Using Synchrotron Radiation X-ray Fluorescence (SRXRF) to Assess the Impacts of Shipping Emissions on the Variations of PM₁₀-bound Elemental Species

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ABSTRACT

Shipping activities significantly contribute to global atmospheric pollutant emissions. Numerous studies have used synchrotron X-ray fluorescence spectroscopy (SRXRF) to identify elemental species in atmospheric particles, yet few studies have applied this technique for assessing PM₁₀-bound chemical species from shipping emissions. In this study, we conducted simultaneous sampling of PM₁₀ at three air quality observation sites located close to Laem Chabang Sea Port (LCSP) from 24 May to 27 June 2020. The PM₁₀ samples were then chemically characterised using SRXRF at the Beam Line 5.1 Wiggler (BL5.1W) in the Siam Photon Source, Synchrotron Light Research Institute (Nakhon Ratchasima, Thailand). We identified unique features in the SRXRF spectra of PM₁₀ samples collected from the site adjacent to LCSP. The average percentage contributions of selected metals at LCSP occurred in the order of Fe > Cu > Te > As > Br > Kr > Mn > Cr > Ni > V > Ti > P > Se > S > Cl, which is in good agreement with the results of previous studies conducted in Bangkok. Although some previous studies highlight the importance of V/Fe as the diagnostic binary ratio that can be used as a chemical proxy for categorizing shipping related particles, this application can be problematic-particularly in the atmospheric environment with high contents of iron-rich dust aerosols. In stead of employing V/Fe, the diagnostic binary ratios of As/V and Se/V can be considered as alternative geochemical tracers for classifying shipping emissions associated aerosols. By applying the concept of enrichment factor (EF), Se is exceedingly enriched in all observatory sites indicating that industrial emissions were the dominant contributor of Se at the ambient air of Lam Chabang. Hierarchical cluster analysis (HCA) successfully classify a group of V, Ti, Ga, and Ni at all sampling sites, which may be caused by shipping activities coupled with industrial emissions.

Keywords: μ -SRXRF spectra, PM₁₀, Rare elements, Heavy metals, Shipping emissions

1 INTRODUCTION

Although there are many advantages, it is necessary to identify and minimise the various environmental impacts from commercial shipping transportation. For instance, low-frequency noise levels from ocean freight shipping activities enhanced by up to 3 dB per decade from the mid-1960s to 2000 (McDonald *et al.*, 2006). Shipping activities also significantly contribute to atmospheric carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and black carbon (BC)

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emissions (Olmer *et al.*, 2017). These emissions are expected to increase with the growth of maritime container shipping, which is expected to enhance the melting of ice and snow—especially in the Arctic region (Corbett *et al.*, 2010). Sulphate aerosol emissions in the Mediterranean and the English Channel/North Sea increased by 60% and 30–35%, respectively (Aksoyoglu *et al.*, 2016). Ocean freight shipping activities also influence the contents of atmospheric chemical species and enhance the deposition of nitrogen and sulphur compounds along the main shipping routes (Aksoyoglu *et al.*, 2016).

Numerous investigations have highlighted the need to quantitatively estimate the contribution of shipping emissions to the concentrations of persistent organic pollutants (POPs) and other elemental species (Pongpiachan *et al.*, 2015; Wen *et al.*, 2018; Xiao *et al.*, 2018; Zhao *et al.*, 2019, 2020). For example, a significant enhancement of PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs) and the mutagenic index (MI) were detected during the docking period in the port area of Rayong province, Thailand (Pongpiachan *et al.*, 2015). Moreover, the atmospheric contents of 17 PAHs, 12 nitro-PAHs, and 4 oxygenated-PAH congeners were successfully characterised in PM_{2.5} emitted from an inland-river bulk freighter and an ocean-going passenger vessel (Zhao *et al.*, 2019). PAH emission factors also show remarkable differences between different fuel types (e.g., heavy fuel oil (HFO) and marine diesel oil (MDO)) in the engine loading of an ocean-going cargo vessel (Zhao *et al.*, 2020). A single particle aerosol mass spectrometer was used to classify the ion mass spectra (with positive and negative ion information) of marine shipping emissions at berth (Xiao *et al.*, 2018). Due to the presence of V in fuels such as HFO, the positive (V⁺) and oxidised (VO⁺) ions of V are considered to be strong chemical tracers of shipping emissions (Xiao *et al.*, 2018). Ni is also considered as a trace marker for HFO combustion in ships (Wen *et al.*, 2018).

