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Airborne persistent toxic substances (PTSs) in China: occurrence and its implication associated with air pollution†

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In recent years, China suffered from extensive air pollution due to the rapidly expanding economic and industrial developments. Its severe impact on human health has raised great concern currently. Persistent toxic substances (PTSs), a large group of environmental pollutants, have also received much attention due to their adverse effects on both the ecosystem and public health. However, limited studies have been conducted to reveal the airborne PTSs associated with air pollution at the national scale in China. In this review, we summarized the occurrence and variation of airborne PTSs in China, especially in megacities. These PTSs included polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), halogenated flame retardants (HFRs), perfluorinated compounds (PFCs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals. The implication of their occurrence associated with air pollution was discussed, and the emission source of these chemicals was concluded. Most reviewed studies have been conducted in east and south China with more developed economy and industry. Severe contamination of airborne PTSs generally occurred in megacities with large populations, such as Guangzhou, Shanghai and Beijing. However, the summarized results suggested that industrial production and product consumption are the major sources of most PTSs in the urban environment, while unintentional emission during anthropogenic activities is an important contributor to airborne PTSs. It is important that fine particles serve as a major carrier of most airborne PTSs, which facilitates the long-range atmospheric transport (LRAT) of PTSs, and therefore, increases the exposure risk of the human body to these pollutants. This implied that not only the concentration and chemical composition of fine particles but also the absorbed PTSs are of particular concern when air pollution occurs.

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Environmental impact

Due to rapidly expanding economic and industrial developments, China, the largest developing country, has suffered from extensive air pollution, especially haze in recent years. Although much attention has been paid to the air quality index (AQI) and control measures have been undertaken, airborne persistent toxic substances (PTSs) associated with air pollution are worth considering because of their adverse effects on human health. However, public awareness about them is still limited in China. The present review summarized the current research status about airborne PTSs in China associated with air pollution and presented their variation and its implication, which may help to gain insight into their environmental behavior and source and enlighten the countries with similar problems, *e.g.*, India, Mexico, *etc.*

1. Introduction

1.1 Persistent toxic substances (PTSs)

Persistent toxic substances (PTSs) generally refer to xenobiotic chemicals in the environment which are characterized by

persistence, and acute or chronic toxicity. Many of these substances could be subject to atmospheric, aquatic or biological transport over long distances, resulting in global distribution and even detectability in areas where they have never been used.¹ In addition, the lipophilic character of some of them is responsible for their bioavailability and accumulation in the tissues of living organisms, leading to body burdens of adverse health effects. Therefore, PTSs and their resulting effects give rise to specific concerns at local, national, regional and global scales.²

PTSs can be manufactured substances for use in various sectors of industry and pesticides, or by-products of industrial processes and combustion. They have been widely studied in

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many typical areas such as the Great Lakes in North America and e-waste dismantling areas in China.¹ Due to the harmful effects on the ecosystem and human body, the transboundary movement of PTSs may be regulated by the Basel Convention regulations. Some PTSs are also covered under the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade.

As a large sub-group of PTSs, persistent organic pollutants (POPs) raised a global public concern due to their serious health and environmental effects, bioaccumulation, environmental persistence and long-range transport potential. They were identified by an international community for international action, known as the Stockholm Convention in 2001, which aims to eliminate or restrict the production and use of POPs. The initial most toxic POPs identified by the United Nations Environment Programme (UNEP) included ten intentionally produced substances (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene and polychlorinated biphenyls (PCBs)), and two unintentional by-products (polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs)). The Stockholm Convention was amended in 2009, 2011, 2013 and 2015 to list 14 new POPs in its Annexes, which include chlordecone, α/β -hexachlorocyclohexane (α/β -HCH),

lindane, technical endosulfan and its related isomers, hexabromobiphenyl (HBB), perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF), commercial pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE), pentachlorobenzene (PeCBz), hexabromocyclododecane (HBCD), hexachlorobutadiene (HCBD), pentachlorophenol (PCP) and its salts and esters, and polychlorinated naphthalenes (PCNs). These compounds could be placed into three categories: pesticides, industrial chemicals and unwanted by-products of industrial processes. The Stockholm Convention took effect in China in 2004, which enforced the Chinese government to eliminate or restrict the production and use of these chemicals.

Another important sub-group of PTSs are heavy metals. They generally refer to the metals with density greater than 5 g cm^{-3} , such as mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), copper (Cu), zinc (Zn), chromium (Cr), and nickel (Ni). Heavy metals have been listed as priority control pollutants by the United States Environmental Protection Agency (US EPA). In China, Hg, Pb, Cd, As, and Cr were designated as priority toxic heavy metals in the Specialized 12th Five-Year-Plan on Comprehensive Control of Heavy Metals Pollution in China issued in 2011.³

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Due to the internal and international demand, an extensive study on PTS distribution and variation in China is required in the next several decades. On the other hand, with the rapidly expanding economic and industrial developments, China suffered from severe environmental pollution at the regional scale, which also caused great concern about the adverse health effects of various pollutants including PTSs.

1.2 Air pollution and megacities in China

Air pollution is the largest single environmental hazard in the world that caused seven million premature deaths in 2012.⁴ With rapid economic growth over the past three decades, China became the biggest energy consumer in 2009 and the world's second largest economy in terms of gross domestic product (GDP) in 2010. However, the extensive industrial development, substantial coal-dependent energy consumption and increasing number of vehicles have caused serious air pollution and substantially reduced visibility. Air pollution was previously estimated to contribute to 1.2 to 2 million deaths annually in China.^{5–7} The air pollution of northern cities is relatively more serious than that of southern cities in China, but the gap has been narrowing with time.⁸ Although the Air Pollution Index (API) had a decreasing trend from 2001–2012,⁸ the air quality of only 21.6% of the cities reached the ambient air quality standard in 2015 according to the Ministry of Environmental Protection (MEP).⁹ In recent years regional haze has been one of the most disastrous weather events in China. In January, 2013, a dense haze covered 1.4 million km² of China and affected more than 800 million people, especially in northern and eastern China, where many megacities are located. A haze episode is a complex pollution process with high levels of fine particulate matter (*i.e.* PM_{2.5}, aero-dynamic diameter ≤ 2.5 μm). Understanding factors contributing to its formation is crucial to mitigate PM_{2.5} pollution, which varies substantially on the daily and city scales.¹⁰ According to the study by Wang *et al.*,¹¹ PM_{2.5} mass concentrations in Beijing reached up to 111.5 μg m^{−3} in 2008, and then showed a declining trend to around 80 μg m^{−3} in 2013, which were still five times higher than the ambient air

quality standard recommended by the US Environmental Protection Agency (15 μg m^{−3}) and eight times the WHO Global Air Quality Guideline (AQG) (10 μg m^{−3}). In Guangzhou, there were 160 days on which the PM_{2.5} concentration exceeded the national daily PM_{2.5} standard (75 μg m^{−3}) during the period of 2012–2015 and the annual average concentration (47.7 μg m^{−3}) was higher than the air quality standard of 35 μg m^{−3} in China.¹²

Apart from PM_{2.5} pollution, it is reported that the severe haze pollution in China was driven to a large extent by secondary aerosol formation and O₃ chemistry in many regions produced through photochemical processing of volatile organic compounds (VOCs).^{13,14} It has been predicted that the emission of VOCs in China will increase by 49% in 2020 compared to that in 2005,¹⁵ and this trend was not predicted to reverse until 2030 under the current legislation.¹⁶ Many VOCs adversely affect public health. The O₃-attributable health burden could increase by up to 46 000 premature deaths in East China under the “maximum technically feasible reduction” scenario when the population growth was considered.¹⁶ Therefore, China faces great pressure on the balance between tackling air pollution and economic development in the near future. The Chinese government has issued several plans to tackle pollution, such as the Action Plan on Prevention and Control of Air Pollution (2013–17), which give priority to the regions that have heavy air pollution and PM_{2.5}.

However, airborne PTSs were not taken as seriously as those pollutants in China, although they have received increasing attention in developed countries. Many studies attempted to reveal the occurrence of airborne PTSs at the regional scale in China, while their distribution and variation at the national scale is still unknown, as well as their association with air pollution.

Megacities are conventionally defined as cities with populations of over 10 million and emerged in the 1990s in China,¹⁷ such as Beijing, Shanghai, Guangzhou, Shenzhen, Xi'an, Shenyang, Chongqing, Nanjing, Wuhan, and Tianjin. Most megacities are located in the three key regions including the Beijing-Tianjin-Hebei (BTH), Yangtze River Delta (YRD), and Pearl River

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Delta (PRD) (Fig. 1), which cover only 6% of the country's land area, but account for nearly 27% of the country's population and 43% of the nation's GDP.¹⁸ Since most PTS emission

sources are closely related to industrialization and urbanization, it is worth evaluating the occurrence of airborne PTSs in megacities and their surrounding areas, which may help to gain

Fig. 1 Spatial distribution of the reported PCDD/Fs (A), PCBs (B), PBDEs and other HFRs (C), PFCs (D), OCPs (E) and PAHs (F) in Chinese air.^{19–120} The dark green represents the areas of the BTH (top), YRD (middle) and PRD (bottom).

insight into the elimination of these pollutants and their adverse health effect. Moreover, air quality management in megacities has tremendous implication on the future development of other cities and even the countries with similar issues, e.g., India and Mexico.

1.3 Data collection and review objectives

This review summarized the results from representative publications about airborne PTSs in megacities including their surrounding areas in China. Some results in domestic publications were also concluded to underline the occurrence of PTSs in specific areas. These references were acquired mainly based on the Web of Science database and published until February 2017.

Most POPs recognized by the Stockholm Convention were summarized as well as some priority organic pollutants and heavy metals. These pollutants are generally present at high levels in various environmental and biotic matrices in urban and industrial areas in China, which may have adverse effects on the human body. The distribution and variation of airborne PTSs in China were first reviewed, especially in the BTH, YRD and PRD regions. Then the implication of their occurrence associated with air pollution was comprehensively discussed. The results may shed light on the elimination of these pollutants in ambient air, and enlighten the countries with similar issues.

2. Airborne PTS distribution and variation in China

2.1 PCDD/Fs

PCDD/Fs are unintentional byproducts of combustion and industrial processes. The environmental levels of PCDD/Fs were generally lower than those of intentionally produced POPs.¹⁹ Although they are trace species in terms of their emission volume (10.2 kg in 2004 in China),²⁰ they captured widespread attention due to their high exposure risk on human health.

As shown in Fig. 1(A) and Table S1,[†] the monitoring campaigns for atmospheric PCDD/Fs were mostly carried out in East China, especially in the BTH, YRD and PRD regions, where industry and economy are more developed. In Beijing, we initially reported PCDD/F occurrence at three urban locations using a high volume air sampler (HVAS) in 2006.²¹ The concentrations of $\sum_{17}$ PCDD/Fs ranged from 0.28 to 10.8 pg m⁻³ (mean 4.36 pg m⁻³), corresponding to 18–644 fg I-TEQ m⁻³ (mean 268 fg I-TEQ m⁻³). In the subsequent study during 2007–2010, the measured concentrations showed a comparable level with a range of 0.22–27 pg m⁻³ (5–470 fg I-TEQ m⁻³), and the rural site presented a significantly lower level ($p < 0.05$) than the urban areas.²² When comparing the data between July and August from 2006 to 2010, PCDD/Fs showed a clearly decreasing trend except for the data during July–August 2008. Thereafter, Zhou *et al.*²³ investigated the ambient levels in six locations around Beijing during 2011–2012, and the concentrations were in the range of 1.75–10.4 pg m⁻³ (mean 3.67 pg m⁻³), corresponding to the TEQ range of 35.0–751 fg I-TEQ m⁻³ (mean 251 fg I-TEQ m⁻³). Zhang *et al.*²⁴ reported that the PCDD/F levels

ranged from 1.5 to 2.8 pg m⁻³ (95.4–175 fg I-TEQ m⁻³) in a suburban area in Beijing in 2014. These were consistent with our previous results.²² Recently, Zhang *et al.*²⁵ reported significantly higher concentrations during haze days (3.98–74.7 pg m⁻³) compared to normal days (0.99–2.85 pg m⁻³), which was attributed to the significantly higher levels of particle concentrations during haze episodes. In Tangshan City, Ren *et al.*²⁶ investigated several POPs in the vicinity of different industrial sources, and the PCDD/F concentrations ranged from 44.2 to 394 fg I-TEQ m⁻³ with an average of 170 fg I-TEQ m⁻³ in 2009. In the Circum-Bohai Sea Gulf Region, Qin *et al.*²⁷ found out that they ranged from 3.07 to 49.5 pg m⁻³ (61.8–1182 fg I-TEQ m⁻³) with an average of 10.2 pg m⁻³ (235 fg I-TEQ m⁻³) in the urban air of Dalian during 2009–2010. These levels were generally comparable to those in Beijing, suggesting regional air pollution in the BTH region.

