153 The three PM fractions collected at NB and UN sites had similar mass concentrations. Although
154 NB site was located in an iron and steelmaking industrial area, PM samples were collected at
155 upwind of emissions as the downwind was the East China Sea. The industrial steelmaking facility
156 at the NB site was also of the most recent age with modern particle capture devices.
157
158 ***Environmental impact assessment***
159 The environmental impact assessment categories investigated in this work using the measured
160 trace metal concentrations and for the three PM fractions are presented in Fig. 3. At the coarse
161 fraction of $PM_{2.1\text{-}9.0}$, the sampling site of KM showed the highest ecotoxicity for freshwater,
162 terrestrial, marine and human, followed by WH, NJ, NB and UN for the same size fraction. This
163 may be because the steelwork at the KM site is the oldest and may be a reflection of the age of the
164 facility. The KM steelwork plant is also located next to a busy main road. According to the previous
165 studies by Barmpadimos *et al.* (2011) and Charron and Harrison (2005), the traffic emissions related
166 to tyre and brake abrasion were also a significant contributor to the coarse PM particles. Hence, the
167 long running operation of KM plant and the surrounded heavy traffic dominated the coarse PM
168 pollution at KM.
169 The same order of KM>WH>NJ>NB>UN at $PM_{2.1\text{-}9.0}$ fractions was also found for the intermodal
170 fraction of $PM_{1.1\text{-}2.1}$ for the human toxicity (Fig. 3). However, the maximum freshwater, marine and
171 terrestrial ecotoxicity were found at the WH site where the steelwork plant was built in 1958 and
172 had the largest annual iron and steel production of 20 million tonnes among the four investigated
173 steelworks.
174 The fine $PM_{1.1}$ particles at WH, NJ, NB and UN had higher values in the categories of freshwater
175 ecotoxicity, terrestrial ecotoxicity, marine ecotoxicity and human toxicity than their corresponding
176 $PM_{1.1\text{-}2.1}$ and $PM_{2.1\text{-}9.0}$ fractions at each site. This is because small particles tend to be more polluted

177 with heavy metals, due to the nucleation and coagulation mode of particle formation mechanisms,
178 than the intermodal and especially the coarse fractions, where the mechanically generated particles
179 dominate (Samara and Voutsa, 2005; Hassanvand *et al.*, 2015). Furthermore, $PM_{1.1}$ particles can
180 travel up to tens of kilometres in the atmosphere (WHO, 2006) posing significant ecological risk as
181 well as carcinogenic and mutagenic respiratory risks to humans over a large geographical area
182 (Saeedi *et al.*, 2012; Zajusz-Zubek *et al.*, 2017).
183
184 ***Freshwater ecotoxicity***
185 The maximum freshwater ecotoxicity was found to be caused by $PM_{2.1\text{-}9.0}$ contamination at the
186 KM steelmaking site (Fig. 4). The largest contributor to freshwater ecotoxicity at $PM_{2.1\text{-}9.0}$ was V
187 with 55% contribution, followed by Cu with 26%, while the contribution of other elements to the
188 freshwater ecotoxicity ranged from 0.05% to 6.6% (Fig. 4). Previous studies showed that V
189 contamination at coarse particles was used as an indicator of diesel combustion (Onat *et al.*, 2013;
190 Wei *et al.*, 2014; Ogundele *et al.*, 2016). Hence, the traffic in addition to the local steelmaking
191 activities were the dominant sources resulting in the freshwater ecotoxicity at the KM sampling site.
192 In addition to KM, the freshwater ecotoxicity at WH, NJ, NB and UN were largely contributed
193 by Cu ranging from 45% to 77% followed by Zn ranging from 10% to 38% (Fig. 4). Cu and Zn
194 contamination have been observed to play a significant negative role in the diversity and trophic
195 structure of the biological communities, such as freshwater mussel and algae in the aquatic systems
196 (Wilde *et al.*, 2006; Wang *et al.*, 2010; Wright *et al.*, 2018).
197
198 ***Terrestrial ecotoxicity***
199 The largest terrestrial ecotoxicity was found in the $PM_{1.1}$ particle size range at WH with 1.31E-
200 09 (kg 1,4-DB eq) (Fig. 5). The dominant contributor was Cu which was responsible for 72% of the

terrestrial ecotoxicity at WH. Compared to $PM_{1.1}$ at WH, $PM_{1.1}$ at NJ posed a slightly lower terrestrial ecotoxicity dominated by Zn with 54% contribution (Fig. 5).

Higher Zn contribution for $PM_{1.1}$ at site NJ compared to WH may be related to the differences in the steelmaking facilities. Steelwork plants at NJ and WH both have blast furnaces (BF) and blast oxygen furnaces (BOF) for steel production, but NJ plant has additional electric arc furnace (EAF) for processing of melting scrap for recycling of steel (Yang *et al.*, 2019). It has been evidenced that EAF generates more Zn emissions than the BF-BOF route (8% vs 19.4%) (Nyirenda, 1991; Jha, 2001).

