concentrations.”

Author response: In the water extraction of the water-soluble metals, we passed all the samples through 0.22 μm pore size filters after sonication and vortexing prior to chemical analysis. Thus, the water-soluble concentrations of metals in the water extraction solutions reported in our study were filterable metals, which include water-soluble metals and potentially colloids and nanoparticles that could penetrate the 0.22 μm pore size filter. We acknowledge the confusion caused by not explicitly stating that we filtered all our samples prior to chemical analysis in the original manuscript. Thus, we have stated that we filtered all our samples prior to chemical analysis in the revised manuscript.

The water extraction protocol we used in this study was adapted from protocols employed in previous studies (Fang et al., 2017; Chen et al., 2019; Jiang et al., 2015; Jiang et al., 2014). While some studies have employed the “3-step leaching” protocol proposed by Perron et al. (2020) to determine the solubility of trace metals in aerosols, we decided to employ a protocol similar to one used by Jiang et al. (2014 and 2015) in their previous studies on aerosol metal solubilities in different parts of Hong Kong. This is to allow us to compare our results more easily with those reported by Jiang et al. (2014 and 2015) to determine how the aerosol metal concentrations at this urban site have changed since 2012/2013. We determined the optimal sonication time, vortexing speed and time by conducting trial tests using ambient filters collected at the urban site outside of our field study period. In these trial tests, we used different combinations of sonication time, vortexing speed and time to extract the water-soluble metals. We found that filter extraction in purified deionized water via 1 hour of sonication, followed by 15 minutes of high speed vortexing at 3000 rpm generally gave us the highest water extraction rates for our species of interest (i.e., water-soluble inorganic species, metals, and organic carbon). Information about our sonication and vortexing protocols have been added to the revised manuscript.

We acknowledge that the referee raised a valid point regarding the possibility of nanoparticles in our water extracts contributing to some of the data points in Figure 6 showing high metal fractional solubilities at low sulfate concentrations. However, we do not know the differences in the nanoparticle size distribution in the water extract before and after our filtration process using 0.22 μm pore size filters. We also did not consider the disaggregation and detachment of nanoparticles from aerosols during the extraction process. Due to the limited number of filters collected in our study, we did not have enough filter samples to conduct additional investigations of the nanoparticle size distribution in the water extracts and explore the possibility of disaggregation and detachment of nanoparticles from aerosols during the extraction process. However, a recent study by Yang et al. (2021) reported that around 84% of Fe and Cu colloidal particles that penetrated through 0.45 μm syringe filters had nominal diameters smaller than 4 nm. The remaining 16% of Fe and Cu colloidal particles had nominal diameters between 4 nm and 0.45 μm, and may be in water-insoluble forms (e.g., Fe and Cu oxides) so they may not be “true” water-soluble species. Thus, based on the observations made by Yang et al (2021), we acknowledge that it is possible that the filterable metal fraction in our water extracts may contain some metals in water-insoluble forms with diameters smaller than 0.22 μm that penetrated through the 0.22 μm pore size syringe filters. This will result in over-estimated metal fractional solubilities, which could explain why some of the data points in Figure 6 showed high metal fractional solubilities at low sulfate concentrations. More research needs to be done to characterize the forms of the metals in the various size fractions of what we operationally define as overall water-soluble metal, and this can be the focus of future studies. Discussions on the possibility of nanoparticles in our water extracts has been added into the revised manuscript.

The following changes have been made to the revised manuscript:

Page 7 line 194: "The filterable metal fraction in the water extracts, defined in this study as water-soluble metals, will include all dissolved metal forms and any colloidal particles with diameters smaller than 0.22 µm. This assumes that all colloidal particles with diameters smaller than 0.22 µm can penetrate through the syringe filter, and that the syringe filter's retention efficiency of particles with diameters larger than 0.22 µm is 100 %. The exact sizes and distribution of metal colloidal particles in the filterable metal fraction in water extracts in this study are not known. However, Yang et al. (2021) recently reported that around 84% of Fe and Cu colloidal particles that penetrated through 0.45 µm syringe filters had nominal diameters smaller than 4 nm. The remaining 16% of Fe and Cu colloidal particles had nominal diameters between 4 nm and 0.45 µm, and they may be in water-insoluble forms (e.g., Fe and Cu oxides) so they may not be "true" water-soluble species. Hence, analogous to observations made by Yang et al (2021), it is possible that the filterable metal fractions in water extracts in this study contain some metals in water-insoluble forms with diameters smaller than 0.22 µm that penetrated through the 0.22 µm pore size filters."

Page 23 line 619: "In addition, a recent study by Yang et al. (2021) reported that the filterable metal fractions in the water extracts may contain some metals in water-insoluble forms with small diameters that allowed them to pass through the pores of syringe filters. This would result in over-estimated metal fractional solubilities, which could explain why some of the data points in Figure 6 showed high metal fractional solubilities at low sulfate concentrations."