In recent years, atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) have been frequently used to chemically characterise the elemental species in aerosols (Ahmad *et al.*, 2019; Almeida *et al.*, 2020; Báez *et al.*, 2007; Leili *et al.*, 2008; Pongpiachan *et al.*, 2017, 2018; Pongpiachan and Iijima, 2016). For instance, the origin of trace elements and heavy metals in PM₁₀ and TSP has been widely investigated globally, such as in Khyber Pakhtunkhwa, Pakistan (Ahmad *et al.*, 2019); Florianópolis, Brazil (Almeida *et al.*, 2020); south of Mexico City, Mexico (Báez *et al.*, 2007); central Tehran, Iran (Leili *et al.*, 2008); and Bangkok, Thailand (Pongpiachan *et al.*, 2017, 2018; Pongpiachan and Iijima, 2016). X-ray fluorescence (XRF) has also been used to chemically analyse aerosols due to its high sensitivity, non-destructive detection, multi-elemental competence, low sample requirement, and the potential to detect amorphous structures (e.g., solid, liquid) at atmospheric pressure (Rivers *et al.*, 1991). The recent improvement of μ -synchrotron radiation XRF (μ -SRXRF) has enabled the continuous identification of elemental species in PM₁₀ at ppm concentrations due to its comparatively high X-ray flux (10^{11-14} ph s⁻¹) and wide energy spectrum (5–30 keV), which covers the binding energies and enables the detection of all elements (Lahiri *et al.*, 2020). As a result, μ -SRXRF has been frequently used to investigate the chemical composition of aerosol particles in both urban and semi-urban sites around the world (Bukowiecki *et al.*, 2005, 2008; Cozzi *et al.*, 2012; López *et al.*, 2011). Numerous studies have demonstrated the promising application of μ -SRXRF for identifying elemental species in atmospheric particles; however, little is known about its application for assessing chemical species in PM₁₀ from shipping emissions. Overall, the main aims of this study were to (i) chemically characterise the elemental species in PM₁₀ using μ -SRXRF, (ii) investigate the impact of shipping emissions on the variability of PM₁₀-bound elemental species, and (iii) apply advanced statistical tools to determine the source apportionment of PM₁₀.

2 MATERIALS AND METHODS

2.1 Sampling Sites

We selected three sampling stations located in Sriracha district, Chon Buri Province, Thailand, due to their distance from Laem Chabang Sea Port (LCSP) (Fig. 1): (1) Laem Chabang Temple Air Quality Observatory Site (LCAS: 13°4'55.42"N 100°52'51.64"E), (2) Laem Thong Temple Air Quality Observatory Site (LTAS: 13°5'29.40"N 100°55'50.12"E), and (3) Waterworks Authority Air Quality Observatory Site (WAAS: 13°6'6.26"N 100°58'14.84"E). As LCAS is the closest monitoring site to LCSP, the PM₁₀ samples from this site were assumed to represent shipping emissions. In

Fig. 1. A map of three air quality observatory sites of this study.

contrast, WAAS is only 3 km southwest of the Pinthong Industrial Estate 1 (PIE1) and is the farthest site from LCSP (see Fig. 1). Pinthong Industrial Park Co., Ltd. (founded in 1995) constructed the PIE1 on an area of 207 rai (i.e., 331,200 m²) in Chon Buri Province in collaboration with the Industrial Estate Authority of Thailand. PIE1 consists of many factories producing various products, including oil filters, engineering plastic parts, plastic compound beads, dye pigments, electronic appliances, iron, stainless steel, alumina ceramic fibre, wooden pallets, wooden boxes, and industrial electric cranes. Hence, the samples from WAAS were assumed to represent industrial emissions from PIE1 factories. Finally, LTAS is located in a residential area, and the samples from this site were representative of urban background emissions.

2.2 PM₁₀ Collection

Instantaneous PM₁₀ sampling was conducted at all three sites from 24 May (Sunday) to 27 June (Saturday), 2020. Continuous 24 hr PM₁₀ sampling began at ~10:00–11:00 AM each day using a high-volume air sampler (Thermo Scientific: G3101) with a constant flow rate of 40 ft³ min⁻¹ (~1.1 m³ min⁻¹). PM₁₀ sampling was performed without the use of the sampler's air pump for the first three (24–27 May, 2020) and last three days (24–27 June, 2020). All PM₁₀ samples were collected on quartz microfibre filters (QMFs) with a pore size of 2.2 µm, a thickness of 0.47 mm, and dimensions of 203 × 254 mm. The filters were placed in a desiccator for 24 h prior to weighing to avoid water vapour contamination. The weights of the filters before and after sampling were measured by an electronic balance (Mettler Toledo ME204). The air temperature (*AT*) and relative humidity (*RH*) were carefully monitored using the meteorological sensor, which combined ambient air temperature, relative humidity, and barometric pressure in a single device (Bosch BME280). In addition, an air pollution rose of PM₁₀ coupled with a wind rose detected at the air quality observatory site of Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MNRE) located at Laem Chabang stadium from 24th May 2020 to 27th June 2020 were illustrated at Figs. S1–S3.

Fig. 2. Schematic Diagram of Beamline 5.1W: X-ray Absorption Spectroscopy & Microbeam X-ray Fluorescence (XAS/ μ XRF) (ASEAN Beamline).

2.3 μ -SRXRF Analysis

The elemental composition of PM_{10} on the filter papers was analysed by SRXRF at the Beam Line 5.1 Wiggler (BL5.1W) in the Siam Photon Source, Synchrotron Light Research Institute, Nakhon Ratchasima, Thailand (Fig. 2). Each QMF sample was randomly cut into three pieces to sizes of approximately 1×1 cm and then sandwiched with Kapton tape and attached to the sample holder, which was positioned at 45° to the direction of the incoming X-ray photons (Fig. S1). The sample was exposed to a 15 keV monochromatic X-ray beam with a size of 2×2 mm, originating from a pair of Si (311) crystals for 5 min. The fluorescence photons generated from the irradiated sample's surface were detected by the Vortex EM[®] silicon drift detector (SDD), which was positioned 30 mm away from the sample surface and perpendicular to the SR beam. The measurement was conducted in an air environment, with three replicates per filter paper sample. The spectral analysis (i.e., energy calibration, peak identification, and peak fitting) was conducted using PyMCA version 5.5.4 (Solé *et al.*, 2007). Relative elemental concentrations were calculated from the peak fit area of each element on the obtained spectra. In addition, all advanced statistical analyses were conducted using IBM SPSS Statistics 23.

