Origins and discrimination between local and regional atmospheric pollution in Haiphong (Vietnam), based on metal(loid) concentrations and lead isotopic ratios in PM10

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RESEARCH ARTICLE

Origins and discrimination between local and regional atmospheric pollution in Haiphong (Vietnam), based on metal(loid) concentrations and lead isotopic ratios in PM_{10}

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Abstract

Southeast Asia is a hotspot of anthropogenic emissions where episodes of recurrent and prolonged atmospheric pollution can lead to the formation of large haze events, giving rise to wide plumes which spread over adjacent oceans and neighbouring countries. Trace metal concentrations and Pb isotopic ratios in atmospheric particulate matter < 10 μm (PM_{10}) were used to track the origins and the transport pathways of atmospheric pollutants. This approach was used for fortnightly PM_{10} collections over a complete annual cycle in Haiphong, northern Vietnam. Distinct seasonal patterns were observed for the trace metal concentration in PM_{10}, with a maximum during the Northeast (NE) monsoon and a minimum during the Southeast (SE) monsoon. Some elements (As, Cd, Mn) were found in excess according to the World Health Organization guidelines. Coal combustion was highlighted with enrichment factors of As, Cd, Se, and Sb, but these inputs were outdistanced by other anthropogenic activities. V/Ni and Cu/Sb ratios were found to be markers of oil combustion, while Pb/Cd and Zn/Pb ratios were found to be markers of industrial activities. Pb isotopic composition in PM_{10} revealed an important contribution of soil dusts (45–60%). In PM_{10}, the Pb fraction due to oil combustion was correlated with dominant airflow pathways (31% during the north-easterlies and 20% during the south-easterlies), and the Pb fraction resulting from industrial emissions was stable (around 28%) throughout the year. During the SE monsoon, Pb inputs were mainly attributed to resuspension of local soil dusts (about 90%), and during the NE monsoon, the increase of Pb inPM_{10} was due to the mixing of local and regional inputs.

Keywords Air pollution · Haiphong · Enrichment factors · Chemical balances · Lead isotopes · Anthropogenic sources · Local and regional inputs

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Introduction

Atmospheric particulate matter (PM) is a complex mixture of various substances (e.g. organic and elemental carbon, SO_4^{2-}, NH_4^+, trace metals) that may carry signatures of its origins (Duce et al., 1975; Patterson and Settle, 1987; Nriagu and Pacyna, 1988). PM occurs along a size continuum that is operationally defined as: coarse particles (PM_{10}, aerodynamic diameter < 10 μm) emitted from natural and anthropogenic sources, fine particles ($PM_{2.5}$) mainly produced from anthropogenic activities, and ultrafine particles ($PM_{0.1}$) derived from PM_{10} and $PM_{2.5}$ transformations (Cohen et al., 2010a, 2010b; Kim et al. 2012).

Nowadays, anthropogenic PM emissions generally exceed crustal derived sources for trace metals owing to the rapid expansion of industrial activities, motorization, and urbanisation processes (Chen et al., 2005; Chen and Zhang, 2010).

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Southeast Asia is one of the most economically dynamic regions in the world. This results in a high production of anthropogenic PM during the combustion of fossil fuels (coal, oil, and natural gas) used for energy production in the residential, commercial and industrial sectors, and for transportation (Duan et al., 2003; Sun et al., 2004; Feng et al., 2005; Wang et al., 2005, 2006a; Okuda et al., 2008). Vietnam has the second largest coal reserves in the region, with 3100 Mt of hard coal and 200 Mt of brown coal at the end of 2011 (BGR, 2013). The majority of these reserves are located in northern Vietnam. The oil produced by the wells located in southeast Vietnam is mainly aimed at the domestic market, with a production of 450 thousand barrels per day. Gas production is exploited offshore southern Vietnam and has grown steadily in the past decade, reaching 9×10^9 m^3 in 2011 (IEA, 2015).

The occurring of large haze events principally made up of anthropogenic PM causes multiple detrimental effects caused by the deterioration of air quality in the region (Ramanathan et al., 2005; Rückerl et al., 2011). In the Asian region, PM composition varies widely in accordance with anthropogenic emissions, as well as natural inputs influenced by the Asian monsoon, which transports desert dust over thousands of kilometres (Cohen et al., 2010b). Trace metal ratios are widely used to infer the origin of PM from their specific chemical composition, by comparing this "fingerprint" with those of potential sources (Nriagu and Pacyna, 1988; Veron et al., 1992; Wedepohl, 1995; Hu et al., 2003). The isotopic composition of an element occurring in PM offers another means of tracking sources of heavy metals and pathways of atmospheric pollution. Although the non-radiogenic lead isotopic composition (^{206}Pb, ^{207}Pb, and ^{208}Pb) is preserved after being naturally transferred in the environment via weathering processes (Murozomi et al., 1969; Doe, 1970; Cumming and Richards, 1975; Stacey and Kramers, 1975; Bollhofer and Rosman, 2000), this composition can vary after mixing with secondary lead sources via industrial processes (Mukai et al., 1991; Wang et al., 2000; Mukai et al., 2001; Zheng et al., 2004; Komárek et al., 2008).

In many developing countries, monitoring of air pollution is still rare. The few studies conducted in the two main Vietnamese cities, Hanoi and Ho Chi Minh City, have showed the impact of monsoon conditions air quality (Hien et al., 2001, 2002, 2004; Cohen et al., 2010a, 2010b; Hai and Kim Oanh, 2013). To quantify and characterise the origin of atmospheric particles, the authors have used positive matrix factorisation (PMF) to circumvent the lack of specific source fingerprints. This statistical model requires a large number of samples, and the chemical composition of emission sources was based on comparison with profiles of North American sources (Henry et al., 1984, Paatero and Tapper, 1994). Other studies have used the HYPSLIT model to identify the origin of PM in a rural site in northern Vietnam (Hoang et al., 2014; Gatari et al., 2006). However, information concerning trace metal emissions in Vietnam is still scarce, and chemical compositions of anthropogenic sources from Vietnam have yet to be determined. For the first time, the present year-round monitoring study reports a quantitative measurement of 22 metal(loid)s (Al, As, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Nd, Ni, Pb, Rb, Sb, Se, Sr, Ti, V, and Zn) present in PM_{10} collected in Haiphong. In order to better understand the impact of monsoon conditions on air quality in the city, we provide an inventory of lead isotopic compositions (^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb) in PM_{10}. To partly fill the knowledge gap, this paper presents characterisations of major emission sources and their relative contributions in Haiphong by discriminating long-range and local inputs. In the present study, we are mainly interested in global atmospheric contamination rather than studying specific extreme events.

Methodology

Study site and PM_{10} sampling

The sampling station is located in Haiphong at about 100 km southeast of Hanoi. With about two million inhabitants, Haiphong is the third largest city in Vietnam and is the main seaport in northern Vietnam. This area is influenced by a subtropical climate with a seasonal differentiation due to the northeast monsoon, which is associated with a dry (cooler) season from November to April and the southeast monsoon itself associated with a wet (warmer) season from May to October (Vu, 1994).

PM_{10} were collected on the roof of the Institute of Marine Environment and Resources (IMER, Haiphong) using a Staplex PM_{10} High Volume Air sampler. The annual survey was conducted from October 2012 to October 2013. Samples were collected every 2 weeks for two consecutive 12-h periods, using quartz fibre filters (Staplex Type TFAQ810 of 20 × 25 cm). A total of 56 filters were used during the sampling period. The average air volume filtered—calculated using the recorded air flow and the sampling time—was 1147 ± 126 m^3 $filter^{-1}$. The quartz filters were stored in plastic bags and frozen until analysis. Field blanks were handled identically to the PM_{10} sampling, but were run on the Staplex sampler for only 1 min (Pekney and Davidson, 2005).

Over the course of the sampling period, the wind speed and wind direction data were recorded continuously using an anemometer (Vantage Pro 2, Davis) installed on the roof of the Institute of Marine Environment and Resources.