In the YRD, Li *et al.*²⁸ revealed PCDD/F and polybrominated dibenzo-*p*-dioxins/dibenzofuran (PBDD/F) pollution in the ambient air of Shanghai in 2006. The concentrations were in the range of 0.1–20.7 pg m⁻³ (corresponding to 2.2–1215 fg I-TEQ m⁻³) and 0.03–4.16 pg m⁻³ (corresponding to 2.2–872 fg I-TEQ m⁻³). The PCDD/F concentration was comparable to the later observation by Die *et al.*²⁹ in industrial sites (0.26–4.93 pg m⁻³). Furthermore, Xu *et al.*³⁰ reported atmospheric PCDD/Fs in the concentration range of 59–3030 (mean 495) fg I-TEQ m⁻³ in a satellite town in Eastern China during 2007–2008. Li *et al.*³¹ obtained the concentrations in the range of 2.33–2.83 pg Nm⁻³ (Nm³, a volume normalized to the standard conditions of 760 mmHg and 298 K) from municipal solid waste incineration (MSWI) and 1.64–2.71 pg Nm⁻³ in adjacent villages in East China. These results were generally comparable to those observed in the BTH region. In the PRD, Yu *et al.*³³ demonstrated the occurrence of particle-bound PCDD/Fs in Guangzhou air in 2004, and the mean concentrations ranged between 3.82 pg m⁻³ (105 fg I-TEQ m⁻³) and 12.8 pg m⁻³ (431 fg I-TEQ m⁻³) for the different sampling sites. This was also consistent with those in the BTH and YRD. Ren *et al.*³⁴ further evaluated the atmospheric deposition of PCDD/Fs in Guangzhou, and the annual deposition fluxes were calculated to be between 170 and 3000 pg m⁻² day⁻¹.

However, significantly higher levels were found in e-waste dismantling areas. In south China, Li *et al.*³⁵ revealed that the atmospheric concentrations of PCDD/Fs were in the range of 64.9–2365 pg m⁻³ (corresponding to 0.972–51.2 pg I-TEQ m⁻³) in Guiyu in 2005, which were the highest documented values in the world. PBDD/Fs were also found at high levels with a concentration range of 8.1–61 pg m⁻³ (corresponding to 1.62–104 fg I-TEQ m⁻³). In another e-waste recycling site (Qingyuan), Xiao *et al.*³⁶ indicated that the mean PCDD/F concentration was 159 pg m⁻³ during 2009–2010, which was approximately 16 to 17 times higher than those in its neighborhoods. In east China, the PCDD/F concentrations were in the range of 2.91–50.6 pg m⁻³, corresponding to 0.20–3.45 pg I-TEQ m⁻³ in the Taizhou area in 2006.³² However, the level showed an apparent declining tendency during 2005–2009 based on the observation in rice hulls,¹²¹ suggesting a direct influence of stricter environmental regulations implemented by the local government in 2005.

Compared to megacities, lower levels of PCDD/Fs were found in background areas in China. Liu *et al.*³⁷ reported that the median PCDD/F concentration was $14.0 \text{ fg TEQ m}^{-3}$ in the air samples collected from 11 background sampling sites across China in 2010. This level was generally comparable to the results from the remote north Atlantic and the Open Mediterranean Sea,^{122,123} but one order of magnitude lower than that in the global oceanic atmosphere.¹²⁴ This suggested that the background levels in China, especially in west China, were not evidently influenced by the megacities, which could also be observed for other PTSS mentioned below.

2.2 PCBs

PCBs were initially identified as POPs in the Stockholm Convention as well. They have been commercially produced for industrial use since the 1930s. Approximately 10 000 tons have been manufactured in China before they were banned in the 1970s.¹²⁵ Meanwhile, PCBs were reported to be formed in various thermal processes, such as waste incineration, metal smelting, coke production and chemical manufacturing.¹²⁶ Unintentionally produced PCBs (UP-PCBs) were also identified in China in recent years, especially in Hebei and Shandong Provinces and surrounding areas, where heavy industries are located.^{20,126–128}

Differently from PCDD/Fs, PCBs were intensively studied across China (Fig. 1(B), Table S2†). Jaward *et al.*³⁸ reported that the atmospheric PCB concentrations were in the range of $7\text{--}117 \text{ pg m}^{-3}$ and $21\text{--}336 \text{ pg m}^{-3}$ for $\sum_7\text{PCBs}$ (sum of 7 indicator PCBs) and $\sum_{29}\text{PCBs}$, respectively across China in 2004 based on passive air sampling (PAS), which were higher than those from other Asian countries (*i.e.* Japan, South Korea and Singapore). They were consistent with the results from 97 sites across China in 2005,³⁹ where the PCB concentrations were the highest at urban sites ($350 \pm 218 \text{ pg m}^{-3}$), followed by rural ($230 \pm 180 \text{ pg m}^{-3}$) and background sites ($77 \pm 50 \text{ pg m}^{-3}$). Generally higher levels of atmospheric PCBs were observed in the southeast areas, especially in the coastal urban sites (Fig. 1(B)). For example, in the PRD, Chen *et al.*⁴⁰ reported the mean concentration of $\sum_{64}\text{PCBs}$ to be 935 pg m^{-3} ($160\text{--}2720 \text{ pg m}^{-3}$) in Guangzhou air in 2004, which was higher than those observed during 2006–2007 (range: $184\text{--}575 \text{ pg m}^{-3}$, mean: 317.6 pg m^{-3}).⁴¹ In the YRD, relatively lower levels were reported. Zhang *et al.*⁴² indicated that the total concentrations (gas + particle phases) of PCBs ranged from 5.00 to 206 pg m^{-3} (mean 65.8 pg m^{-3}) in Suzhou, Wuxi and Nantong during 2009–2010. This was slightly higher than the results in the following study across the YRD during 2010–2011 ($\sum_7\text{PCBs}$: $35.0 \pm 27.3 \text{ pg m}^{-3}$).⁴³ In north China, the mean concentrations were 45.3 pg m^{-3} ($\sum_7\text{PCBs}$) and 122 pg m^{-3} ($\sum_{29}\text{PCBs}$) in Beijing in 2004,³⁸ while a generally lower level ($\sum_{19}\text{PCBs}$: $22\text{--}65 \text{ pg m}^{-3}$) was obtained in Beijing during 2006–2007.⁴⁵ These were comparable to the observations in the YRD, whereas higher levels were also observed in northeast China. Yang *et al.*⁴⁶ reported that the annual mean concentration of $\sum_7\text{PCBs}$ was 120 pg m^{-3} ($40.7\text{--}226 \text{ pg m}^{-3}$) in Qingdao in 2009, which was still lower than the previous results in 2003 ($166\text{--}551 \text{ pg m}^{-3}$ with a mean of 360 pg m^{-3}).⁴⁷

Severe PCB pollution was observed in e-waste dismantling areas. Han *et al.*⁴⁸ investigated atmospheric PCBs in Taizhou during 2006–2007 using HVAS. The average $\sum_{38}\text{PCB}$ concentration (gas + particle phase) near the e-waste dismantling area was $12\,407 \pm 9592 \text{ pg m}^{-3}$ in winter, which was much higher than those observed in megacities. However, it was still lower than that reported one decade ago, suggesting an impact of historical dismantling of PCB containing equipment. In south China, Wang *et al.*⁴⁹ observed total particulate PCB concentrations to be $27.6\text{--}1704 \text{ pg m}^{-3}$ at an abandoned e-waste recycling site, which was even lower than those obtained at the nearby village of Longtang ($7825\text{--}76\,330 \text{ pg m}^{-3}$).⁵⁰

Despite that, much lower levels were reported in remote areas. In the air samples taken from 11 background sites geographically distributed across China in 2007–2008, the $\sum_7\text{PCB}$ concentrations ranged between 4.0 and 27.5 pg m^{-3} and the TEQ ranged from 0.3 to 11.3 fg m^{-3} .⁵¹ In the Tibetan Plateau, Wang *et al.*⁵² reported the air concentrations of $\sum_{15}\text{PCBs}$ in the range of $1.8\text{--}8.2 \text{ pg m}^{-3}$ at 16 locations in 2007–2008 based on XAD-2 resin PAS. Moreover, He *et al.*⁵³ found that the PCB concentrations were $0.92\text{--}3.8 \text{ pg m}^{-3}$ in the air samples collected along the Yellow River, which had a significantly positive relationship with the concentrations in the bark samples. These results were generally consistent with those obtained at other remote areas in the world.⁵¹

2.3 Halogenated flame retardants (HFRs)

Halogenated flame retardants (HFRs) are organic compounds containing chlorine or bromine bonded to carbon and can prevent combustion and reduce the flammability of products, such as PBDEs, HBCD, tetrabromobisphenol A (TBBPA) and dechlorane plus (DP). They were extensively used in a variety of products, such as electronic equipment, plastics, textiles, polyurethane foam, wires, and cables. These compounds generally have low vapor pressures and high octanol–water partition coefficients (K_{ow}), and tend to bind to particulate matter in ambient air.⁶⁰ Therefore, they may be more resistant to photo-degradation and metabolic breakdown.^{66,129} Commercial penta-BDE and octa-BDE, and HBCD have been listed as POPs, and their production and use have been under restriction in many countries. Recently, novel brominated flame retardants (NBFRs), relating to BFRs which are new to the market or newly/recently observed in the environment,¹³⁰ have raised great concern due to their similar properties to POPs, such as decabromodiphenyl ethane (DBDPE), 2,3,4,5-tetrabromobenzoate (TBB), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), tetrabromophthalate (TBPH) and 1,2-bis(2,4,6 tribromophenoxy)ethane (BTBPE). As a high production and consumption country in the world, China received great attention due to environmental pollution associated with these chemicals, especially PBDEs, which have been widely detected in Chinese air (Table S3†).

As shown in Fig. 1(C), the spatial distribution of the PBDE sampling sites was quite similar to that of PCBs. As Yang *et al.*⁵⁷ indicated, the $\sum_{12}\text{PBDE}$ concentrations in air (gas + particle phases) were in the range of $11.0\text{--}838 \text{ pg m}^{-3}$ (mean $232 \pm$

72 pg m⁻³) at 15 sites across China during 2008–2009. They were generally in the order of urban (306 ± 20.0 pg m⁻³) > suburban (67.0 ± 14.0 pg m⁻³) > background/rural (14.0 ± 1.00 pg m⁻³). The highest concentration was observed in Guangzhou (mean: 838 pg m⁻³), followed by Beijing (mean: 781 pg m⁻³) and Chengdu (mean: 502 pg m⁻³), a megacity in southwest China. Zhao *et al.*⁵⁸ investigated BFRs based on gridded field observations coupled with PAS in north China in 2011. The highest concentrations of $\sum_{10}$ PBDEs were found in the region of Beijing-Tianjin, followed by Shandong Province and Hebei Province. The highest values of the two most abundant compounds of BFRs, DBDPE and BDE-209, mainly occurred in the region around Laizhou Bay, Shandong Province, where some manufacturing plants were located. Li *et al.*⁵⁹ demonstrated the distribution of BFRs including PBDEs and NBFRs in Chinese air during China's POPs Soil and Air Monitoring Program phase I and phase II, which covered the sampling period of 2005–2010. A significant increase in $\sum_{12}$ PBDEs and $\sum_6$ NBFR concentrations was found in phase II, indicating increasing pollution of atmospheric BFRs in China. The highest values of $\sum_{18}$ BFRs were observed in Guangzhou air over the entire sampling period, followed by Beijing and Shanghai. Recently, Liu *et al.*⁶⁰ revealed the occurrence of HFRs in PM_{2.5} at 10 urban sites in China during 2013–2014. The highest $\sum_9$ PBDE concentrations were also observed in Guangzhou with a range of 2.5–1000 pg m⁻³ (mean 210 pg m⁻³), which was nearly 10- to 100-fold higher than those in the other sites. The lowest values were recorded in Wuhan (2.0 ± 1.4 pg m⁻³) and Guiyang (2.2 ± 2.2 pg m⁻³), two large cities in south-central China. The DBDPE concentrations varied from 0.24 to 1000 pg m⁻³ at all sites, with the highest value obtained in Guangzhou air.

In specific regions, Chen *et al.*⁶¹ first reported that the atmospheric concentrations of $\sum_{10}$ PBDEs (gas + particle phases) ranged from 41.5 to 6594 pg m⁻³ in Guangzhou in 2004, and BDE-209 was in the range of 99.9–1464 pg m⁻³. This was generally comparable to the results reported by Pan *et al.*⁴¹ ($\sum_{31}$ PBDEs: 240–1189 pg m⁻³) during 2006–2007 and Shi *et al.*⁶² (240–9440 pg m⁻³) in 2007. Deng *et al.*⁶³ compared PBDE distributions in air particle samples simultaneously collected from Guiyu (an e-waste dismantling area) and two major urban centers of the PRD (Hong Kong and Guangzhou) in 2004. The mean concentrations of $\sum_{22}$ PBDEs in TSP were in the range of 33.8–358 pg m⁻³ and 204–372 pg m⁻³ in Hong Kong and Guangzhou, respectively, while much higher levels were obtained in Guiyu with a concentration range of 13.2–45.4 ng m⁻³. This high level was comparable to the observation by Chen *et al.*⁶⁴ in Guiyu and its neighboring areas (0.35–41.5 ng m⁻³). Wang *et al.*⁶⁵ also compared PBDE levels in indoor air from different households of Hong Kong and Guangzhou in 2010. $\sum_{26}$ PBDEs in PM_{2.5} in Guangzhou (52.9–2030 pg m⁻³, mean 239 pg m⁻³) were significantly higher than those in Hong Kong (0.25–160 pg m⁻³, mean 43.8 pg m⁻³) ($p < 0.05$). Ding *et al.*⁶⁶ also investigated the occurrence of BFRs in indoor and outdoor air in Guangzhou in 2013. The outdoor air concentrations of PBDEs (1.21–1522 pg m⁻³; mean 404 pg m⁻³) were significantly higher than those in indoor air (1.43–57 pg m⁻³). DBDPE showed a similar distribution pattern (median: 127 pg m⁻³ in outdoor

air versus 74.9 pg m⁻³ in indoor air). However, the detection frequencies and levels of other target BFRs were generally at very low levels, such as BTBPE, PBBs, PBEB, 2,3,5,6-tetrabromop-xylene (pTBX) and pentabromotoluene (PBT).