3 RESULTS AND DISCUSSION

3.1 Meteorological Data

Chonburi Province is situated 12 m above sea level. According to the Köppen climate classification, Chonburi Province is categorised as tropical savanna climate, or tropical wet and dry climate (Barton, 1962). The measured atmospheric PM_{10} contents at LCAS, LTAS, and WAAS were $53 \pm 82 \mu\text{g m}^{-3}$, $29 \pm 39 \mu\text{g m}^{-3}$, and $29 \pm 13 \mu\text{g m}^{-3}$, respectively, and the ambient air temperatures were $34.2 \pm 1.72^\circ\text{C}$, $31.0 \pm 1.19^\circ\text{C}$, and $31.6 \pm 1.34^\circ\text{C}$, respectively. The average RH of the three sampling sites was $62.3 \pm 6.3\%$.

3.2 SRXRF Spectra and Percentage Contributions of Elemental Species

Numerous studies have quantitatively characterised the elemental compositions of aerosols to evaluate the emissions strength of contaminant sources (Ahmad *et al.*, 2019; Almeida *et al.*, 2020; Báez *et al.*, 2007; Leili *et al.*, 2008; Pongpiachan *et al.*, 2017, 2018; Pongpiachan and Iijima, 2016); however, innovative analytical techniques are still required to enhance data interpretation. In this study, we used the SRXRF spectra to distinguish shipping emission aerosols from urban background particles. LCAS, LTAS, and WAAS were classified into three main groups: Port Area, Urban Background, and Industrial Area, respectively (See Fig. 1). The average SRXRF spectra of the three clusters were carefully examined and compared (See Fig. 3). We determined the atmospheric percentage contributions of 16 selected elemental species from a total of 84 samples collected at LCAS, LTAS, and WAAS from 27 May to 23 June 2020, as shown in Fig. 4. As all PM_{10} samples were collected on QMFs, all SRXRF spectra of the aerosol samples were subtracted from those of the field blanks.

All three clusters exhibited similar spectral features. We observed four noticeable characteristics that were mutually inclusive to all spectra. First, we observed high contributions from three major elements in all samples, namely Fe (K_α at 6.404 keV, K_β at 7.058 keV), Cu (K_α at 8.048 keV, K_β at 8.905 keV), and As (K_α at 10.543 keV, K_β at 11.726 keV), with total contributions of 87%, 83%, and 83% for LCAS, LTAS, and WAAS, respectively (See Fig. 4). Second, all PM_{10} samples showed moderate contributions from Br (K_α at 11.924 keV, K_β at 13.291 keV), Kr (K_α at 12.649 keV, K_β at

Fig. 3(A). Spectrum of μ -SRXRF in PM₁₀ collected at LCAS, LTAS, and WAAS from May 2020 to June 2020.

Fig. 3(B). First derivative of μ -SRXRF spectrum in PM₁₀ collected at LCAS, LTAS, and WAAS from May 2020 to June 2020.

14.112 keV), Mn (K_{α} at 5.899 keV, K_{β} at 6.490 keV), and Cr (K_{α} at 5.415 keV, K_{β} at 5.947 keV), with total contributions of 6.9%, 8.2%, and 8.9% for LCAS, LTAS, and WAAS, respectively. Third, Ni (K_{α} at 7.478 keV, K_{β} at 8.265 keV), V (K_{α} at 4.925 keV, K_{β} at 5.427 keV), Ti (K_{α} at 4.510 keV, K_{β} at 4.932 keV), P (K_{α} at 2.014 keV, K_{β} at 2.139 keV), Se (K_{α} at 11.222 keV, K_{β} at 12.496 keV), S (K_{α} at 2.308 keV, K_{β} at 2.464 keV), and Cl (K_{α} at 2.622 keV, K_{β} at 2.816 keV) occurred at extremely low levels, with total contributions of 2.3%, 2.9%, and 2.67% for LCAS, LTAS, and WAAS, respectively. Based on these results, we found that all elemental species in the PM₁₀ samples shared comparable spectral features.

Fig. 3(C). Second derivative of μ -SRXRF spectrum in PM₁₀ collected at LCAS, LTAS, and WAAS from May 2020 to June 2020.

Although all PM₁₀ samples showed relatively similar SXRF spectral distribution patterns in the photon energy range of 2–12 keV, noticeable comparative alterations can be magnified by calculating the first and second-order derivative of the raw spectra (Bhagavathy *et al.*, 1991; Hong *et al.*, 2019; Li *et al.*, 2020; Pongpiachan *et al.*, 2013). The calculation of the first-order derivative provides curves with peaks indicating the maximum alteration rate of the original spectral curves, while horizontal lines indicate no fluctuation in the slope of the spectral curves. As illustrated in Fig. 3(B), LCAS has a unique first-order derivative spectral curve, which differs from that of LTAS and WAAS. The LCAS first-order derivative spectral curve can be categorised by its major positive and negative peaks between 6 and 7 keV (Fig. 3(B)). Similarly, the LCAS second-order derivative spectral curve showed two major positive peaks and one major negative peak between 6 and 7 keV (Fig. 3(C)). Moreover, the absence of major positive peaks for Ga, As, Br, and Kr at the energy range of 8–12 keV in all spectral curves for both first and the second-order derivative forms suggests that these elements occurred at extremely low levels. In addition, the absence of major positive peaks for Ti, V, Cr, and Mn at the energy range of 4–6 keV suggests that these elements had comparatively low percentage contribution.