Analytical procedures

Determination of trace metals in PM_{10} was conducted following the Standard Operating Procedure in the US Environmental Protection Agency (Method IO-3.5, EPA, 1999). All samples were processed and analysed in a trace metal clean HEPA filtered laboratory (ISO 7), using high purity acids (Fisher, Optima grade) and milliQ water. PFA beakers were cleaned in HNO_3 (10%), sonicated for 2 h, rinsed, and dried in a laminar flow cabinet (class 10). Samples were leached with 10 mL of a pure acids mixture ($HF/HCl/HNO_3$, 1:6:2), sonicated for 2 h, and heated on a hot-block (100 °C, 4 h). The solutions thus obtained were cooled and diluted in 10 mL of HNO_3 (2%) before analysis. Some elements (Al, Fe, K, Mn, Mg, Na, Se, and V) were analysed with an inductively coupled plasma optical spectrometer (ICP-OES, Perkin Elmer, Optima 8000DV) using an ICP multi-elemental commercial solution (Merck, Certipur) to control the performance of external calibration. Other elements (As, Cd, Co, Cr, Cu, Nd, Ni, Pb, Rb, Sb, Sr, Ti, Zn) were measured by inductively coupled plasma mass spectrometry (Q-ICP-MS, Perkin Elmer, NexION 300X) using Sc and In as internal standards to correct for instrumental mass bias. The digestion procedure was assessed using a certified material for marine sediments (IAEA 433) and a certified material for atmospheric PM (NIOH, SRM B3). All elements were within the satisfactory target recovery of 100 ± 15%, except for Cd (134%). Trace metal concentrations in blank filters were less than 1% of the average trace metal concentrations measured in PM_{10} samples. Precision and accuracy of analysis were checked with a certified reference material (NIST 1643e). The analytical detection limits were well below the analysed samples. More detailed are presented in Table S1 as Supplementary information.

Lead isotopic analyses (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) were performed with a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu Instruments, Nu Plasma) at a concentration of 200 ppb (Ortega et al. 2012). In order to minimise matrix effects during analysis, lead was extracted and purified by an ion exchange resin (Dowex 1X8, 100–200 mesh, Acros Organics) according to a conventional protocol (Manhès et al., 1978; Monna et al., 1997). An internal isotopic standard of Tl (NIST 997) was added to all samples to correct the instrumental drift. In addition, a standard bracketing method was applied to correct fractionation effects using isotopic standard of Pb (NIST 981). The combination of Tl normalisation and classical bracketing method provided an analytical precision (‰) of 0.0033, 0.0007, and 0.0004 for $^{208/206}Pb$, $^{207/206}Pb$, and $^{206/204}Pb$, respectively.

An AMA 254 mercury analyser (Leco, USA) was used for the determination of total Hg concentration by direct analysis of samples with an AS 254 autosampler. The method does not require any special preparation of samples (Wiśniewska et al., 2017). Analytical uncertainties were evaluated by measurements of the certified reference material BCR 482 with a recovery of 83.5% and a detection limit of 0.005 μg g^{-1}.

Trajectory cluster analysis

Weather in Haiphong is under the influence of the Asian monsoon, itself characterised by a marked change of wind direction. After meteorological analysis, we classified seasonality during dry (cooler temperature, lower rainfall), transition, and wet (higher temperature, higher rainfall) periods. In order to characterise transport of pollutants, isentropic trajectories extending 48 h backwards at the site were calculated at three different altitudes (500, 1000, and 1500 m) using the NOAA HYSPLIT-4 model (Draxler and Rolph, 2003). However, the accuracy of an individual trajectory is limited by various uncertainties, leading to coarse approximation of air mass origin (Draxler et al., 1999). Large numbers of trajectories were statistically used to identify homogeneous groups of transport pathways. The air trajectories arriving at the site were computed throughout the sampling period from October 2012 to October 2013. For each day, four 6-hourly trajectories with ending times of 00:00, 06:00, 12:00, and 18:00 GMT were calculated, and the data set was split according to seasonality (dry, transitional, and wet periods). Cluster analysis was applied separately to each of the three periods. A detailed description of the clustering process can be found in the NOAA HYSPLIT-4 user's guide.

Cluster analysis showed differing air mass back trajectories according to seasonal differentiation (Fig. 1, Table S2). Due to regional emission zones, the area surrounding Haiphong was classified in three sectors: the northeast (NE) pathway over China; the southeast (SE) pathway over the South China Sea and southern Vietnam; and the southwest (SW) pathway over northern Vietnam, Laos, and Thailand. Clustering results presented a dominant airflow (81%) from the NE sector in the dry season, which decreased in the transitional period (65%). The mean direction of the north-easterly flow moved further south in the wet season. Clustering presented different airflow pathways: 45% from NE, 32% from SE, and 23% from SW. To provide a more precise view of atmospheric pollution in Haiphong, our results are presented and discussed using the NE or SE dominant airflow pathways rather than seasonal differentiation.

Results and discussion

Chemical composition of PM_{10} and comparison with the literature

Variations of elemental PM_{10} levels measured in Haiphong according to the dominant airflow pathway are presented in

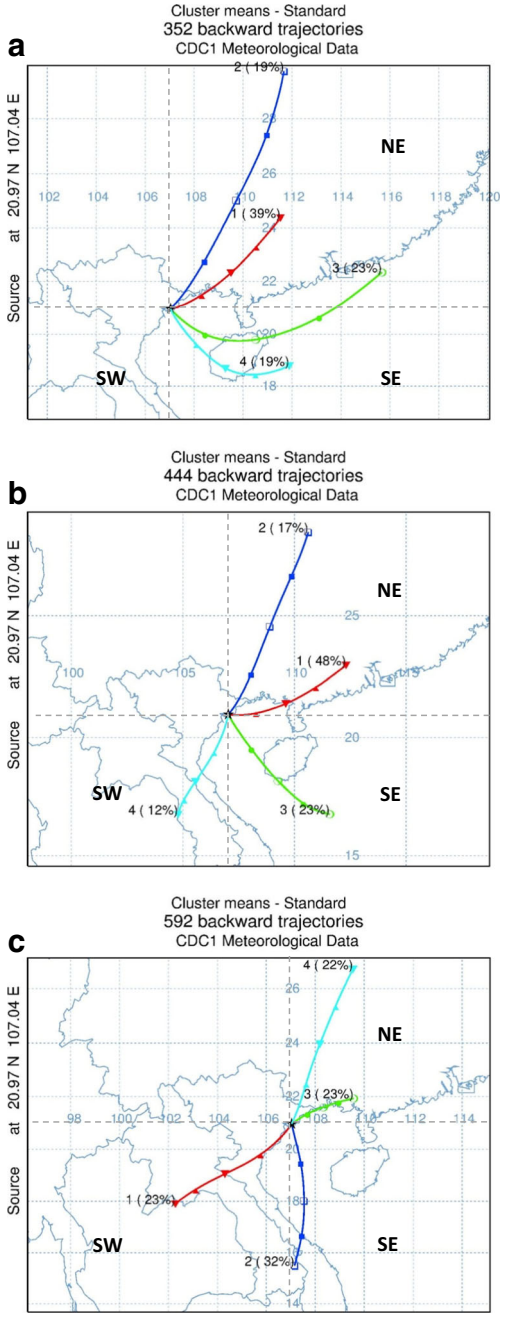

Fig. 1 Statistical cluster analysis of air mass backward trajectories showing the path of air parcels prior to arrival at Haiphong during **a** wet, **b** transitional, and **c** dry periods. Trajectories were calculated using the hybrid single-particle Lagrangian trajectory (HYSPLIT 4) model (NOAA Air Resources Laboratory; www.arl.noaa.gov/ready/hystplit4.html) with meteorological data collected from October 2012 to October 2013

Fig. 2, and concentrations are detailed in Table S3 as supplementary information. PM_{10} metal concentrations showed significant variations from day to day, with a maximum in January and a minimum in July. As expected, higher PM_{10} metal concentrations were observed during the NE monsoon, and lower metal concentrations were measured in south-easterly wind conditions. With a NE dominant airflow pathway, high PM_{10} levels in Haiphong could be linked to the stable atmospheric conditions, which often originated in China (Cohen et al., 2010b; Hai and Kim Oanh, 2013). The anti-cyclonic conditions implied a higher potential of long-range dust transport in the upper cold air mass, and the subsidence temperature inversion in the near ground layer favoured the accumulation of aerosols (Hien et al., 2002). These particular weather conditions allowed both a regional and a local accumulation of particles, considerably worsening atmospheric pollution in Haiphong. During the SE monsoon, a high-pressure system moves toward the north of the southern hemisphere. The weather in northern Vietnam is governed by moist air masses coming from the Indian Ocean and the South China Sea. Aerosol composition stems from two sources: both from the sea itself in the form of spray from the bursting of bubbles and from the land surface in the form of dust from natural erosion and anthropogenic activities. Therefore, atmospheric trace metal concentrations should be lower during this period due to air mass dilution and washout removal by rainfalls.