In general, lower levels of HFRs were observed in ambient air in the YRD. Zhang *et al.*^{42,67} assessed PBDEs in three cities (Suzhou, Wuxi and Nantong) during 2009–2011. BDE-209 was the most abundant congener (4.11–2840 pg m⁻³). The sum concentrations of tri- to hepta-BDEs ranged from <LOD to 275 pg m⁻³ (mean 38.4 pg m⁻³), which was higher than those derived from PAS ($\sum_{13}$ PBDEs: 0.20–43 pg m⁻³).⁶⁷ Yu *et al.*⁶⁸ indicated that the mean concentrations of particle-bound PBDEs and DP were in the range of 108 ± 34–744 ± 152 pg m⁻³ and 2.32 ± 0.50–5.48 ± 1.28 pg m⁻³, respectively in different districts in Shanghai. Li *et al.*⁶⁹ also revealed the occurrence of atmospheric HBCD in Shanghai, and its concentrations varied from 3.21 to 123 pg m⁻³. The industrial area showed about three times higher HBCD levels than the urban areas.

The atmospheric levels of HFRs in Beijing were commonly comparable to those of the YRD (Fig. 1(C)). As Hu *et al.*⁷⁰ reported, the total concentrations of PBDEs and HBCD during 2008–2009 were in the range of 57–470 and 20–1800 pg m⁻³, respectively. The PBDE level was slightly lower than the results from Yang *et al.*⁵⁷ (mean 781 ± 107 pg m⁻³), whereas a large variation of $\sum_{42}$ PBDE (gas + particle phases) concentrations was obtained at the solid waste incineration plant (60.5–216 pg m⁻³), chemical plant (71.8–7500 pg m⁻³), and coal-fired thermal power plant (34.4–454 pg m⁻³).⁷¹ Furthermore, in north China, Yang *et al.*⁷² reported that the annual mean concentrations of $\sum_{12}$ PBDEs (gas + particle phases) were 104 ± 95 pg m⁻³ in Dalian during 2008–2009. Qi *et al.*⁷³ revealed that the annual mean concentrations of $\sum_{13}$ PBDEs and 9 alternative BFRs were 69 pg m⁻³ (range 2.0–320 pg m⁻³) and 180 pg m⁻³ (range 5.3–6900 pg m⁻³), respectively in Harbin air during 2007–2008. Li *et al.*⁷⁴ found that 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) and bis(2-ethylhexyl) tetrabromophthalate (BEHTBP) were frequently detected at mean concentrations of 5.2 ± 20 and 30 ± 200 pg m⁻³, respectively, while *syn*-DP and *anti*-DP showed much lower levels with mean values of 1.9 ± 5.1 and 5.8 ± 18 pg m⁻³, respectively. The temporal trend indicated that the concentrations of these compounds were significantly increased over 2008–2013, possibly suggesting their increasing usage in China. Noticeably, distinctively higher levels of BFRs were obtained by He *et al.*⁵³ along the Yellow River, where PBDE concentrations were 310–5200 pg m⁻³, and they were 5.4–130 pg m⁻³, 2.2–140 pg m⁻³ and 4.0–86 pg m⁻³ for PBBz, HBB and PBT, respectively. The reason was unknown. As expected, significantly lower PBDEs were observed in the Tibetan Plateau, where the concentrations of $\sum_9$ PBDEs ranged between 0.1 and 8.3 pg m⁻³ at 16 locations during 2007–2008, which reflected a baseline level of PBDEs in China.⁵²

2.4 PFCs

Perfluorinated compounds (PFCs) are hydrophobic and oleophobic organic compounds of which all hydrogen atoms on the carbon chain are substituted by fluorine atoms. PFCs were commonly used in textiles, furniture manufacture, plastics,

leather, coating, construction and other fields. They are known to be persistent, bioaccumulative and have possible detrimental effects on humans and wildlife.^{131,132} Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), two of the most widely produced compounds, have been commonly found in water bodies and soils.^{75,131,132} They can also enter ambient air *via* air-surface exchange and are subject to long-range atmospheric transport (LRAT).⁷⁵

Some studies have revealed the occurrence of airborne PFCs in North American^{133,134} and Europe,^{135,136} while limited data could be obtained in China to date (Fig. 1(D), Table S4†). Li *et al.*⁷⁵ reported the occurrence of molecular PFCs such as fluorotelomer olefins (FTOs), acrylates (FTAs), fluorotelomer alcohols (FTOHs), fluorooctane sulfonamides (FOSAs), and fluorooctane sulfonamidoethanols (FOSEs) in the Asian atmosphere in 2009 using PAS. The concentrations of $\sum$ FTOHs, $\sum$ FTAs, $\sum$ FOSAs and $\sum$ FOSEs in Chinese air were in the range of 51.4–936 (253 ± 216) pg m^{-3} , 0.20–5.80 (1.64 ± 1.56) pg m^{-3} , 3.48–23.1 (12.8 ± 4.95) pg m^{-3} and 7.44–94.0 (40.0 ± 18.9) pg m^{-3} , respectively. They were generally at a similar level to those in Japan and India. Very high levels of 8 : 2 FTO, 8 : 2 FTOH, and 10 : 2 FTOH were found in the BTH, YRD and PRD regions, as well as the southwest developed region (Chongqing). The level of PFCs at two background sites (Tuoji and Jianfeng Mountains) was significantly lower than that at the urban sites, while the concentrations of FOSAs and FOSEs were consistent across China. Liu *et al.*⁷⁶ investigated the occurrence of PFCs in the atmosphere of Shenzhen, China. $\sum$ PFC concentrations ranged from 3.4 to 34 pg m^{-3} with an average of 15 pg m^{-3} . PFOS and PFOA were the two most abundant PFCs and accounted for 35% and 22% of $\sum$ PFCs on average. Although the spatial distribution of airborne PFCs across China was not available, it is expected that higher PFC levels are present in ambient air around manufacturing plants, such as those in Wuhan, where very high concentrations of PFOS and PFOA were found in dust from the manufacturing facility, and PFOS, PFOA and perfluorohexane sulfonate (PFHxS) were also detected in dust, water, soil, and chicken eggs.¹³⁷ It is noteworthy that there was a general decline in PFC concentration from urban, rural, to remote locations in the Asian atmosphere observed by Li *et al.*,⁷⁵ which suggested an apparently elevated level of airborne PFCs in megacities. More complementary research is warranted to assess their distribution in China and the possible exposure risk to human health.

2.5 OCPs

Organochlorine pesticides (OCPs) were once widely produced and used globally with a long history. Nine of them have been initially listed as POPs in the Stockholm Convention. Although HCB has never been registered as a pesticide in China, it can be released as a by-product of chlorination processes such as those in pesticide production and some chemical industries. The primary sources of OCPs such as DDTs and HCHs have been reduced in the past several decades,¹³⁸ and as a result, their atmospheric levels presented a decreasing tendency on a global scale.¹³⁹ However, the data on the nationwide distribution of atmospheric OCPs are rather sparse in China (Table S5†). Liu

*et al.*⁸⁰ obtained seasonal data from 37 Chinese cities and three background sites in 2005. In general, DDTs and HCHs showed relatively high levels in the cities of southern, southwestern and central parts of China, such as Guangzhou, Zhuzhou, Chongqing, Chengdu, Fuzhou, *etc.* (Fig. 1(E)). As reviewed by Wang *et al.*,⁸¹ HCB levels increased from south China to north China in most of the environmental compartments including air, and hotspots were identified near factories producing and using HCB. This spatial distribution of airborne OCPs is slightly different from those of other PTSs, which may be related to their extensive agricultural application.

In specific regions, according to our observation on the Beijing 325 m meteorological tower during 2006–2007,⁴⁵ the air concentrations of γ -HCH were in the range of 39–242 pg m^{-3} , while those of α -HCH, *p,p'*-DDT and HCB were lower with ranges of 20–86 pg m^{-3} , 7.3–78 pg m^{-3} and 15–160 pg m^{-3} , respectively. Zhang *et al.*^{82,83} also revealed the occurrence of atmospheric OCPs in Beijing over 2005–2009. HCB, HCH and DDT isomers were the most abundant OCPs with concentration ranges of 27–1400 pg m^{-3} , <LOD–2000 pg m^{-3} and <LOD–850 pg m^{-3} , respectively. HCB levels showed no obvious temporal trend over the sampling period, except for a decline in 2008. In the YRD, Qiu *et al.*⁸⁴ reported OCPs in the air around the Taihu Lake, one of the most densely populated areas in China. The concentrations of α - and β -HCH were in the range of 21–164 pg m^{-3} and 18–96 pg m^{-3} in 2002, while the concentrations of individual DDT isomers were in the range of n.d.–2753 pg m^{-3} , which were dominated by *o,p'*-DDT. Besides, α -endosulfan contributed a high level of n.d.–888 pg m^{-3} , followed by HEPT (18–173 pg m^{-3}) and HCB (18–109 pg m^{-3}). Zhang *et al.*⁴² observed that HCB and *p,p'*-DDE were the most abundant OCPs in Suzhou, Wuxi and Nantong cities during 2009–2010, with concentration ranges of 10.0–778 pg m^{-3} and 18.8–384 pg m^{-3} , respectively. These were generally consistent with the results from PAS across the YRD region during 2010–2011,⁴³ and those in the Taihu area⁸⁴ and Beijing.^{82,83} In the PRD, Li *et al.*⁸⁵ compared the OCP distributions in Guangzhou and Hong Kong during 2003–2004. The mean concentrations of *t*-CHL, *c*-CHL, *o,p'*-DDT, *p,p'*-DDT and α -endosulfan ranged from 103 to 1440 pg m^{-3} . The concentrations of HCHs, CHLs, *o,p'*-DDT, and α -endosulfan were significantly ($p < 0.05$) higher in the air of Guangzhou than those in Hong Kong. The subsequent investigations indicated a lower level in Guangzhou in general. For example, Pan *et al.*⁴¹ found that the annual average $\sum$ OCP concentration was 345.6 pg m^{-3} during 2006–2007 at a low latitude station in Tianhe District. Wang *et al.*⁸⁶ obtained that the concentrations of $\sum$ HCHs and $\sum$ DDTs were in the range of 40.5–235 pg m^{-3} and 39.1–939 pg m^{-3} in agricultural paddy fields in the suburban areas of Guangzhou.

In other areas, $\sum$ HCH concentrations were found to be in the range of <200–742 pg m^{-3} (mean 314 pg m^{-3}) in Qingdao City in 2003, followed by $\sum$ DDTs (88–263 pg m^{-3}).⁴⁷ The concentrations of mirex and chlordane were in the range of 6.6–255 pg m^{-3} and <6–71 pg m^{-3} , respectively at the coast sites, while aldrin, dieldrin and endrin were mostly found below 10 pg m^{-3} . Yang *et al.*⁴⁶ obtained lower levels of $\sum$ HCHs and $\sum$ DDTs in near-surface atmospheric aerosols in the same area during 2009–2010 (the annual mean concentrations:

32.4 pg m⁻³ and 59.4 pg m⁻³, respectively). In the Tibetan Plateau, Li *et al.*⁸⁷ reported that the air concentrations of α -HCH and α -endosulfan were in the ranges of 8.7–25.9 pg m⁻³ and 8.8–71.1 pg m⁻³, respectively in the Mt. Everest region in 2002. This was comparable to the following observations in Nam Co⁸⁸ and across the Tibetan Plateau,⁵² but generally lower than those from the southeastern Tibetan Plateau^{89,90} and Lhasa Region,⁹¹ where more anthropogenic activities exist. Similarly to PBDEs, He *et al.*⁵³ found a relatively high level of OCPs in air samples collected along the Yellow River in 2012 (range 120–6700 pg m⁻³). HCB, HCHs, and DDTs were the predominant OCPs. Only eight paired air and tree bark samples were collected from these sites, and further study is needed to explain the cause of such high levels of OCPs and PBDEs.

2.6 PAHs

Polycyclic aromatic hydrocarbons (PAHs) are emitted from natural and anthropogenic sources *via* incomplete combustion activities of carbon containing materials, such as coal combustion, vehicle emission, biomass burning and industrial processes.^{92,140} PAHs present carcinogenic, mutagenic, and toxic effects and have been listed as priority pollutants by both the United States Environmental Protection Agency (EPA) and the European Community.¹⁴¹ In China, because of the fast development of industry and large consumption of fossil fuels, PAHs were ubiquitously detected at ng m⁻³ levels in air (Table S6†), which are much higher than those of many other PTSs. PAH sampling campaigns were mostly conducted in the BTH, YRD and PRD regions, and this spatial distribution was generally comparable to that of PCDD/Fs (Fig. 1(F)).