3.3. Diagnostic Binary Ratios and Enrichment Factors

As, Cr, Cu, Mn, Ni, and Pb are key species representing coal combustion (Cercasov *et al.*, 1998; Deng *et al.*, 2014; Galvagno *et al.*, 2002; Manoli *et al.*, 2002; Pastuszka *et al.*, 2010; Tian *et al.*, 2010, 2012; Weckwerth, 2001; Xia and Gao, 2011; Yang *et al.*, 2003; Zhang *et al.*, 2009), and As, Cu, Mn, and Zn are potential chemical proxies for smelting furnaces and steel smelting (Querol *et al.*, 2006; Yang *et al.*, 2003). Moreover, V and Ni are widely used as indicators of heavy oil combustion, such as that of HFO in ship engines (Cercasov *et al.*, 1998; Chu-Van *et al.*, 2020; Tian *et al.*, 2012, 2013). As illustrated in Table 1, the diagnostic binary ratios of Ni/V collected from LCAS, LTAS, and WAAS were 1.6, 1.2, and 1.0, respectively. These values are similar to those of urban background samples collected from Antwerpen (1.4), Gent (1.4), Bruges (1.2), and Oostende (1.1) in Belgium (Maenhaut *et al.*, 2016), as well as that of traffic road samples collected from Hornsgatan in Stockholm (1.2), Sweden (Johansson *et al.*, 2009). In contrast, an exceedingly high Ni/V ratio of 5.6 was detected at the Daejeon Industrial Complex (DIC) in South Korea (Lim *et al.*, 2010). As Ni is a marker element of coal combustion and V is a chemical tracer of oil burning (Lim *et al.*, 2005), the comparatively high Ni/V is likely due to the contribution of coal combustion for power generation in the DIC. According to the coal information overview provided by the

Fig. 4. Percentage contribution of selected element species in PM₁₀ collected at LCAS, LTAS, and WAAS from May 2020 to June 2020.

International Energy Agency, South Korea has shown an increasing trend in total coal imports by major importers from 1978 to 2019 (<https://www.iea.org/reports/coal-information-overview>). In agreement, South Korea ranked in the top 10 electricity producing countries in 2014 (Di Gianfrancesco, 2017).

We also assessed the diagnostic binary ratios of V/Fe, As/V, and Se/V in this study. Fe is a major crustal element (e.g., Al, Si, K, Ca, and Ti) and is predominantly observed in aerosols (Gaonkar *et al.*, 2020; Lawson and Winchester, 1979); hence, V/Fe can be used as an effective chemical proxy

Table 1. Diagnostic binary ratios of particulate elemental species collected at LCAS, LTAS, and WAAS from May 2020 to June 2020.

Sampling Site	LCAS	LTAS	WAAS	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Area Type	PA	UB	IA	UB	UB	UB	UB	IA	UB	UB	UB	UB	PA	BB	BB	TR	URD	URD	URD
Country	Thailand	Thailand	Thailand	Belgium	Belgium	Belgium	Belgium	Korea	India	India	Colombia	Taiwan	China	USA	USA	Sweden	Spain	Spain	Spain
Reference	This study	This study	This study	[1]	[1]	[1]	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[8]	[9]	[10]	[10]	[10]
Ni/V	1.6	1.2	1.0	1.4	1.4	1.2	1.1	5.6	N.A.	N.A.	N.A.	N.A.	0.80	N.A.	N.A.	1.2	0.13	N.A.	N.A.
Mn/Cr	1.05	1.4	1.3	3.5	5.6	6.8	4.4	2.8	N.A.	0.30	N.A.	0.65	2.1	9.5	1.6	2.6	5.8	N.A.	N.A.
V/Fe	0.005	0.007	0.007	0.005	0.006	0.008	0.01	0.004	N.A.	N.A.	N.A.	N.A.	37	0.06	0.04	N.A.	0.001	N.A.	0.00009
Cu/Fe	0.18	0.20	0.17	0.04	0.028	0.034	0.036	N.A.	0.03	0.02	0.11	0.02	24	0.33	0.29	N.A.	0.01	0.02	0.07
As/V	10.4	10.9	12.5	0.72	0.28	0.31	0.20	0.57	N.A.	N.A.	N.A.	N.A.	0.17	0.16	0.17	0.43	0.53	N.A.	N.A.
Se/V	0.51	0.54	0.50	N.A.	N.A.	N.A.	N.A.	0.36	N.A.	N.A.	N.A.	N.A.	0.17	0.092	0.073	N.A.	N.A.	N.A.	N.A.