To evaluate air pollution levels, the World Health Organization (WHO) Air quality guidelines were used as a reference with a focus on As, Cd, Mn, Ni, Pb, and V in PM_{10} (Table 1). Concentrations of As measured in Haiphong were consistently 6- to 12-fold over the WHO guideline, underlining a threat to human health. The concentrations of PM_{10} observed in Haiphong were equivalent to those of Tokyo, where the atmosphere is known to be seriously polluted by toxic heavy metals (Furuta et al., 2005). In comparison with a rural site located in northern Vietnam (i.e. Tam Dao, Vietnam) or with remote islands (Rishiri, Japan; Jeju, Korea), PM_{10} concentrations in Haiphong were several times higher (Okuda et al., 2006; Kim et al., 2012; Hoang et al., 2014). All metal concentrations in PM_{10} were about 5–10 times higher than those observed in other regions. In particular, Al was 18 times higher than in Tam Dao; As was up to 55 times higher than in Rishiri and Tokyo; Cd was 12–13 times higher than in the remote islands (Rishiri and Jeju); Cu was 26 and 41 times higher than in Tam Dao and Jeju, respectively; Sb was 18 times higher than in Rishiri; Se was 5 and 10 times higher than in Tokyo and Rishiri, respectively; and Zn was up to 28 times higher than in Tam Dao and Rishiri, making these elements good tracers of anthropogenic activities in Haiphong. Conversely, PM_{10} metallic levels were approximately 5-fold lower than concentrations measured in Beijing and 5 to 20 times lower than in Delhi (Okuda et al., 2008; Kumar et al., 2016), two mega-cities known to rank amongst the most polluted cities in the world (WHO, 2016). These findings indicate that atmospheric particles in Haiphong are heavily impacted by trace metal concentrations and may thus have repercussions on human health.

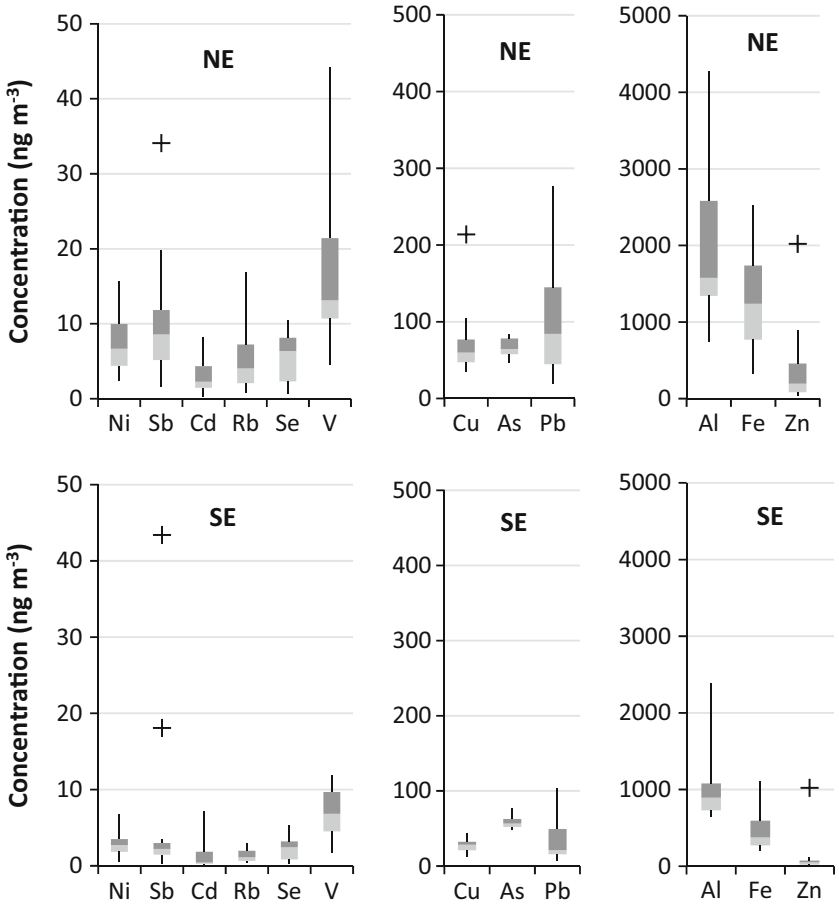

Fig. 2 Box and whisker plots of elemental PM_{10} levels according to dominant airflow pathway (NE for northeast and SE for southeast) during seasonal sampling from October 2012 to October 2013. The boundary between light and dark grey boxes indicates the median; the light and dark grey boxes indicate the 25th and 75th percentile, respectively; whiskers mark the highest and lowest values of the results. Outliers are represented by "+" symbol. Variations of elements during the study are detailed in Tables 1 and S3

Enrichment factors

The concept of enrichment factor (EF) was developed in the seventies (Chester and Stoner, 1973) to evaluate the anthropogenic contribution of a metal (x) above an uncontaminated background level, which was in the same matrix as the examined sample. EF is calculated as:

$$EF_x = \frac{\left(C_x/C_{ref}\right)_{PM_{10}}}{\left(C_x/C_{ref}\right)_{background}}$$

where C_x is the metal concentration and C_{ref} is the concentration of a reference element in PM_{10} and the background matrix, respectively. Since soil dust contributes to atmospheric PM_{10}, the upper continental crust is usually chosen as background matrix (Chester et al., 1991; Okuda et al., 2008). Concentrations of metals in the upper continental crust were reported in Reimann and Caritat (1998). However, absolute EF values must be used cautiously because there is no consensus on the average elemental composition and literature data vary by several orders of magnitude. Furthermore, the choice of the reference element can also affect the absolute value of EF. The reference element should be chosen free from contamination, stable, and reflecting geogenic sources. Although several lithogenic elements (Al, Fe, Li, Cs, Rh, etc.) can be used as reference element to estimate EF, Al is the most commonly used due to its high concentration in the lithosphere (Grousset et al., 1995; Reimann and Caritat, 2000; Bergamaschi et al., 2004). Nevertheless, anthropogenic inputs of Al from aluminium smelters, cement plants, and other industrial activities could bias EF values. Contrary to Al, Rb has a very low concentration in the lithosphere and is generally not impacted by anthropogenic activities (Reimann and Caritat, 1998). Despite these theoretical considerations that have been the subject of much discussion (Reimann and Caritat, 1998; 2000; 2005), EFs are commonly used to assess the current level of environmental contamination. EF index includes three classes which ranges depend on the atmospheric PM size. For PM_{10} (coarse particles from natural and anthropogenic sources), $EF < 10$ is considered to be a crustal origin, $10 < EF < 500$ comes from mixed sources (natural and anthropogenic), and $EF > 500$ indicates a highly enriched element (Wang et al., 2006a, b; Shelley et al., 2015). For $PM_{2.5}$ (fine particles mainly from anthropogenic sources), $EF < 1$ is considered to be crustal origin, $1 < EF < 5$ shows

Table 1 Geometric mean and min-max metal concentrations in PM_{10} (ng m^{-3}) measured in Haiphong during the study, compared with values (average ± σ; ng m^{-3}) in different sites and the WHO air quality guideline in Asia