Marine ecotoxicity

Similar to terrestrial ecotoxicity, $PM_{1.1}$ at WH and NJ were found to contribute to higher marine ecotoxicity (Fig. 6). Cu in $PM_{1.1}$ at WH and NJ contributed 76% and 45% of the total terrestrial ecotoxicity. In addition to Cu, the Zn contamination in $PM_{1.1}$ was responsible for 19% and 46% of marine ecotoxicity at WH and NJ, respectively.

Both Cu and Zn are essential elements with functions in oxygen transport (e.g. Cu) (Kim *et al.*, 2008) and enzyme co-factors or metalloenzymes (e.g. Cu and Zn) (Soetan *et al.*, 2010). However, elevated Cu and Zn concentrations can result in marine pollution, damaging the quality of sediments (Miller *et al.*, 2000) and posing a risk to marine animals (Lavery *et al.*, 2009) and other organisms (Debelius *et al.*, 2009).

Human toxicity

$PM_{1.1}$ had significantly higher human toxicity than the corresponding fractions of $PM_{1.1\text{-}2.1}$ and $PM_{2.1\text{-}9.0}$ at the five sampling sites (Fig. 7). PM emissions at the three size fractions in KM, WH and NJ posed higher health risks to humans than UN as a background site and NB site which has a flue

gas recirculation system with 45% reduction of PM emissions during the steelmaking process (CEIA, 2017).

The human toxicity of PM emissions was dominated by Pb contamination, especially for the fine $PM_{1.1}$ particles. For example, the contribution of Pb on human toxicity of $PM_{1.1}$ size fraction for sites KM and NJ was up to 87% and 76%, respectively (Fig. 7). Airborne Pb emissions have cumulative toxic impacts on humans and adversely affect the neurological, hematological, gastrointestinal, cardiovascular and renal systems (U.S. EPA, 2017). As a result, around 0.6% of the global burden of disease is estimated to be associated with exposure to Pb (WHO, 2010b).

The contributions of As contamination to human toxicity were stable at the three size fractions which were 8% – 19% at $PM_{2.1\text{-}9.0}$, 6% – 26% at $PM_{1.1\text{-}2.1}$ and 6% – 26% at $PM_{1.1}$ particles. Long-term exposure to airborne As emissions can increase the risks of developing lung cancer, especially at fine particles of $PM_{1.1}$ which can penetrate deep into the alveolar regions of the human lungs (WHO, 2010a; Poh *et al.*, 2018).

In addition to As and Pb contamination, airborne Mn was responsible for 2% – 11% of human toxicity at $PM_{1.1}$, but increased to 8% – 18% at $PM_{1.1\text{-}2.1}$ and reached maximum contribution of 23% – 34% at $PM_{2.1\text{-}9.0}$ size fractions. Unlike As and Pb, which are classified as carcinogenic to humans (Group 1) and possibly carcinogenic to humans (Group 2A), respectively (WHO, 2010a, b), Mn is considered as a nutritient under a safe limit (ATSDR, 2012). However, exceeding Mn concentrations can cause environmental implications with potential risks to human health (Elder *et al.*, 2006), especially for the children population. A number of studies documented the neurotoxic effects of Mn associated with learning disabilities and deficits in intellectual functions of children (Riojas-Rodriguez *et al.*, 2010).

CONCLUSION

This study aimed to investigate the contamination of PM particles near iron and steelmaking areas in China. PM samples at ranges of less than 1.1 μm, 1.1 – 2.1 μm and 2.1 – 9.0 μm in diameter were collected in this study. All the samples were subject to mass concentration and trace element analyses. LCIA method was used to assess the impact of trace element contamination at different PM fractions on human and ecological health.

The mass concentration results showed that PM samples collected from intensive iron and steelmaking areas were higher than those collected from background areas and the published $PM_{2.5}$ and PM_{10} data online at each city, confirming the industrial emission played a significant role to the local air quality. The LCIA ~~R~~results showed that PM metal emission had a much higher human toxicity than freshwater, terrestrial and marine ecotoxicity. Among the three PM fractions, $PM_{1.1}$ particles posed significantly higher risks to both human and ecosystem health than the other two fractions. This study further revealed that the Cu and Zn contamination were the key contributors to freshwater, marine and terrestrial ecotoxicity, while Pb was the dominant contributor to human toxicity. Findings presented in this study provide a potential guideline to help the steel mills make effective actions to control the key toxic metals present in the PM emissions, improving the local environmental quality and reducing the risks to public health.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR). Public Health Statement for Manganese, https://www.atsdr.cdc.gov/phs/phs.asp?id=100&tid=23, Last Access: September 10, 2019.

Barmpadimos, I., Nufer, M., Oderbolz, D.C., Keller, J., Aksoyoglu, S., Hueglin, C., Baltensperger, U. and Prévôt, A.S.H. (2011). The weekly cycle of ambient concentrations and traffic emissions of coarse (PM_{10}–$PM_{2.5}$) atmospheric particles. *Atmos. Environ.* 45: 4580-4590.