Sampling Site

A: Antwerpen, B: Gent, C: Brugge, D: Oostende, E: Daejeon Industrial Complexes, F: Darjeeling, G: Nainital, H: Bagota, I: Changua, J: Xiamen University, K: Belle Glade, Florida, L: Delray Beach, Florida, M: Hornsgatan, Stockholm, N: Campo Martires da Patria, O: Boavista Avenue, P: Fernao Magalhães

Area Type

UB: Urban Background, TR: Traffic Road, URD: Urban Road Dust, PA: Port Area, IA: Industrial Area, BB: Biomass Burning

Reference

- [1] Maenhaut *et al.*, 2016 [6] Hsu *et al.*, 2016
- [2] Lim *et al.*, 2010 [7] Wu *et al.*, 2020
- [3] Sharma *et al.*, 2020a [8] Sevimglu *et al.*, 2019
- [4] Sharma *et al.*, 2020b [9] Johansson *et al.*, 2009

for classifying shipping emission aerosols. As displayed in Table 1, the V/Fe value at LCAS was almost 7,400 times lower than that of the port area in China (Wu *et al.*, 2020). Fe was found to be the second highest element in PM₁₀ in ambient air in Bangkok (Pongpiachan and Iijima, 2016), which is located ~125 km northwest of LCSP. The application of V/Fe as a chemical tracer of shipping emissions can therefore be problematic—especially in ambient air with high concentrations of iron-rich dust particles. In contrast, the diagnostic binary ratios of As/V at LCAS, LTAS, and WAAS were excessively high compared with that of other aerosol types. For instance, As/V at LCAS was 14, 18, and 65 times higher than those detected at Antwerpen (Maenhaut *et al.*, 2016), DIC (Lim *et al.*, 2010), and Belle Glade (Florida) (Sevimoğlu and Rogge, 2019), respectively. Similarly, Se/V at LCAS was 1.4, 5.5, and 7.0 times greater than those observed at DIC (Lim *et al.*, 2010), Belle Glade, and Delray Beach (Florida) (Sevimoğlu and Rogge, 2019), respectively. These findings suggest that the application of some diagnostic binary ratios are potentially inaccurate and must be considered with caution.

The enrichment factor (*EF*) has been extensively used to assess the contribution of traffic emissions (Pongpiachan *et al.*, 2017; Pongpiachan and Iijima, 2016; Taghavi *et al.*, 2019), industrial releases (Almasoud *et al.*, 2015; Mingorance *et al.*, 2007), and municipal solid waste combustion (Tang *et al.*, 2015) to selected elemental concentrations. Previous studies have used Fe as a reference element for *EF* calculations (López *et al.*, 2005; Pongpiachan *et al.*, 2017; Pongpiachan and Iijima, 2016). Rudnick (2003) proposed the use of Fe to represent crustal contributions. The *EF* of element *E* in a PM₁₀ sample can be described as follows:

$$EF = \frac{(E/R)_{Air}}{(E/R)_{Crust}} \quad (1)$$

where *R* is a reference element. An *EF* of ~1 suggests that crustal emissions are the major source of the target element, while an *EF* of > 1 suggests that anthropogenic activities are the major source of the target element. As displayed in Fig. 5, the logarithms of *EF* of the 13 selected elemental species in PM₁₀ were categorised into four groups (arbitrary scale):

(i) S, Cl, V, and Mn are not enriched ($\text{Log}(EF) < 1$); (ii) Cr, Ni, and Ga are slightly enriched ($\text{Log}(EF)$ close to 1); (iii) Cu, As, Br, and Tl are moderately enriched ($\text{Log}(EF) = 2-3$); and (iv) Se is exceedingly enriched ($\text{Log}(EF) > 3$). The above-mentioned distribution patterns were relatively common for the three air quality observation sites. However, we also noted other prominent features. First, we detected an extremely high $\text{Log}(EF)$ for Se (> 4) at WAAS, which suggests that industrial emissions were the dominant sources of Se at this observation site. This interpretation is reasonable, as the WAAS is located only 3 km southwest of PIE1 and thus likely represents anthropogenic emissions from the industrial estate. Furthermore, numerous anthropogenic activities, such as coal and oil combustion, refuse incineration, and non-ferrous metal production, have been identified as major sources of atmospheric Se (Mosher and Duce, 1987; Nriagu, 1989; Nriagu and Pacyna, 1988). Second, LCAS showed a different $\text{Log}(EF)$ distribution pattern for As, Se, and Br, possibly due to the prevailing shipping emissions at LCSP.

3.4 Pearson's Correlation Coefficient (PCC) and Hierarchical Cluster Analysis (HCA)

The Pearson's Correlation Coefficients (PCC) of 16 elements in PM₁₀ collected at LCAS, LTAS, and WAAS are presented in Tables 2–4. The Pearson's correlation results indicated exceedingly strong positive correlations (i.e., $0.9 \leq R < 1.0$) for Ti vs. V and Mn vs. Cr in PM₁₀ samples collected at WAAS (Table 4). These high positive correlations were likely caused by industrial emissions from PIE1 due to its close proximity to WAAS. Previous studies detected comparatively high As, Cu, Mn, and Zn contents emitted from smelting furnaces and steel smelting (Querol *et al.*, 2006; Yang *et al.*, 2003). Moreover, rare earth elements, such as Cd, Co, Cu, Ni, Cr, Pb, and Hg, are endocrine disruptors that combine with oestrogen receptors and are also abundant in construction materials and the plastics industry (Iavicoli *et al.*, 2009; Philippat *et al.*, 2017). Cr, Mn, and Cu are also used as chemical tracers of iron and steel production (Dai *et al.*, 2015), and both steel production and plastic plants are major industries in PIE1. As Ni is considered as a chemical marker of industrial emissions from metal-assembly facilities and alloy manufacturing, the strong