Site region	Haiphong[a]			Tamdao[b]	Beijing[c]	Tokyo[d]	Rishiri[e]	Jeju[f]	New Delhi[g]	WHO
	Vietnam			Vietnam	Chine	Japan	Japan	Korea	India	
	Mean	Min	Max							
Al	1543	647	5232	100 ± 100	3968 ± 3350	1355 ± 492	251 ± 371	683.9	N/A	N/A
As	63.7	41.5	120	N/A	58.3 ± 60.0	2.14 ± 0.32	1.20 ± 2.10	N/A	31.0	6.6
Cd	1.46	0.135	9.01	1 ± 0	9.02 ± 10.3	2.18 ± 0.28	0.19 ± 0.33	0.2	24.5	5
Co	0.900	0.448	1.90	1 ± 0	5.28 ± 5.37	0.69 ± 0.06	0.18 ± 0.25	1.7	N/A	N/A
Cr	7.82	0.921	35.2	30 ± 10	22.7 ± 19.3	10.9 ± 0.31	2.0 ± 2.2	10.7	170	N/A
Cu	48.2	12.3	214	2 ± 1	146 ± 149	73.7 ± 4.52	7.40 ± 10.2	1.3	294	N/A
Fe	828	205	2524	400 ± 200	6200 ± 4714	1392 ± 180	356 ± 645	471	17,380	N/A
Hg	0.065	0.007	0.831	N/A	N/A	N/A	N/A	N/A	N/A	1000
K	978	315	4506	N/A	N/A	N/A	N/A	198.4	N/A	N/A
Mg	433	203	885	100 ± 100	N/A	N/A	N/A	200.9	N/A	N/A
Mn	44.6	6.65	278	10 ± 20	293 ± 224	43.0 ± 5.51	8.60 ± 12.0	9	N/A	150
Na	923	217	5044	N/A	N/A	576 ± 14.8	N/A	252.4	N/A	N/A
Nd	0.363	0.041	1.992	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Ni	4.69	0.478	15.6	5 ± 0	21.6 ± 21.0	4.64 ± 1.29	1.90 ± 3.40	4.4	42.3	25
Pb	56.0	6.83	349	10 ± 10	570 ± 638	N/A	16 ± 30	8.9	1926	500
Rb	2.64	0.445	16.9	N/A	N/A	1.46 ± 0.26	N/A	N/A	N/A	N/A
Sb	5.52	0.321	43.4	N/A	40.1 ± 42.5	20.1 ± 1.47	0.46 ± 0.62	N/A	73.5	N/A
Se	3.37	0.225	23.5	N/A	12.9 ± 13.8	0.93 ± 0.14	0.49 ± 0.65	N/A	9.00	N/A
Sr	6.43	2.05	48.9	1 ± 0	N/A	N/A	N/A	2.6	145	N/A
Ti	13.0	3.30	36.5	20 ± 10	408 ± 320	140 ± 22.4	27 ± 38	23.7	N/A	N/A
V	10.6	1.63	44.2	6 ± 0	14.1 ± 11.4	6.20 ± 0.55	1.30 ± 1.60	6.6	55.3	1000
Zn	145	14.3	2021	30 ± 20	996 ± 913	271 ± 40.3	16 ± 20	10.3	1843	N/A

N/A not available

[a] This study

[b] Hoang et al. (2014)

[c] Okuda et al. (2008)

[d] Mizohata et al. (2000)

[e] Okuda et al. (2006)

[f] Kim et al. (2012)

[g] Kumar et al. (2016)

other inputs beside crustal source, and EF > 5 suggests predominant anthropogenic emissions (Yin et al., 2012).

In this study, EFs were calculated as a first indication of the relative sources, using Al as the reference element. In order to produce reliable information concerning pollution trends, we also used Rb as a reference element and compared EF values with Al normalisation (Fig. 3). Rb or Al normalisation presented similar patterns during the NE and SE airflow pathways. Low EF values (< 10) were found for Al, Co, Fe, K, Mg, Mn, Na, Nd, Rb, Sr, and Ti. These metals showed natural origins due to the long-range transport from desert or marine inputs (Duce et al., 1980; Okuda et al., 2006; Kim et al., 2012; Hoang et al., 2014). Some elements (i.e. Cr, Cu, Hg, Ni, Pb, V, and Zn) showed EFs between 10 and 500, suggesting anthropogenic contamination from urban and industrial activities (Nriagu and Pacyna, 1988; Sun et al., 2004; Furuta et al., 2005). Only Se, As, Cd, and Sb were highly enriched (EF ≫ 500), indicating major contaminations from the combustion of fossil fuels in power plants, heating plants, and individual heating facilities (Wang et al., 1999, Tian et al., 2010). Mosher and Duce (1987) estimated that 50% of worldwide anthropogenic Se emissions originated from coal combustion. In addition, Se is often found associated with As, Cd, and Sb in coal combustion (Zeng et al., 2001; Li et al., 2014). EF was a first approach used to identify natural

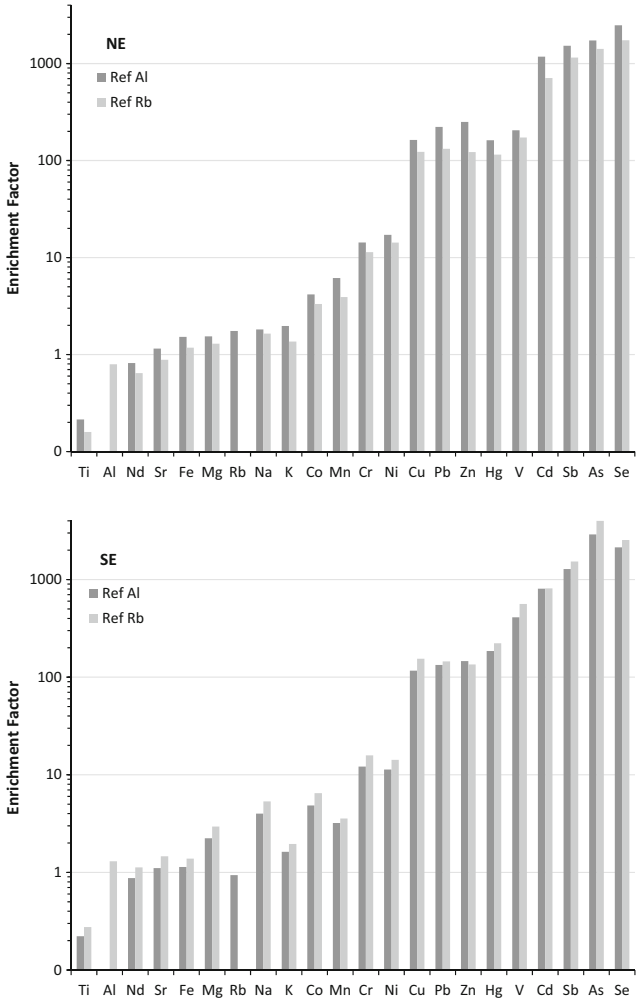

Fig. 3 Average enrichment factors with respect to Al and Rb content (dark and light grey, respectively) in PM_{10} samples according to air dominant trajectories (NE for northeast and SE for southeast) in Haiphong between October 2012 and October 2013

versus anthropogenic sources in the atmosphere, and Al or Rb were used as reference elements at the sampling site.

Characterisation of anthropogenic emissions

Atmospheric PM is composed of a mixture of elements, which come from different origins. To better assess the emission sources, elemental ratios are often used as markers of PM. However, ratios used in the literature can vary by a factor of 2 to 10 (Nriagu and Pacyna, 1988). Basically, ratios depend on the initial concentration of the trace metals in the raw material and on the primary energy sources used in industrial activities. Atmospheric concentrations of Al and Fe are good indicators of desert dusts (Duce et al., 1975; Kowalczyk et al., 1978) or coal emissions (Gao and Anderson, 2001). In this study, Fe/Al ratios showed variations between 0.3 and 1.5, which is very similar to values obtained from crustal soil (i.e. 0.4) and coal (i.e. 1.1) (Table 2). If natural and anthropogenic inputs have similar chemical balances, the differentiation between sources cannot be clearly established. Nevertheless, our results indicate that Fe/Al ratios were highly correlated with south-easterly wind conditions (mean 0.47 ± 0.17), indicating a typical crustal source (Fig. 4a). Higher concentrations of Fe and Al were observed during the NE airflow pathway. The scattering of elemental ratios up to 1.5 suggested a second source with the possible influence of coal activities during the long-range transport.