3. Referee comment: "*l.224: How did you consider the activity coefficient?*"

Author response: The thermodynamic model used in this study, ISORROPIA-II, assumes that the molality based activity coefficient of the hydronium ion is equal to unity. This is stated explicitly in the revised manuscript:

Page 9 line 263: "Fine aerosol pH values were calculated based on the molal definition (Pye et al., 2020):

$$pH = -\log_{10}\gamma_{H^+}H^+_{aq} = -\log_{10}\frac{1000H^+_{air}}{W_i+W_o} \cong -\log_{10}\frac{1000H^+_{air}}{W_i} \quad (1)$$

where γ_{H^+} is the hydronium ion activity coefficient, H^+_{aq} is the hydronium ion concentration within the ambient aerosol liquid water (mol L^{-1}), H^+_{air} is the hydronium ion concentration per volume of air (µg m^{-3}), and W_i and W_o are the aerosol liquid

water concentrations (µg m^{-3}) associated with inorganic and organic species, respectively. H^{+}_{air} and W_i are the outputs provided by the ISORROPIA-II model, which assumes that γ_{H^+} is equals to unity.”

4. Referee comment: “*Fig. S3 and Fig. S4: How do you explain the high contributions of dust for Cu in Fig. S3 as opposed to Fig. S4? How do you explain the low contributions of dust for Fe and Mn in Fig. S4 as opposed to Fig. S3? How do you explain the high contributions of industrial 1 and ship emissions for Mn in Fig. S4 as opposed to Fig. S3? How do you interpret the high contribution of dust for Co? How do you interpret the high contribution of sea salt for Fe?*”

Author response: The arrangement of the sources for some of the metals in Figure S4 of the original manuscript were incorrect; this caused the discrepancies between Figures S3 and S4 of the original manuscript. We thank the referee for pointing out our mistake. This mistake has been corrected in the revised manuscript.

Regarding the high contribution of Co in the dust factor, dust is one of the natural emission sources of Co. Co is widely found in rocks, soil, water, and plants, and it is the 33rd abundant elements in Earth’s crust with an average concentration of 20 µg/g (Lison, 1996). While Co can also be emitted from anthropogenic sources such as coal-fired power generation, vehicle exhaust, and mining activities, these sources were not resolved in this work since we did not measure their source-specific tracers (Wu et al., 2022; Johansson et al., 2009). This information has been included into the revised manuscript.

The high contribution of Fe in the sea salt factor could be explained by the presence of Fe in aerosols originating from marine areas. Some previous studies have also reported a noticeable high contribution of Fe in the sea salt factor in their source apportionment studies (Han et al., 2006; Seneviratne et al., 2017). Fe is present in marine waters due to the deposition of Fe-containing aerosols to marine waters. Fe emissions are dominated by mineral source (41 Tg yr^{-1}) on the global scale. However, substantial Fe concentrations have been found in aerosols over marine areas due to the transport of mineral dust aerosols to these areas. For instance, Fe concentrations (> 0.1 µg m^{-3}) have been reported for aerosols measured over a large region of the Atlantic Ocean due to the outflow of dust from the Sahara Desert, while large Fe concentrations (> 0.5 µg m^{-3}) have been reported for aerosols measured over the Arabian Sea and the Indian Ocean due to the outflow of dust from the Arabian, Lut and Thar deserts (Ito, 2013; Wang et al., 2015). Previous studies have also reported that biomass burning and oil fly ash from fossil fuel combustion contribute to aerosol Fe deposition to marine waters (Matsui et al., 2018). This information has been included into the revised manuscript.

The following changes have been made to the revised manuscript:

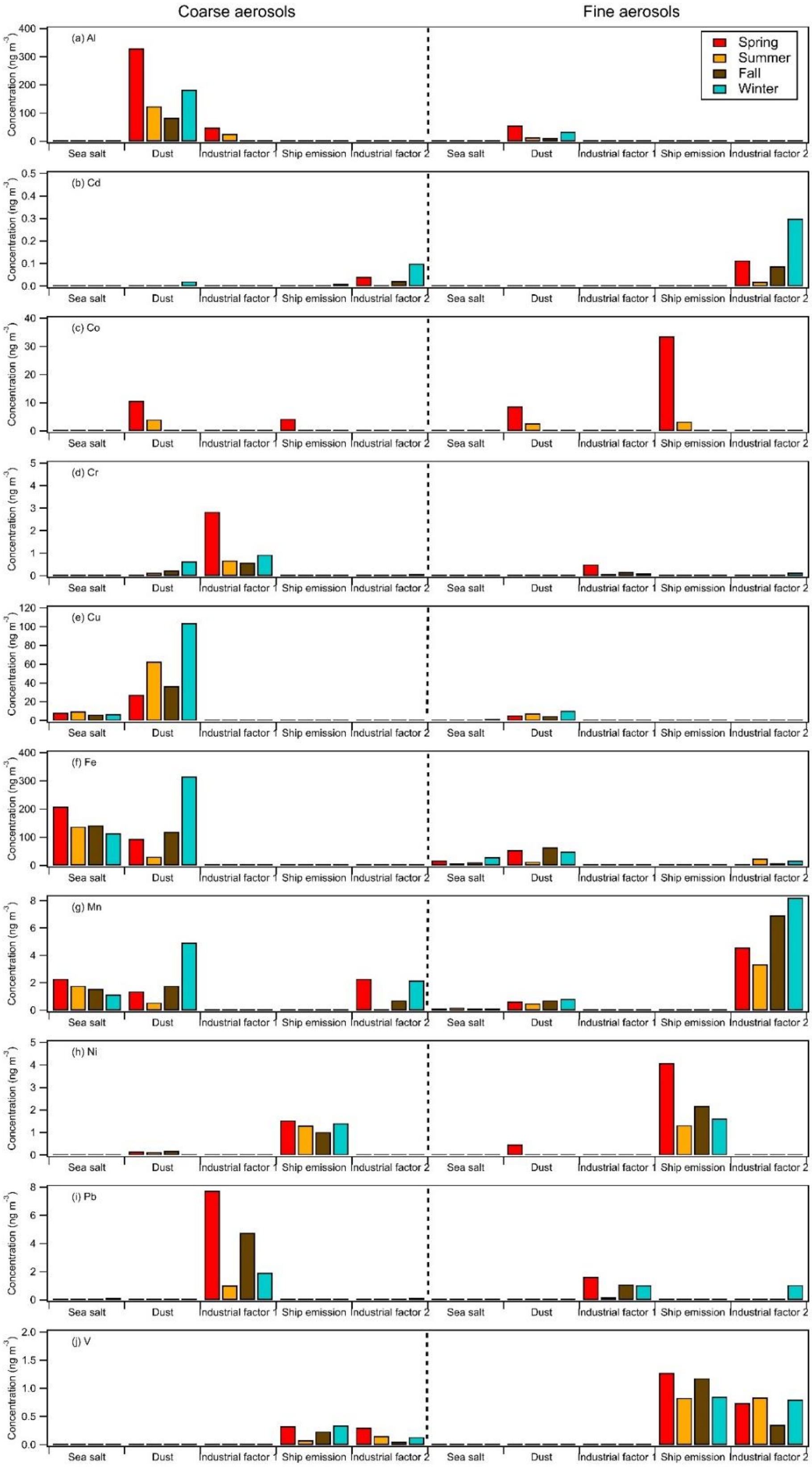

Figure S5: Seasonal mass contributions of each source to each species in coarse and fine aerosols.

SI Page 15 line 250: "The first factor was marked by the high loadings of common sea salt tracers Na^+, Cl^-, and Mg^{2+}, thus it was identified as "sea salt" (Chow et al., 2022). Interestingly, the "sea salt" factor had a noticeably high Fe loading. Previous studies have reported Fe deposition to marine waters from continental outflows of mineral dust, biomass burning aerosols, and oil fly ash (Ito, 2013; Wang et al., 2015; Matsui et al., 2018). This could result in substantial concentrations of Fe in sea salt, which in turn would lead to the high loading of Fe in the "sea salt" factor."

SI Page 15 line 256: "The second factor was identified as "dust" due to its high loadings of Al, Fe, and Mn, which are known mineral dust tracers (Chow et al., 2022). Cu is also a dominant species in this second factor. Previous studies have attributed Cu to brake/tire wear, and Fe and Mn to both dust and brake/tire wear (Garg et al., 2000; Adachi and Tainosho, 2004; Lough et al., 2005). Thus, resuspended road dust containing brake/tire wear particles could have contributed to this "dust" factor. Interestingly, the "dust" factor had a noticeably high Co loading. This could be explained by Co being widely found in rocks, soil, water, and plants. It is the 33rd abundant elements in Earth's crust with an average concentration of 20 µg/g (Lison, 1996). While Co can also be emitted from anthropogenic sources such as coal-fired power generation, vehicle exhaust, and mining activities (Wu et al., 2022; Johansson et al., 2009), these sources were not resolved in this work since we did not measure their source-specific tracers."

5. Referee comment: "*l.473: Fig. 6 does not show strong correlations (R > 0.7) between the fractional solubilities except Cu and sulfate. Please rephrase this.*"

Author response: We have made the following changes in the revised manuscript.

Page 22 line 594: "Together, the statistically significant positive correlations between the fractional solubilities of Cr, Fe, Co, Cu, Pb, and Mn and sulfate, W_i, and H^+_{air} indicated that acid processing likely played an important role in enhancing the solubilities of these six metals."