Fig. 5. Logarithms of EF of 13 selected elemental species in PM_{10} collected at LCAS, LTAS, and WAAS from May 2020 to June 2020.

positive correlations of Ni vs. Kr ($0.8 \leq R < 0.9$) and Ni vs. Ga ($0.7 \leq R < 0.8$) suggest that Ni and Ga can be used as tracers of steel industrial emissions. Notably, we also observed other strong positive correlations between elements at LCAS: S vs. P ($0.8 \leq R < 0.9$), Kr vs. Cr ($0.8 \leq R < 0.9$), Kr vs. Ga ($0.8 \leq R < 0.9$), Cu vs. Fe ($0.7 \leq R < 0.8$), Ga vs. Cr ($0.7 \leq R < 0.8$), As vs. Cr ($0.7 \leq R < 0.8$), Se vs. Ni ($0.7 \leq R < 0.8$), Br vs. Ti ($0.6 \leq R < 0.7$), Br vs. Ti ($0.6 \leq R < 0.7$), Ni vs. V ($0.6 \leq R < 0.7$), Ni vs. Cr ($0.6 \leq R < 0.7$), As vs. Ga ($0.6 \leq R < 0.7$), Kr vs. Mn ($0.6 \leq R < 0.7$), Te vs. Cr ($0.6 \leq R < 0.7$), Te vs. Ni ($0.6 \leq R < 0.7$), and Te vs. Se ($0.6 \leq R < 0.7$). These correlations are likely related to the significant contribution of shipping emissions at LCSP, which is located only a few hundred metres from LCAS.

Table 2. Pearson's Correlation Coefficients (PCC) of 16 elements in PM₁₀ collected at LCAS from May 2020 to June 2020. Any values that higher than 0.5 will be highlighted as bold.

	P	S	Cl	Ti	V	Cr	Mn	Fe	Ni	Cu	Ga	As	Se	Br	Kr	Te
P	1.00															
S	.832**	1.00														
Cl	.699**	.412*	1.00													
Ti	–0.22	–0.20	–0.28	1.00												
V	.380*	.436*	0.04	0.21	1.00											
Cr	0.16	0.30	–0.15	0.04	.575**	1.00										
Mn	0.11	0.21	–0.12	0.17	.511**	.585**	1.00									
Fe	–0.396*	–0.25	–0.36	0.11	–0.29	–0.670**	1.00	1.00								
Ni	.537**	.535**	0.20	–0.02	.633**	.635**	.435*	–0.499*	1.00							
Cu	0.31	0.04	.544**	–0.425*	–0.06	0.10	–0.29	–0.716**	0.05	1.00						
Ga	–0.10	0.26	–0.453*	0.16	.445*	.787**	.573**	–0.22	.497**	–0.37	1.00					
As	.434*	.563**	0.10	0.01	.405*	.740**	.534**	–0.537*	.543**	0.03	.653**	1.00				
Se	0.30	0.30	0.21	0.25	.487**	.593**	.527**	–0.573**	.764**	0.04	.477*	.566**	1.00			
Br	–0.13	–0.10	–0.25	.638**	0.05	.376*	0.11	–0.31	0.22	–0.23	.386*	0.21	.506**	1.00		
Kr	–0.34	–0.11	–0.511**	0.23	0.35	.800**	.620**	–0.30	0.36	–0.22	.858**	.538**	.422*	.414*	1.00	
Te	.387*	0.35	0.12	–0.01	.519**	.655**	.433*	–0.623**	.622**	0.08	.457*	.536**	.634**	0.32	0.34	1.00

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 3. Pearson's Correlation Coefficients (PCC) of 16 elements in PM₁₀ collected at LTAS from May 2020 to June 2020. Any values that higher than 0.5 will be highlighted as bold.

	P	S	Cl	Ti	V	Cr	Mn	Fe	Ni	Cu	Ga	As	Se	Br	Kr	Te
P	1.00															
S	.437*	1.00														
Cl	-.053	-.410*	1.00													
Ti	-.142	-.044	-.542**	1.00												
V	.008	-.375*	.292	.044	1.00											
Cr	-.079	-.342	.327	-.240	.781**	1.00										
Mn	.004	-.273	.277	-.361	-.113	-.058	1.00									
Fe	-.437*	-.584**	-.018	.271	-.137	-.301	.249	1.00								
Ni	-.045	.062	-.079	.080	.143	.254	-.590**	-.319	1.00							
Cu	-.056	.170	.030	.102	-.069	-.059	-.403*	-.538**	.395*	1.00						
Ga	.099	.045	-.017	-.246	.380*	.614**	-.061	-.191	.175	-.450*	1.00					
As	-.030	-.011	.521**	-.368	.186	.452*	-.016	-.447*	.352	.275	.336	1.00				
Se	.010	.005	.132	-.137	.422*	.414*	-.133	-.072	.148	-.201	.489**	.223	1.00			
Br	-.134	.065	-.093	-.122	.055	.182	-.046	-.376*	-.018	.084	-.001	-.139	-.033	1.00		
Kr	.156	.579**	-.266	-.046	-.301	-.063	-.390*	-.455*	.375*	.137	.396*	.235	.013	-.018	1.00	
Te	-.135	-.530**	.336	-.204	.840**	.881**	.117	-.112	.051	-.152	.432*	.216	.258	.270	-.383*	1.00

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 4. Pearson's Correlation Coefficients (PCC) of 16 elements in PM₁₀ collected at WAAS from May 2020 to June 2020. Any values that higher than 0.5 will be highlighted as bold.