According to the evaluation by Xu *et al.*,¹⁴² the total PAH emission in China was 25 300 tons in 2003. Sichuan Province, located in southwest China, contributed the largest portion of PAH emission, followed by Shanxi, Hebei and Shandong Provinces. In north China PAHs were investigated with PAS in 90 gridded sites in 2011.⁹² The average concentration of $\sum_{15}$ PAHs was 220 $\pm$ 14 ng m⁻³, with the highest in Shanxi Province, followed by Shandong Province and the BTH, which was consistent with the evaluation by Xu *et al.*¹⁴² In the BTH, the concentrations of $\sum_{16}$ PAHs in the gas phase varied from 20 to 479 ng m⁻³ with a mean of 119 $\pm$ 105 ng m⁻³ in 2008.⁹³ This was comparable to the results from Gao *et al.*,⁹⁴ where the concentrations of $\sum_{14}$ PAHs ranged from 31.8 to 440 ng m⁻³ (mean 250 ng m⁻³) in 2013. They were also consistent with the observation by Qin *et al.*⁹⁵ at Lake Small Baiyangdian, a shallow lake in the BTH, where the $\sum_{16}$ PAH concentration was 417 $\pm$ 300 ng m⁻³ in the gas phase, and 151 $\pm$ 99.2 ng m⁻³ in the particulate phase during 2007–2008. However, lower levels of PAHs and their derivatives, nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs), were reported in Beijing as well. Wang *et al.*⁹⁶ observed that the mean $\sum_{16}$ PAH concentrations (molecular weight < 300) were 8.9 $\pm$ 3.6 ng m⁻³ and 19.0 $\pm$ 12.2 ng m⁻³ during the source control period for the Beijing Olympic Games and the non-source control period in 2008. Correspondingly, $\sum_{11}$ NPAH and $\sum_5$ OPAH concentrations were 0.42 $\pm$ 0.31 and 0.79 $\pm$ 0.55 ng m⁻³, and 0.70 $\pm$ 0.25 and 1.03 $\pm$ 0.47 ng m⁻³ during the

different periods. Lin *et al.*⁹⁷ found that the median concentration of $\sum_{23}$ PAHs, $\sum_{15}$ NPAHs, $\sum_{16}$ hydroxylated PAHs (OHPAHs), and $\sum_7$ OPAHs was 53.8, 1.14, 1.40, and 3.62 ng m⁻³, respectively in PM_{2.5} in Beijing during 2012–2013. This level was in agreement with the results at Yucheng, Shandong Province,⁹⁸ where the average $\sum_{12}$ PAH concentration in PM_{2.5} samples was higher during haze episodes (28.3 $\pm$ 8.4 ng m⁻³) compared to that during non-haze episodes (23.7 $\pm$ 4.2 ng m⁻³) in 2013.

In the YRD, Zhang *et al.*⁴² found that the $\sum_{16}$ PAH concentrations ranged from 13.9 to 229 ng m⁻³ with an overall average of 88.2 ng m⁻³ in Suzhou, Wuxi and Nantong cities. This was comparable to the results in an industrial area of Shanghai in 2004–2005,⁹⁹ where the PM₁₀-bound $\sum_{16}$ PAH concentrations ranged from 0.07 to 270 ng m⁻³ with a mean of 64.9 ng m⁻³. Lower levels were observed recently. Wang *et al.*¹⁰⁰ reported that the concentrations of $\sum_{37}$ PAHs were in the range of 4.58–14.5 ng m⁻³ and 1.82–8.56 ng m⁻³ in TSP and PM_{1.1} in 2015, which were in agreement with his another study on PM_{2.5}-bound PAHs during 2014–2015 (annual average: 6.9 ng m⁻³).¹⁰² By contrast, Liu *et al.*¹⁰¹ reported extremely high PAH concentrations with a range of 3100–11 307 ng m⁻³ in an urban tunnel of Shanghai. The levels at the exit of the tunnel were significantly ($p < 0.01$) higher than those at the entrance,¹⁴³ suggesting vehicle traffic as a main contributor to PAH emission.

In the PRD, Liu *et al.*¹⁰³ observed that the annual average concentration of PAHs in PM_{2.5} was 33.89 ng m⁻³ (6.99–106 ng m⁻³) in Guangzhou during 2012–2013, and benzo(a)pyrene (BaP) was the dominant PAH. This was consistent with the observation in an industrial complex site and an e-waste recycling site (7.38–113 ng m⁻³).¹⁰⁴ Relatively higher levels were found in agricultural paddy fields in the suburban areas of Guangzhou ($\sum_{12}$ PAHs: 40.9–333 ng m⁻³),⁸⁶ which were comparable to the previous results.^{105,106} According to the study by Huang *et al.*,¹⁰⁷ the abundance of $\sum$ NPAHs and $\sum$ OPAHs was 4.14 $\pm$ 2.37 ng m⁻³ and 13.0 $\pm$ 6.63 ng m⁻³, respectively in a rural site in 2010, which was approximately one order of magnitude lower than the PAH concentrations (mean 91.5 $\pm$ 36.1 ng m⁻³).

In central China, Liu *et al.*¹⁰⁸ characterized the occurrence and size distributions of ten species of PAHs in the ambient air of coking plants in Shanxi Province. The concentrations of total particulate-matter PAHs reached up to 2241 ng m⁻³ in 2009. Wang *et al.*¹¹⁰ also widely detected PAHs (mean 197 ng m⁻³) and OPAHs (mean 29.4 ng m⁻³) in 19 sites in PM_{2.5} from Xi'an, Shaanxi Province in 2013. Shi *et al.*¹⁰⁹ introduced the study on 16 PAHs in PM_{2.5} and PM₁₀ in 2011 and 2012 in Chengdu. The mean concentrations were 41.5 ng m⁻³ in PM₁₀ and 36.8 ng m⁻³ in PM_{2.5}, respectively. These studies revealed a generally high level of PAHs and their derivatives in megacities across China.

2.7 Heavy metals

Heavy metals enter into the surrounding environment *via* (1) the weathering of their parent materials, and (2) emission from human activities such as mining, electroplating, smelting and some other industrial processes.¹⁴⁴ According to the first national soil pollution survey, Chinese soils have been contaminated by heavy metals with varying degrees.¹⁴⁴ The soil metal pollution in

southern provinces was more serious than in the other provinces. However in air, generally higher levels were obtained in the PRD, BTH and central China (Zhengzhou, Xi'an, *etc.*) as reviewed by Duan and Tan.¹⁴⁵ The mean atmospheric concentrations of Zn, Pb, Mn, Cu and Cr were $425 \pm 337 \text{ ng m}^{-3}$, $261 \pm 276 \text{ ng m}^{-3}$, $199 \pm 363 \text{ ng m}^{-3}$, $117 \pm 163 \text{ ng m}^{-3}$ and $85.7 \pm 111 \text{ ng m}^{-3}$, respectively during the last few decades across China. Recently, there were some studies on heavy metals at the regional scale as well, which possibly shed light on the variation of airborne heavy metals around China. For example, Duan *et al.*¹⁴⁶ reported that the mean concentration of atmospheric Pb was 281.6 ng m^{-3} in Beijing in 2006.¹⁴⁵ Gao *et al.*⁹⁴ indicated that the total concentration of ten measured elements ranged from 0.02 to $1.14 \mu\text{g m}^{-3}$ at each functional area in Beijing in 2013. Zn and Ba showed the highest concentrations among non-carcinogenic metals. Differently, the level of particulate mercury (HgP) was relatively low with the monthly concentrations between 0.08 ± 0.04 and $1.81 \pm 0.47 \text{ ng m}^{-3}$ in aerosols in Beijing over 2005–2011.¹⁴⁷ In Shanghai, Chen *et al.*¹⁴⁸ observed that the concentrations of Zn, Pb, Cu, Cr, As and Cd were in the range of 20–1163, 12–460, 5–109, 5–134, 1–92 and $0.2\text{--}12.2 \text{ ng m}^{-3}$, respectively in $\text{PM}_{2.5}$ at four sites. The level and distribution pattern were generally comparable to the observation by Bian *et al.*¹⁴⁹ in the Taihu Basin in 2013, where the Zn and Pb concentrations in $\text{PM}_{2.5}$ were much higher than those of Cu, As, Cd, and Cr. In the PRD, Lee *et al.*¹⁵⁰ collected TSP samples in the urban and suburban areas of Hong Kong and Guangzhou from 2003–2005. The annual concentrations of Cd, Cr, Cu, Pb and Zn were 1.61–7.83, 12.4–20.9, 30.8–82.3, 53.5–269 and 241–1190 ng m^{-3} , respectively. The levels of most heavy metals were higher in the urban and suburban areas of Guangzhou than those in Hong Kong, indicating significant atmospheric trace metal pollution in Guangzhou. These results were generally comparable to the reviewed concentrations across China.¹⁴⁵ However, a higher level was observed in an e-waste recycling zone in Qingyuan in 2012,¹⁵¹ where the sum concentrations of 15 heavy metals ranged between 670 and 5200 ng m^{-3} , and Zn and Pb represented the highest levels with the concentrations of 160–1600 ng m^{-3} and 45–280 ng m^{-3} . Besides, the mean concentration of 8 heavy metals (Cr, Ni, Cu, Cd, Pb, Zn, Mn and Co) was reported to be $0.80 \mu\text{g m}^{-3}$ in the $\text{PM}_{2.5}$ from Taiyuan, a typical coal-burning city in Shanxi Province, which was much higher than those in other areas of China.¹⁵² These studies comprehensively revealed a large variation of airborne heavy metals in different areas. In general, higher levels were obtained in the areas with more developed industries, such as the PRD, BTH, YRD and megacities in central China (*e.g.*, Zhengzhou, Taiyuan, Xi'an, *etc.*). This suggested that airborne heavy metals should also be of special concern in megacities other than other PTSS.

3. The implication associated with air pollution

As introduced in Section 1.2, air pollution in China, especially in megacities, is characterized by fine particles, *i.e.*, $\text{PM}_{2.5}$. The partitioning of PTSS in fine particles is therefore vital to understand their atmospheric fate and environmental

behavior.¹⁵³ Many studies indicated that in general heavier PTSS tend to be adsorbed in the particle phase, and the sizes of suspended particles influence their distribution more than temperature and humidity.^{145,154,155} This suggested a certain correlation between the variation of airborne PTSS and air pollution in China. Here we assume that fine particles serve as a major carrier of airborne PTSS and facilitate their LRAT, while industrial production and product consumption are the major sources of most pollutants, and unintentional emission would be an important contributor to airborne PTSS. These assumptions are expected to explain the relationship between the occurrence of airborne PTSS and the sources, as well as the implication associated with air pollution.

3.1 Fine particles as a major carrier of airborne PTSS

Many heavier PTSS have been found dominantly in the particulate phase.^{153,154} For example, PCDD/Fs and PBDD/Fs in the particle phase made an average contribution of >90% to the total concentrations.^{21,28} The alternative HFRs (EHTBB, BEHTBP and DP) were frequently detected in the particle phase and their concentrations showed positive and significant correlations with the TSP concentrations.⁷⁴ The distribution of BFR output mass showed that PBDEs and HBCD were emitted mainly by airborne particles (51% and 62%), followed by residual ash (44% and 24%) and the gas phase (5.1% and 14%).¹⁵⁶ For PCBs, although gas-phase PCBs accounted for >70% of the total concentration, higher chlorinated CBs tended to partition more to fine particles.⁴⁸ For PAHs, the compounds with molecular weights (MWs) lower than 210 were mainly distributed in the gas phase with a percentage range of 73.7–98.4%, while those with $\text{MW} > 210$ were mainly distributed in the particle phase with a percentage range of 54.9–99.5%.⁴² Ma *et al.*⁹³ also indicated that the ratios of the particle phase for individual PAHs increase with their molecular weight. This suggested that air particles are an important carrier of many airborne PTSS when they were diffused from sources to the surroundings.