6. Referee comment: "*How do you explain higher solubilities at lower sulfate and Wi concentrations if acid processing played a major role in enhancing the solubilities of these six metals?*"

Author response: We assume that the referee made this comment based on what we showed in Figure 6. At present, we are unable to explain why some of the data points in Figure 6 showed higher solubilities at lower sulfate and/or W_i concentrations. It is possible that this could be a result of the sulfate, water, levels of acidity, total and water-soluble metal concentrations being different in individual aerosol particles, which would not be captured by the bulk chemical analysis and thermodynamic modeling we performed in this study. The metal dissolution rates in individual aerosol particles could also be significantly different due to differences in metal mineralogy, aerosol acidity levels etc. in individual aerosol particles (Oakes et al., 2012; Longo et al., 2016; Ingall et al., 2018). The question posed by the referee could potentially be answered using a single-particle analytical techniques similar to the ones used by Li et al. (2017), and could be a subject of future studies. In addition, as discussed in our reply to the referee's comment 2, it is possible that the filterable metal fraction in our water extracts may contain some metals in water-insoluble forms with diameters smaller than 0.22 μm that penetrated through the 0.22 μm pore size syringe filters. This will result in over-estimated metal fractional solubilities, which could explain why some of the data points in Figure 6 showed high metal fractional solubilities at low sulfate concentrations. More research needs to be done to characterize the forms of the metals in the various size fractions of what we operationally define as overall water-soluble metal, and this can be the focus of future studies.

The following changes were made to the revised manuscript:

Page 23 line 611: "Despite the statistically significant positive correlations between the fractional solubilities of Cr, Fe, Co, Cu, Pb, and Mn and sulfate, W_i, and H^+_{air} (Table 1), there was significant scatter in the datasets (Figures 6, S7, and S8). This scatter could be a result of the sulfate, W_i, H^+_{air}, total and water-soluble metal concentrations being substantially different in individual aerosol particles, which would not be captured by the bulk chemical analysis and thermodynamic modeling performed in this study. The metal dissolution rates in individual aerosol particles could also be significantly different due to differences in metal mineralogy, aerosol acidity levels, etc. in individual aerosol particles. In addition, a recent study by Yang et al. (2021) reported that the filterable metal fraction in the water extracts may contain some metals in water-insoluble forms with small diameters that allowed them to pass through the pores of syringe filters. This would result in over-estimated metal fractional solubilities, which could explain why some of the datasets in Figure 6 showed high metal fractional solubilities at low sulfate concentrations."

7. Referee comment: "*Why don't you analyze the correlation for each factor? Please discuss the reasons of the stronger correlation between WS metals and sulfate than between the fractional solubility of metals and sulfate.*"

Author response: Based on his comment, we assumed that the referee is suggesting that we perform additional correlation analysis between the metal fractional solubilities and other aerosol components, pH, temperature, and RH. In addition to sulfate, ammonium and nitrate were the other abundant inorganic components measured in fine aerosols. Thus, we performed additional correlation analysis between the metal fractional solubilities and ammonium, nitrate, pH, temperature, and RH. These results are presented in the revised manuscript. The correlations between the metal fractional solubilities and ammonium, nitrate, pH, temperature, and RH were mostly lower than the correlations between the metal fractional solubilities and sulfate.

V and Cd are the metals where the correlations between sulfate concentration and their water-soluble concentrations are significantly stronger compared to the correlations between sulfate concentration and their fractional solubilities. We hypothesize that this could be due to a large fraction of the measured water-soluble V and Cd having the same sources as sulfate and its precursor SO_2. In the case of V, it is known to be present in substantial quantities in the ship emissions, thus it is commonly used as a tracer for ship emissions in source apportionment studies (as was the case for our PMF analysis). Celo et al. (2015) previously reported that substantial concentrations of water-soluble aerosol metals (including V), sulfate, and SO_2 are present in exhaust emissions from the main engines of commercial marine vessels. It is possible that a substantial fraction of water-soluble V measured in our study originated from shipping emissions, instead of being formed from the sulfate-driven acid dissolution of water-insoluble V. Our PMF analysis attributed Cd to industrial emissions. We hypothesize that it is possible that a substantial fraction of water-soluble Cd measured in our study originated from industrial emissions. However, we were unable to find a previous study that explicitly measured water-soluble Cd concentrations emitted from industrial activities.

The following changes were made to the revised manuscript:

Page 20 line 552: "It is possible that the strong correlations of sulfate concentration with water-soluble V and Cd concentrations but not with V and Cd fractional solubilities were due to a large fraction of water-soluble V and Cd having the same sources as sulfate and its precursor (i.e., SO_2). For instance, Celo et al. (2015) reported that substantial concentrations of water-soluble aerosol metals (including V), sulfate, and SO_2 are present in exhaust emissions from the main engines of commercial marine vessels."

