



Metallic elements emitted from industrial sources in Taiwan: Implications for source identification using airborne PM

Yu-Chi Lin^{a,b,c,*}, Shih-Chieh Hsu^b, Shuen-Hsin Lin^b, Yi-Tang Huang^b

^a Yale-NUIST Center on Atmospheric Environment, International Joint Laboratory on Climate and Environment Change, Nanjing University of Information Science and Technology, Nanjing, 210044, China

^b Research Center for Environmental Changes (RCEC), Academia Sinica, Taipei, 115, Taiwan

^c Key Laboratory Meteorological Disaster, Ministry of Education & Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disaster, Nanjing University of Information Science and Technology, Nanjing, 210044, China



ARTICLE INFO

Keywords:

Filterable stack particulate matter
Heavy metals
Industrial emissions
FCC petroleum refinery
Lanthanum to lanthanides ratios

ABSTRACT

Filterable stack total suspended particle (TSP) samples emitted from electric arc furnace (EAF) steel manufacturing plants, coal-fired power plants (CPP), cement mills (CM), and petroleum refineries (PR), were isotopically collected using an in-stack PM device and analyzed for thirty-one targeted elements. The results showed that metallic elements constituted a majority (43–61%) of stack TSP mass in EAF steel plants and CM whereas contributed to a less fraction (11–27%) in CPP and PR. The coefficient of divergence (COD) values varied from 0.58 to 0.81, indicating that the elemental profiles between each industrial source were very distinct. Geological elements such as Al, Fe, Ca, Na, Mg, and K were the dominant elements in all industrial sources (50–96% of elemental mass). Besides, Zn was another dominant metal (22–40% of element mass) in addition to Fe in EAF steel plants and Ni (~3.6%) was the most predominant metal in oil-refinery. Tracers in different industrial sectors were also identified by source marker calculations. Moreover, the ratios of La/Ce (1.8) and La/Nd (6.0) in fluidized bed catalytic cracking (FCC) were 20–30 times higher than those of other industrial sectors. Utilizing both La/Ce and La/Nd ratios, the contribution of FCC PR to ambient primary TSP surrounding by the petroleum refinery was estimated to be 0.6%, which was comparable to the Taiwan Emission Data (0.7%). This highlighted that La/Ce and La/Nd ratios can be able to track the influence of petroleum refining sources on airborne particles in an industrial urban area in Taiwan.

1. Introduction

Industrial emissions are major sources of airborne particulate matter (PM) in many urban areas (Thurston et al., 1994; Tsuang et al., 2003; Chan et al., 2008; Viana et al., 2008; Zhang et al., 2013). PM derived from industries not only deteriorates air quality and atmospheric visibility, but also exerts adverse effects on human health because it contains many toxic elements such as As, Ni, Cr, Cd, Pb, and Co, which are categorized into carcinogens or probably carcinogens to human by the International Agency for Research on Cancer.

Numerous studies have established the elemental profiles of PM emitted from industrial emissions (Olmez et al., 1988; Watson et al., 2001; Chow et al., 2004; Machemer, 2004; Tsai et al., 2007; Cheng et al., 2008; Yatkin and Bayram, 2008; Hleis et al., 2013; Patil et al., 2013). These studies have suggested that the elemental compositions of industry-emitted PM vary with sources, manufacturing processes, and

operating conditions. Consequently, some metals can be considered as markers to track specific sources of airborne PM. For instance, Fe and Mn concentrations are much higher in electric arc furnace (EAF) steel manufacturing plants than in other emission sources; thus, both metals are the preferred indicators of steel manufacturing plants (Sweet et al., 1993; Patil et al., 2013). Coal-fired power plants (CPP) are characterized by high S, As and Se concentrations (Chow et al., 2004). Lanthanum (La) and other lanthanides are commonly used as markers of fluidized bed catalytic cracking (FCC) in petroleum refineries (PR); therefore, the ratios of La to other lanthanides are useful fingerprints for petroleum refining (Kulkarni et al., 2006, 2007). The study has shown that stack PM emitted from an oil-refinery is characterized by high concentrations of V, Ni, La, and Sb (Chow et al., 2004).

Establishing elemental profiles for stack PM is necessary for several reasons. First, elemental profiles of stack PM can enable to estimate toxic and hazardous metal emissions that are useful to assess health

Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

* Corresponding author.

E-mail addresses: yuchilin@nuist.edu.cn, yclin1226@outlook.com (Y.-C. Lin).

<https://doi.org/10.1016/j.apr.2020.01.005>

Received 22 August 2019; Received in revised form 8 January 2020; Accepted 8 January 2020

Available online 12 January 2020

1309-1042/ © 2020 Turkish National Committee for Air Pollution Research and Control. Production and hosting by Elsevier B.V. All rights reserved.

risks caused by specific industrial sources (Chow et al., 2004). Second, elemental profiles can be used to create speciated chemical emission inventories (Pacyna and Pacyna, 2001; Bhanarkar et al., 2005). Finally, elemental profiles can facilitate the verification of profiles derived from ambient measurements by using the positive factorization matrix model and factor analysis (Lee et al., 1999).

Taiwan has been experiencing a severe PM problem for a long time. Previous studies showed industrial emissions were one of the major sources for airborne PM (Yuan et al., 2000; Tsuang et al., 2003; Chio et al., 2004). These particles, containing a large quantity of toxic metals, have adverse effects on human respiratory, cardiovascular, nerves and digestion systems (Lin et al., 2016; Huang et al., 2018); therefore, assessments of toxic element exposure of residents living in the neighboring areas of specific industrial plants have become an important issue in Taiwan. To achieve this goal, establishments of metal profiles in stack PM are needed (Chio et al., 2014). So far, there are very few data relevant to heavy metals emitted from industrial emissions in Taiwan. Consequently, we collected filterable stack PM emitted from the four integrated industrial emissions, including electrical arc furnace steel manufacturing, coal-fired power plants, cement plants (CM) and petroleum refineries, in order to characterize heavy metals derived from various industries. Thirty-one metallic elements in each filterable stack PM sample were analyzed through inductively coupled plasma mass spectrometry (ICP-MS). In this study, we characterized the elemental compositions and identified potential markers of filterable stack PM produced from the various industries. Moreover, the fingerprinting ratios of FCC petroleum refining were assessed and were subsequently applied to qualitatively and quantitatively estimate the effects of a petroleum refining source on ambient primary PM in an industrial metropolitan area of northern Taiwan.

2. Methods

2.1. Stack TSP sampling

In this work, we collected filterable total suspended particulate (TSP) samples in stack from four integrated industrial sources in Taiwan, namely electrical arc furnace steel manufacturing plants, coal-fired power plants, cement mills, and petroleum refineries. All filterable TSP samples were collected using an in-stack device following the USEPA Method 5 procedure (US EPA, 2001). A stack TSP system consists of a commercial sampling nozzle (APEX, NG7-13AB), temperature sensor, cylindrical filter holder, cooling device, and pump in addition to a dry gas meter (DGM) to measure and control the sampling flow rate. Before collection of the stack TSP samples, the temperature, pressure and chemical compositions (CO, CO₂ and O₂) of stack gas were needed to be measured. During sampling, the nozzle was placed into the stack sampling position, and the TSP sampling was conducted under isokinetic conditions by adjusting the suction orifice to achieve a sampling velocity similar to that of the flue gas (see in *supplementary S1*). The details of this method can be found elsewhere (US EPA, 2001).

During the sampling, the TSP sample of each stack was conducted with triplicate measurements and each sample was collected for at least 1 h to obtain sufficient particle mass for further elemental analyses. Quartz filter membranes (Pall, 7205, 82.6 mm in OD) were used to collect the samples. Each filter was conditioned before and after sampling for 48 h at 23 °C and 30% ± 5% relative humidity. Gravimetric measurements were subsequently performed using a microbalance (Mettler Toledo, MX5, AX205; precision, 1 µg) to measure the net mass of the collected aerosol particles. This net mass was required to calculate the mass concentrations of stack TSP (C_s , mg m⁻³) in dry basis under standard conditions. C_s can be obtained by (US EPA, 2001):

$$C_s = \frac{M_s}{V_s} \quad (1)$$

where M_s is the total amount of TSP collected (mg); V_s is the volume (m³) of gas samples measured by the DGM, which is corrected to standard conditions. The V_s can be calculated as:

$$V_s = \frac{K_1 V_m \left[P_{bar} + \left(\frac{\Delta H}{13.6} \right) \right]}{T_m} \quad (2)$$

where V_m is the volume of gas sample measured by the DGM and P_{bar} is barometric at the sampling site in mm Hg. ΔH is the average pressure differential across the orifice meter with a unit in mm H₂O. T_m is the average temperature of DGM during the sampling period with a unit of °K. K_1 is a coefficient of 0.3858 K mm⁻¹. More details can be seen in US EPA (2001).