Borggaard, O.K., Hansen, H.C.B., Holm, P.E., Jensen, J.K., Rasmussen, S.B., Sabiene, N., Steponkaite, L. and Strobel, B.W. (2009). Experimental assessment of using soluble humic substances for remediation of heavy metal polluted soils. *Soil Sediment Contam.* 18: 369-382.

Calderon, J., Navarro, M.E., Jimenez-Capdeville, M.E., Santos-Diaz, M.A., Golden, A., Rodriguez-Leyva, I., Borja-Aburto, V. and Diaz-Barriga, F. (2001). Exposure to arsenic and lead and neuropsychological development in Mexican children. *Environ. Res.* 85: 69-76.

Charron, A. and Harrison, R.M. (2005). Fine ($PM_{2.5}$) and coarse ($PM_{2.5\text{-}10}$) particulate matter on a heavily trafficked London highway: sources and processes. *Environ. Sci. Technol.* 30: 7768-7776.

Cheng, F.-J., Lee, K.-H., Lee, C.-W. and Hsu, P.-C. (2019). Association between particulate matter air pollution and hospital emergency room visits for pneumonia with septicemia: A retrospective analysis. *Aerosol Air Qual. Res.* 19: 345-354.

China Environmental Impact Assessment 环境保护部环境工程评估中心 (CEIA) (2017). Methods and Strategies to Reduce Emissions of Atmospheric Particles in Iron and Steelmaking Indutries 钢铁行业大气污染防治最佳可行技术及减排潜力分析报告, Beijing, p. 73.

Debelius, B., Forja, J.M., DelValls, A. and Lubian, L.M. (2009). Toxicity and bioaccumulation of copper and lead in five marine microalgae. *Ecotoxicol. Environ. Saf.* 72: 1503-1513.

291 Elder, A., Gelein, R., Silva, V., Feikert, T., Opanashuk, L., Carter, J., Potter, R., Maynard, A., Ito,
292 Y., Finkelstein, J. and Oberdorster, G. (2006). Translocation of inhaled ultrafine manganese oxide
293 particles to the central nervous system. *Environ. Health Perspect.* 114: 1172-1178.
294 Hassanvand, M.S., Naddafi, K., Faridi, S., Nabizadeh, R., Sowlat, M.H., Momeniha, F.,
295 Gholampour, A., Arhami, M., Kashani, H., Zare, A., Niazi, S., Rastkari, N., Nazmara, S., Ghani,
296 M. and Yunesian, M. (2015). Characterization of PAHs and metals in indoor/outdoor
297 $PM_{10}/PM_{2.5}/PM_1$ in a retirement home and a school dormitory. *Sci. Total Environ.* 527-528: 100-
298 110.
299 Jha, M.K. (2001). Review of hydrometallurgical recovery of zinc from industrial wastes. *Resour.*
300 *Conserv. Recy.* 33: 1-22.
301 Jiang, N., Liu, X., Wang, S., Yu, X., Yin, S., Duan, S., Wang, S., Zhang, R. and Li, S. (2019).
302 Pollution characterization, source identification, and health risks of atmospheric-particle-bound
303 heavy metals in PM_{10} and $PM_{2.5}$ at multiple sites in an emerging megacity in the central region
304 of China. *Aerosol Air Qual. Res.* 19: 247-271.
305 Kim, B.E., Nevitt, T. and Thiele, D.J. (2008). Mechanisms for copper acquisition, distribution and
306 regulation. *Nat. Chem. Biol.* 4: 176-185.
307 Lavery, T.J., Kemper, C.M., Sanderson, K., Schultz, C.G., Coyle, P., Mitchell, J.G. and Seuront, L.
308 (2009). Heavy metal toxicity of kidney and bone tissues in South Australian adult bottlenose
309 dolphins (Tursiops aduncus). *Mar. Environ. Res.* 67: 1-7.
310 Liu, J., Zheng, B.S., Aposhian, H.V., Zhou, Y.S., Chen, M.L., Zhang, A.H. and Waalkes, M.P.
311 (2002). Chronic arsenic poisoning from burning high‐arsenic‐containing coal in Guizhou,
312 China. *Environ. Health Perspect.* 110: 119-122.
313 Miller, B.S., Pirie, D.J. and Redshaw, C.J. (2000). An assessment of the contamination and toxicity
314 of marine sediments in the Holy Loch, Scotland. *Mar. Pollut. Bull.* 40: 22-35.