Table 1: Spearman rank correlations between the metal fractional solubilities and W_i and H^+_{air} in fine aerosols[a]

Metal	Sulfate	W_i	H^+_{air}	pH
Cr	**0.62**	**0.42**	**0.48**	-0.16
Al	0.14	0.08	0.14	-0.06
Fe	**0.53**	**0.31**	**0.50**	**-0.33**
Ni	0.03	0.01	0.18	**-0.26**
Co	**0.41**	**0.41**	**0.23**	-0.05
Cu	**0.74**	**0.72**	**0.24**	-0.07
Pb	**0.53**	**0.41**	**0.34**	-0.13
Mn	**0.49**	**0.43**	**0.23**	-0.01
V	0.14	0.01	0.21	-0.20
Cd	0.04	0.10	0.13	0.22

[a] Bold: statistically significant ($p < 0.05$)"

Table S3: Spearman rank correlations between the metal fractional solubilities and aerosol components and properties[a]

Metal	Nitrate	Ammonium	RH	Temp
Cr	**0.67**	**0.51**	**-0.53**	**-0.78**
Al	-0.05	0.09	-0.07	-0.09
Fe	-0.04	**0.39**	0.01	0.06
Ni	**-0.26**	-0.05	**0.25**	**0.77**
Co	0.16	**0.33**	-0.01	0.02
Cu	**0.67**	**0.59**	0.00	0.00
Pb	**0.34**	**0.38**	-0.25	-0.12

Mn	0.14	**0.22**	0.02	-0.11
V	**-0.29**	**0.23**	0.18	0.10
Cd	-0.16	0.11	0.08	-0.17

[a] Bold: statistically significant ($p < 0.05$)”

Additional revisions

The stage with nominal cut points of 1.8 µm was mistakenly put in “coarse mode” for Figure 2, Figure 4, and Table S1. We have made the following revisions in the revised manuscript:

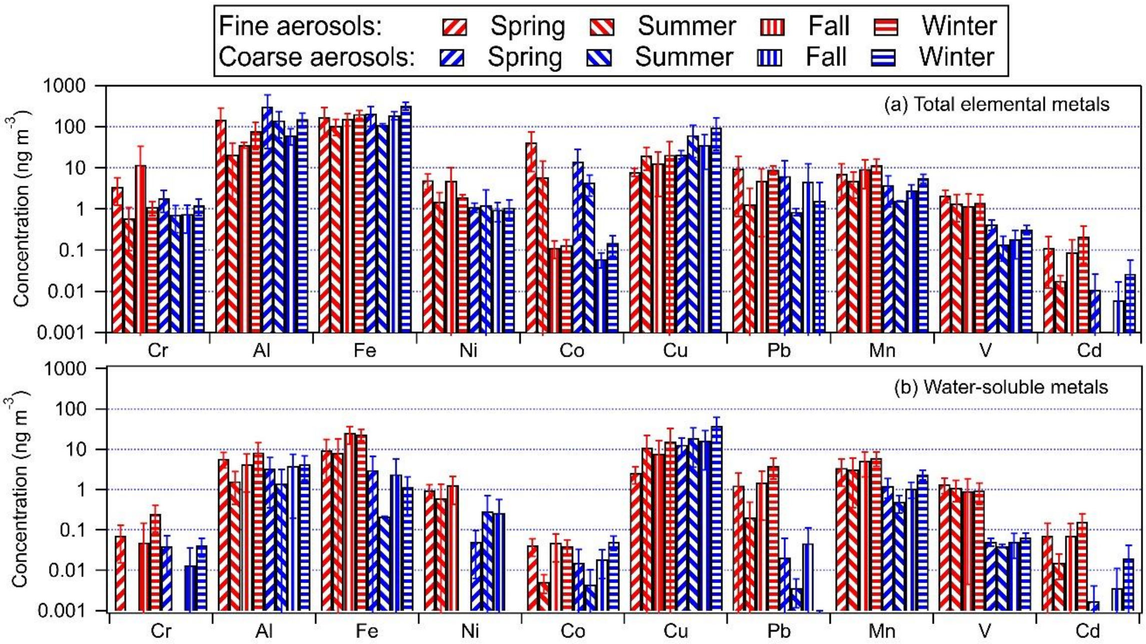

Figure 2: Seasonal average mass concentrations of (a) total metals and (b) water-soluble metals in fine (red) and coarse (yellow) aerosols. The error bars represent one standard deviation. The y axes are on logarithm scales.