2.2. Chemical analysis

To analyze the concentrations of metals in stack TSP, two-thirds of weighed TSP samples were subjected to acidic digestion by using an ultrahigh throughput microwave digestion system (MARSXpress, CEM Corporation, Matthews, NC, USA). Each sampled filter was put into the vessel and digested in an acid mixture (4 mL of 60% HNO₃ + 2 mL of 48% HF). The digestion process was performed in three steps: (1) heating to 170 °C for 8 min and maintaining this temperature for 7 min at 1440 W, (2) heating to 200 °C for 7 min and maintaining this temperature for 15 min at 1600 W, and (3) cooling for 60 min. After digestion, the vessels were transferred to XpressVap™ accessory sets (CEM Corporation) for the evaporation of the remaining acids until nearly dry. Approximately 2 mL of concentrated HNO₃ was added into each vessel, followed by reheating. The resulting solution was subsequently diluted with Milli-Q water to a final volume of 50 mL before injection into the ICP-MS system. The detailed digestion procedure can be found elsewhere (Hsu et al., 2010).

A total of 31 target metals/elements in the filterable stack PM samples were analyzed through ICP-MS (Elan 6100, Perkin Elmer™ SCIEX, USA). A multi-element standard, prepared from stock (Merck) composed of 2% HNO₃ solution, was used for calibration of seven diluted concentrations. Typically, the calibration ranges for Al, Fe, Na, Mg, K, Ca, and P were 0.1–1000 ppb, whereas those for Sr, Ba, Ti, Mn, Co, Ni, Cu, Zn, Cd, Sn, Sb, Tl, Pb, V, Cr, As, Se, Ge, Rb, Cs, and Ga were in the ranges of 0.01–100 ppb. For rare earth elements (REEs), including La, Ce, and Nd, the calibration ranges were 0.01–1 ppb. Because of high PM loading in the sampling filters, some samples required dilution with Milli-Q water by a factor of 5–20. *Table S1* lists the operating conditions for ICP-MS. To reduce the isobaric interference and formation of doubly charged ions and oxides, some operating parameters were adjusted. For example, the nebulizer gas flow rate was set at 0.85 L min⁻¹. The CeO/Ce and Ba⁺⁺/Ba ratios were lower than the recommended values of 0.020 and 0.012, respectively. However, 10 ng mL⁻¹ concentration of indium (In) was added to the digests as an internal standard to correct instrumental drift. In each run, a blank reagent and three filter membrane blanks were subjected to the procedure same as that used for the samples. Accuracy and precision were calculated by replicate analyses (N = 7) of the standard reference material NIST SRM 1648, following total digestion. *Table S2* lists the recovery and accuracy for each analyzed element. The recoveries of most elements were 90–110%. The precision for most elements was less than 5%. The average ratio of each elemental concentration in blank to real stack PM samples (B/S) was 2.5% (from 0.9% for Mn to 4.8% for Ni), indicating that the concentrations of elements in stack PM samples exceeded that in blank by factors of 20–100 and therefore the data was reliable for further scientific discussion.

3. Results and discussion

Fig. 1 illustrates the average concentrations of elements in filterable

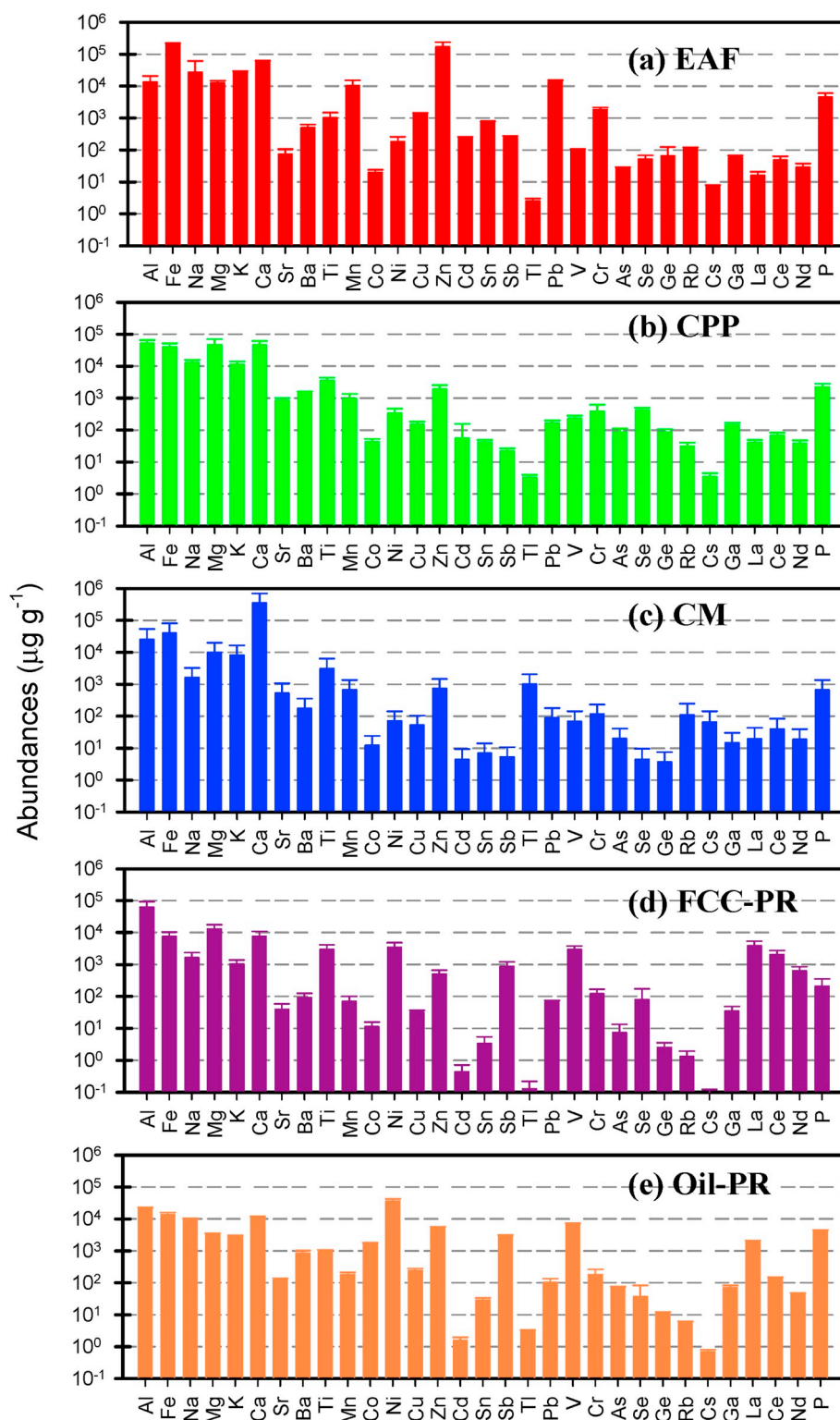


Fig. 1. The average elemental compositions of stack TSP emitted from industry emission sources: (a) EAF steel manufacturing plants; (b) CPP; (c) CM; (d) FCC petroleum refinery and (e) oil-refinery. The solid line in this figure represent standard deviations.

stack TSP emitted from various industrial emissions. The abundance of each metal was calculated by subtracting the blank level and subsequently dividing them by the TSP mass concentration. The average concentrations of heavy metals in each filterable stack TSP sample are listed in Table S3. The details of the elemental compositions of the stack PM samples are discussed in the following sections.

3.1. Concentrations of heavy metals in different industrial sectors

3.1.1. EAF steel manufacturing plants

In the EAF steel industry sector, the samples were collected from two steel manufacturing plants. Briefly, scrap steel is used as feedstock in both plants, and the output rates of iron-related products composed mainly of billet or liquid steel (see in Table 1). The baghouse (BH)

Table 1
Descriptions of industrial stacks for elemental compositions investigations in this study.