The relationship between PTSS and air particles was demonstrated in many cases. The atmospheric PCDD/F level showed a declining trend in Beijing during 2006–2010, and there was a significant correlation between PCDD/F and TSP concentrations ($p < 0.01$).²² Furthermore, PCDD/F concentrations in air in 2008 decreased by approximately 70% compared with the 2007 level. This was attributed to the fact that the Beijing Municipal Government implemented strict emission control measures including vehicle restrictions before the 29th Beijing Olympic Games (BOG) in 2008, which resulted in a significant reduction of TSP concentrations during the BOG with a decrease of 52% compared to 2007.²² This was considered to contribute to the variations of airborne PAHs during the 29th BOG as well.^{93,96} Zhang *et al.*^{82,83} also observed that the pattern of HCB concentrations was consistent with PM_{10} /TSP variation during the BOG. Although HCB was basically detected in the gas phase, the increase of HCB levels in wintertime was mainly contributed by the high TSP from combustion processes according to the gas-particle partitioning results. In addition, Lu *et al.*^{98,112} found that the average $\sum_{12}\text{PAH}$ concentration in

PM_{2.5} samples was higher during haze episodes compared to non-haze episodes. The percentage of high molecular weight PAHs increased from 62.3% on normal days to 67.9% during the haze periods.⁹⁸ Chi *et al.*^{54,55} found that the ambient PCDD/F concentrations increased during the Asian Dust Storm (ADS) episode of 3rd Mar 2008 and a northeast monsoon episode on 3rd Dec 2008 in northern Taiwan. There were significantly positive correlations between PCDD/F and TSP concentrations. However, the PCB concentrations did not vary significantly before or after the ADS episode, which was attributed to the fact that the majority of the airborne PCBs were present in the vapour phase.¹²⁸ By contrast, our observation in Beijing indicated a comparable level of PCDD/Fs during the dust event (average 2489 fg m⁻³) with that during the non-dust event (average 3671 fg m⁻³).²¹ This was consistent with the observation of Lee *et al.*¹⁵⁷ in southeastern Korea. The reason could be that the particulate fractions during the dust event were dominant with diameters between 3.67 and 10 µm, while PCDD/Fs were dominantly distributed in fine particles with diameter <2.1 µm,¹⁵⁸ which resulted in limited influence of the dust events on the gas-particle partitioning of PCDD/Fs. This may also explain the variation of PCDD/Fs during Taiwan dust episodes,^{54,55} because the dust originated from Central Asia and the ratio of fine particles were probably elevated due to the fact that coarse particles are deposited easily over long distances.⁵³

The particle size distribution of airborne PTSSs was also demonstrated recently. Han *et al.*⁴⁸ found that the PM_{2.5}/TSP ratios of PCB congeners increased along with increasing chlorine numbers (44% for 3 Cl PCBs increasing to 67% for 10 Cl PCBs), suggesting that higher chlorinated CBs tended to partition more to fine particles. Furthermore, PCBs were mainly in the <0.5 µm cut, accounting for 44% of the total PCBs in fine particles, and more lower chlorinated congeners were found in the 1.3–2.5 µm cut than in other size cuts.⁴⁸ Zhang *et al.*²⁵ indicated that both particle and PCDD/F concentrations were significantly lower during normal days compared to haze days ($p < 0.05$). PCDD/F concentrations increased as particle sizes decreased and 95% of the particle-bound PCDD/Fs were associated with inhalable fine particles (PM_{2.5}). This was consistent with another study on both PCDD/Fs and PBDD/Fs.²⁴ A similar distribution was also observed for PAHs.^{98,108,109,113} Ren *et al.*¹¹³ revealed that, among four size ranges (<1.1, 1.1–3.3, 3.3–9.0 and >9.0 µm), PAHs of PM_{1.1} account for 60 ± 6.7% and 61 ± 33% of the total airborne particulate PAHs in winter and summer in Xi'an, which even accounted for 79 ± 19% and 78 ± 5.2%, respectively in Guangzhou. Furthermore, the results in Beijing air indicated that 72.1% of PBDEs in particulate matters were found in PM_{2.5–10} and PM_{2.5} samples, and more than 50% of PBDEs were found in PM_{2.5}.⁷¹ A similar result was obtained in two major urban centers of the PRD, where PBDEs were measured in PM_{2.5}, TSP and dust samples, and PM_{2.5} accumulated the highest concentration among residential particles especially for BDE-209.⁶⁵ For heavy metals, most heavy metals were enriched in fine particles as reviewed by Duan and Tan.¹⁴⁵ Pb, Cd, As and Zn existed mostly in accumulation mode, and V, Mn and Cu were in both coarse and accumulation modes, while Ni and Cr existed in all of the three modes. Huang *et al.*¹⁵¹

indicated that anthropogenic metals (Zn, Se, Pb, Sb, As, and Cd) were predominantly enriched in the particles with diameter <1.8 µm, which also increased the potential health risk of residents through inhalation exposure to size-fractionated particle-bound heavy metals. Regarding PFCs, the total concentration significantly correlated with PM_{2.5} ($p < 0.05$, $R^2 = 0.11$) and PM₁₀ ($p < 0.01$, $R^2 = 0.45$).⁷⁶ This indicated that PFCs were more likely to adhere to particles with relatively large sizes, which was in agreement with the observation of Murakami and Takada¹⁵⁹ in Japanese residential areas. The reason for the discrepancy of particle size distributions between PFCs and other PTSSs is unclear and requires further investigation.

In summary, most of the heavier PTSSs in air tended to be bounded to particles, and the mass ratios of the particle phase for individual compounds generally increase with their molecular weight. Furthermore, the particle-bound PTSSs were more associated with fine particles, *i.e.* PM_{2.5}, and even smaller particles. This suggested that fine particles served as a major carrier of most airborne PTSSs, which facilitates their LRAT and increases the exposure risk of the human body to these pollutants. Therefore, to some extent, fine particles play a vital role in understanding the atmospheric fate of PTSSs and their potential adverse effect on human health.

3.2 Industrial production/use as a primary source of most PTSSs

Most PTSSs were produced for commercial use except those unintentional by-products, *e.g.*, PCDD/Fs, PAHs, *etc.* Thus, industrial production and commercial use could lead to release of PTSSs into the surrounding environment. Based on gridded field observation in north China, Zhao *et al.*⁵⁸ indicated that BDE-209 and DBDPE in air were mainly from point sources, particularly in the manufacturing base of BFRs around Laizhou Bay, Shandong Province. Li *et al.*⁵⁹ and Wang *et al.*¹¹¹ also found a high OCP level in air apart from PBDEs and other commercial halogenated compounds including NBFRs in Laizhou Bay. Yu *et al.*⁶⁸ observed that the levels of particle-bound PBDEs and DP exhibited the changing trend of industrial areas > urban areas in Shanghai, and the results from multiple linear regression analyses suggested that the deca-BDE mixture was the most important contributor to the particulate PBDEs. Furthermore, extremely higher concentrations of DP were observed in the air samples close to the Chinese DP manufacturing plant in Huai'an City, Jiangsu Province,^{77,78} indicating an impact of industrial production of HFRs on the surroundings.

In general, higher levels of PTSSs could be found in the global urban environment due to their large consumption and their resultant release into the surroundings, such as PBDEs,^{129,160} PFCs,⁷⁵ HBCDs,^{130,160} and DPs.¹⁶¹ In China, as Yang *et al.*⁵⁷ indicated, the atmospheric PBDE levels were in the order of urban > suburban > background/rural at 15 sites across China. Significantly positive correlations were found between the concentrations and urban population ($R = 0.69$, $p < 0.05$) and gross industrial output values ($R = 0.87$, $p < 0.001$). Li *et al.*⁵⁹ also found significantly higher levels of $\sum$ PBDEs and $\sum$ NBFRs in urban sites compared with those in rural sites and background sites. A

significant correlation between BFR concentrations and GDP was observed as well. Spatial distribution revealed hotspots in megacities, such as Guangzhou, Beijing and Shanghai. Li *et al.*⁷⁵ reported the occurrence of molecular PFCs in the Asian atmosphere in 2009. Very high levels of 8 : 2 FTO, 8 : 2 FTOH, and 10 : 2 FTOH were measured in the BTH (Beijing and Tianjin), YRD (Hangzhou), PRD (Guangzhou), and Chongqing (a new rapidly developed region in west China). This trend was attributed to the fact that their source appeared to be directly related to human population density. In north China, Zhao *et al.*⁵⁸ observed that $\sum_{10}$ PBDEs, BDE-209, and DBDPE were significantly higher in Beijing and Tianjin than those in town or countryside areas ($p < 0.05$). The gridded field observation suggested that 78% of $\sum_{10}$ PBDEs were from nonpoint emissions.⁵⁸ In northeast China, Li *et al.*⁷⁴ identified strong local sources for the alternative HFRs (EHTBB, BEHTBP and DP). The significantly increased concentrations over 2008–2013 were attributed to their possible increasing usage in China from 2008 to 2013. In the YRD, significantly higher levels of OCPs were observed in the metropolitan areas and development zones compared to the background areas ($p < 0.01$), and technical product (*i.e.* DDT and chlordane) input was considered a main source.⁴² PBDEs were also present at a higher level in the development zones than in the background areas ($p = 0.03$), and the ratios of the signature congeners deriving from the technical formulations were similar to the technical penta-mixture, indicating their production or use in Wuxi and Nantong cities.⁴² In the PRD, Wang *et al.*⁶⁵ observed that PBDEs in air of the households in Guangzhou were significantly higher than those in Hong Kong, which was attributed to the fact that large amounts of BFRs are consumed in Guangzhou due to the boom in electronics.

Some studies also elucidated the influence of volatilization from contaminated soils on airborne PTSs. Chen *et al.*⁴⁰ observed that the homologue composition of PCBs in Guangzhou air differed from that in Chinese transformer oils, while it is similar to that in sediment and soil subjected to arbitrary disposal of used electronic appliances in this region. This suggested that volatilization is a major source of PCBs in the atmosphere of Guangzhou. Li *et al.*⁸⁵ also found that atmospheric α -HCH in summer time was mainly from evaporation from soil in the PRD, while in winter, it may be the combined effect of evaporation from soils and atmospheric transport from external sources. Wang *et al.*⁸⁶ indicated that HCHs above paddy fields originated from the emission of both technical HCHs and lindane, and were mainly governed by local sources in Guangzhou. DDTs also have a similar source pattern with a combination of fresh input and historical emission. Therefore, the airborne PTSs volatilized from contaminated soils were ultimately ascribed to the use of these chemicals in the local area.

Above all, industrial production and commercial use lead to release of PTSs into surroundings, especially urban areas characterized by higher population density. Higher levels of airborne PTSs associated with air pollution (characterized by $PM_{2.5}$) in the urban environment will cause more exposure risk to these pollutants.

3.3 Unintentional emission as an important contributor to airborne PTSs

Some PTSs are produced unintentionally during steel smelting, power generation, and chemical and combustion processes, such as PCDD/Fs, PAHs, PCBs, PBDEs and heavy metals. In China, many studies have identified the unintentional emission sources of these chemicals. Wang *et al.*¹⁶² established a comprehensive emission inventory of multiple air pollutants from iron and steel production for the historical period of 1978–2011 across China. Emissions of gaseous pollutants (SO_2 , NO_x , and CO), PCDD/Fs, heavy metals (Hg, Pb, As, Cd, Cr and Ni) and particulate matter ($TSP/PM_{10}/PM_{2.5}$) have experienced a gradually increasing tendency since 2000. The Bohai economic circle including the BTH was identified as the top emission intensity region since iron and steel smelting plants are densely built. Ren *et al.*²⁶ indicated the coke industry as a high potential emission source for PCDD/Fs in Tangshan city in the BTH region. As Nie *et al.*¹²⁸ reported, in a typical magnesium smelting plant, dioxin-like PCB (DL-PCB) concentrations could be up to 3780 pg Nm⁻³ and 54 pg g⁻¹ in stack gas and fly ash samples, respectively. Similarly in a coke plant, they could reach up to 4648 pg Nm⁻³ in stack gas samples.¹²⁷ This indicated that unintentional emission of PCBs may intensively occur during industrial processes. As estimated by Cui *et al.*,¹⁶³ total UP-PCB emissions in China were estimated to be 146 t from 1950 to 2010, among which 98.1% was from cement and steel industries. UP-PCB emission seems to be responsible for the increase of PCBs in Chinese air as a whole from 2004 to 2008. Recently, Zhao *et al.*¹⁶⁴ estimated long-term emission trends of PCBs in China using a dynamic fate model. Primary sources still dominate, while UP-PCB emissions are predicted to account for up to 91% of PCB emission in the future (2040–2100). Industrial activities also act as atmospheric emission sources of some BFRs (*e.g.*, PBDEs). Dong *et al.*⁷¹ observed the highest level of PBDEs in the sites of a solid waste incineration plant and coal-fired thermal power plant in Beijing, and the concentration in the thermal power plant was significantly higher ($p = 0.017$) than those in other sites. Ni *et al.*¹⁵⁶ estimated BFR emissions from the open burning of five plastic wastes. Accordingly, PBDE release to air and land from MSWI plants could be 105 kg per year and 7124 kg per year in China in 2015. The data for HBCD were 25.5 and 71.7 kg per year, respectively. This suggested that unintentional emission from point sources (*i.e.* industrial production) had an apparent effect on airborne PTS distribution at the regional scale.

Several studies have also revealed the emission from other anthropogenic activities in urban areas, such as domestic heating, biomass burning and vehicle emissions. Zhang *et al.*^{82,83} indicated that the increase of HCB levels in wintertime was ascribed to coal combustion, waste incineration and fuel combustion in Beijing during 2005–2009. As we investigated during the BOG in 2008,²² significant reduction of PCDD/F levels was found after the emission control measures in Beijing, indicating an impact of strict restrictions on vehicle and industrial production. This was also consistent with the observations for PAHs.^{93,96} In the Circum-Bohai Sea Gulf Region,

Qin *et al.*²⁷ found that the source of airborne PCDD/Fs in Dalian was characterized for thermal source pollution, *i.e.* various combustion processes for thermoelectricity, domestic heating, and vehicle emissions. Yu *et al.*³³ suggested that industrial activities had tremendous influence on the atmospheric distribution of particle-bound PCDD/Fs in Guangzhou. However, detailed source appointment demonstrated that PCDD/Fs were derived from small diffuse combustion sources, such as domestic burning of fossil fuels, traffic sources, and non-industrial and industrial combustion sources. Ren *et al.*³⁴ further indicated that vehicle exhaust might be an important source *via* analysis of similarities in PCDD/F homolog patterns and the differences in deposition fluxes between samples from heavy-traffic roadsides and nearby residence house roofs in Guangzhou. Li *et al.*¹⁶⁵ specially investigated PTS pollution in a microenvironment and confirmed vehicle emission as an important contribution to air pollution in China. Moreover, vehicle parking areas exhibited higher levels of PBDEs, PBDD/Fs, and DP than their adjacent urban area.¹⁶⁶ According to a review by Duan and Tan,¹⁴⁵ vehicle emission is also an important source of urban atmospheric heavy metal pollution other than coal-burning and iron and steel industries. Anthropogenic Hg, Cd, Cr and Pb emission increased significantly during the last few decades due to these unintentional emission sources.