	P	S	Ti	V	Cr	Mn	Fe	Ni	Cu	Ga	As	Se	Br	Kr	Te
P	1.00														
S	.818**	1.00													
Ti	.112	.116	1.00												
V	.110	.247	.914**	1.00											
Cr	.065	.071	-.050	-.038	1.00										
Mn	.014	.028	-.072	-.074	.991**	1.00									
Fe	-.332	-.408*	-.205	-.302	-.396*	1.00									
Ni	-.103	.108	-.277	-.122	-.091	-.114	1.00								
Cu	.527**	.352	.653**	.658**	.004	-.057	-.368	1.00							
Ga	-.249	.039	-.566*	-.380*	-.093	-.092	.170	.720**	1.00						
As	.175	.199	-.178	-.162	-.094	-.111	-.629**	-.095	-.146	.093	1.00				
Se	.588**	.443*	-.052	-.052	-.009	-.090	-.207	.173	.394*	-.066	-.013	1.00			
Br	-.295	-.105	.067	.087	-.084	-.127	-.235	.095	-.206	.239	.030	-.094	1.00		
Kr	-.243	-.087	-.295	-.168	-.201	-.236	.172	.822**	-.296	.707**	-.108	.156	.144	1.00	
Te	-.507**	-.193	-.622**	-.433*	.036	.034	.206	.446*	-.663**	.698**	-.140	-.112	.348	.447*	1.00

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

We applied the agglomerative hierarchical clustering algorithm (HCA) on the percentage element contributions from the SRXRF spectra to produce a dendrogram of PM₁₀-bound selected elements from the three air quality observation sites. After importing the data into SPSS Statistics 23, the HCA indicated the presence of three major clusters. The first major cluster consisted of S, Cl, Se, P, Ni, Ga, V, Ti, Kr, Cr, Mn, Br, As, and Te; and the second and the third clusters included Cu and Fe, respectively. As the horizontal axis of the dendrogram reflects the distance of dissimilarity between the clusters, we conclude that the emission source of Fe was entirely different from that of the other elements. This interpretation is consistent with numerous studies identifying crustal emissions as a major source of Fe (Gaonkar *et al.*, 2020; Lawson and Winchester, 1979). Another prominent feature is the proximity of V, Ti, Ga, and Ni at all observation sites, which may be due to the burning of ship engine HFO coupled with the prevalence of heavy oil combustion at PIE1 factories (Cercasov *et al.*, 1998; Chu-Van *et al.*, 2020; Tian *et al.*, 2012, 2013).

3.5 Principal Component Analysis (PCA)

PCA is a widely adopted statistical technique for data reduction. Instead of applying several diagnostic binary ratios, PCA decreases the information of various detected parameters into a smaller set of original variables (i.e., selected elemental contents in PM₁₀ samples); this allows for the extraction of principal components (PCs) to assess the relationships between measured parameters. PCA has therefore been widely used as a receptor modelling method to determine the source apportionment of urban air pollutants (Pongpiachan *et al.*, 2015, 2017; Pongpiachan and Iijima, 2016). In this study, original parameters were organised into a matrix where individual columns corresponded to a single variable, and each row reflected the number of samples. The PCA was then used to investigate the summarised data in data matrixes (see Tables 5–7). As displayed in Table 5, the PCA patterns of the varimax-rotated components at LCAS were composed of five principal components (PC1, PC2, PC3, PC4, and PC5) that accounted for 23.8%, 17.7%, 16.5%, 15.5%, and 12.4% of the total variance, respectively. We observed strong positive correlation coefficients for Cr ($R = 0.803$), Ga ($R = 0.895$), and Kr ($R = 0.852$) at PC1, which is consistent with their strong positive correlation coefficients determined from the Pearson's correlation analysis (i.e., Kr vs. Cr ($0.8 \leq R < 0.9$), Kr vs. Ga ($0.8 \leq R < 0.9$)); this suggests that these three elements can be used as chemical markers for ship engine HFO combustion. We also observed positive correlations for V ($R = 0.842$), Mn ($R = 0.690$), Ni ($R = 0.596$), and Se ($R = 0.552$) at PC3. As previously mentioned in section 3.3, the high *EF* value of Se (i.e., $EF > 3$) suggests that

Table 5. Principal component analysis (Varimax rotation) of particulate elemental species collected at LCAS from May 2020 to June 2020.