Emission sources	Electric Arc Furnace		Coal-fired power plant		Cement mills		Petroleum refining	
	Stack ID	Sampling date	Feedstock (Fuel)	Main products	Stack ID	Sampling date	Feedstock (Fuel)	Main products
	EAF1	2014/5/2	Scrap steel: 67 tons h ⁻¹	Liquid steel: 60.7 tons h ⁻¹	CPP1	2014/5/6	Coal:226 tons h ⁻¹	Power:545 MW h ⁻¹
	EAF2	2014/6/4	Scrap steel: 211 tons h ⁻¹	Billet steel: 165.1 tons h ⁻¹	CPP2	2014/7/22	Coal:214 tons h ⁻¹	Power: 547 MW h ⁻¹
					CM1	2014/6/12	Limestone: 267 tons h ⁻¹	CM: 235.78 tons h ⁻¹
					CM2	2014/9/5	Limestone: 220 tons h ⁻¹	CM: 300 tons h ⁻¹
APCD ^a	BH	25.4	50.0	BH	ESP	73.9	none	PR1(FCC)
Stack height (m)	4.2	79.4	79.8	FGD, SCR, ESP	ESP	61	204	2017/8/19
Stack diameter (m)	79.4	79.4	79.8	FGD, SCR, ESP	ESP	3.6	204	boil water: 180 tons h ⁻¹
Temperature of stack gas (°C)	3.3	10246	28291	FGD, SCR, ESP	ESP	72.8	204	Propylene:20.0 kl h ⁻¹
Moisture of stack gas (%)	18.5	0.6	0.1 ± 0.03	FGD, SCR, ESP	ESP	28.0	10.6	LPG:41.0 kl h ⁻¹
Gas flow rate (Nm ⁻³ min ⁻¹)	0.6 ± 0.1	0.6 ± 0.1	0.1 ± 0.03	FGD, SCR, ESP	ESP	4673	487	Pyrolysis gasoline: 178.0 kl h ⁻¹
O ₂ (%)	18.5	0.6	0.1 ± 0.03	FGD, SCR, ESP	ESP	2.2	6.2	Venturi Scrubber
CO ₂ (%)	0.6	0.6	0.1 ± 0.03	FGD, SCR, ESP	ESP	15.3	11.2	73.9
CO (%)	< 0.1	< 0.1	< 0.1	FGD, SCR, ESP	ESP	< 0.1	< 0.1	3.6
TSP mass (mg m ⁻³)	0.6 ± 0.1	0.6 ± 0.1	0.1 ± 0.03	FGD, SCR, ESP	ESP	42.9 ± 2.7	11.9 ± 1.4	72.8

^a APCD: air pollution control device; BH: baghouse; FGD: flue gas desulfurization; SCR: selective catalytic reduction; ESP: electrostatic precipitator.

equipment is used to reduce PM pollution in both plants. Fig. 1(a) plots the average abundances of heavy metals in stack TSP emitted from two EAF steel manufacturing plants. The concentrations of elements in stack TSP in each EAF steel plant are listed in Table S3. In FCC steel plants, Fe (21% for stack TSP mass) was the predominant species, followed by Zn (17%), Ca (5.5%), Na (2.7%), K (2.6%), Pb (1.4%), Al (1.4%), Mg (1.3%) and Mn (1.0%). The rest of other elements accounted for 1% of the stack PM mass.

Compared to other industrial sources (the abundances of Fe varied from 0.7% for FCC refining to 4% for cement mills), the concentration of Fe in steel manufacturing plants was considerably higher. The high concentration of Fe in electrical arc furnace steel manufacturing plants was attributed to scrap steel, which is a raw material in the steel industry. On the other hand, the concentrations of Zn, Mn and Pb in the EAF steel plants were 1–2 orders of magnitude higher than those of other industrial sectors, suggesting that enriched-Zn, -Mn and -Pb particles were found and these elements might be considered important markers of electrical arc furnace steel manufacturing plants in addition to Fe.

3.1.2. Coal-fired power plants

Coal combustion in Taiwan is mainly used for power generation, with 1.33 M tons of coal consumption in 2014. In addition to secondary aerosols, primary PM from coal-fired power plants severely deteriorates air quality in neighboring areas (Tsuang et al., 2003; Malm et al., 2004). In the current work, the elemental compositions of stack PM were investigated in samples collected from two coal-fired power plants. Both plants use bituminous coal from India and Australia as feedstock, and the electrostatic precipitator (ESP) is used to reduce PM emissions from stack. As seen in Fig. 1(b), the dominant elements of stack PM of coal-fired power plants were Al (5.2%), Mg (4.7%), Ca (4.6%) and Fe (4.0%), indicating that crustal materials dominated elemental compositions in CPP. Previously, numerous studies have characterized stack PM from coal-fired power plant and have suggested that CPP-derived PM contains certain trace metals, such as As, Se and Hg; As and Se are often used as specific markers for this industrial sector (Song et al., 2001; Watson et al., 2001; Chow et al., 2004; Ge et al., 2004). As seen in Fig. 1(b), Se and As concentrations were 419 and 88 μg g⁻¹, respectively. The Se concentrations in CPP were much higher than those emitted from other industrial sectors (ranging from 4.4 μg g⁻¹ for cement plants to 80 μg g⁻¹ for petroleum refinery), suggesting that Se was an unique element released from coal-fired power plant in this study.

3.1.3. Cement mills

Fig. 1(c) plots the average concentrations of elements in stack TSP samples collected from cement plants. Both plants used limestone as the raw material for cement production and were equipped with ESP to reduce PM emissions (see in Table 1). Calcium (Ca) was the dominant metal in cement plants, which accounted 35% for total stack TSP mass. Ca concentrations in cement plants exceeded the concentrations in other sectors by factors of 3–30. The enriched-Ca particles in cement plants might be due to the use of limestone, composed mainly of CaO, as a raw material of cement production. In addition to Ca, Fe (4.0%), Al (2.5%) and Mg (1.0%) concentrations were also high in CM. The concentrations of other crustal elements, such as K, Ti and Na were lower than 1% (ranging from 0.2% for Na to 0.8% for K). It is noted that the concentrations of Tl, a toxic element, were extremely high in cement plants, which were two orders of magnitude higher than those in other industries. The high concentration of Tl in cement plants might be because of pyrite or troilite minerals, which are raw materials in cement production in addition to limestone and clay (Xiao et al., 2012). Because of its high concentration, Tl has been used as a specific marker for CM emissions in previous studies (Santacatalina et al., 2010; Lin et al., 2016). Besides, enriched-Cs particles were also found; exceeded those of other sectors by factors of 8–66. As results, cement plants are a

crucial source of airborne particulate Cs in addition to soil, particularly in large particles.

3.1.4. Petroleum refining

Figs. 1(d) and (e) show the elemental profiles obtained from two different petroleum refineries: one is a fluidized bed catalytic cracking petroleum refining and another one is an oil-refinery. In terms of FCC petroleum refinery, Al (6.3%) dominated the stack TSP, followed by Mg (1.3%), Ca (0.8%), and Fe (0.8%). The concentrations of La, Ni, Ti, and V were 0.3–0.4% and those of Ce, Na, and K were 0.1–0.2%. The concentrations of La (0.4%), Ce (0.2%), and Nd (0.06%) in this sector were higher than those of other industries by one to two orders of magnitude. The high concentrations of these REEs indicated that enriched-REE particles were released into the atmosphere during catalyst PR operation; thereby, La, Ce and Nd were appropriate tracers to track petroleum refinery emissions for airborne PM (Kulkanri et al., 2006 ; , 2007). The relevant application will be discussed in section 3.5.

In oil-refinery, Ni was the most predominant species (3.6%), followed by Al (2%), Fe (1.3%), and Ca (1.1%), and then followed by Na (0.9%), V (0.7%), and Zn (0.5%). The concentrations of Ni and V in this source were two orders of magnitude higher than those in other industries. The high concentrations of Ni and V were attributed to oil-fired processes because both species are markers for oil-fired boiler (OFB) emissions (Olmez et al., 1988; Querol et al., 2007; Cheng et al., 2008).

3.2. Coefficient of divergence (COD) analysis

To evaluate the differences and similarities among our profiles, coefficient of divergence (COD) was used. It can be calculated as (Bano et al., 2018; Matawle et al., 2015):

$$COD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}} \right)^2} \quad (3)$$

where j and k are different elemental profiles. p denotes the number of investigated elements; X_{ij} and X_{ik} represent the mean concentrations of element i in profile j and k . If the COD value is close to zero, two elemental profiles are similar. If the COD value approaches to 1, significant discrepancy is found between the two profiles.