Oil combustion is another potential source of metals in PM_{10}. V and Ni have been considered as specific metals from oil combustion in residential, commercial, and industrial applications (Kowalczyk et al., 1978; Pacyna and Pacyna, 2001, Okuda et al., 2007). Traffic is a major source of ground air pollution, especially in urban areas. In Haiphong, with a

Table 2 Selected elemental ratios in natural or anthropogenic sources

Date	Cu/Sb	Zn/Pb	Pb/Cd	Sb/Cd	Fe/Al	V/Ni	
Soil							
Chinese soil	19	2.9	260	12	0.44	3.1	Pan et al. (2013)
Crustal soil	77	3.3	185	2.6	0.4	2.9	Reimann and Caritat (1998)
Coal							
Vietnamese coal[a]	9.8	0.7	269	30	N/A	0.55	This study
Chinese coal	22	2.7	50	2.7	1.1	2.6	Pan et al. (2013)
Pretroleum fuels							
Gasoil[b]	3.1	3869	156	114	N/A	0.15	This study
Diesel	10	32	81	44	N/A	0.09	This study
Traffic	6.2	1.7	N/A	5	N/A	1.49–2.4[c]	Thorpe and Harrison (2008)
Industrial activities							
Steel production	20	0.73	46	0.11	N/A	N/A	Pacyna and Pacyna (2001)
Steel production	N/A	3.5	34	N/A	N/A	N/A	Oravisjarvi et al. (2003)

N/A not available

[a] Coc Sau mine

[b] #92 unleaded

[c] Lee et al. (2000)

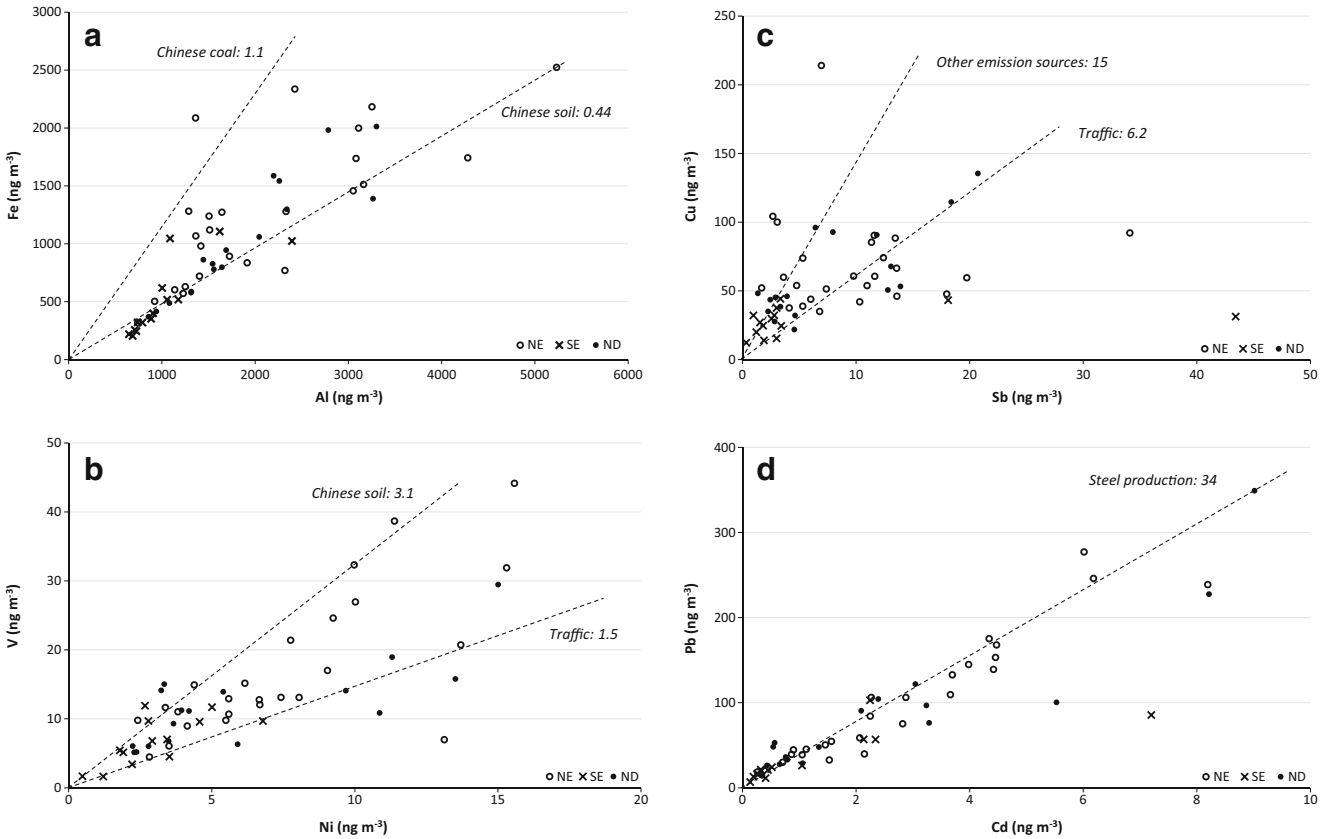

Fig. 4 Chemical balances in PM_{10} collected during sampling periods: **a** Fe vs Al, **b** V vs Ni, **c** Cu vs Sb, **d** Pb vs Cd. Data are presented according dominant air flow pathway using the NOAA HYSPLIT-4 model. Due to the complex back trajectories into transport patterns, we assigned the dominant wind direction as follow: open circles for northeast (NE), crosses for southeast (SE), and black points for not defined (ND) wind directions. Elemental concentrations are expressed in ng m^{-3}

population of about two million people and a density of 3600 people km^{-2}, particles emitted from diesel engines accounted for 25% of the local road resuspension (Vu et al., 2013). In the present study, V/Ni ratios varied between 0.5 and 4.5 with a mean value of 2.4 (Fig. 4b). Elsewhere, a similar range (i.e. 1.49 to 1.9) was obtained in residual oil used in power plants (Swietlicki and Krejci, 1996), and V/Ni values up to 2.4 have been reported by Lee et al. (2000) in oil combustion for domestic heating. The variable ratios between V and Ni mass concentrations in collected samples may result from a spatial and temporal evolution of PM_{10}. Indeed, Sb is commonly used as a flame retardant and is also present in exhaust gas from diesel engine combustion. According to Dietl et al. (1997), road traffic could contribute up to 20% of Sb emissions. Typically, a Cu/Sb ratio of 6 can be imputed to brake lining wear (Thorpe and Harrison, 2008), while higher values (i.e. from 15 to 42) are representative of coal, crustal soil, or steel production (Pacyna and Pacyna, 2001; Zhang et al., 2004; Pan et al., 2013). Within 150 km of Haiphong, there are four coal-fired power stations burning more than 2 million tons of anthracite, three major cement production plants and at least four significant non-ferrous metal factories (Cohen et al., 2010b). In our samples, these elements presented fingerprints similar to those found in industrial activities of this type (Fig. 4c). Higher Cu/Sb values (between 10 and 30) were not only from crustal soil but also from dust mixed with other anthropogenic emissions. Lower Cu/Sb ratios (between 3 and 10) may be due to dust mixing with fuel oil combustion, as used by road and maritime traffic (respectively, 10 and 3.1, Table 2). The influence of air masses was not clearly established, but the increase of anthropogenic metal concentrations in PM_{10} samples can be explained by the mixing of particles during long-range transport and road dust resuspension. The relative discrepancy of these elements in PM_{10} suggests that much of the ambient pollution, which is not associated with extreme events, is produced locally.

Many other trace metals are emitted from anthropogenic sources. The non-ferrous metal industry accounts for a large fraction of Cd, Cu, Pb (in addition to gasoline combustion), and Zn emitted in the atmosphere. Due to the wide variety of production technologies, it is difficult to select the correct values, but a reasonable range of emission factors can be advanced to highlight this source. Pb/Cd ratios around 40 and Zn/Pb ratios between 0.7 and 3.5

can be used as chemical fingerprints in most non-ferrous emissions (Niagru and Pacyna, 1988; Pacyna and Pacyna, 2001; Oravisjarvi et al., 2003; Sun et al., 2004). Elemental values for the PM_{10} collected in Haiphong from October 2012 to October 2013 correlated with ratios reported in the literature (Fig. 4d; Fig. S1). The Pb/Cd and Zn/Pb ratios highlighted an enrichment of metallic compounds in atmospheric particles from industrial smelters. As can be seen from the discussion above, the increase of anthropogenic metal concentrations in PM_{10} samples was made possible via the mixing and the accumulation of particles during long-range transport and road dust resuspension. The study of chemical balances showed that the main anthropogenic sources of PM_{10} in Haiphong were fossil fuel combustion and industrial activities. Coal combustion was found to be a contributor of Fe and Al in PM_{10} samples. Oil combustion resulted in the emission of Ni and V into the atmosphere. The non-ferrous metal industry accounted for a fraction of Cu and Zn, with Pb and Sb (in addition to gasoline combustion) also emitted. However, the complex nature of PM_{10} means that the quantitative estimation of the contribution to each emission source remains difficult and may not be elucidated by chemical element ratios alone.