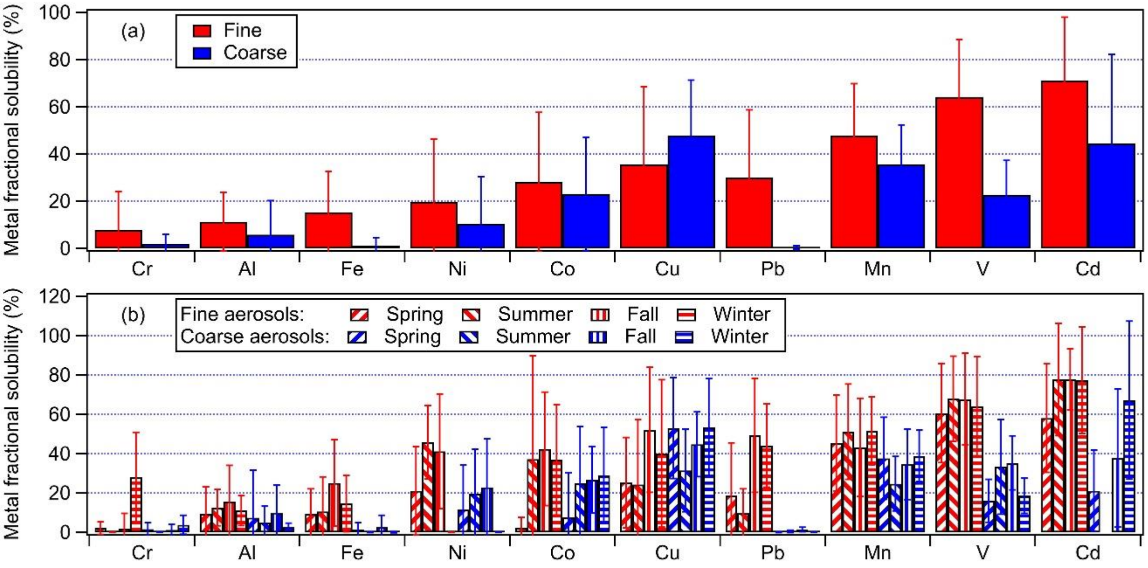

Figure 4: (a) Study-averaged fractional solubilities of metals in fine and coarse aerosols. (b) Seasonal average fractional solubilities of metals in fine and coarse aerosols. The error bars represent one standard deviation.

Table S1: Comparison of average total metal concentrations (ng m^{-3}) in 2012/2013 by Jiang et al. (2015) and 2021/2022 (this study) at a Kowloon Tong in Hong Kong

(a) Comparison of winter mass concentrations

Metal	Jiang et al. (2015)[a]		This study[b]	
	Fine	Coarse[c]	Fine	Coarse[c]
Cr	3	2.7	1.11	0.94
Al	254	301.2	78.53	135.12
Fe	137	142	204.71	301.22
Ni	4.4	1.6	1.97	0.84
Cu	19.7	4	20.61	61.20
Pb	49.4	2.9	8.98	0.86
Mn	17.1	5.2	11.82	5.18
V	9.2	0.9	1.41	0.30
Cd	1.1	0.1	0.22	0.03

[a] Measurements were performed from 12 November 2012 to 10 December 2012.

[b] Measurements were performed from 15 December 2021 to 26 January 2022.

[c] Mass concentrations measured for the MOUDI impactor stage 11 (18 µm nominal cutoff) was excluded in this comparison since Jiang et al. (2015) reported mass concentrations for $PM_{2.5\text{-}10}$ for their coarse aerosol measurements.

(b) Comparison of spring/summer mass concentrations

Metal	Jiang et al. (2015)[a]		This study[b]	
	Fine	Coarse[c]	Fine	Coarse[c]
Cr	7.2	1.5	2.53	1.24
Al	591	528.9	107.14	237.76

Fe	190.6	153	150.33	163.59
Ni	10	1.3	3.84	0.94
Cu	21.6	5.5	11.98	24.16
Pb	52.7	2.8	6.92	3.69
Mn	19.3	5	6.45	2.87
V	25.6	1.8	1.90	0.31
Cd	1.2	0.1	0.08	0.01

[a] Measurements were performed from 8 April 2013 to 13 May 2013.

[b] Measurements were performed from 7 March 2021 to 4 April 2021, 23 to 30 June 2021, and 7 to 14 July 2021.

[c] Mass concentrations measured for the MOUDI impactor stage 11 (18 µm nominal cutoff) was excluded in this comparison since Jiang et al. (2015) reported mass concentrations for $PM_{2.5-10}$ for their coarse aerosol measurements.

Page 1 line 22: "The study-averaged metal fractional solubilities spanned a wide range for both fine (7.8 % to 71.2 %) and coarse (0.4 % to 47.9 %) aerosols, but higher fractional solubilities were typically observed for fine aerosols."

Page 10 line 288: "The metals could be arranged in the following order based on their abundances: Fe > Al > Cu > Co > Mn > Pb > Cr > Ni > V > Cd."

Page 12 line 342: "As shown in Table S1, lower mass concentrations were measured in fine (21 % to 93 % lower) and coarse (0.5 % to 92 % lower) aerosols for most of the metals in this study."

Page 15 line 428: "The study-averaged metal fractional solubilities spanned a wide range for both fine (7.8 % to 71.2 %) and coarse (0.4 % to 47.9 %) aerosols. With the exception of Cu, the metals generally exhibited higher fractional solubilities in fine aerosols compared to coarse aerosols."