Table 2 lists the results of COD in the different emission sources. The COD values ranged from 0.58 to 0.81, with a highest value between steel industry and FCC-refinery, and a lowest value between steel industry and coal-fired power plant. Wongphatarakul et al. (1998) suggested that the COD value should be less than 0.269 if two profiles were similar. Based on our results, all the COD values were higher than 0.269, reflecting the significant discrepancies of elemental profiles were found among all industrial sectors.

3.3. Source markers

In this section, we identified source markers for different industrial sectors as (Bano et al., 2018; Kong et al., 2011; Yang et al., 2002):

Table 2
Coefficient of divergence (COD) for filterable stack TSP in different industrial sectors.

	EAF	CPP	CM	FCC-PR	Oil-refinery
EAF	0.00				
CPP	0.58	0.00			
CM	0.69	0.61	0.00		
FCC-PR	0.81	0.78	0.69	0.00	
Oil-refinery	0.71	0.62	0.70	0.64	0.00

Table 3
Identified potentially elemental markers of stack PM for different industrial emissions in this work and other studies.

Industrial sectors/stack PM sizes	Source markers	References
EAF steel industry		
TSP	Zn, Pb, Cr, Mn and Fe	this work
TSP	Fe, Zn, Cr, Cu, Mn, Ni and Pb	Chow (1995)
PM _{2.5-10}	Cr, K, Mg, Mn and Pb	Bano et al. (2018)
PM _{2.5}	Fe, Zn, Pb, Mn and Cr	Ouerol et al. (2007)
Coal-fired power plant		
TSP	Se, Cd, Ge, Sr and As	this work
TSP	As and Se	Hien et al. (2001)
TSP	S, As, Sb, Se and Hg	Chow (1995)
PM ₁₀	As, Sb, Se, Sn Pb and Zn	Xie et al. (2006)
PM _{2.5-10}	As and S	Bano et al. (2018)
PM _{2.5}	S, As and Se	Chow et al. (2004)
PM _{2.5}	As, Cr, S and Al	Matawle et al. (2014)
Cement plants		
TSP	Tl, Cs, Rb Ca, and Sr	this work
PM _{2.5-10}	Al, Ca, Cu and Mg	Bano et al. (2018)
PM ₁₀	Tl, Ti, Cs and Rb	Santacatalina et al. (2010)
PM _{2.5}	S, Cr, Cu, Al, Mo and Mg	Matawle et al. (2014)
FCC-refinery		
TSP	La, Sb, Ce, Ni, and Nd	this work
TSP	La, Ce, Nd and Sm	Bozlaker et al. (2013)
PM _{2.5}	La, Nd, Pr and Sm	Kulkarni et al. (2006, 2007)
Oil-refinery		
TSP	Ni, Sb, La, Co and V	this work
TSP ^a	Ni, V	Chow (1995)
PM ₁₀ ^a	Ni and V	Cheng et al. (2008)
PM _{2.5}	V, Ni, La and Sb	Chow et al. (2004)
PM _{2.5} ^a	V and Ni	Watson et al. (2008)

^a The source profiles were established for heavy-oil boiler.

$$R_{j,i} = \frac{(X_i / \sum X)_j}{(X_i / \sum X)_{\min}} \quad (4)$$

where X_i is the concentration of i th element and $(X_i / \sum X)_j$ is the quotient of the concentration of i th element divided by the sum of 31 species concentrations in emission source j . $(X_i / \sum X)_{\min}$ is the minimum quotient of the concentration of i th element divided by the sum of 31 species concentrations. In this equation, a normalize procedure was needed. Normalized value of i th element was calculated by i th elemental concentration dividing by the sum of i th elemental concentrations in all sources (Bano et al., 2018; Kong et al., 2011). Without analyzing water-soluble ions and carbon contents, we selected the five highest R_{ji} values as potential markers for specific emissions sources. In supplementary S2, we give an example to explain details of this concept.

Table 3 lists the potential markers for various industrial emissions calculated by Eq. (4). The source markers obtained from other studies are also listed in this table. Zinc (Zn), Pb, Cr, Mn and Fe could be used as indicators for electric arc furnace steel industries. These source markers were in line with those reported by Querol et al. (2007). For coal-fired power plant, As and Se were commonly considered as markers (Bano et al., 2018; Chow et al., 2004; Xie et al., 2006; Matawle et al., 2014). In fact, the element enriched in coal is dependent on the source of coal. In this study, we found that enriched Cd, Ge and Sr in CPP emissions, suggesting that these elements might be potential source markers other than As and Se in coal-fired power plants.

In case of cement plants, Tl, Cs, Rb and Ca were regarded as representative species, especially for Tl, whose concentrations in cement emissions were two orders of magnitude higher than those derived from other industries, could be used as a good marker for CM emissions in

this work. Nevertheless, in Texas, Chow et al. (2004) found that the concentration of Tl ($\sim 2400 \mu\text{g g}^{-1}$) in stack PM of cement industry was similar to that ($2500 \mu\text{g g}^{-1}$) of coal-fired power plant and even lower than that ($\sim 3900 \mu\text{g g}^{-1}$) of catalytic cracker refinery, suggesting that Tl might not be an marker of cement industry in Texas. This indicated that consideration of Tl as a marker of CM was regional differences. Lanthanum (La), Ce and Nd were found to be good markers for FCC petroleum refining. This was in agreement with those reported by Kulkarni et al. (2006, 2007). Abundant La, Sb, V and Ni were found in oil-refinery, suggesting these elements were good indicators for this industrial sector.

3.4. Inter-elemental ratios for FCC-refinery

Numerous studies have suggested that the inter-elemental ratios of stack PM, including V/Ni, As/Se, Sb/Cu and Tl/Ca, can be used as potential fingerprints to track specific emission sources for airborne PM (Kavouras et al., 2001; Arditoglou and Samara, 2005; Mazzei et al., 2008; Hsu et al., 2010; Lin et al., 2016). Ratios of La to other lanthanides have been successfully employed to differentiate dust from FCC catalyst petroleum refining emissions (Kulkarni et al., 2006, 2007). Rare earth elements are commonly associated with crustal materials. In addition to natural dust, anthropogenic emissions can be sources of airborne REEs (Olmez and Gordon, 1985). For instance, La, Ce, and Nd were synchronously used as catalysts in the fluidized bed catalytic cracking petroleum refinery, and Ce was used as an additive in motor engines. Even in oil-refinery emissions, enriched La was also detected in stack PM (Chow et al., 2004).

In the current work, the elemental ratios of La to Ce and La to Nd of various industrial sectors are shown in Fig. 2. The La/Ce and La/Nd ratios in crust, traffic emissions and FCC petroleum refinery in Houston are also plotted here for comparisons (Taylor, 1964; Kulkarni et al., 2006; Lin et al., 2015). Note that the Y-axis is presented in log scale. In FCC refining, the ratios of La/Ce and La/Nd were 1.8 and 6.0, respectively. The ratio of La/Ce in this study was slightly lower than the average value (4.3) for the FCC petroleum refinery in Houston (Kulkarni et al., 2006, see in Fig. 2); the La/Nd ratio was nearly the same as that in Houston (6.4). However, both ratios in FCC petroleum refinery were higher than those in other anthropogenic emissions and natural crustal materials. For the oil refinery, La/Ce (13.9) and La/Nd (44.7) ratios were high, and both ratios were 20–30 times higher than those for other emissions. The findings did claim that higher La/Ce and La/Nd ratios for both catalytic and oil refineries; thus, these ratios can be used as efficient tools to diagnose whether ambient PM is contaminated by refining emissions, as will be discussed in section 3.5.