315 Mohiuddin, K., Strezov, V., Nelson, P.F. and Evans, T. (2016). Bonding Structure and Mineral
316 Analysis of Size Resolved Atmospheric Particles nearby Steelmaking Industrial Sites in Australia.
317 *Aerosol Air Qual. Res.* 16: 1638-1650.
318 Mohiuddin, K., Strezov, V., Nelson, P.F. and Stelcer, E. (2014). Characterisation of trace metals in
319 atmospheric particles in the vicinity of iron and steelmaking industries in Australia. *Atmos.*
320 *Environ.* 83: 72-79.
321 Nyirenda, R.L. (1991). The processing of steelmaking flue-dust: A review. *Miner. Eng.* 4: 1003-
322 1025.
323 Ogundele, L.T., Owoade, O.K., Olise, F.S. and Hopke, P.K. (2016). Source identification and
324 apportionment of $PM_{2.5}$ and $PM_{2.5–10}$ in iron and steel scrap smelting factory environment using
325 PMF, PCFA and UNMIX receptor models. *Environ. Monit. Assess.* 188.
326 Onat, B., Sahin, U.A. and Akyuz, T. (2013). Elemental characterization of $PM_{2.5}$ and PM_{1} in dense
327 traffic area in Istanbul, Turkey. *Atmos. Pollut. Res.* 4: 101-105.
328 Poh, T.Y., Ali, N., Mac Aogain, M., Kathawala, M.H., Setyawati, M.I., Ng, K.W. and Chotirmall,
329 S.H. (2018). Inhaled nanomaterials and the respiratory microbiome: clinical, immunological and
330 toxicological perspectives. *Part. Fibre. Toxicol.* 15: 46.
331 Riojas-Rodriguez, H., Solis-Vivanco, R., Schilmann, A., Montes, S., Rodriguez, S., Rios, C. and
332 Rodriguez-Agudelo, Y. (2010). Intellectual function in Mexican children living in a mining area
333 and environmentally exposed to manganese. *Environ. Health Perspect.* 118: 1465-1470.
334 Saeedi, M., Li, L.Y. and Salmanzadeh, M. (2012). Heavy metals and polycyclic aromatic
335 hydrocarbons: Pollution and ecological risk assessment in street dust of Tehran. *J. Hazard. Mater.*
336 227-228: 9-17.
337 Samara, C. and Voutsa, D. (2005). Size distribution of airborne particulate matter and associated
338 heavy metals in the roadside environment. *Chemosphere* 59: 1197-1206.

339 Sarkodie, S.A., Strezov, V., Jiang, Y. and Evans, T. (2019). Proximate determinants of particulate
340 matter (PM2.5) emission, mortality and life expectancy in Europe, Central Asia, Australia,
341 Canada and the US. *Sci. Total Environ.* 683: 489-497.
342 Semlali, R.M., Dessogne, J.B., Monna, F., Bolte, J., Azimi, S., Navarro, N., Denaix, L., Loubet, M.,
343 Chateau, C. and Van Oort, F. (2004). Modeling lead input and output in soils using lead isotopic
344 geochemistry. *Environ. Sci. Technol.* 38: 1513-1521.
345 Soetan, K.O., Olaiya, C.O. and Oyewole, O.E. (2010). The importance of mineral elements for
346 humans, domestic animals and plants-A review. *Afr. J. Food Sci.* 4: 200-222.
347 Taylor, M.P., Isley, C.F. and Glover, J. (2019). Prevalence of childhood lead poisoning and
348 respiratory disease associated with lead smelter emissions. *Environ. Int.* 127: 340-352.
349 U.S. EPA (2016a). National Lakes Assessment 2012 Results, Washington, DC, p. 2.
350 U.S. EPA (2016b). National Rivers and Streams Assessment 2008-2009, Washington, DC, p. 2.
351 U.S. EPA. Basic Information about Lead Air Pollution, https://www.epa.gov/lead-air-
352 pollution/basic-information-about-lead-air-pollution#health, Last Access: September 10, 2019.
353 Wang, N., Ingersoll, C.G., Ivey, C.D., Hardesty, D.K., May, T.W., Augspurger, T., Roberts, A.D.,
354 van Genderen, E. and Barnhart, M.C. (2010). Sensitivity of early life stages of freshwater mussels
355 (Unionidae) to acute and chronic toxicity of lead, cadmium, and zinc in water. *Environ. Toxicol.*
356 *Chem.*: 2053-2063.
357 Wasserman, G.A., Liu, X., Parvez, F., Factor-Litvak, P., Kline, J., Siddique, A.B., Shahriar, H.,
358 Uddin, M.N., van Geen, A., Mey, J.L., Balac, O. and Graziano, J.H. (2016). Child intelligence
359 and reductions in water arsenic and manganese: A two-year follow-up study in bangladesh.
360 *Environ. Health Perspect.* 124: 1114-1120.
361 Wei, Z., Wang, L.T., Chen, M.Z. and Zheng, Y. (2014). The 2013 severe haze over the Southern
362 Hebei, China: $PM_{2.5}$ composition and source apportionment. *Atmos. Pollut. Res.* 5: 759-768.

Wesely, M.L. and Hicks, B.B. (2000). A review of the current status of knowledge on dry deposition. *Atmos. Environ.* 34: 2261-2282.