Lead isotopic source apportionment

Atmospheric emissions are the main cause of metal accumulation in the environment (Nriagu and Pacyna, 1988). The discrimination between these different sources can be assessed by Pb isotopic analysis. In order to estimate the contribution of anthropogenic activities with the greatest accuracy, we used $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios. Quantification of sources was calculated with a linear mixing model (Monna et al., 1997):

$$\left(\frac{^{207}Pb}{^{206}Pb}\right)_m = x_1\left(\frac{^{207}Pb}{^{206}Pb}\right)_1 + x_2\left(\frac{^{207}Pb}{^{206}Pb}\right)_2 + x_3\left(\frac{^{207}Pb}{^{206}Pb}\right)_3$$

$$\left(\frac{^{208}Pb}{^{206}Pb}\right)_m = x_1\left(\frac{^{208}Pb}{^{206}Pb}\right)_1 + x_2\left(\frac{^{208}Pb}{^{206}Pb}\right)_2 + x_3\left(\frac{^{208}Pb}{^{206}Pb}\right)_3$$

$$x_1 + x_2 + x_3 = 1$$

where m is the measured sample, the numbers in subscript (1, 2, and 3) represent sources, and x their relative contribution. Lead isotopic ratios of PM_{10} collected in Haiphong during our study varied from 0.8373 to 0.8704 for $^{207}Pb/^{206}Pb$ and from 2.0788 to 2.1208 for $^{208}Pb/^{206}Pb$ (Fig. 5, Table S4). These ratios were in agreement with recent measurements of Pb isotopic composition in Tay Ho, an urban lake located in the north of Hanoi. Isotopic ratios in the top sediment layer varied from 0.840 to 0.855 for $^{207}Pb/^{206}Pb$ and from 2.075 to 2.120 for $^{208}Pb/^{206}Pb$ (Kikuchi et al., 2010). The cities of Hanoi and Haiphong presented a similar isotopic signature, which indicates the same origins of Pb, probably due to atmospheric deposition from long-range dust transport and local resuspension. As discussed earlier, anthropogenic Pb pollution in Haiphong originates mainly from fossil fuel combustion, industrial smelting, and urban activities. The predominant origin

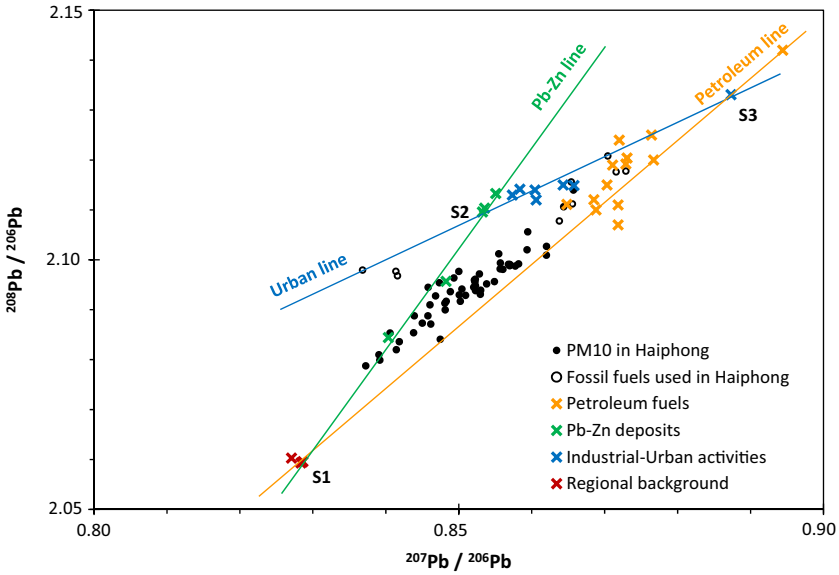

Fig. 5 Relationship between $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios in Haiphong. The black dots are data from PM_{10} samples and open circles are data from fossil fuels used in Haiphong (Table S4 for description). The coloured data are source values of samples collected in East Asia (see Table 3 for description). The blue line is based on data for urban-industrial activities; the green line corresponds to the Pb isotopic fractionation in Pb-Zn ores, and the orange line corresponds to the Pb isotopic fractionation of petroleum fuels

of Pb in the PM_{10} collected in Haiphong was further evidenced by plotting Pb isotopic compositions from natural and anthropogenic sources in the same geochemical province.

The majority of countries in the Asia-Pacific region have phased-out leaded gasoline since 2000, with Indonesia being the last of the larger Asian countries to do so in 2006. Other countries, such as Cambodia, Bhutan, Laos, Mongolia, Myanmar, and North Korea, are presumably still using local leaded gasoline, but in quite low amounts (i.e. 2%) comparative to quantities of imported unleaded gasoline (www.acfa.org.sg). Because the isotopic signature of Pb in gasoline has changed substantially due to the discontinuation of alkyl-lead, we limit our comparison to the most recently published references, i.e. those obtained after 2000 (Mukai et al., 2001; Duzgoren-Aydin et al., 2004; Chen et al., 2005; Yao et al., 2015). Lead fingerprints of other anthropogenic activities (mining, smelting, coal combustion, waste incineration, etc.) have been identified by numerous studies (Mukai et al., 1993; Zhu, 1998; Sangster et al., 2000; Bollhofer and Rosman, 2000; Zhu et al., 2001, 2003; Zheng et al., 2004; Chen et al., 2005; Duzgoren-Aydin, 2007; Diaz-Somoano et al., 2009; Zhao et al., 2015). The quantification of anthropogenic inputs also depends on the establishment of natural sources. Haiphong is surrounded by seven geochemical provinces (North China, Northeast China, North Xinjiang, Tibet, Cathaysia, Yangtze, and the Indochinese Peninsula) with different Pb isotopic fingerprints (Zhu et al., 2003; Gallon et al., 2011). Lead isotope composition in natural samples, including basaltic and granitic rocks from the Earth's mantle, shows wide variations. Due to the high heterogeneity in Asian crustal soils, the localization of the natural Pb isotopic background is a complex task. Furthermore, owing to the accelerated population growth and increasing industrial activities in the past decades, it is clear that Pb present in soils comes from a mix of natural and anthropogenic sources. In the Pearl River Delta, no anthropogenic Pb isotopic evidence from continental China could be detected in recent pelagic sediments (Zhu et al., 2003). As sediments in the South China Sea are derived from the lands surrounding the Indochinese Peninsula and the Cathaysian geochemical province in China, the Pb isotopic composition in silty clays was chosen to provide a record of regional background.

The compilation of $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios in different Pb origins is detailed in Table 3. We used the less radiogenic ratios ($^{207}Pb/^{206}Pb = 0.827$ and $^{208}Pb/^{206}Pb = 2.060$) as source S1 to represent the regional background, which reflects the actual combination of natural and anthropogenic background contribution. With the discontinuation of leaded gasoline, the Pb contribution was reduced and the $^{207}Pb/^{206}Pb$ increased gradually to approach the Earth growth curve, making this source identification difficult (Cumming and Richards, 1975; Wang et al., 2006a, b). In urban areas, dust resuspension due to road traffic cannot be disregarded. Pb emissions from industrial or domestic activities may therefore be responsible for a significant portion of Pb atmospheric inputs. In a conventional isotope $^{207}Pb/^{206}Pb$ vs $^{208}Pb/^{206}Pb$ plot, the mixing between three sources is characterised by a scattering of the sample within a triangle defined by the end members in the bi-dimensional isotope space (Fig. 5). As shown above, coal activity influences Pb levels in PM_{10}. Indeed, the published lead isotope ratios for coal samples from the SE Asian region overlap Haiphong PM_{10} isotopic ratio ranges (Fig. S2). However, in addition to coal combustion, the Asian region is also known to have numerous Pb-Zn deposits whose lead isotopic composition can be used as a tracer of anthropogenic inputs. Observing the intercept of the "Pb-Zn line" and the "Urban line," we found that source S2 was located in the closest Chinese province of Cathaysia, in the Fankou Pb-Zn ore deposit ($^{207}Pb/^{206}Pb = 0.853$ and $^{208}Pb/^{206}Pb = 2.110$). Furthermore, the intercept between the two linear trends, the "petroleum line" and the "urban line," clearly identified the vehicle exhaust source S3 with Pb isotopic fingerprints ($^{207}Pb/^{206}Pb = 0.8873$ and $^{208}Pb/^{206}Pb = 2.1331$) obtained from Bangkok, a mega-city with more than 8.2 million automobiles registered in 2013 (Zhu et al., 2003; Narut et al., 2016).