3.5. Tracking petroleum sources by REEs

As mentioned above, La/Ce and La/Nd ratios can be considered as potential markers for petroleum sources; in the section, we attempted to apply both ratios to estimate the influence of a FCC petroleum refining (PR1) on ambient PM in an industrialized city in northern Taiwan. The ambient TSP samples were synchronously collected using high-volume aerosol samplers at four sampling sites encompassing the FCC petroleum refinery (PR1) in Taoyuan City in northern Taiwan (as shown in Fig. 3) from August 19 to 22 2014. The sampling sites A and B are located in the suburban areas of Taoyuan City and are approximately 5 km west to the FCC petroleum refinery. Site C, situated at Waishe hill (approximately 150 m above sea level), is a lightly populated area. Site D is located in the downtown of Guishan District and thereby is characterized by relatively high traffic emissions compared with the other sites. Each aerosol sample was collected over a period of 12 h, either from 8 a.m. to 8 p.m. or from 8 p.m. to 8 a.m. After sampling, the aerosol samples were analyzed 31 target elements through ICP-MS, following the same procedure as that used for stack PM samples. The wind profiles for this region were obtained from the various monitoring

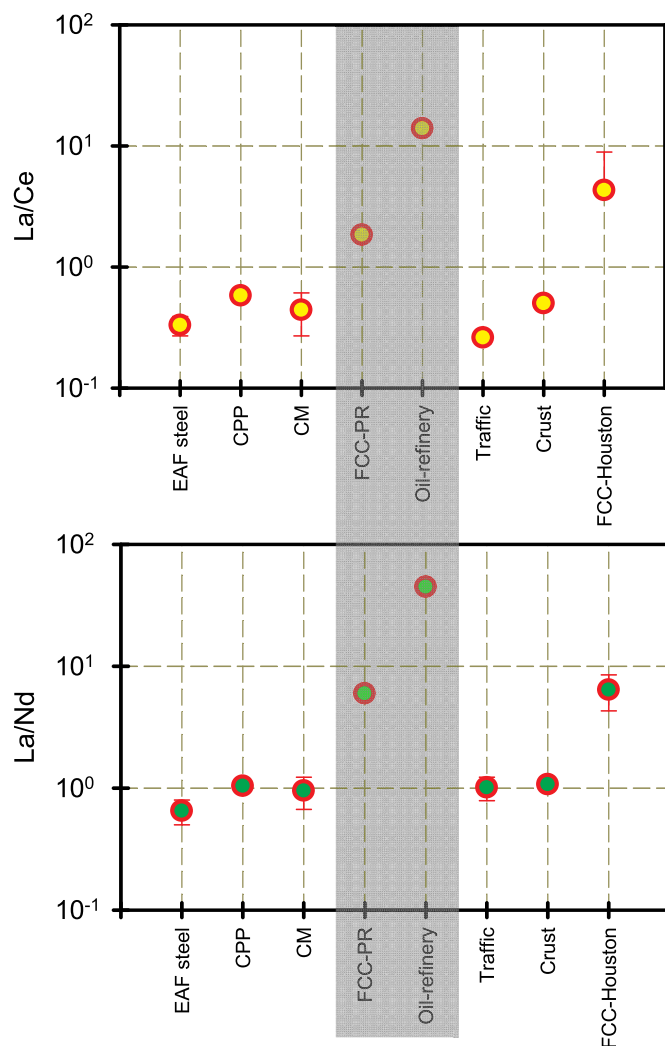


Fig. 2. Ratios of La/Ce and La/Nd in filterable stack PM emitted from various sectors. The same ratios of traffic emissions (Lin et al., 2016), natural crust (Taylor, 1964) and FCC refinery in Houston (Kulkarni et al., 2006) are also shown in this figure.

stations, namely Linkou (W1), Taoyuan (W2), Luzhu (W3), Chungli (W4), and Pushin (W5) (Fig. 3), operated by the Central Weather Bureau (CWB) of Taiwan.

Fig. S1 shows the time series of hourly wind speed (WS) and wind direction (WD) from August 19 to 22 in Taoyuan City. Sea-land breeze was apparent only at the Luzhu coastal station, resulting in prevailing north and northwesterly wind at daytime and prevalent southwesterly flow at nighttime. Nevertheless, at the other CWB stations, the WS was frequently lower than 1 m s^{-1} . During the sampling period, the TSP mass concentrations were, on average, $24, 25, 21,$ and $27 \mu\text{g m}^{-3}$ at sites A, B, C, and D, respectively. The TSP mass concentration at site C was significantly lower ($p < 0.05$) than that at other sites. This might be because hilly areas, which was less impact of anthropogenic emissions. Fig. 4 shows the average concentrations of heavy metals in TSP samples at the sampling stations. On average, the analyzed metallic elements accounted for approximately 8.6–9.2% of the ambient TSP mass at each station. Sodium (Na) was the most predominant species at the all stations, accounting for approximately 2% of the TSP mass. In addition to Fe (1.5–1.8% at each station), Al, Ca, and K (up to 1%) were the major elements, followed by Zn (0.25–0.42%), Mg (0.27–0.34%), and Ti (0.09–0.11%). The concentrations of the remaining elements were lower than 0.1%. Different sites showed fairly similar elemental patterns in TSP samples; however, similar to the TSP mass,

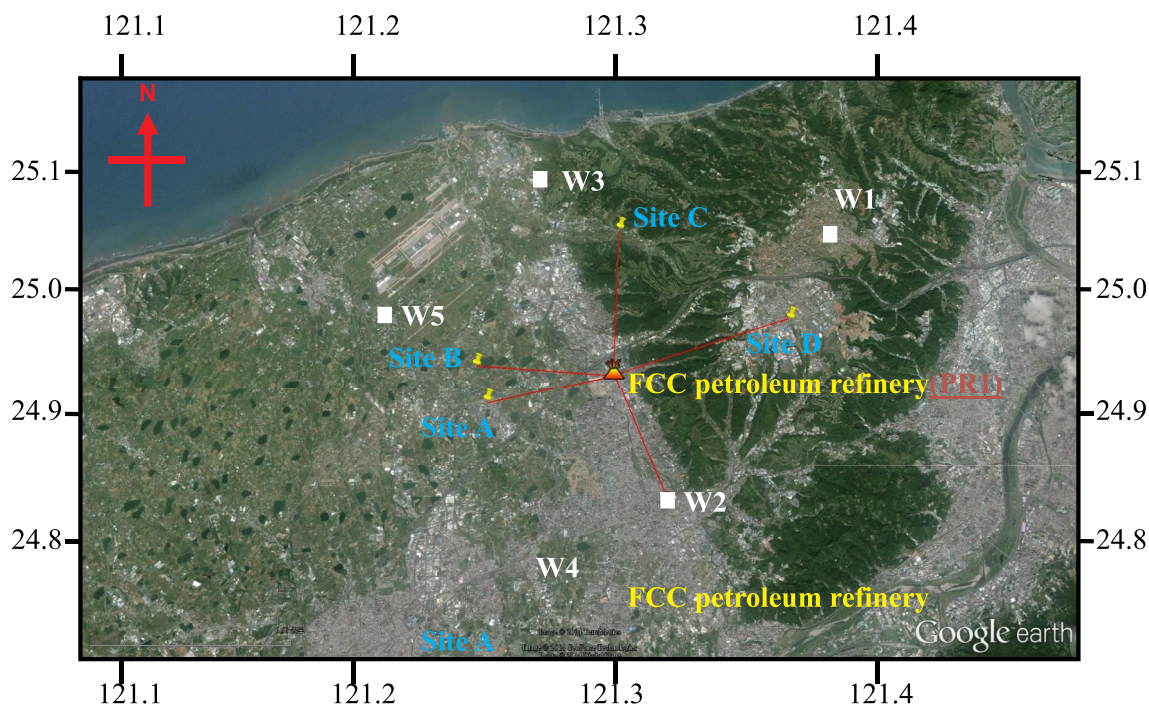


Fig. 3. Relative locations of four airborne TSP sampling sites (A, B, C, and D) and a FCC petroleum refinery in Taoyuan City of northern Taiwan. The white squares (W1, W2, W3, W4 and W5) are the Taiwan CWB monitoring stations.

concentrations of elements were always lower at site C. The levels of Zn, Pb, and Mo were clearly higher at site D, suggesting more contributions of vehicle emissions (Lin et al., 2015). The average concentration of La, a marker for FCC refining, was 0.5–0.9 ng m⁻³ with a maximum and minimum value at sites A and C, respectively.