	Principal Component				
	PC1	PC2	PC3	PC4	PC5
P	−0.139	0.895	0.235	0.250	−0.077
S	0.176	0.926	0.161	−0.040	−0.111
Cl	−0.460	0.566	0.099	0.499	−0.105
Ti	−0.063	−0.184	0.209	−0.297	0.818
V	0.186	0.227	0.842	−0.007	0.040
Cr	0.803	0.097	0.410	0.320	0.111
Mn	0.470	0.022	0.690	−0.143	0.002
Fe	−0.337	−0.194	−0.183	−0.878	−0.156
Ni	0.338	0.462	0.596	0.225	0.147
Cu	−0.173	0.050	−0.099	0.907	−0.261
Ga	0.895	0.053	0.274	−0.178	0.153
As	0.708	0.496	0.205	0.169	0.073
Se	0.312	0.262	0.552	0.323	0.480
Br	0.318	−0.048	−0.049	0.088	0.910
Kr	0.852	−0.314	0.304	−0.001	0.164
Te	0.0392	0.282	0.484	0.365	0.200
% of Variance	23.8	17.7	16.5	15.5	12.4

Table 6. Principal component analysis (Varimax rotation) of particulate elemental species collected at LTAS from May 2020 to June 2020.

	Principal Component				
	PC1	PC2	PC3	PC4	PC5
P	0.037	0.606	−0.163	0.071	0.115
S	−0.191	0.873	0.149	−0.139	0.061
Cl	0.089	−0.320	−0.098	0.833	−0.030
Ti	−0.122	−0.265	0.304	−0.743	−0.097
V	0.727	−0.380	0.124	0.085	0.319
Cr	0.808	−0.206	0.168	0.308	0.316
Mn	−0.110	−0.129	−0.779	0.352	−0.005
Fe	−0.092	−0.606	−0.420	−0.336	−0.546
Ni	0.206	0.056	0.813	0.033	−0.084
Cu	−0.443	−0.018	0.731	0.228	0.305
Ga	0.865	0.326	−0.036	−0.055	−0.138
As	0.256	0.090	0.394	0.757	−0.135
Se	0.670	0.073	0.056	0.053	−0.157
Br	0.025	0.082	−0.031	−0.105	0.813
Kr	0.079	0.722	0.406	−0.037	−0.226
Te	0.698	−0.435	−0.060	0.221	0.465
% of Variance	20.4	17.0	15.6	14.4	10.1

Table 7. Principal component analysis (Varimax rotation) of particulate elemental species collected at WAAS from May 2020 to June 2020.

	Principal Component				
	PC1	PC2	PC3	PC4	PC5
P	−0.237	0.055	0.910	0.015	0.111
S	0.080	0.147	0.799	0.068	0.272
Ti	−0.278	0.920	−0.006	−0.056	−0.014
V	−0.080	0.948	0.047	−0.019	0.059
Cr	−0.061	−0.021	0.038	0.993	0.040
Mn	−0.101	−0.069	−0.022	0.987	−0.005
Fe	0.088	−0.266	−0.283	−0.352	−0.807
Ni	0.888	−0.078	0.153	−0.051	−0.116
Cu	−0.403	0.675	0.491	−0.020	−0.073
Ga	0.826	−0.404	−0.087	−0.051	0.117
As	−0.164	−0.293	0.130	−0.165	0.847
Se	0.146	0.015	0.781	−0.037	−0.054
Br	0.391	0.257	−0.396	−0.052	0.476
Kr	0.865	−0.069	0.038	−0.172	−0.125
Te	0.658	−0.412	−0.349	0.114	0.007
% of Variance	21.2	18.6	18.2	14.5	11.6

Se can be used as a chemical tracer of industrial emissions; thus, the high positive correlations of other elements in PC3 (i.e., V, Mn, Ni, and Se) are also likely due to anthropogenic emissions from PIE1 industrial factories. Strong positive correlations between Ti, V, and Cu were also observed at PC2 (Table 7), which is likely explained by shipping emissions; PC2 contributed almost 18.6% (PC2) to the total variance—even at WAAS, which is the farthest sampling site from LCSP.

4 CONCLUSIONS

Both the first and the second-order derivatives of all SRXRF spectra exhibited prominent features at LCAS where ocean container vessels frequently dock to discharge and load containers.

Our results suggest that Ni/V can be used as an effective chemical tracer for aerosol identification from coal-fired power plant emissions. However, V/Fe was relatively ineffective at classifying shipping emissions, especially in atmospheric environments with high concentrations of iron-rich dust particles. Instead, As/V and Se/V can be used as alternative diagnostic binary ratios for classifying shipping emission aerosols. The extremely high Log(*EF*) of Se detected at WAAS suggests that Se can be used as a chemical tracer of industrial emissions. We observed strong positive Pearson's correlation coefficients between numerous elements at LCAS, signifying the high contribution of ship engine HFO combustion to selected elements in the sea port area. HCA classified Fe as an outlier crustal element in all observation sites. Moreover, the closeness of V, Ti, Ga, and Ni in the dendrograms indicated the strong influence of anthropogenic activities on the air quality at all monitoring stations. In addition, PCA highlights the importance of Kr, Cr, and Ga as three metals that can be used as chemical tracers for categorizing shipping emission aerosols. It is also crucial to highlight that the comparatively high correlation coefficients of V, Mn, Ni, and Se detected at PC3 of LCAS can be interpreted as a consequence of industrial emissions during the observatory period. Overall, our findings highlight the possible use of SRXRF (a relatively rapid, highly sensitive, and non-destructive approach) to characterise shipping emission aerosols as well as other anthropogenically released particles.

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SUPPLEMENTARY MATERIAL

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