Page 24 line 651: "The total metals could be arranged in the following order based on their abundances: Fe > Al > Cu > Co > Mn > Pb > Cr > Ni > V > Cd."

References:

Adachi, K. and Tainosho, Y.: Characterization of heavy metal particles embedded in tire dust, Environment International, 30, 1009-1017, https://doi.org/10.1016/j.envint.2004.04.004, 2004.

Celo, V., Dabek-Zlotorzynska, E., and McCurdy, M.: Chemical Characterization of Exhaust Emissions from Selected Canadian Marine Vessels: The Case of Trace Metals and Lanthanoids, Environmental Science & Technology, 49, 5220-5226, https://doi.org/10.1021/acs.est.5b00127, 2015.

Chen, Q., Wang, M., Wang, Y., Zhang, L., Li, Y., and Han, Y.: Oxidative Potential of Water-Soluble Matter Associated with Chromophoric Substances in PM2.5 over Xi'an, China, Environmental Science & Technology, 53, 8574-8584, https://doi.org/10.1021/acs.est.9b01976, 2019.

Chow, W. S., Huang, X. H. H., Leung, K. F., Huang, L., Wu, X., and Yu, J. Z.: Molecular and elemental marker-based source apportionment of fine particulate matter at six sites in Hong Kong, China, Science of The Total Environment, 813, 152652, https://doi.org/10.1016/j.scitotenv.2021.152652, 2022.

Costa, D. L. and Dreher, K. L.: Bioavailable transition metals in particulate matter mediate cardiopulmonary injury in healthy and compromised animal models, Environmental Health Perspectives, 105, 1053-1060, https://doi.org/10.1289/ehp.97105s51053, 1997.

Fang, T., Guo, H., Verma, V., Peltier, R. E., and Weber, R. J.: PM2.5 water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies, Atmos. Chem. Phys., 15, 11667-11682, https://doi.org/10.5194/acp-15-11667-2015, 2015.

Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, Environmental Science & Technology, 51, 2611-2620, https://doi.org/10.1021/acs.est.6b06151, 2017.

Gao, D., Mulholland, J. A., Russell, A. G., and Weber, R. J.: Characterization of water-insoluble oxidative potential of PM2.5 using the dithiothreitol assay, Atmospheric Environment, 224, https://doi.org/10.1016/j.atmosenv.2020.117327, 2020.

Garg, B. D., Cadle, S. H., Mulawa, P. A., Groblicki, P. J., Laroo, C., and Parr, G. A.: Brake Wear Particulate Matter Emissions, Environmental Science & Technology, 34, 4463-4469, https://doi.org/10.1021/es001108h, 2000.

Han, J. S., Moon, K. J., Lee, S. J., Kim, Y. J., Ryu, S. Y., Cliff, S. S., and Yi, S. M.: Size-resolved source apportionment of ambient particles by positive matrix factorization at Gosan background site in East Asia, Atmos. Chem. Phys., 6, 211-223, 10.5194/acp-6-211-2006, 2006.

He, X., Liu, P., Zhao, W., Xu, H., Zhang, R., and Shen, Z.: Size distribution of water-soluble metals in atmospheric particles in Xi'an, China: Seasonal variations, bioavailability, and health risk assessment, Atmospheric Pollution Research, 12, 101090, https://doi.org/10.1016/j.apr.2021.101090, 2021.

Heal, M. R., Elton, R. A., Hibbs, L. R., Agius, R. M., and Beverland, I. J.: A time-series study of the health effects of water-soluble and total-extractable metal content of airborne particulate matter, Occupational and Environmental Medicine, 66, 636-638, https://doi.org/10.1136/oem.2008.045310, 2009.

Hopke, P. K., Lamb, R. E., and Natusch, D. F. S.: Multielemental characterization of urban roadway dust, Environmental Science & Technology, 14, 164-172, https://doi.org/10.1021/es60162a006, 1980.

Ingall, E. D., Feng, Y., Longo, A. F., Lai, B., Shelley, R. U., Landing, W. M., Morton, P. L., Nenes, A., Mihalopoulos, N., Violaki, K., Gao, Y., Sahai, S., and Castorina, E.: Enhanced Iron

Solubility at Low pH in Global Aerosols, Atmosphere, 9, 201, 2018.

Ito, A.: Global modeling study of potentially bioavailable iron input from shipboard aerosol sources to the ocean, Global Biogeochemical Cycles, 27, 1-10, https://doi.org/10.1029/2012GB004378, 2013.

Jiang, S. Y., Kaul, D. S., Yang, F., Sun, L., and Ning, Z.: Source apportionment and water solubility of metals in size segregated particles in urban environments, Science of The Total Environment, 533, 347-355, https://doi.org/10.1016/j.scitotenv.2015.06.146, 2015.

Jiang, S. Y. N., Yang, F., Chan, K. L., and Ning, Z.: Water solubility of metals in coarse PM and PM2.5 in typical urban environment in Hong Kong, Atmospheric Pollution Research, 5, 236-244, https://doi.org/10.5094/APR.2014.029, 2014.