Fig. 5 presents the scatter plots of La against Nd and La against Ce at the four sampling sites. It is found that La correlated moderately with Ce and Nd, suggesting that the origins of airborne La, Ce and Nd were different in part. Fig. S2 plots the enrichment factor (EF) values of elements in each sampling site. The details of EF analysis are written in supplementary S3. Here, Al was used as a reference element (Taylor,

1964). Lanthanum (La) exhibited an EF value of approximately 10 at each sampling site, suggesting that anthropogenic emissions were a major source. Cerium (Ce) and Nd had an EF value of approximately 3, reflecting a mixed source of soil dust and anthropogenic emissions. The La/Ce ratio was 1.5–1.9, and the La/Nd ratio was 3.3–3.8 (see in Fig. 5). Both the La/Ce and La/Nd ratios were markedly higher than those of EAF steel manufacturing plants, coal-fired power plant, cement mills, and vehicle emissions together with natural soil emissions, but were in concordance with those of local FCC petroleum emissions (Fig. 2). In addition, the La/Ce and La/Nd ratios were markedly higher than those (La/Ce, approximately 0.62 and La/Nd, approximately 1.06, both ratios

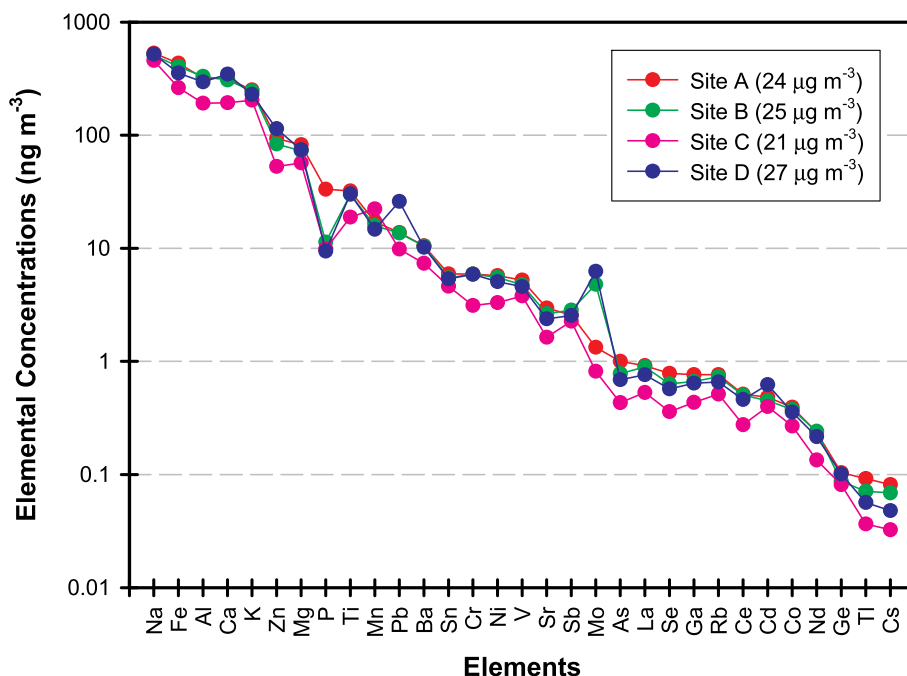


Fig. 4. The average concentrations of elements in TSP samples at the all stations during the sampling period.

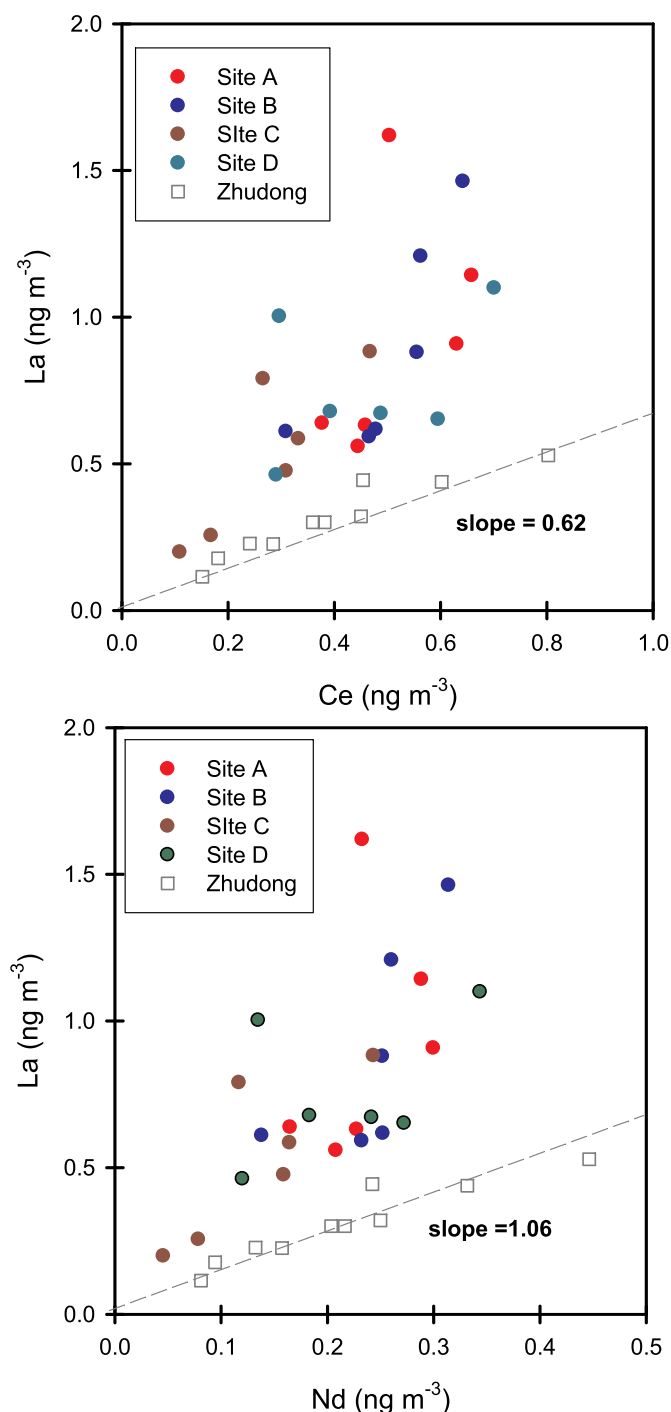


Fig. 5. Scatter plots of La against Ce and La against Nd in ambient TSP samples observed at the sampling sites in Taoyuan City from August 19 to 22, 2014. The grey dash lines denote the slopes of La/Ce and La/Nd at the Zhudong background site.

were close to natural dust) at the Zhudong sampling site, which is located 20 km southwest to the FCC refinery and is isolated from FCC contamination (Chou et al., 2014). Consequently, the high La/Ce and La/Nd ratios in Taoyuan City were considered to be influenced by anthropogenic emissions, and the FCC refinery was a candidate.

To quantitatively estimate the contribution of the FCC refinery to airborne TSP in Taoyuan City, the La/Ce and La/Nd ratios were used. Assuming that the La/Ce ratio at the Zhudong station was a background ratio, we can define excessive-La (La_{EX}) that are additional quantities relative to what the soil dust could contribute, as follow:

$$[La]_{EX} = [La]_{amb} - \left(\frac{[La]}{[Ce]} \right)_{bk} \times [Ce]_{amb} \quad (5)$$

where $[La]_{amb}$ and $[Ce]_{amb}$ are La and Ce concentrations, respectively, in ambient TSP. $([La]/[Ce])_{bk}$ is a mass ratio of La to Ce in ambient TSP at the Zhudong sampling site. Consequently, the atmospheric TSP concentrations (C) from the FCC refinery can be directly calculated using the following equation (Lin et al., 2016):

$$C (\mu\text{g m}^{-3}) = [La]_{EX} (\text{ng m}^{-3}) / [Abu]_{PR} (\mu\text{g g}^{-1}) \times 1000 \quad (6)$$

where $[Abu]_{PR}$ represents the concentration of La (in $\mu\text{g g}^{-1}$) from a FCC PR-derived particles; this value was $3815 \mu\text{g g}^{-1}$ in the current study (PR1 in Table S3). Finally, we estimated that approximately $0.13 \mu\text{g m}^{-3}$ (from $0.10 \mu\text{g m}^{-3}$ at site C to $0.16 \mu\text{g m}^{-3}$ at site A) of TSP was directly contributed by the FCC petroleum refinery during the sampling period. Assuming that the ambient primary TSP were summed as metallic elements and primary carbon (19% of the ambient TSP mass) (Chou et al., 2010), we subsequently estimated that the average contribution of the FCC refinery to ambient primary TSP in Taoyuan City was 0.6% (from 0.4% for site C to 0.7% for site A). Furthermore, we used the same approach involving the La/Nd ratio for the estimations. The results revealed that approximately 0.7% of the ambient primary TSP was contributed by the PR plant. This value was in agreement with that of Taiwan emission data systems (TEDs, 8.1), which suggested that approximately 0.7% of ambient primary TSP was released from PR emissions in Taoyuan City. In spite of existence of uncertainty for the estimations, the inter-elemental ratios of La/Ce and La/Nd can provide us a direct evidence to track a FCC source contributing to ambient particulates.