WHO (2006). Health Risks of Particulate Matter From Long-Range Transboundary Air Pollution, Denmark, p. 113.

WHO (2007). Health Risks of Heavy Metals From Long-Range Transboundary Air Pollution, Germany, p. 144.

WHO (2010a). Exposure to Arsenic: A Major Public Health Concern, Geneva, Switzerland.

WHO (2010b). Exposure to Lead: A Major Public Health Concern Geneva, Switzerland, p. 6.

WHO (2013). Health Effects of Particulate Matter - Policy Implications For Countries In Eastern Europe, Caucasus And Central Asia, Denmark, p. 20.

WHO. Ambient (Outdoor) Air Quality and Health, https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health, Last Access: September 13, 2019.

Wilde, K.L., Stauber, J.L., Markich, S.J., Franklin, N.M. and Brown, P.L. (2006). The effect of pH on the uptake and toxicity of copper and zinc in a tropical freshwater alga (*chlorella* sp.). *Arch. Environ. Contam. Toxicol.* 51: 174-185.

Wright, L.P., Zhang, L., Cheng, I., Aherne, J. and Wentworth, G.R. (2018). Impacts and Effects Indicators of Atmospheric Deposition of Major Pollutants to Various Ecosystems - A Review. *Aerosol Air Qual. Res.* 18: 1953-1992.

Wright, R.O., Amarasiriwardena, C., Woolf, A.D., Jim, R. and Bellinger, D.C. (2006). Neuropsychological correlates of hair arsenic, manganese, and cadmium levels in school-age children residing near a hazardous waste site. *Neurotoxicology* 27: 210-216.

Yang, X., Zhou, X., Kan, T., Strezov, V., Nelson, P., Evans, T. and Jiang, Y. (2019) Characterization of size resolved atmospheric particles in the vicinity of iron and steelmaking industries in China. Sci. Total Environ., DOI: 10.1016/j.scitotenv.2019.07.340.

Zajusz-Zubek, E., Radko, T. and Mainka, A. (2017). Fractionation of trace elements and human health risk of submicron particulate matter (PM_1) collected in the surroundings of coking plants. *Environ. Monit. Assess.* 189.

Table Titles

Table 1. Background information at sampling cities Kunming (KM), Wuhan (WH), Nanjing (NJ) and Ningbo (NB). Population data was obtained from National Bureau of Statistics of China, 2017. The meteorological information during sampling period was obtained from China National Environmental Monitoring Centre.

Cities	Population (million)	Sampling date	$PM_{2.5}$ ($\mu g\ m^{-3}$)	PM_{10} ($\mu g\ m^{-3}$)	Relatively humidity (%)	Temperature (℃)	Wind speed (m/s)	Precipitation (mm)
			Min – max					
KM	5.6	2017/04/29 – 05/05	22 – 38	63 – 95	--	10 – 26	0.2 – 2.9	0
WH	8.5	2017/05/14 – 05/20	41 – 75	89 – 163	49 – 100	18 – 33	0.1 – 4.6	5.6
NJ	6.8	2017/05/28 – 06/04	25 – 72	77 – 118	21 – 86	19 – 34	0.2 – 6.8	0
NB	6.0	2017/06/13 – 06/19; 2017/06/29 – 07/01[a]	13 – 35	18 – 65	49 – 96	17 – 28	0.1 – 6.4	67[a]
		2017/05/17 – 05/23[b]						0[b]

a. sampling period near iron and steelmaking area

b. sampling period on UN campus

--no available data

Figure Captions

Fig. 1. Sampling locations in this study.

Fig. 2. Average mass concentrations (μg m^{-3}) at fractions of $PM_{2.1\text{-}9.0}$, $PM_{1.1\text{-}2.1}$ and $PM_{1.1}$ across five sampling sites.

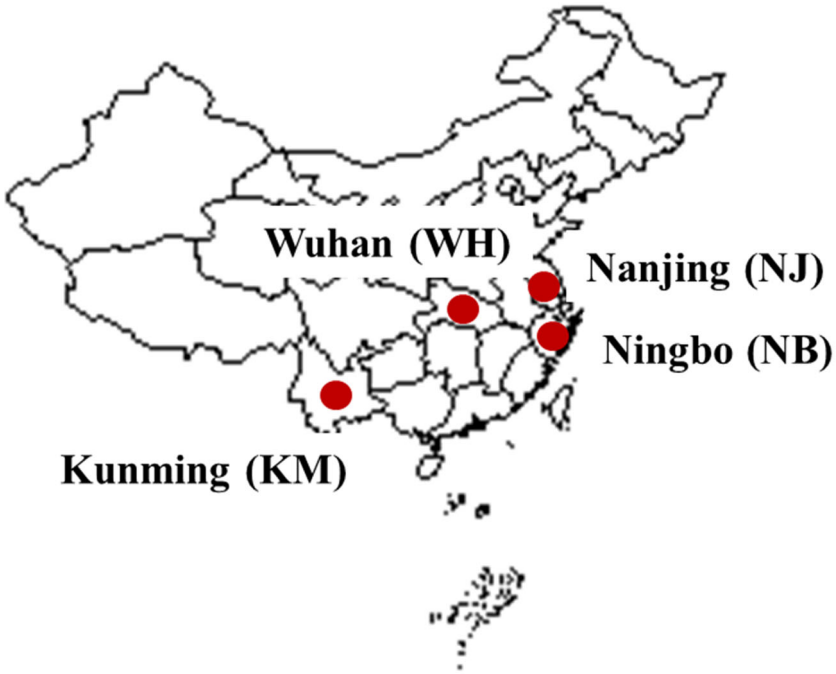
Fig. 3. Life cycle impact assessment of metal concentrations at fractions of $PM_{2.1\text{-}9.0}$, $PM_{1.1\text{-}2.1}$ and $PM_{1.1}$.