Our Pb isotopic fingerprinting approach clearly demonstrated that PM_{10} in Haiphong were composed of a mixture of soil dusts and two main anthropogenic inputs from vehicle exhaust and non-ferrous smelters. The contribution of each source was calculated using equations from the linear model (Fig. 6, Table S5). Lead atmospheric inputs were highly influenced by source S1. The average contributions of the regional background varied between 41.5% during the NE airflow pathway and 51.6% with south-easterly wind conditions. These results were easily attributable to Asian dust storms, which transport fine, dry soil particles over vast areas. The increase of the soil dust fraction during the SE monsoon was due to aerosol mixing, with marine airflow less impacted by anthropogenic activities. As discussed above, soil dusts evaluated from source S1 had a combination of natural and anthropogenic inputs. Thus, the contribution of natural dusts from pristine soils may be lower than our estimation (S1), as the overestimation of S1 implies an underestimation of S2 + S3. These considerations show that dominant Pb inputs are from anthropogenic activities. The oil combustion fraction in PM_{10} samples presented seasonal variations. The average contribution varied between 31.5% during the NE airflow pathway to 20.2% in south-easterly wind conditions. The production of Chinese electricity depends on both industrial demand and outdoor temperature. Firstly, due to low temperatures between October and April, the increase in Chinese energetic demand is supplied via oil combustion (Tian et al., 2012). Secondly, Vietnam's oil consumption is about 450,000 barrels per day, with an expected increase of 10% per year up to 2020 (IEA, 2015). During the NE monsoon, Haiphong received

Table 3 A comparison of Pb isotope composition from different sources in Asia

Location	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	Sample origin	Reference
Regional soil					
South China Sea	0.828	2.059	18.74	Silty clay	Zhu et al. (2003)
South China Sea	0.827	2.060	19.02	Silty clay	Zhu et al. (2003)
South China Sea	0.829	2.060	19.02	Silty clay	Zhu et al. (2003)
Coal					
Haiphong (Vietnam)	0.8368	2.0979	18.84		This study
Haiphong (Vietnam)	0.8414	2.0977	N/A		This study
Haiphong (Vietnam)	0.8416	2.0968	N/A		This study
Ho Chi Minh (Vietnam)	0.87	2.10	18.01		Bolhofer and Rosman (2000)
Hanoi (Vietnam)	0.86	2.10	18.25		Bolhofer and Rosman (2000)
Indonesia	0.8459	2.0897	N/A		Diaz-Somoano et al. (2009)
Indonesia	0.8472	2.1013	N/A		Diaz-Somoano et al. (2009)
Indonesia	0.8417	2.0878	N/A		Diaz-Somoano et al. (2009)
China	0.8661	2.1249	N/A		Diaz-Somoano et al. (2009)
China	0.849	2.101	N/A		Mukai et al. (1993)
Shanghai (Yangtze Province)	0.8600	2.1111	N/A		Chen et al. (2005)
Dafang (Southern Province)	0.832	2.083	18.75		Zhao et al. (2015)
Guiyang (Southern Province)	0.824	2.060	18.99		Zhao et al. (2015)
Guiyang (Southern Province)	0.804	2.002	19.53		Zhao et al. (2015)
Shanxi (North Province)	0.839	2.071	18.56		Zhao et al. (2015)
Shandong (North Province)	0.837	2.065	18.65		Zhao et al. (2015)
Pb-Zn deposit					
North Province	0.896	2.188	17.23		Zhu et al. (2003)
Cathaysia Province	0.855	2.113	18.42		Zhu et al. (2003)
Indonesia Province	0.840	2.084	18.67		Zhu et al., 2003
Foshan (Cathaysia Province)	0.8535	2.1104	N/A		Zhu (1998)
Fankou (Cathaysia Province)	0.853	2.110	18.35		Sangster et al. (2000)
Jinding (Southern Province)	0.848	2.096	18.45		Sangster et al. (2000)
Petroleum fuels					
Haiphong (Vietnam)	0.8638	2.1078	18.09	Diesel[a]	This study
Haiphong (Vietnam)	0.8654	2.1156	N/A	Diesel[a]	This study
Haiphong (Vietnam)	0.8656	2.1112	N/A	Diesel[a]	This study
Haiphong (Vietnam)	0.8644	2.1106	N/A	#92 gasoline[a]	This study
Haiphong (Vietnam)	0.8729	2.1178	17.86	#92 gasoline[a]	This study
Haiphong (Vietnam)	0.8716	2.1176	N/A	#92 gasoline[a]	This study
Shanghai (Yangtze province)	0.872	2.124	N/A	Traffic	Chen et al. (2005)
Guiyang (Southern Province)	0.8648	2.1111	18.07	Traffic	Zhao et al. (2015)
Hong Kong (Cathaysia Province)	0.8685	2.1120	N/A	Traffic	Duzgoren-Aydin et al. (2004)
Surgut (Russia)	0.88	2.12	17.69	Oil field	Mukai et al. (2001)
Nizhnevartovsk (Russia)	0.89	2.14	17.36	Oil field	Mukai et al. (2001)
Taipei (Taiwan)	0.870	2.115	17.89	Diesel[b]	Yao et al. (2015)
Taipei (Taiwan)	0.872	2.107	17.87	#98 gasoline[b]	Yao et al. (2015)
Taipei (Taiwan)	0.869	2.110	17.94	#95 gasoline[b]	Yao et al. (2015)
Taipei (Taiwan)	0.872	2.111	17.86	#92 gasoline[b]	Yao et al. (2015)
Taipei (Taiwan)	0.871	2.119	17.89	Diesel[c]	Yao et al. (2015)
Taipei (Taiwan)	0.873	2.119	17.85	#98 gasoline[c]	Yao et al. (2015)
Taipei (Taiwan)	0.876	2.125	17.78	#95 gasoline[c]	Yao et al. (2015)
Taipei (Taiwan)	0.873	2.120	17.84	#92 gasoline[c]	Yao et al. (2015)
Industrialised zone					
Bangkok (Thailand)	0.8873	2.1331	17.6	Urban city	Zhu et al. (2003)
Shanghai (Yangtze Province)	0.8606	2.112	18.16	Residencial	Zheng et al. (2004)
Shanghai (Yangtze Province)	0.8643	2.115	18.12	Residencial	Zheng et al. (2004)
Hong Kong (Cathaysia Province)	0.8658	2.1149	N/A	Residencial	Duzgoren-Aydin (2007)
Foshan (Cathaysia Province)	0.860	2.114	N/A	Industrial	Zhu et al. (2001)
Foshan (Cathaysia Province)	0.858	2.114	N/A	Industrial	Zhu et al. (2001)
Foshan (Cathaysia Province)	0.857	2.113	N/A	Industrial	Zhu et al. (2001)

N/A not available

[a] Vietnam National Petroleum Group (Petrolimex)