4. Conclusion

In this study, we characterized the elemental profiles of filterable stack TSP emitted from integrated industrial emission sources in Taiwan, namely EAF steel manufacturing plants, CPP, CM, and PR. The elemental profile of stack TSP in each industrial sector showed very different based on COD analysis. Geological elements including Al, Fe, Ca, Na, K and Mg were the dominant species in coal-fired power plants, cement mills and FCC petroleum refining. However, Zn was a dominant element in addition to Fe in EAF steel plants and Ni constituted a major fraction in oil-refinery. Furthermore, we identified source markers of different emissions by source marker calculations. The results suggested that Zn, Pb, Cr, Mn and Fe were appropriate indicators for EAF steel industry. As, Se, Cd and Ge were markers for coal-fired power plants. Tl, Cs, Rb and Ca were signatures for cement mills while La, Sb, Ce and Nd were strong indicators for FCC refining emissions. Finally, Ni, Sb, La, Co and V were selected as tracers for oil-refinery. The mass ratios of La/Ce (1.8) and La/Nd (6.0) were fingerprinting ratios of FCC petroleum refinery. We employed the identified La/Ce and La/Nd ratios to assess the effects of an FCC PR on the ambient TSP, and approximately 0.6% of the ambient primary TSP was contributed by FCC petroleum emissions during the summertime in an industrial urban area of northern Taiwan.

In this study, we built elemental profiles and source markers of filterable stack TSP from various industrial emissions. The similar studies have been done in other regions over the last two decades (Chow, 1995; Chow et al., 2004; Watson et al., 2001; Xie et al., 2006; Bano et al., 2018). Indeed, the elemental concentrations of stack PM in the same industrial sectors would be different via the different feedstock, raw materials, operating conditions and air pollutant control devices (Chow et al., 2004). Thus, the elemental profiles built in this work might be only applicable in Taiwan. On the contrary, the markers of EAF steel manufacturing, coal combustion and FCC-petroleum refinery along with oil-refinery in different studies were much similar, suggesting that source marker established in this work can be used in other places in the world.

CRedit authorship contribution statement

Yu-Chi Lin: Conceptualization, Methodology, Formal analysis, Writing - original draft. **Shih-Chieh Hsu:** Conceptualization, Methodology. **Shuen-Hsin Lin:** Data curation. **Yi-Tang Huang:** Data curation.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Acknowledgements

This study was financially supported by Taiwan Environmental Protection Administration (No. EPA-103-1602-02-06).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2020.01.005>.