Fig. 4. Life cycle impact assessment of freshwater ecotoxicity based on metal concentrations at fractions of $PM_{2.1\text{-}9.0}$, $PM_{1.1\text{-}2.1}$ and $PM_{1.1}$.

Fig. 5. Life cycle impact assessment of terrestrial ecotoxicity based on metal concentrations at fractions of $PM_{2.1\text{-}9.0}$, $PM_{1.1\text{-}2.1}$ and $PM_{1.1}$.

Fig. 6. Life cycle impact assessment of marine ecotoxicity based on metal concentrations at fractions of $PM_{2.1\text{-}9.0}$, $PM_{1.1\text{-}2.1}$ and $PM_{1.1}$.

Fig. 7. Life cycle impact assessment of human toxicity based on metal concentrations at fractions of $PM_{2.1\text{-}9.0}$, $PM_{1.1\text{-}2.1}$ and $PM_{1.1}$.

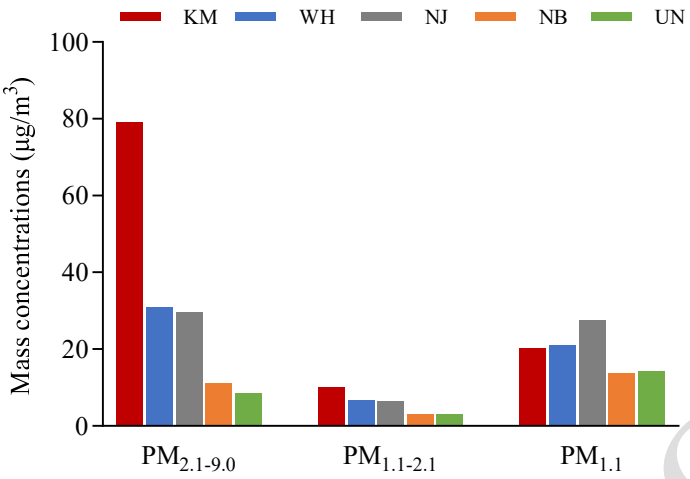


417

418 **Fig. 1.**

419

420

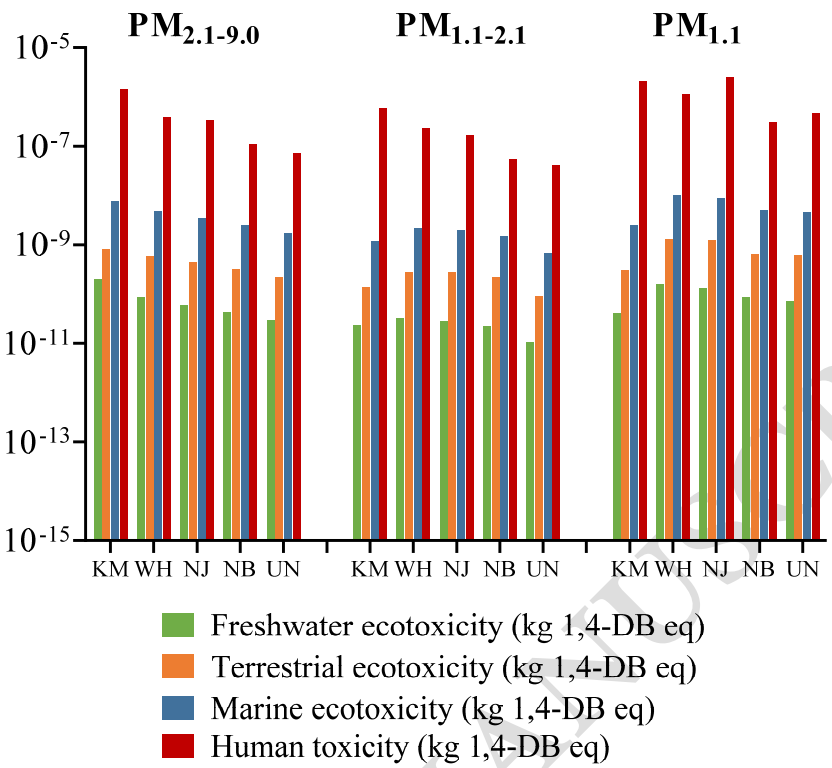


421

422 **Fig. 2.**

423

424



425

426 **Fig. 3.**

427

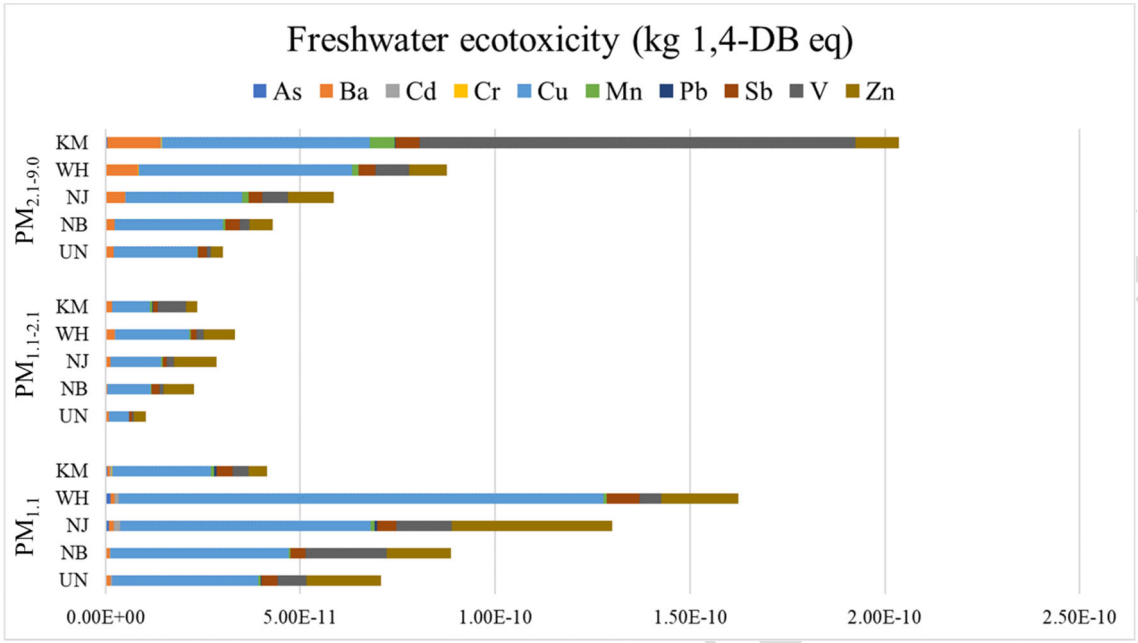


Fig. 4.

