



# Occurrence and profile of organophosphorus compounds in fine and coarse particulate matter from two urban areas of China and Pakistan<sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 24 April 2017

Received in revised form

4 August 2017

Accepted 27 September 2017

### Keywords:

Organophosphorus compounds

Flame retardants

Particulate matter

Seasonal variation

OPs distribution

## ABSTRACT

Seven organophosphorus compounds (OPs) were measured in urban fine and coarse particulate matter (PM) collected from two sites of Nanjing (XCNUC), China and Islamabad (APHSP), Pakistan. The fine PM mass at APHSP site was significantly higher ( $p = 0.005$ ) in the spring (mean  $22.5 \mu\text{g}/\text{m}^3$ ) than in the summer (mean  $12.7 \mu\text{g}/\text{m}^3$ ). The total concentration,  $\sum^7\text{OPs}$ , of samples collected at APHSP was found significantly higher in coarse (range  $672\text{--}47621 \text{ pg}/\text{m}^3$ ) than in fine PM (range  $1200\text{--}15213 \text{ pg}/\text{m}^3$ ); while  $\sum^7\text{OPs}$  from XCNUC in fine (range  $1696\text{--}15063 \text{ pg}/\text{m}^3$ ) and coarse PM (range  $2053\text{--}5379 \text{ pg}/\text{m}^3$ ) were statistically different in samples during summer, based on two-sample  $t$ -test at 0.05 confidence interval. Seasonally,  $\sum^7\text{OPs}$  was found to be higher in the samples of Nanjing ( $9510 \pm 3633 \text{ pg}/\text{m}^3$ ) in the summer than in the spring. In contrast, the samples of Islamabad had higher  $\sum^7\text{OPs}$  ( $25558 \pm 16255 \text{ pg}/\text{m}^3$ ) in the spring than in the summer. Tri(chloropropyl) phosphate (TCEP) was found at higher concentration than any other OPs in the samples from the XCNUC site. Triphenyl phosphate (TPHP) was found at extremely high levels from APHSP, which may attributed to its use in jet fuel. Most of the  $\sum\text{OPs}$  concentrations were found significantly different in both PMs at both sites due to their diverse sources. Both sites showed strong correlation of  $\sum\text{OPs}$  with TCEP in both PMs, indicating similar mode of transfer from sources like plastics, lacquer, paint, glue, industrial processes and foam fillers. Relative abundance of OPs in fine and coarse PM differs amongst OP congeners and concerning seasons, with these variations attributed to different mechanisms of mass transfer such as volatilization, condensation and abrasions. Moreover, triphenylphosphine oxide (TPPO) has been reported in outdoor PMs. This is the first study on the occurrence of OPs in atmospheric fine and coarse PM and their seasonal variation from Pakistan and China.

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## 1. Introduction

Human exposure to complex Semi-Volatile Organic Compounds (SVOCs) is a ubiquitous issue in the modern era. Among the SVOCs, organophosphorus compounds (OPs) are commonly used as flame retardants and plasticizers, as well as anti-foaming agent, stabilizers, and wetting agents in products such as floor polishes, hydraulic liquids, paints, lubricants, textiles, and a variety of plastic

materials (van der Veen and de Boer, 2012; Wei et al., 2015). As additives, OPs are not chemically bonded but simply mixed with the bulk raw material, so they are easily released into the environment via abrasion and volatilization processes during product use (Cao et al., 2014a; Kemmlein et al., 2003). OPs have been found in high concentrations in indoor dust (Faiz et al., 2016).

The phase distribution of organic pollutants in the environment has critical impact on the pathways of human exposure to these chemicals (Cao et al., 2014a). In ambient air, many OPs are mainly associated with airborne particulate matter (PM), and gas phase fractions are relatively minor (Liu et al., 2014; Möller et al., 2011; Salamova et al., 2014). This implies that OPs could be shielded from photolytic degradation thus are atmospherically persistent

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and therefore could transport over medium to long-distances (Möller et al., 2012). PM is an important part of atmospheric environment that concerns air pollution. Transportation has been one of the major contributors to PM emissions (Moss et al., 2010; Yan et al., 2011). PM is the most harmful pollutant from vehicles (Yan et al., 2014), railway locomotives and aircrafts (Masiol and Harrison, 2014). Various contaminants have been effectively associated with PM. Consequently, it poses serious health concerns for all possible human exposures (Faiz et al., 2016). In addition, it has been established that the PM size is a crucial factor in the distribution of organic pollutants not only between gas and particle phases but also among particle size fractions (Cao et al., 2012; Ruby and Lowney, 2012). For instance, OPs distribution in different size fractions of air particulates was found to be related to their vapor pressures and other physicochemical properties (Yang et al., 2014). However, PM size specific data are extremely scarce for atmospheric OPs.