Similar emission sources were assigned to PAHs.^{140,167} As evaluated by Xu *et al.*,¹⁴² domestic coal, firewood, and coking industries contributed 39.9%, 24.8%, and 17.6% of the PAH emission in China, respectively. As Lin *et al.*⁹⁷ indicated, traffic emission was determined as the primary source in the non-heating season, while coal combustion and biomass burning were the major sources in the heating season in Beijing. Secondary formation made a significant contribution to their derivatives (NPAHs and OPAHs) in the non-heating season, implying an impact of atmospheric transformation on PM_{2.5} toxicity. A similar result was obtained by Qin *et al.*⁹⁵ at Lake Small Baiyangdian. In the YRD, a potential source of PAHs was identified using diagnostic ratios of individual PAH compounds, and petroleum combustion was suggested a main source in Suzhou, Wuxi and Nantong,⁴² while in Shanghai, the major sources of PAHs were fossil fuel combustion, coal-burning, cement plants, wood combustion and industrial furnaces in the industrial area.⁹⁹ In Xi'an, a megacity in central China, biomass burning was recognized as the most dominant pollution source for PAHs, while vehicle emission and coal combustion were also important contributors.¹¹⁰ As evaluated by Zhang and Tao,¹⁶⁷ residential solid fuel combustion dominated the pattern of seasonal variation of airborne PAHs, while wild fires and open fire straw burning made a large contribution during the spring and summer.

E-waste dismantling activities were also identified as a typical source of airborne PTSs in China. Although these activities occurred scarcely in megacities, long-range transport may affect the PTS distribution in the adjacent areas. Our results^{32,79} in Taizhou indicated that the atmospheric levels of PCDD/Fs, PCBs, PBDEs and DP were higher than those in other urban sites in China. Deng *et al.*⁵⁶ also observed that, due to the

crude dismantling of e-wastes, the PCDD/F concentration in Guiyu was 1.5 times that of Guangzhou and 3.1 times that of Hong Kong sites in 2005. Significantly higher levels of PAHs were also obtained at e-waste sites than urban sites in south China.¹¹⁴ In addition, Han *et al.*⁴⁸ observed that the PCB level near an e-waste dismantling area was 54 times higher than that in a reference urban site. Wang *et al.*⁴⁹ indicated that the particulate PCB concentration at an abandoned e-waste recycling site was much lower than that with e-waste dismantling activities at the nearby village.⁵⁰ As evaluated by Wang *et al.*,¹⁶⁸ the health risks from PCBs for migrant workers in an e-waste recycling area were 3.8 times greater than those of local residents, which suggested severe influence of e-waste dismantling activities on human health.

In summary, unintentional emission from either industrial production or other anthropogenic activities could be an important contributor to airborne PTSs, especially PCDD/Fs, PAHs, PCBs, PBDEs and heavy metals. Even though many of the sources are located in the surrounding areas rather than the cities, airborne PTSs could undergo LRAT, and finally affect their distribution at the regional scale including megacities.

4. Conclusion and recommendations

With the rapidly expanding economic and industrial developments, China suffered from extensive air pollution in recent years. Although the API had a decreasing trend since the 2000s,⁸ severe impact of air pollution on human health has raised great concern currently, especially for inhalable fine particles. As a large group of environmental pollutants, PTSs showed adverse effects on both the ecosystem and public health. More and more studies are inclined to reveal their occurrence and potential impact in China. As summarized above, most studies on airborne PTSs have been conducted in east and south China, where the economy and industry are more developed. The results indicated more severe contamination of airborne PTSs in megacities with large populations in general, such as Guangzhou, Shanghai and Beijing. Some research studies revealed significantly positive correlations between airborne PTS concentrations and urban populations, suggesting a large consumption of chemical-containing products in megacities, such as HFRs^{58,59} and PFCs.⁷⁵ Many studies also observed evidently high levels of PTSs in their production areas, *e.g.*, HBCD,¹⁶⁹ DP^{77,170} and PFCs,⁷⁵ indicating an apparent emission during their industrial production. On the other hand, industrial activities lead to the unintentional emission of some PTSs, such as PCDD/Fs,^{19,20,127,128} PAHs,^{96,104,142,171} PCBs,^{126,128} PBDEs^{71,156} and heavy metals.^{145,162} The emission even tends to be responsible for the increase of some PTSs in Chinese air.^{163,164} Moreover, vehicle emission and e-waste dismantling activities have been confirmed as important contributors to air pollution in some specific areas, especially for airborne PTSs.^{35,48,50,63,145,151,165,166,168} These studies suggested that industrial production and product consumption are the major sources of most PTSs, while unintentional emission during anthropogenic activities is an important contributor to airborne PTSs.

The majority of studies indicated that heavier PTSs tend to be absorbed in the particle phase, and the sizes of suspended particles influence the distribution of airborne PTSs more than temperature and humidity.^{154,155} Furthermore, inhalable fine particles (*i.e.* PM_{2.5}) generally accumulated the most abundant organic pollutants rather than coarse aerosols, such as PCDD/Fs,^{24,25,158} PAHs,^{42,98,108,109} PBDEs^{65,71} and HBCD.¹⁵⁶ A similar distribution has been observed for heavy metals, with their predominant enrichment in fine particles.^{145,151} That is, fine particles may serve as a major carrier of most airborne PTSs, which facilitates the LRAT of PTSs, and therefore, increases the exposure risk of the human body to these pollutants.

In China, air pollution is characterized by fine particles (*i.e.* PM_{2.5}), which implies that fine particle may pose a serious threat to human health not only due to its concentration and chemical composition,¹⁷² but also the absorbed PTS. Although there is evidence to support the causal relationship between fine particles and some typical diseases, *e.g.*, lung cancer,^{10,173,174} limited data could be obtained associated with the relationship between particle-bound PTSs and human respiratory disease. It is expected that the environmental health effect of airborne PTSs will be a potential research hotspot in the near future. On the other hand, PTSs have caused concern due to increasing understanding of their toxicity and the potential risk to human health. A large number of studies have been conducted on PTSs associated with air pollution, which have revealed their temporal and spatial variation at the regional and national scales. However, it is inadequate that only a few studies demonstrated the distribution of novel PTSs across China, such as organophosphate flame retardants (OPFRs) and NBFRs, which gradually become the main force of commercial FRs in the world. Thus, special attention needs to be paid to these compounds in ambient air in future.

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References

- 1 M. H. Wong, F. W. K. Lee and M. K. F. Fung, in *Environmental Principles and Ethics*, WORLD SCIENTIFIC, 2012, pp. 109–122, DOI: 10.1142/9789812773340_0009.
- 2 M. Porta, *Environ. Sci. Pollut. Res.*, 2015, **22**, 14560–14565.
- 3 S. Wu, N. Sun, R. Lu, Y. Zhao and Z. Wang, *J. Environ. Manage.*, 2015, **7**, 21–28.
- 4 W. H. O. (WHO), 7 million premature deaths annually linked to air pollution, <http://www.who.int/mediacentre/news/releases/2014/air-pollution/en/>.
- 5 W. H. O. (WHO), Burden of disease from household and ambient air pollution for 2012, http://www.who.int/phe/health_topics/outdoorair/databases/AP_jointeffect_BoD_results_March2014.pdf.
- 6 G. Yang, Y. Wang, Y. Zeng, G. F. Gao, X. Liang, M. Zhou, X. Wan, S. Yu, Y. Jiang, M. Naghavi, T. Vos, H. Wang, A. D. Lopez and C. J. L. Murray, *Lancet*, 2013, **381**, 1987–2015.
- 7 R. A. Rohde and R. A. Muller, *PLoS One*, 2015, **10**, e0135749.
- 8 J. Bao, X. Yang, Z. Zhao, Z. Wang, C. Yu and X. Li, *Int. J. Environ. Res. Public Health*, 2015, **12**, 15875–15887.
- 9 m. o. e. p. (MEP), <MEP releases the 2015 Report on the State of the Environment in China.pdf>, http://english.sepa.gov.cn/News_service/news_release/201606/t20160603_353406.shtml.
- 10 L. H. Guo, *Natl. Sci. Rev.*, 2016, **3**, 412–413.
- 11 H. Wang, J. Gao, H. Li, H. Wang, Q. Li, S. Wang and F. Chai, *Res. J. Environ. Sci.*, 2016, **29**, 783–790.
- 12 H. Lin, T. Liu, J. Xiao, W. Zeng, X. Li, L. Guo, Y. Xu, Y. Zhang, M. G. Vaughn, E. J. Nelson, Z. Qian and W. Ma, *Atmos. Environ.*, 2016, **137**, 38–44.
- 13 L. K. Xue, T. Wang, J. Gao, A. J. Ding, X. H. Zhou, D. R. Blake, X. F. Wang, S. M. Saunders, S. J. Fan, H. C. Zuo, Q. Z. Zhang and W. X. Wang, *Atmos. Chem. Phys.*, 2014, **14**, 13175–13188.
- 14 J. Li, R. Wu, Y. Li, Y. Hao, S. Xie and L. Zeng, *Sci. Total Environ.*, 2016, **557–558**, 531–541.
- 15 J. Xing, S. X. Wang, S. Chatani, C. Y. Zhang, W. Wei, J. M. Hao, Z. Klimont, J. Cofala and M. Amann, *Atmos. Chem. Phys.*, 2011, **11**, 3119–3136.
- 16 L. Madaniyazi, T. Nagashima, Y. Guo, X. Pan and S. Tong, *Environ. Int.*, 2016, **92–93**, 165–172.
- 17 National Bureau of Statistics of China, *Urban Statistical Yearbook of China 2005*, China Statistics Press, Beijing, 2006.
- 18 Greenpeace, Ranking Eastern Chinese Cities by their “Clean Air” Actions, <http://www.greenpeace.org/eastasia/publications/reports/climate-energy/2012/ranking-cities-air-action/>, accessed April 7th, 2017.
- 19 G. J. Zheng, A. O. Leung, L. P. Jiao and M. H. Wong, *Environ. Int.*, 2008, **34**, 1050–1061.
- 20 G. R. Liu and M. H. Zheng, *Sci. Sin.: Chim.*, 2013, **43**, 265.
- 21 Y. Li, G. Jiang, Y. Wang, Z. Cai and Q. Zhang, *Atmos. Environ.*, 2008, **42**, 2037–2047.
- 22 Y. Li, T. Wang, P. Wang, L. Ding, X. Li, Y. Wang, Q. Zhang, A. Li and G. Jiang, *Environ. Sci. Technol.*, 2011, **45**, 3304–3309.
- 23 Z. G. Zhou, B. Zhao, L. Qi, P. J. Xu, Y. Ren, N. Li, S. Zheng, H. Zhao, S. Fan, T. Zhang, A. M. Liu, Y. R. Huang and L. Shen, *Aerosol Air Qual. Res.*, 2014, **14**, 1269–1278.
- 24 X. Zhang, Q. Q. Zhu, S. J. Dong, H. X. Zhang, X. K. Wang, M. Wang, L. R. Gao and M. H. Zheng, *Aerosol Air Qual. Res.*, 2015, **15**, 1933–1943.
- 25 X. Zhang, M. Zheng, Y. Liang, G. Liu, Q. Zhu, L. Gao, W. Liu, K. Xiao and X. Sun, *Sci. Total Environ.*, 2016, **573**, 876–882.
- 26 Z. Ren, B. Zhang, P. Lu, C. Li, L. Gao and M. Zheng, *J. Environ. Sci.*, 2011, **23**, 228–235.
- 27 S. Qin, X. Zhu, W. Wang, J. Chen, Y. Ni, X. Li, J. Mu, Q. Xu and K.-W. Schramm, *Chin. Sci. Bull.*, 2012, **57**, 3442–3451.