Johansson, C., Norman, M., and Burman, L.: Road traffic emission factors for heavy metals, Atmospheric Environment, 43, 4681-4688, https://doi.org/10.1016/j.atmosenv.2008.10.024, 2009.

Li, W., Xu, L., Liu, X., Zhang, J., Lin, Y., Yao, X., Gao, H., Zhang, D., Chen, J., Wang, W., Harrison, R. M., Zhang, X., Shao, L., Fu, P., Nenes, A., and Shi, Z.: Air pollution–aerosol interactions produce more bioavailable iron for ocean ecosystems, Science Advances, 3, e1601749, https://doi.org/10.1126/sciadv.1601749, 2017.

Lison, D.: Human Toxicity of Cobalt-Containing Dust and Experimental Studies on the Mechanism of Interstitial Lung Disease (Hard Metal Disease), Critical Reviews in Toxicology, 26, 585-616, https://doi.org/10.3109/10408449609037478, 1996.

Longo, A. F., Feng, Y., Lai, B., Landing, W. M., Shelley, R. U., Nenes, A., Mihalopoulos, N., Violaki, K., and Ingall, E. D.: Influence of Atmospheric Processes on the Solubility and Composition of Iron in Saharan Dust, Environmental Science & Technology, 50, 6912-6920, https://doi.org/10.1021/acs.est.6b02605, 2016.

Lough, G. C., Schauer, J. J., Park, J.-S., Shafer, M. M., DeMinter, J. T., and Weinstein, J. P.: Emissions of Metals Associated with Motor Vehicle Roadways, Environmental Science & Technology, 39, 826-836, https://doi.org/10.1021/es048715f, 2005.

Matsui, H., Mahowald, N. M., Moteki, N., Hamilton, D. S., Ohata, S., Yoshida, A., Koike, M., Scanza, R. A., and Flanner, M. G.: Anthropogenic combustion iron as a complex climate forcer, Nature Communications, 9, 1593, https://doi.org/10.1038/s41467-018-03997-0, 2018.

Oakes, M., Ingall, E. D., Lai, B., Shafer, M. M., Hays, M. D., Liu, Z. G., Russell, A. G., and Weber, R. J.: Iron Solubility Related to Particle Sulfur Content in Source Emission and Ambient Fine Particles, Environmental Science & Technology, 46, 6637-6644, https://doi.org/10.1021/es300701c, 2012.

Perron, M. M. G., Strzelec, M., Gault-Ringold, M., Proemse, B. C., Boyd, P. W., and Bowie, A. R.: Assessment of leaching protocols to determine the solubility of trace metals in aerosols, Talanta, 208, 120377, https://doi.org/10.1016/j.talanta.2019.120377, 2020.

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr, J. L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I. T., McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles and clouds, Atmos. Chem. Phys., 20, 4809-4888, https://doi.org/10.5194/acp-20-4809-2020, 2020.

Seneviratne, S., Handagiripathira, L., Sanjeevani, S., Madusha, D., Waduge, V. A. A., Attanayake, T., Bandara, D., and Hopke, P. K.: Identification of Sources of Fine Particulate Matter in Kandy, Sri Lanka, Aerosol and Air Quality Research, 17, 476-484, 10.4209/aaqr.2016.03.0123, 2017.

Wang, R., Balkanski, Y., Boucher, O., Bopp, L., Chappell, A., Ciais, P., Hauglustaine, D., Peñuelas, J., and Tao, S.: Sources, transport and deposition of iron in the global atmosphere, Atmos. Chem. Phys., 15, 6247-6270, https://doi.org/10.5194/acp-15-6247-2015, 2015.

Wu, Y., Liu, Q., Ma, J., Zhao, W., Chen, H., and Qu, Y.: Antimony, beryllium, cobalt, and vanadium in urban park soils in Beijing: Machine learning-based source identification and health risk-based soil environmental criteria, Environmental Pollution, 293, 118554, https://doi.org/10.1016/j.envpol.2021.118554, 2022.

Zhou, Y., Zhang, Y., Griffith, S. M., Wu, G., Li, L., Zhao, Y., Li, M., Zhou, Z., and Yu, J. Z.: Field Evidence of Fe-Mediated Photochemical Degradation of Oxalate and Subsequent Sulfate Formation Observed by Single Particle Mass Spectrometry, Environmental Science & Technology, 54, 6562-6574, https://doi.org/10.1021/acs.est.0c00443, 2020.

Zhu, X., Prospero, J. M., Savoie, D. L., Millero, F. J., Zika, R. G., and Saltzman, E. S.: Photoreduction of iron(III) in marine mineral aerosol solutions, Journal of Geophysical Research: Atmospheres, 98, 9039-9046, https://doi.org/10.1029/93JD00202, 1993.