Quite a few studies have been conducted on seasonal variations of atmospheric OPs (Möller et al., 2012; Ohura et al., 2006; Salamova et al., 2014). The concentrations of  $\Sigma$ OP have been found generally higher in the summer due to higher temperatures (Salamova et al., 2014). Therefore, reporting these OPs bound to suspended particulates and their seasonal variations in outdoors from these regions is required (OR, 2015), especially during hot seasons (Wei et al., 2015). Moreover, seasonal variations in OPs concentration would lead to better understand the extent of fluctuations in the ultimate estimation of doses through inhalation, dermal and ingestion exposures throughout the year (OR, 2015). The objective of the present study was to evaluate the levels and seasonal profiles (spring and summer) of OPs in outdoor fine and coarse PM collected from the urban areas of China and Pakistan. This is the first comprehensive report on the occurrence and seasonal variations in atmospheric OP concentrations in fine and coarse PM from China and Pakistan, although OPs have been reported in a few microenvironments of Pakistan (Ali et al., 2013). Moreover, triphenylphosphine oxide (TPPO) has been reported in wastewater effluent (Rodil et al., 2012), rivers (Wang et al., 2015) and indoor air (Faiz et al., 2016), but this is the first study of the existence of TPPO in outdoor PM. If TPPO is used as flame retardants in indoor artifacts (Hu et al., 2009), it may result in its presence outdoors. Therefore, TPPO was also investigated as its occurrence in outdoor PM has not been reported so far. The current study provides comparison of the two urban sites from different countries.

## 2. Materials and method

### 2.1. Sampling

A total of 88 PM samples, including 52 (fine PM = 26; coarse PM = 26) from the Pakistan site and 36 (fine PM = 18; coarse PM = 18) from China site were collected. At both sites, active air sampling (AAS) was conducted on average for 24-h periods.

The first site (N32° 7, E118° 57) was located in the city of Nanjing in China. It is a Xianlin Campus of Nanjing University which is located in the urban area of Nanjing city, China (denoted as XCNUC, Fig. S1, Supporting information). Nanjing has a population of >3,600,000 and a variety of industries like cars, electronics, petrochemicals, rubber & plastic, fire-fighting equipment and other related industries. Sampling took place during the spring (March and April 2014) and the summer (July and August 2014), on the roof of the School of the Environment building, ~18 m above ground level.

The second site (N33° 35, E73° 07) was located at the junction of twin cities of Rawalpindi/Islamabad in Pakistan (Fig. S2). It is a densely populated urban site impacted by different type of

emission sources including chemical, pharmaceutical, textile industries and an international airport. The site is located in a housing society called the Airport Housing Society near Benazir Bhutto International Airport (denoted as APHSP, Fig. S2). The sampling spot is located about 2 km away from the Airport, and approximately 500 m away from both heavy vehicular traffic road (Islamabad Expressway) and railway tracks. From February 2012 to August 2012, on the roof of domestic building, ~15 m above ground level.

Gent stacked filter unit (SFU) sampler was operated at flow rate 16 L/min using 47 mm diameter Nuclepore polycarbonate filter to collect fine PM (0.4  $\mu$ m pore size) and coarse PM (8  $\mu$ m pore size) samples. Sampling procedures were quite similar in both sites. Further details of sampling procedures were described in our earlier work (Waheed et al., 2012).

Before and after sampling, the filters were enclosed with aluminum foil, sealed in an airtight glass container and placed in a fridge overnight to be conditioned (4° C and 40% relative humidity) for steady weight measurements. Each filter was weighed before and after the sampling three times and the average value of three weight measurements was used. The mass of PM was determined gravimetrically as the difference in weight of each filter before and after sampling. The loaded filters from the Pakistani site along with some blank filters were transported by air in a hand carry to the School of the Environment, Nanjing University for the analysis of OPs.

### 2.2. Laboratory analyses

Chemical standards for all seven targeted OPs (Table 1) were acquired from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Tri-*n*-butyl- $d_{27}$ -phosphate (TnBP- $d_{27}$ ) and tri-phenyl- $d_{15}$ -phosphate (TPHP- $d_{15}$ ) were obtained from Cambridge Isotope Laboratories (Andover, USA) and used as surrogates. Internal standard used was 2,3,3',4,4',5-hexachlorobiphenyl- $d_3$  (PCB-156- $d_3$ ), acquired from Sigma-Aldrich (Germany). HPLC grade solvents such as ethyl acetate, toluene and cyclohexane were obtained from Merck (Darmstadt, Germany). Solid phase extraction cartridges (1.0 g/6 ml Florisil cartridge, Sep-Pak<sup>®</sup>, Waters, USA) were used for sample cleaning. TSQ Quantum GC-EI-MS/MS (Thermo Scientific, USA) equipped with DB-5 column (15 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m film thickness, J&W Scientific, USA) was used for analysis. Final residue extract was prepared in 500  $\mu$ l in toluene containing 25 ng of internal standard PCB-156- $d_3$  for instrument analysis.

### 2.3. Quality assurance/quality control (QA/QC)

Detailed procedures of pre-treatment, extraction, purification, instrumental analysis, and QA/QC have been published in our earlier work (Faiz et al., 2016). Concisely, two surrogates (TnBP- $d_{27}$  and TPHP- $d_{15}$ , 100 ng) were spiked to each filter before sample extraction. Internal standard (PCB-156- $d_3$ , 25 ng) was used to improve precision and accuracy of results. Instrument limit of detection (iLOD) was defined as the lowest amount of a target that was detectable by the instrument (Table S1). Method detection limit (MDL) was specified as three times SD of blank samples plus the mean of the corresponding blanks of compounds (Table S1). Average procedural blank levels of OPs are given in Table S2. The sample concentrations more than the MDL were measured and blank corrected by subtracting the average blanks from the sample values of each compound. The spiked laboratory control samples ( $n = 7$ , added at 50 ng/sample) showed relative standard deviation (RSD) of <20.0% for all OPs. Average recoveries of OPs were in the range of 87.0–109% and those of the surrogates, TPHP- $d_{15}$  & TnBP- $d_{27}$ , were 83% & 118%, respectively.

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