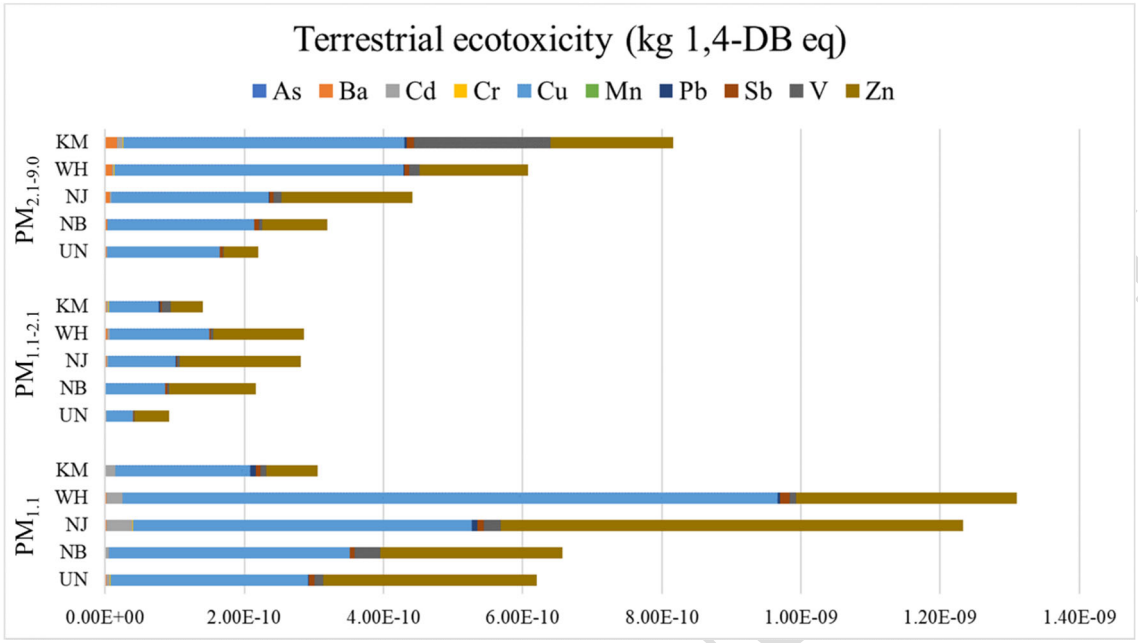


Fig. 5

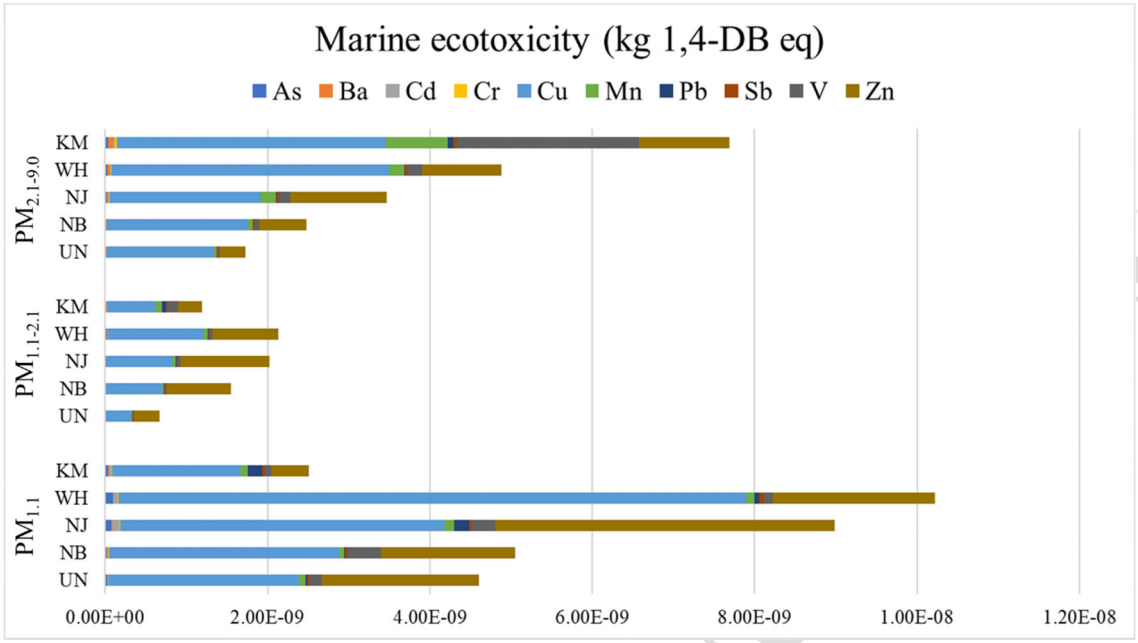