- 28 H. Li, J. Feng, G. Sheng, S. Lu, J. Fu, P. Peng and R. Man, *Chemosphere*, 2008, **70**, 576–583.
- 29 Q. Die, Z. Nie, F. Liu, Y. Tian, Y. Fang, H. Gao, S. Tian, J. He and Q. Huang, *Atmos. Environ.*, 2015, **119**, 220–227.
- 30 M. X. Xu, J. H. Yan, S. Y. Lu, X. D. Li, T. Chen, M. J. Ni, H. F. Dai, F. Wang and K. F. Cen, *Chemosphere*, 2009, **76**, 1540–1549.
- 31 J. Li, H. Dong, J. Sun, J. Nie, S. Zhang, J. Tang and Z. Chen, *Sci. Total Environ.*, 2016, **571**, 876–882.
- 32 Y. Li, G. Jiang, Y. Wang, T. Wang and Q. Zhang, *Sci. Bull.*, 2008, **53**, 521–528.
- 33 L. Yu, B. Mai, X. Meng, X. Bi, G. Sheng, J. Fu and P. A. Peng, *Atmos. Environ.*, 2006, **40**, 96–108.
- 34 M. Ren, P. A. Peng, S. Zhang, L. Yu, G. Zhang, B. Mai, G. Sheng and J. Fu, *Atmos. Environ.*, 2007, **41**, 592–605.
- 35 H. Li, L. Yu, G. Sheng, J. Fu and P. Peng, *Environ. Sci. Technol.*, 2007, **41**, 5641.
- 36 X. Xiao, J. Hu, P. Chen, D. Chen, W. Huang, P. Peng and M. Ren, *Environ. Toxicol. Chem.*, 2014, **33**, 500–507.
- 37 G. Liu, M. Zheng, G. Jiang, Z. Cai and Y. Wu, *TrAC, Trends Anal. Chem.*, 2013, **46**, 178–188.
- 38 F. M. Jaward, G. Zhang, J. J. Nam, A. J. Sweetman, J. P. Obbard, Y. Kobara and K. C. Jones, *Environ. Sci. Technol.*, 2005, **39**, 8638.
- 39 Z. Zhang, L. Liu, Y. F. Li, D. Wang, H. Jia, T. Harner, E. Sverko, X. Wan, D. Xu and N. Ren, *Environ. Sci. Technol.*, 2008, **42**, 6514–6518.
- 40 L. Chen, X. Peng, Y. Huang, Z. Xu, B. Mai, G. Sheng, J. Fu and X. Wang, *Arch. Environ. Contam. Toxicol.*, 2009, **57**, 437–446.
- 41 J. Pan, Y.-L. Yang, G. Zhang, J.-L. Shi, X.-H. Zhu, Y. Li and H.-Q. Yu, *Atmos. Environ.*, 2011, **45**, 3371–3380.
- 42 L. Zhang, T. Zhang, L. Dong, S. Shi, L. Zhou and Y. Huang, *Sci. Total Environ.*, 2013, **454–455**, 619–626.
- 43 L. Zhang, L. Dong, W. Yang, L. Zhou, S. Shi, X. Zhang, S. Niu, L. Li, Z. Wu and Y. Huang, *Environ. Pollut.*, 2013, **181**, 159–166.
- 44 Y. Tian, Z. Nie, J. He, Q. Die, Y. Fang, F. Liu, Y. Yang, X. Gao and Q. Huang, *Environ. Sci. Pollut. Res.*, 2016, **23**, 3376.
- 45 Y. Li, Q. Zhang, D. Ji, T. Wang, Y. Wang, P. Wang, L. Ding and G. Jiang, *Environ. Sci. Technol.*, 2009, **43**, 1030.
- 46 Y.-L. Yang, N. Gai, C.-Z. Geng, X.-H. Zhu, Y. Li, Y. Xue, H.-Q. Yu and K.-Y. Tan, *Atmos. Environ.*, 2013, **79**, 802–810.
- 47 G. Lammel, Y.-S. Ghim, A. Grados, H. Gao, H. Hühnerfuss and R. Lohmann, *Atmos. Environ.*, 2007, **41**, 452–464.
- 48 W. Han, J. Feng, Z. Gu, M. Wu, G. Sheng and J. Fu, *J. Environ. Sci.*, 2010, **22**, 589–597.
- 49 Y. Wang, X. Wu, M. Hou, H. Zhao, R. Chen, C. Luo and G. Zhang, *Sci. Total Environ.*, 2017, **578**, 34–39.
- 50 S. J. Chen, M. Tian, J. Zheng, Z. C. Zhu, Y. Luo, X. J. Luo and B. X. Mai, *Environ. Sci. Technol.*, 2014, **48**, 3847–3855.
- 51 J. Wu, M. Teng, L. Gao and M. Zheng, *Sci. Total Environ.*, 2011, **409**, 1818–1823.
- 52 X. Wang, P. Gong, T. Yao and K. C. Jones, *Environ. Sci. Technol.*, 2010, **44**, 2988–2993.
- 53 C. He, J. Jin, G. Li and Y. Wang, *Chemosphere*, 2016, **153**, 478–484.
- 54 K. H. Chi, *Aerosol Air Qual. Res.*, 2014, **14**, 1279–1291.
- 55 K. H. Chi, S. C. Hsu, S. H. Wang and M. B. Chang, *Sci. Total Environ.*, 2008, **401**, 100–108.
- 56 W. Deng, *J. Environ. Sci. Eng. B*, 2013, **2**, 319–331.
- 57 M. Yang, H. Qi, H. L. Jia, N. Q. Ren, Y. S. Ding, W. L. Ma, L. Y. Liu, H. Hung, E. Sverko and Y. F. Li, *Environ. Sci. Technol.*, 2013, **47**, 8978–8984.
- 58 Y. Zhao, J. Ma, X. Qiu, Y. Lin, Q. Yang and T. Zhu, *Environ. Sci. Technol.*, 2013, **47**, 8123–8129.
- 59 W.-L. Li, H. Qi, W.-L. Ma, L.-Y. Liu, Z. Zhang, M. O. A. Mohammed, W.-W. Song, Z. Zhang and Y.-F. Li, *Atmos. Environ.*, 2015, **117**, 156–161.
- 60 D. Liu, T. Lin, K. Shen, J. Li, Z. Yu and G. Zhang, *Environ. Sci. Technol.*, 2016, **50**, 9846–9854.
- 61 L. G. Chen, B. X. Mai, X. H. Bi, S. J. Chen, X. M. Wang, Y. Ran, X. J. Luo, G. Y. Sheng, J. M. Fu and E. Y. Zeng, *Environ. Sci. Technol.*, 2006, **40**, 1190.
- 62 T. Shi, S. J. Chen, X. J. Luo, X. L. Zhang, C. M. Tang, Y. Luo, Y. J. Ma, J. P. Wu, X. Z. Peng and B. X. Mai, *Chemosphere*, 2009, **74**, 910–916.
- 63 W. J. Deng, J. S. Zheng, X. H. Bi, J. M. Fu and M. H. Wong, *Environ. Int.*, 2007, **33**, 1063–1069.
- 64 D. Chen, X. Bi, M. Liu, B. Huang, G. Sheng and J. Fu, *Chemosphere*, 2011, **82**, 1246–1252.
- 65 W. Wang, J. Zheng, C.-Y. Chan, M.-j. Huang, K. C. Cheung and M. H. Wong, *Atmos. Environ.*, 2014, **89**, 786–796.
- 66 N. Ding, T. Wang, S. J. Chen, M. Yu, Z. C. Zhu, M. Tian, X. J. Luo and B. X. Mai, *Environ. Pollut.*, 2016, **212**, 457–463.
- 67 L. Zhang, L. Dong, Y. Huang, S. Shi, W. Yang and L. Zhou, *Chemosphere*, 2016, **150**, 438–444.
- 68 Z. Yu, R. Liao, H. Li, L. Mo, X. Zeng, G. Sheng and J. Fu, *Environ. Pollut.*, 2011, **159**, 2982–2988.
- 69 H. Li, L. Mo, Z. Yu, G. Sheng and J. Fu, *Environ. Pollut.*, 2012, **165**, 140–146.
- 70 J. Hu, J. Jin, Y. Wang, Z. Ma and W. Zheng, *Chemosphere*, 2011, **84**, 355–360.
- 71 Y. Dong, S. Fu, Y. Zhang, H. Nie and Z. Li, *Chemosphere*, 2015, **123**, 33–42.
- 72 M. Yang, H.-L. Jia, W.-L. Ma, H. Qi, S. Cui and Y.-F. Li, *Atmos. Environ.*, 2012, **55**, 73–79.
- 73 H. Qi, W. L. Li, L. Y. Liu, W. W. Song, W. L. Ma and Y. F. Li, *Sci. Total Environ.*, 2014, **491–492**, 60–66.
- 74 W. L. Li, L. Y. Liu, W. W. Song, Z. F. Zhang, L. N. Qiao, W. L. Ma and Y. F. Li, *Sci. Total Environ.*, 2016, **539**, 286–293.
- 75 J. Li, S. Del Vento, J. Schuster, G. Zhang, P. Chakraborty, Y. Kobara and K. C. Jones, *Environ. Sci. Technol.*, 2011, **45**, 7241–7248.
- 76 B. Liu, H. Zhang, D. Yao, J. Li, L. Xie, X. Wang, Y. Wang, G. Liu and B. Yang, *Chemosphere*, 2015, **138**, 511–518.
- 77 Q. Zhang, C. Zhu, H. Zhang, P. Wang, Y. Li, D. Ren and G. Jiang, *Sci. Bull.*, 2015, **60**, 792–797.
- 78 D. G. Wang, M. Yang, H. Qi, E. Sverko, W. L. Ma, Y. F. Li, M. Alaei, E. J. Reiner and L. Shen, *Environ. Sci. Technol.*, 2010, **44**, 6608–6613.
- 79 H. Sun, Y. Li, P. Wang, S. Zheng, J. Matsiko, D. Wang, W. Zhang, Y. Hao, Q. Zhang and G. Jiang, *Sci. China: Chem.*, 2016, **60**, 319–331.