[b] Chinese Petroleum Corporation

[c] Formosa Plastics Corporation

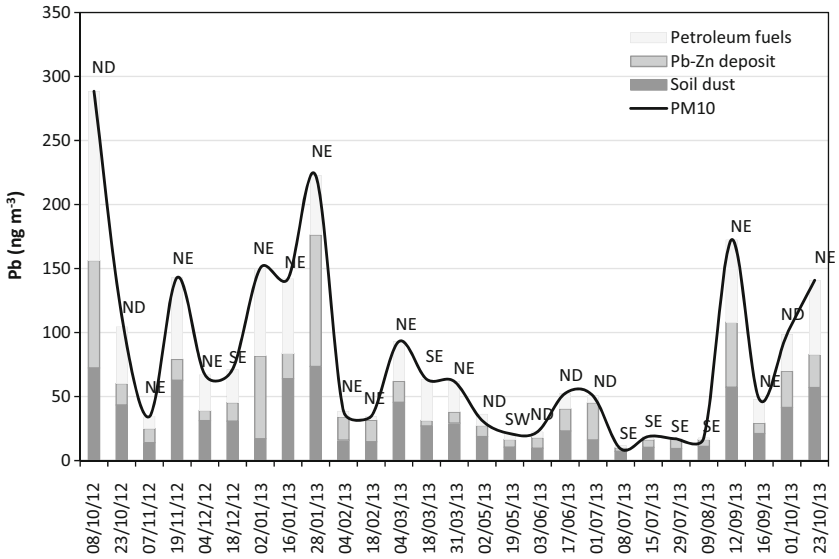

Fig. 6 Variation of Pb content and relative contributions of Pb sources in Haiphong atmospheric particles during the sampling period (October 2012–October 2013). Data are presented according dominant air flow pathway using the NOAA HYSPLIT-4 model. Due to the complex back trajectories into transport patterns, we assigned the dominant wind direction as follow: open circles for northeast (NE), crosses for southeast (SE), and black points for not defined (ND) wind directions. Elemental concentrations are expressed in ng m^{-3} The plot figure illustrates the average of two consecutive 12-h sampling periods. For details see Table S5

atmospheric pollution from both the long-range transport of regional dust and from local urban soil resuspension, which increased the contribution of petroleum fuels in PM_{10} samples. In addition to oil combustion, Pb-Zn ore related to industrial emissions also contributed to atmospheric Pb contamination. The average Pb-Zn ore fraction in atmospheric particles varied from 27.0% during the NE airflow pathway to 28.2% during the SE wind events. No seasonal pattern was observed, suggesting a constant Pb-Zn industrial activity over time. In the Pb isotope plot, the Pb-Zn source was clearly located in the Chinese province of Cathaysia, indicating that atmospheric Pb in Haiphong partly results from long-range transport. During the SE monsoon, anthropogenic particles were diluted with marine aerosols. The constant Pb-Zn contribution also suggests a steady contribution from soil dusts.

To determine whether long-range transport or urban soil resuspension drove atmospheric pollution in Haiphong, a binary mixing model was used to attribute a regional-type and a local-type to the Pb-PM_{10} seasonal variations:

$$PM_{10} = x_r \cdot \text{Regional}-\text{type} + x_l. \cdot \text{Local}-\text{type}$$

$$x_r + x_l = 1$$

where x_r and x_l represented the contributions of regional and local inputs, respectively. As discussed above, Pb atmospheric concentrations were influenced by both local and regional transport during the NE monsoon. However, rainfalls are known to limit soil dust resuspension by leaching surfaces. In our study, the maximum Pb-PM_{10} level was collected on 28–29 January 2013 during both NE dominant airflow and a rainfall event, suggesting that regionally emitted Pb might be much more significant than Pb from local inputs. Therefore, the maximum Pb-PM_{10} over 24-h sampling (222.5 ng m^{-3}, 28–29/01/2013) was attributed as regional-type. Conversely, during the SE monsoon, high temperatures favoured air convection and higher wind speed caused the local dispersion of atmospheric particles. In addition, the sub-tropical climate also favoured rainfall, which prevented the resuspension of soil dusts. Local-type was selected during stable SE airflow and a limited rainfall event. These meteorological conditions were recorded on the 08–09 July 2013 with a mean Pb-PM_{10} measured at 9.19 ng m^{-3} over 24-h sampling. As expected, the local-PM_{10} increased with wind speed at the site with a maximal and stable fraction (about 90%) during the SE monsoon and a highly variable fraction with north-easterly wind conditions (Fig. 7, Table S6). Fluctuations with the NE airflow pathway indicated that long-range transport was not negligible. Depending on the regional meteorological event, the regional-PM_{10} fraction could represent from 70 to 100% of atmospheric particles in Haiphong. Our results were in good agreement with a recent study realised in Guiyang (SE China). Indeed, Zhao et al. (2015) have shown that Pb in atmospheric particles was characterised by a decrease in coal combustion and an increase in Pb-Zn industrial emissions, indicating that the locally emitted Pb should be more significant than that from long-range transport.

Conclusion

The combined use of metal measurements with Pb isotopic analysis allowed us to assess contamination levels and

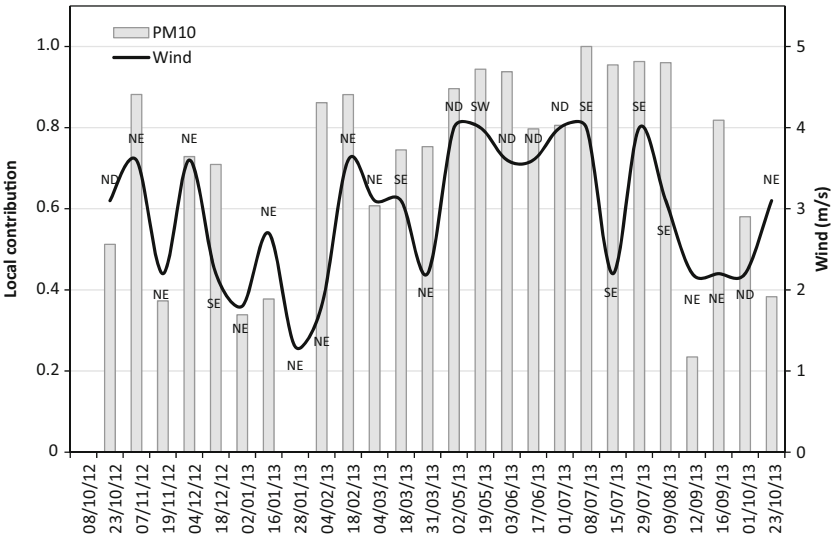

Fig. 7 Variation of contribution of soil dust resuspension as a function of wind speed (m s^{-1}) in Haiphong during the sampling period (October 2012 to October 2013). Data are presented according dominant air flow pathway using the NOAA HYSPLIT-4 model. Due to the complex back trajectories into transport patterns, we assigned the dominant wind direction as follow: open circles for northeast (NE), crosses for southeast (SE), and black points for not defined (ND) wind directions. The plot figure illustrates the average of two consecutive 12-h sampling periods. For details see Table S6

to identify and quantify the sources of PM_{10} in Haiphong. This approach was also used to infer the contribution of specific inputs. High variability of trace metal concentrations was observed in atmospheric particles and revealed a seasonal trend: elevated levels during the NE monsoon and low levels in south-easterly wind conditions. Some elements (As, Cd, Mn) were found in excess of the WHO guidelines, thus posing a potential threat to health and environmental resources. EFs revealed that the composition of PM_{10} collected in Haiphong had various origins. Elements, such as Al, Co, Fe, K, Mg, Mn, Na, Nd, Rb, Sr, and Ti, originated from crustal sources, while other trace metals (Cr, Cu, Hg, Ni, Pb, V, and Zn) were emitted from urban/industrial activities. Coal combustion was highlighted with EFs of As, Cd, Se, and Sb, whose values largely exceeded all others. The study of chemical balances showed that atmospheric pollution in Haiphong was mainly controlled by industrial and/or vehicle exhaust emissions with typical markers of oil combustion such as V/Ni and Cu/Sb ratios (1.5 and 6.2, respectively) and typical markers of industrial activities, such as Pb/Cd and Zn/Pb ratios (34 and 3.5, respectively). The Pb isotope and concentration analyses were used to quantify inputs and to study aerosol transport. PM_{10} showed an important soil dust contribution (constant annual fraction 45% with a relative maximum up to 60% during SE monsoon). Anthropogenic Pb was estimated as the dominant input. Sources were assigned to vehicle exhaust and Pb-Zn smelters as markers of oil combustion and industrial activities, respectively. Whereas oil combustion input was correlated to the dominant airflow pathway (31% during the north-easterly winds and 20% during the south-easterlies), the industrial activity contribution was stable (around 28%) over the year. This distribution can be explained by the transport of local and regional air masses. During the SE monsoon, anthropogenic Pb was mainly assigned to local soil dust resuspension (about 90%), and during the NE monsoon, the increase of Pb-PM_{10} was due to the mixing of local and regional inputs.

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