Fig. 6.

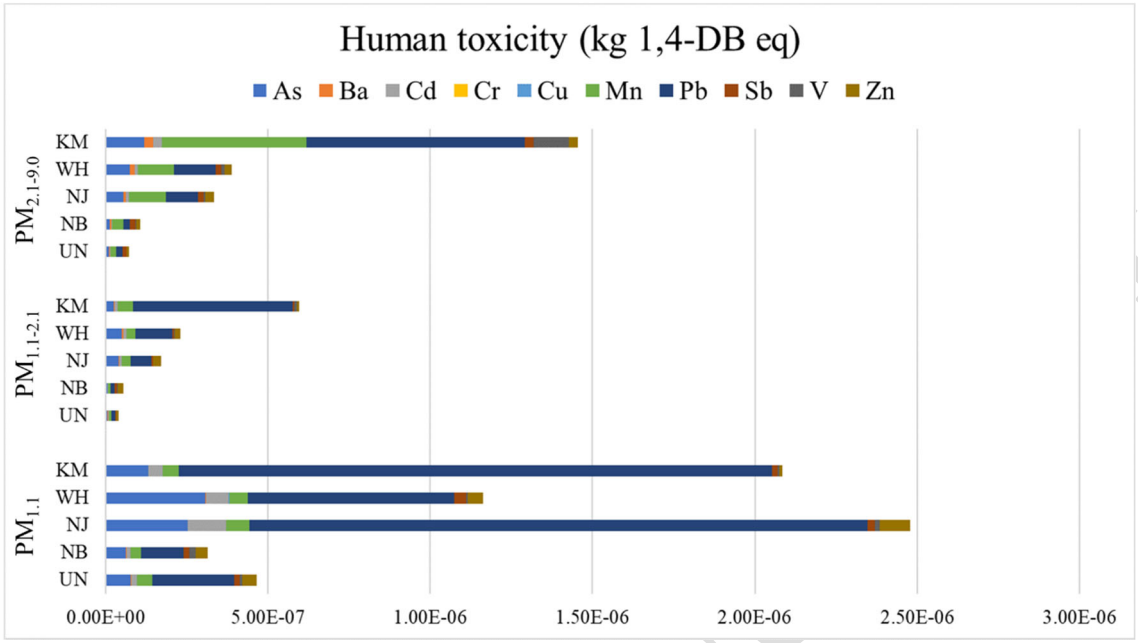


Fig. 7.