- 80 X. Liu, G. Zhang, J. Li, L.-L. Yu, Y. Xu, X.-D. Li, Y. Kobara and K. C. Jones, *Environ. Sci. Technol.*, 2009, **43**, 1316–1321.
- 81 G. Wang, Y. Lu, J. Han, W. Luo, Y. Shi, T. Wang and Y. Sun, *Environ. Int.*, 2010, **36**, 122–130.
- 82 L. Zhang, Y. Huang, L. Dong, S. Shi, L. Zhou, T. Zhang, F. Mi, L. Zeng and D. Shao, *Arch. Environ. Contam. Toxicol.*, 2010, **61**, 159–165.
- 83 L. Zhang, Y. Huang, S. Shi, L. Zhou, T. Zhang, L. Dong and D. Shao, *Bull. Environ. Contam. Toxicol.*, 2010, **85**, 1–4.
- 84 X. Qiu, T. Zhu, J. Li, H. Pan, Q. Li, G. Miao and J. Gong, *Environ. Sci. Technol.*, 2004, **38**, 1368.
- 85 J. Li, G. Zhang, L. Guo, W. Xu, X. Li, C. S. L. Lee, A. Ding and T. Wang, *Atmos. Environ.*, 2007, **41**, 3889–3903.
- 86 Y. Wang, Q. Li, S. Wang, Y. Wang, C. Luo, J. Li and G. Zhang, *Atmos. Environ.*, 2015, **112**, 208–215.
- 87 J. Li, T. Zhu, F. Wang, X. H. Qiu and W. L. Lin, *Ecotoxicol. Environ. Saf.*, 2006, **63**, 33–41.
- 88 H. Xiao, S. Kang, Q. Zhang, W. Han, M. Loewen, F. Wong, H. Hung, Y. D. Lei and F. Wania, *J. Geophys. Res.: Atmos.*, 2010, **115**, 751–763.
- 89 J. Ren, X. Wang, Y. Xue, P. Gong, D. R. Joswiak, B. Xu and T. Yao, *Environ. Pollut.*, 2014, **194**, 210–216.
- 90 N. Zhu, K. W. Schramm, T. Wang, B. Henkelmann, X. Zheng, J. Fu, Y. Gao, Y. Wang and G. Jiang, *Environ. Pollut.*, 2014, **191**, 166–174.
- 91 P. Gong, X. P. Wang, J. J. Sheng and T. D. Yao, *Atmos. Environ.*, 2010, **44**, 2518–2523.
- 92 Y. Zhang, Y. Lin, J. Cai, Y. Liu, L. Hong, M. Qin, Y. Zhao, J. Ma, X. Wang, T. Zhu, X. Qiu and M. Zheng, *Sci. Total Environ.*, 2016, **565**, 994–1000.
- 93 W. L. Ma, D. Z. Sun, W. G. Shen, M. Yang, H. Qi, L. Y. Liu, J. M. Shen and Y. F. Li, *Environ. Pollut.*, 2011, **159**, 1794–1801.
- 94 Y. Gao, X. Guo, H. Ji, C. Li, H. Ding, M. Briki, L. Tang and Y. Zhang, *Atmos. Res.*, 2016, **178–179**, 6–16.
- 95 N. Qin, X. Z. Kong, Y. Zhu, W. He, Q. S. He, B. Yang, H. L. Ou-Yang, W. X. Liu, Q. M. Wang and F. L. Xu, *Sci. World J.*, 2012, **2012**, 416321.
- 96 W. Wang, N. Jariyasopit, J. Schrlau, Y. Jia, S. Tao, T. W. Yu, R. H. Dashwood, W. Zhang, X. Wang and S. L. Simonich, *Environ. Sci. Technol.*, 2011, **45**, 6887–6895.
- 97 Y. Lin, Y. Ma, X. Qiu, R. Li, Y. Fang, J. Wang, Y. Zhu and D. Hu, *J. Geophys. Res.: Atmos.*, 2015, **120**, 7219–7228.
- 98 W. Lu, L. Yang, J. Chen, X. Wang, H. Li, Y. Zhu, L. Wen, C. Xu, J. Zhang, T. Zhu and W. Wang, *Air Qual., Atmos. Health*, 2015, **9**, 823–833.
- 99 J. Cheng, T. Yuan, Q. Wu, W. Zhao, H. Xie, Y. Ma, J. Ma and W. Wang, *Water, Air, Soil Pollut.*, 2007, **183**, 437–446.
- 100 Q. Wang, K. Kobayashi, S. Lu, D. Nakajima, W. Wang, W. Zhang, K. Sekiguchi and M. Terasaki, *Environ. Pollut.*, 2016, **214**, 149–160.
- 101 Y. Liu, Y. Gao, N. Yu, C. Zhang, S. Wang, L. Ma, J. Zhao and R. Lohmann, *Chemosphere*, 2015, **134**, 52–59.
- 102 Q. Wang, M. Liu, Y. Yu and Y. Li, *Environ. Pollut.*, 2016, **218**, 118–128.
- 103 J. Liu, R. Man, S. Ma, J. Li, Q. Wu and J. Peng, *Mar. Pollut. Bull.*, 2015, **100**, 134–143.
- 104 S. Wei, B. Huang, M. Liu, X. Bi, Z. Ren, G. Sheng and J. Fu, *Atmos. Res.*, 2012, **109–110**, 76–83.
- 105 X. Bi, G. Sheng, P. A. Peng, Y. Chen, Z. Zhang and J. Fu, *Atmos. Environ.*, 2003, **37**, 289–298.
- 106 Y. Yang, P. Guo, Q. Zhang, D. Li, L. Zhao and D. Mu, *Sci. Total Environ.*, 2010, **408**, 2492–2500.
- 107 B. Huang, M. Liu, X. Bi, C. Chaemfa, Z. Ren, X. Wang, G. Sheng and J. Fu, *Atmos. Pollut. Res.*, 2014, **5**, 210–218.
- 108 X. Liu, L. Peng, H. Bai, L. Mu and C. Song, *Environ. Geochem. Health*, 2014, **36**, 531–542.
- 109 G. L. Shi, X. Y. Zhou, S. Y. Jiang, Y. Z. Tian, G. R. Liu, Y. C. Feng, G. Chen and Y. K. Liang, *Environ. Toxicol. Chem.*, 2015, **34**, 480–487.
- 110 J. Wang, S. S. Hang Ho, R. Huang, M. Gao, S. Liu, S. Zhao, J. Cao, G. Wang, Z. Shen and Y. Han, *Chemosphere*, 2016, **159**, 367–377.
- 111 Y. Wang, M. Xu, J. Jin, S. He, M. Li and Y. Sun, *Sci. Total Environ.*, 2014, **482–483**, 276–282.
- 112 H. Lu, S. S. Wang, Z. L. Wu, S. L. Yao, J. Y. Han, X. J. Tang and B. Q. Jiang, *Environ. Sci. Pollut. Res.*, 2017, **24**, 135–145.
- 113 Y. Q. Ren, B. H. Zhou, J. Tao, J. J. Cao, Z. S. Zhang, C. Wu, J. Y. Wang, J. J. Li, L. Zhang, Y. N. Han, L. Liu, C. Cao and G. H. Wang, *Atmos. Res.*, 2017, **183**, 322–330.
- 114 S. J. Chen, J. Wang, T. Wang, T. Wang, B. X. Mai and S. L. M. Simonich, *Sci. Total Environ.*, 2016, **573**, 115–122.
- 115 Y. Chen, J. Cao, J. Zhao, H. Xu, R. Arimoto, G. Wang, Y. Han, Z. Shen and G. Li, *Sci. Total Environ.*, 2014, **470–471**, 9–18.
- 116 C. Wang, X. Wang, P. Gong and T. Yao, *Environ. Pollut.*, 2014, **184**, 138–144.
- 117 X. Wang, P. Gong, J. Sheng, D. R. Joswiak and T. Yao, *Atmos. Environ.*, 2015, **115**, 124–131.
- 118 Y. C. Chen, H. C. Chiang, C. Y. Hsu, T. T. Yang, T. Y. Lin, M. J. Chen, N. T. Chen and Y. S. Wu, *Environ. Pollut.*, 2016, **218**, 372–382.
- 119 S. Liu, S. Tao, W. Liu, H. Dou, Y. Liu, J. Zhao, M. G. Little, Z. Tian, J. Wang, L. Wang and Y. Gao, *Environ. Pollut.*, 2008, **156**, 651–656.
- 120 W. Li, C. Wang, H. Wang, J. Chen, H. Shen, G. Shen, Y. Huang, R. Wang, B. Wang, Y. Zhang, H. Chen, Y. Chen, S. Su, N. Lin, J. Tang, Q. Li, X. Wang, J. Liu and S. Tao, *Environ. Pollut.*, 2014, **192**, 83–90.
- 121 J. Fu, T. Wang, P. Wang, G. Qu, Y. Wang, Q. Zhang, A. Zhang and G. Jiang, *Chemosphere*, 2012, **88**, 330–335.
- 122 J. I. Baker and R. A. Hites, *Environ. Sci. Technol.*, 2015, **33**, 2389–2393.
- 123 J. Castrojiménez, S. J. Eisenreich, M. Ghiani, G. Mariani, H. Skejo, G. Umlauf, J. Wollgast, J. M. Zaldívar, N. Berrojalbiz and H. I. Reuter, *Environ. Sci. Technol.*, 2010, **44**, 5456.
- 124 L. Morales, J. Dachs, B. Gonzalez-Gaya, G. Hernan, M. Abalos and E. Abad, *Environ. Sci. Technol.*, 2014, **48**, 10198–10207.
- 125 K. Breivik, A. Sweetman, J. M. Pacyna and K. C. Jones, *Sci. Total Environ.*, 2002, **290**, 296–307.
- 126 G. Liu, M. Zheng, M. Cai, Z. Nie, B. Zhang, W. Liu, B. Du, S. Dong, J. Hu and K. Xiao, *Chemosphere*, 2013, **90**, 2453–2460.

- 127 G. Liu, M. Zheng, W. Liu, C. Wang, B. Zhang, L. Gao, G. Su, K. Xiao and P. Lv, *Environ. Sci. Technol.*, 2009, **43**, 9196–9201.
- 128 Z. Nie, M. Zheng, W. Liu, B. Zhang, G. Liu, G. Su, P. Lv and K. Xiao, *Chemosphere*, 2011, **85**, 1707–1712.
- 129 R. A. Hites, *Environ. Sci. Technol.*, 2004, **38**, 945–956.
- 130 A. Covaci, S. Harrad, M. A. Abdallah, N. Ali, R. J. Law, D. Herzke and C. A. de Wit, *Environ. Int.*, 2011, **37**, 532–556.
- 131 L. Ahrens, *J. Environ. Monit.*, 2011, **13**, 20–31.
- 132 P. Zareitalabad, J. Siemens, M. Hamer and W. Amelung, *Chemosphere*, 2013, **91**, 725–732.
- 133 B. Boulanger, A. M. Peck, J. L. Schnoor and K. C. Hornbuckle, *Environ. Sci. Technol.*, 2005, **39**, 74–79.
- 134 J. Mühle, A. L. Ganesan, B. R. Miller, P. K. Salameh, C. M. Harth, B. R. Greally, M. Rigby, L. W. Porter, L. P. Steele and C. M. Trudinger, *Atmos. Chem. Phys.*, 2010, **10**, 5145–5164.
- 135 J. L. Barber, U. Berger, C. Chaemfa, S. Huber, A. Jahnke, C. Temme and K. C. Jones, *J. Environ. Monit.*, 2007, **9**, 530.
- 136 R. Bossi, K. Vorkamp and H. Skov, *Environ. Pollut.*, 2016, **217**, 4–10.
- 137 Y. W. Wang, J. J. Fu, T. Wang, L. Yong, Y. Y. Pan, Y. Cai and G. B. Jiang, *Environ. Sci. Technol.*, 2010, **44**, 8062–8067.
- 138 K. Breivik, R. Alcock, Y.-F. Li, R. E. Bailey, H. Fiedler and J. M. Pacyna, *Environ. Pollut.*, 2004, **128**, 3–16.
- 139 H. Hung, A. A. Katsoyiannis, E. Brorström-Lundén, K. Olafsdottir, W. Aas, K. Breivik, P. Bohlin-Nizzetto, A. Sigurdsson, H. Hakola and R. Bossi, *Environ. Pollut.*, 2016, **217**, 52–61.
- 140 K. H. Kim, S. A. Jahan, E. Kabir and R. J. Brown, *Environ. Int.*, 2013, **60**, 71–80.
- 141 L. H. Keith, *Polycyclic Aromat. Compd.*, 2015, **35**, 147–160.
- 142 S. Xu, W. Liu and S. Tao, *Environ. Sci. Technol.*, 2006, **40**, 702–708.
- 143 Y. Liu, S. Wang, R. Lohmann, N. Yu, C. Zhang, Y. Gao, J. Zhao and L. Ma, *Atmos. Environ.*, 2015, **107**, 129–136.
- 144 H. Chen, Y. Teng, S. Lu, Y. Wang and J. Wang, *Sci. Total Environ.*, 2015, **512–513**, 143–153.
- 145 J. Duan and J. Tan, *Atmos. Environ.*, 2013, **74**, 93–101.
- 146 J. Duan, J. Tan, J. Hao and F. Chai, *J. Environ. Sci.*, 2014, **26**, 189–196.
- 147 N. J. Schleicher, J. Schäfer, Y. Chen, G. Blanc, Y. Chen, F. Chai, K. Cen and S. Norra, *Atmos. Environ.*, 2016, **124**, 396–403.
- 148 J. Chen, M. Tan, Y. Li, J. Zheng, Y. Zhang, Z. Shan, G. Zhang and Y. Li, *J. Hazard. Mater.*, 2008, **156**, 36–43.
- 149 B. Bian, L. J. Zhou, L. Li, L. Lv and Y. M. Fan, *Environ. Sci. Pollut. Res.*, 2015, **22**, 7794–7807.
- 150 C. S. L. Lee, X. D. Li, G. Zhang, J. Li, A. J. Ding and T. Wang, *Atmos. Environ.*, 2007, **41**, 432–447.
- 151 C. L. Huang, L. J. Bao, P. Luo, Z. Y. Wang, S. M. Li and E. Y. Zeng, *J. Hazard. Mater.*, 2016, **317**, 449–456.
- 152 Y. Zhang, X. Ji, T. Ku, G. Li and N. Sang, *Environ. Pollut.*, 2016, **216**, 380–390.
- 153 R. Lohmann, T. Harner, G. O. Thomas and K. C. Jones, *Environ. Sci. Technol.*, 2014, **34**, 4943–4951.
- 154 O. Correa, H. Rifai, L. Raun, M. Suarez and L. Koenig, *Atmos. Environ.*, 2004, **38**, 6687–6699.
- 155 K. Martínez, E. Abad, L. Gustems, A. Manich, R. Gómez, X. Guinart, I. Hernández and J. Rivera, *Atmos. Environ.*, 2006, **40**, 567–573.
- 156 H. G. Ni, S. Y. Lu, T. Mo and H. Zeng, *Environ. Pollut.*, 2016, **214**, 70–76.
- 157 S.-J. Lee, H. Park, S.-D. Choi, J.-M. Lee and Y.-S. Chang, *Atmos. Environ.*, 2007, **41**, 5876–5886.
- 158 H. J. In and S. U. Park, *Atmos. Environ.*, 2003, **37**, 4625–4636.
- 159 M. Murakami and H. Takada, *Chemosphere*, 2008, **73**, 1172.
- 160 R. J. Law, D. Herzke, S. Harrad, S. Morris, P. Bersuder and C. R. Allchin, *Chemosphere*, 2008, **73**, 223–241.
- 161 P. Wang, Q. Zhang, H. Zhang, T. Wang, H. Sun, S. Zheng, Y. Li, Y. Liang and G. Jiang, *Environ. Int.*, 2016, **88**, 206–220.
- 162 K. Wang, H. Tian, S. Hua, C. Zhu, J. Gao, Y. Xue, J. Hao, Y. Wang and J. Zhou, *Sci. Total Environ.*, 2016, **559**, 7–14.
- 163 S. Cui, H. Qi, L.-Y. Liu, W.-W. Song, W.-L. Ma, H.-L. Jia, Y.-S. Ding and Y.-F. Li, *Atmos. Environ.*, 2013, **67**, 73–79.
- 164 S. Zhao, K. Breivik, G. Liu, M. Zheng, K. C. Jones and A. J. Sweetman, *Environ. Sci. Technol.*, 2017, **51**, 2838–2845.
- 165 H. Li, L. Zhou, M. Ren, G. Sheng, J. Fu and P. Peng, *Chemosphere*, 2014, **94**, 128–134.
- 166 H. Li, H. Liu, L. Mo, G. Sheng, J. Fu and P. A. Peng, *Environ. Sci. Pollut. Res.*, 2016, **23**, 10702–10713.
- 167 Y. Zhang and S. Tao, *Environ. Pollut.*, 2008, **156**, 657–663.
- 168 Y. Wang, J. Hu, W. Lin, N. Wang, C. Li, P. Luo, M. Z. Hashmi, W. Wang, X. Su, C. Chen, Y. Liu, R. Huang and C. Shen, *Environ. Int.*, 2016, **87**, 33–41.
- 169 G. Yu, Q. Bu, Z. Cao, X. Du, J. Xia, M. Wu and J. Huang, *Chemosphere*, 2016, **150**, 479–490.
- 170 H. Zhang, P. Wang, Y. Li, H. Shang, Y. Wang, T. Wang, Q. Zhang and G. Jiang, *Environ. Sci. Technol.*, 2013, **47**, 10567–10573.
- 171 D. Wu, Z. Wang, J. Chen, S. Kong, X. Fu, H. Deng, G. Shao and G. Wu, *Atmos. Res.*, 2014, **149**, 217–229.
- 172 A. F. Sarofim, J. S. Lighty and E. G. Eddings, *Fuel Chem.*, 2002, **47**, 618–621.
- 173 J. Lepeule, F. Laden, D. Dockery and J. Schwartz, *Environ. Health Perspect.*, 2012, **120**, 965–970.
- 174 T. Yorifuji and S. Kashima, *Lancet Oncol.*, 2013, **14**, 788.