References

- Arditsoglou, A., Samara, C., 2005. Levels of total suspended particulate matter and major trace element in Kosovo: a source identification and apportionment study. *Chemosphere* 59, 669–678.
- Bano, S., Pervez, S., Chow, J.C., Matawle, J.L., Watson, J.G., Sahu, R.K., Srivastava, A., Tiwari, S., Pervez, Y.F., Deb, M.K., 2018. Coarse particle (PM_{2.5-10}) source profiles for emissions from domestic cooking and industrial process in central India. *Sci. Total Environ.* 627, 1137–1145.
- Bhanarkar, A.D., Rao, P.S., Gajghate, D.G., Nema, P., 2005. Inventory of SO₂, PM and toxic metals emissions from industrial sources in greater Mumbai, India. *Atmos. Environ.* 39, 3851–3864.
- Bozlake, A., Buzcu-Güven, B., Fraser, M.P., Chellam, S., 2013. Insights into PM10 sources in Houston, Texas: role of petroleum refineries in enriching lanthanoid metals during episodic emission events. *Atmos. Environ.* 69, 109–117.
- Chan, Y.-C., Cohen, D.D., Hawas, O., Stelcer, E., Simpson, R., Denison, L., Wong, N., Hodge, M., Comino, E., Carswell, S., 2008. Apportionment of sources of fine and coarse particles in four major Australian cities by positive matrix factorisation. *Atmos. Environ.* 42, 374–389.
- Cheng, M.-T., Chio, C.-P., Huang, C.-Y., Chen, J.-M., Wang, C.-F., Kuo, C.-Y., 2008. Chemical composition of fine particulates emitted from oil-fired boilers. *J. Environ. Eng. Manag.* 18, 355–362.
- Chio, C.-P., Cheng, M.-T., Wang, C.-F., 2004. Source apportionment to PM10 in different air quality conditions for Taichung urban and coastal areas, Taiwan. *Atmos. Environ.* 38, 6893–6905.
- Chio, C.-P., Yuan, T.-H., Shie, R.-H., Chan, C.-C., 2014. Assessing vanadium and arsenic exposure of people living near a petrochemical complex with two stage dispersion models. *J. Hazard Mater.* 271, 98–107.
- Chou, C.C.-K., Lee, C.-T., Cheng, M.T., Yuan, C.S., Chen, S.J., Wu, Y.L., Hsu, W.C., Lung, S.C., Hsu, S.C., Lin, C.Y., Liu, S.C., 2010. Seasonal variation and spatial distribution of carbonaceous aerosols in Taiwan. *Atmos. Chem. Phys.* 10, 9563–9578.
- Chou, C.C.-K., Hsu, S.-C., Lin, Y.-C., Lin, S.-H., Chen, F.-Y., Huang, Y.-T., Huang, C.-H., Hu, S.-C., 2014. Technical Establishment and Evaluation of Characteristics and Signatures of Anthropogenic PM. (Taiwan EPA report).
- Chow, J., 1995. Measurements method to determine compliance with ambient quality standards for suspended particles. *J. Air Waste Manag. Assoc.* 45, 320–382.
- Chow, J.C., Watson, J.G., Kuhns, H., Etyemezian, V., Lowenthal, D.H., Chow, D., Kohl, S.D., Engelbrecht, J.P., Green, M.C., 2004. Source profiles for industrial, mobile, and area sources in the big blend regional aerosol visibility and observational study. *Chemosphere* 54, 185–208.
- Ge, S., Xu, X., Chow, J.C., Watson, J.G., Sheng, Q., Liu, W., Bai, Z., Zhu, T., Zhang, J., 2004. Emissions of air pollutants from household stoves: honeycomb coal versus coal cake. *Environ. Sci. Technol.* 38, 4612–4618.
- Hien, P.D., Binh, N.T., Truong, Y., Ngo, N.T., Sieu, L.N., 2001. Comparative receptor modelling study of TSP, PM₂ and PM_{2.5-10} in Ho chi minh city. *Atmos. Environ.* 35, 2669–2678.
- Hleis, D., Fernández-Olmo, I., Ledoux, F., Kfoury, A., Courcot, L., Desmonts, T., Courcot, D., 2013. Chemical profiles identification of fugitive and confined particle emissions from an integrated iron and steelmaking plant. *J. Hazard Mater.* 250–251, 246–255.
- Hsu, S.C., Liu, S.C., Tsai, F., Engling, G., Lin, I.I., Chou, C.K.C., Kao, S.J., Lung, S.C.C., Chan, C.Y., Lin, S.C., Huang, J.C., Chi, K.H., Chen, W.N., Lin, F.J., Huang, C.H., Kuo, C.L., Wu, T.C., Huang, Y.T., 2010. High wintertime particulate matter pollution over an offshore island (Kinmen) off Southeastern China: an overview. *J. Geophys. Res.* Atmos. 115, D17309.
- Huang, R.J., Chen, R., Jing, M., Yang, L., Li, Y., Chen, Q., Chen, Y., Yan, J., Lin, C., Wu, Y., Zhang, R., Haddad, J.E., Prevot, A.S.H., O'Dowd, C.D., Cao, J., 2018. Source-specific health risk analysis on particulate trace elements: coal combustion and traffic emission as major contributors in wintertime Beijing. *Environ. Sci. Technol.* 52, 10967–10974.
- Kavouras, I.G., Koutrakis, P., Cereceda-Balic, F., Oyola, P., 2001. Source apportionment of PM₁₀ and PM_{2.5} in five Chilean cities using factor analysis. *J. Air Waste Manag. Assoc.* 51, 451–464.
- Kong, S., Ji, Y., Lu, B., Chen, L., Han, B., Li, Z., Bai, Z., 2011. Characterization of PM₁₀ source profiles for fugitive dust in Fushun—a city famous for coal. *Atmos. Environ.* 45, 5351–5365.
- Kulkarni, P., Chellam, S., Fraser, M.P., 2006. Lanthanum and lanthanides in atmospheric fine particles and the appointment to refinery and petrochemical operations in Houston, TX. *Atmos. Environ.* 40, 508–520.
- Kulkarni, P., Chellam, S., Fraser, M.P., 2007. Tracking petroleum refinery emission event using lanthanum and lanthanides as elemental markers for PM_{2.5}. *Environ. Sci. Technol.* 41, 6748–6754.
- Lee, E., Chan, C.K., Paatero, P., 1999. Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong. *Atmos. Environ.* 33, 3201–3212.
- Lin, Y.-C., Tsai, C.-J., Wu, Y.-C., Zhang, R., Chi, K.-H., Huang, Y.-T., Lin, S.-H., Hsu, S.-C., 2015. Characteristics of trace metals in traffic-derived particles in Hsuehshan Tunnel, Taiwan: size distribution, potential source, and fingerprinting metal ratio. *Atmos. Chem. Phys.* 15, 4117–4130.
- Lin, Y.-C., Hsu, S.-C., Chou Charles, C.-K., Zhang, R., Wu, Y., Kao, S.-J., Luo, L., Huang, C.-H., Lin, S.-H., Huang, Y.-T., 2016. Wintertime haze deterioration in Beijing by industrial pollution deduced from trace metal fingerprints and enhanced health risk by heavy metals. *Environ. Pollut.* 208, 284–293.
- Machemer, S.D., 2004. Characterization of airborne and bulk particulate from iron and steel manufacturing facilities. *Environ. Sci. Technol.* 38, 381–389.
- Malm, W.C., Schichtel, B.A., Pitchford, M.L., Ashbaugh, L.L., Eldred, R.A., 2004. Spatial and monthly trends in speciated fine particle concentration in the United States. *J. Geophys. Res.* 109, D3.
- Matawle, J.L., Pervez, S., Dewangan, S., Shrivastava, A., Tiwari, S., Pant, P., Deb, M.K., Pervez, Y., 2014. PM_{2.5} chemical source profiles of emissions resulting from industrial and domestic burning activities in India. *Aerosol Air Qual. Res.* 14, 2051–2066.
- Matawle, J.L., Pervez, S., Dewangan, S., Shrivastava, A., Tiwari, S., Pant, P., Deb, M.K., Pervez, Y., 2015. Characterization of PM_{2.5} source profiles for traffic and dust sources in Rapir, India. *Aerosol Air Qual. Res.* 15, 2537–2548.
- Mazzei, F., D'Alessandro, A., Lucarelli, F., Nava, S., Prati, P., Valli, G., Vecchi, R., 2008. Characterization of particulate matter sources in an urban environment. *Sci. Total Environ.* 401, 81–89.
- Olmez, I., Gordon, G.E., 1985. Rare earths: atmospheric signatures for oil-fired power plant and refineries. *Science* 229, 966–968.
- Olmez, I., Sheffield, A.E., Gordon, G.E., Houck, J.E., Pritchett, L.C., Cooper, J.A., Dzubay, T.G., Bennett, R.I., 1988. Compositions of particles from selected sources in Philadelphia for receptor modeling applications. *J. Air Waste Manag. Assoc.* 38, 1392–1402.
- Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* 9, 269–298.
- Patil, R.S., Kumar, R., Menon, R., Shah, M.K., Stehi, V., 2013. Development of particulate matter speciation profiles for major sources in six cities in India. *Atmos. Res.* 132–133, 1–11.
- Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., Sánchez de la Campa, A., Artíñano, B., Salvado, P., García Dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Gil, J.I., Inza, A., Ortega, L.A., Santamaría, J.M., Zabalza, J., 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. *Atmos. Environ.* 41, 7219–7231.
- Santacatalina, M., Reche, C., Minguillón, M.C., Escrig, A., Sanfelix, V., Carratalá, A., Nicolás, J.F., Yubero, E., Crespo, J., Alastuey, A., Monfort, E., Miró, J.V., Querol, X., 2010. Impact of fugitive emissions in ambient PM levels and composition: a case study in Southeast Spain. *Sci. Total Environ.* 409, 4999–5009.
- Song, X.-H., Polissar, A.V., Hopke, P.K., 2001. Sources of fine particle composition in the northeastern US. *Atmos. Environ.* 35, 5277–5286.
- Sweet, C.W., Vermette, S.J., Landsberger, S., 1993. Sources of toxic elements in urban air in Illinois. *Environ. Sci. Technol.* 27, 2502–2510.
- Taylor, S.R., 1964. Abundance of chemical elements in the continental crust: a new table. *Geochem. Cosmochim. Acta* 18, 1273–1285.
- Thurston, G.D., Ito, K., Lall, R., 1994. A source apportionment of U.S. fine particulate matter air pollution. *Atmos. Environ.* 45, 3924–3936.
- Tsai, J.-H., Lin, K.-H., Chen, C.-Y., Ding, J.-Y., Choa, C.-G., Chiang, H.-L., 2007. Chemical constituents in particulate emissions from an integrated iron and steel facility. *J. Hazard Mater.* 147, 111–119.
- Tsuang, B.-J., Chen, C.-L., Lin, C.-H., Cheng, M.-T., Tsai, Y.-I., Chio, C.-P., Pan, R.-C., Kuo, P.-H., 2003. Quantification on the source/receptor relationship of primary pollutants secondary aerosols by a Gaussian plume trajectory model: Part II Case study. *Atmos. Environ.* Times 37, 3993–4006.
- U.S. EPA, 2001. Determination of Particulate Emission from Stationary Sources, vol. 40 CFR Part 60, Appendix A, Method 5.
- Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winwarther, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wählin, P., Vecchi, R., Miranda, A.I., Kasper-Giebl, A., Maenhaut, W., Hitenberger, R., 2008. Source apportionment of particulate matter in Europe: a review of methods and results. *J. Aerosol Sci.* 39, 827–849.
- Watson, J.G., Chen, L.-W.A., Chow, J.C., Doraiswamy, P., Lowenthal, D.H., 2008. Source Apportionment: Findings from the U.S. Superfund Program. *Journal of the Air & Waste Management Association* 58 (2), 265–288.
- Watson, J.G., Chow, J.C., Houck, J.E., 2001. PM_{2.5} chemical source profiles for vehicle

- exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995. *Chemosphere* 43, 1141–1151.
- Wongphatarakul, V., Friedlander, S.K., Pinto, J.B., 1998. A comparative study of PM_{2.5} ambient aerosol chemical datasets. *Environ. Sci. Technol.* 32, 3926–3934.
- Xiao, T., Yang, F., Li, S., Zheng, B., Ning, Z., 2012. Thallium pollution in China: a geo-environmental perspective. *Sci. Total Environ.* 421–422, 51–58.
- Xie, R., Seip, H.M., Wibetoe, G., Nori, S., Mcleod, W., 2006. Heavy coal combustion as the dominant source of particulate pollution in Taiyuan, China, corroborated by high concentrations of arsenic and selenium in PM₁₀. *Sci. Total Environ.* 370, 409–415.
- Yang, H.-H., Lai, S.-O., Hsieh, L.-T., Hsueh, H.-J., Chi, T.-W., 2002. Profile of PAH emission from steel and iron industries. *Chemosphere* 48, 1061–1074.
- Yatkin, S., Bayram, A., 2008. Determination of major natural and anthropogenic source profiles for particulate matter and trace elements in Izmir, Turkey. *Chemosphere* 71, 685–696.
- Yuan, C.-S., Lee, C.-G., Liu, S.-H., 2000. Characterization and sources apportionment of ambient particulate matter in southern Taiwan. *J. Aerosol Sci. Suppl.* 1, S368–S369.
- Zhang, R., Jing, J., Tao, J., Hsu, S.-C., Wang, G., Cao, J., Lee, C.S.L., Zhu, L., Chen, Z., Chao, Y., Shen, Z., 2013. Chemical characterization and source apportionment of PM_{2.5} in Beijing: seasonal perspective. *Atmos. Chem. Phys.* 13, 7053–7074.