Environmental Pollution xxx (2016) 1–11

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Evaluating spatial distribution and seasonal variation of phthalates using passive air sampling in southern India[☆]

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ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form
26 November 2016
Accepted 2 December 2016
Available online xxx

Keywords:
Air pollution
Phthalates
Passive air sampling
GC-MS
Human exposure assessment
India

ABSTRACT

Usage of phthalates as plasticizers has resulted in worldwide occurrence and is becoming a serious concern to human health and environment. However, studies on phthalates in Indian atmosphere are lacking. Therefore, we studied the spatio-temporal trends of six major phthalates in Tamil Nadu, southern India, using passive air samplers. Phthalates were ubiquitously detected in all the samples and the average total phthalates found in decreasing order is pre-monsoon (61 ng m^{-3}) > summer (52 ng m^{-3}) > monsoon (17 ng m^{-3}). Largely used phthalates, dibutylphthalate (DBP) and diethylhexlphthalate (DEHP) were predominantly found in all the seasons with contribution of 11–31% and 59–68%, respectively. The highest total phthalates was observed in summer at an urban location (836 ng m^{-3}). Furthermore, through principal component analysis, potential sources were identified as emissions from additives of plasticizers in the polymer industry and the productions of adhesives, building materials and vinyl flooring. Although inhalation exposure of infants was higher than other population segments (toddlers, children and adults), exposure levels were found to be safe for people belonging to all ages based on reference dose (RfD) and tolerable daily intake (TDI) values. This study first attempted to report seasonal trend based on atmospheric monitoring using passive air sampling technique and exposure risk together.

1. Introduction

Phthalates are also known as phthalic acid esters, which are widely used as catalysts in manufacturing plasticizers. They are also used as additives in about 80–85% of the consumer products in the plasticizer market, such as cosmetics, shampoos, soaps, lubricants, pesticides and paints (Lenoir et al., 2012; Guo and Kannan, 2013). High-molecular-weight phthalates (C_7–C_{11}) are primarily used as plasticizers in polyvinyl chlorides (PVCs), whereas low-molecular-weight phthalates (C_3–C_6) are widely used in consumer products such as toys, adhesives, building material, personal-care products, electronics and medical devices (Jonsson et al., 2003) (SI Table 1). Global phthalates production was estimated as 4.9 million tons per annum during 2010, which accounts for 84% of the total plasticizers produced. The consumption of phthalates was highest in Asia (52%), whereas in Europe, North America, Latin America and rest of the world it was found to be 18%, 13%, 6% and 11%, respectively (Cullen, 2012). Further China was found to be the highest consumer (38%) of plasticizer in the global market whereas rest of the Asian countries collectively consumed 21%, followed by Western Europe (16.0%) and North America (about 13%). This heavy demand for plasticizers in the Asia-Pacific region was due to the growing industrial sectors.

Phthalates are not chemically bonded to the polymer matrix, so they can easily enter into different environmental matrices (Bošnir et al., 2003). Hence, they were ubiquitously found in air (Xie et al., 2005, 2007; Teil et al., 2006; Wang et al., 2008; Fu et al., 2010; Kong et al., 2013), airborne particulate matter $PM_{2.5}$ and PM_{10} (Ma et al., 2014), surface waters (Latini, 2005; Sánchez-Avila et al., 2012; Zhang et al., 2012) and sediment (Fromme et al., 2002; Zeng

☆ This paper has been recommended for acceptance by Dr. Hageman Kimberly Jill.
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http://dx.doi.org/10.1016/j.envpol.2016.12.003
0269-7491/

et al., 2008; Srivastava et al., 2010). The phthalates in atmosphere are subjected to photo-degradation with a half-life of about 28 days (Stales et al., 1997). Nevertheless, they shall associate with gas or particulate phase to undergo long-range transport and eventually enters the food chain (FEA, 2007). Among them, low-molecular-weight (LMW) phthalates like diethyl phthalate are more bio-accumulative than high-molecular-weight (HMW) phthalates (Stales et al., 1997) (SI Table 1).

Phthalates, as a result of wider application and inclusion in both industrial processes and consumer products, were sometimes detected in indoor (home and occupation) air and dust (Wensing et al., 2005; Tran and Kannan, 2015), at levels several hundreds of nanogram m^{-3} which were higher than the outdoor environment (Fu et al., 2010; Kong et al., 2013). These compounds prevail in the atmosphere either in gas phase and/or associated with particulate matter which has the capacity to enter and penetrate into the respiratory system and cause health effects (Salgueiro-González et al., 2015). Moreover, inhalation is considered as the major route of exposure next to dietary/oral intake.

The implications of air pollution on human health can be mild to severe, leading to lung cancer. In order to protect human health, world health organization (WHO) has classified the constituents of outdoor air into different categories (WHO, 2013). According to Lyche et al. (2009), phthalates are highly considered for its reproductive and developmental toxicity. Among the six presently studied phthalates designated as priority pollutants by USEPA, DEHP has been classified as carcinogen (class B2), butylbenzylphthalate (BBP) as possible carcinogen (class C), whereas due to lack of evidences DBP, diethylphthalate (DEP) and dimethylphthalate (DMP) were placed under class D (not yet classified as a human carcinogen) by the USEPA (Alatriste-Mondragon et al., 2003).

As a result of wide exposure, phthalates and their metabolites have also been detected in human body fluids such as amniotic fluid (Silva et al., 2004a), saliva (Silva et al., 2004b), breast milk, cord blood and urine (Silva et al., 2005; Högberg et al., 2008). A study by Guo et al. (2011), reported phthalates and their metabolites in urine samples collected from seven Asian countries with highest median concentration in Kuwait (1050 ng mL^{-1}) followed by India (389 ng mL^{-1}). Since phthalates are high in Indian population, in order to understand the scenario, awareness on examining phthalates exposure through food and environment has gained momentum. To fill the existing knowledge gap, Das et al. (2014) analyzed phthalates in Indian food items and reported adult daily intake of DMP, DEP, DBP, BBP, and DEHP as 37, 52, 38, 36, and 70 $\mu g\ kg^{-1}\ day^{-1}$, respectively. Further, they also identified that the exposure was higher than in some of the developed countries (European Union, Japan, Germany and USA) and China. Apart from food products, phthalates were also found in river water and bottled water up to 1640 (Selvaraj et al., 2015) and 7820 ng L^{-1} (Selvaraj et al., 2016), respectively. However, information regarding atmospheric exposure is scanty and therefore our investigation will help to evaluate the risks associated with inhalation of phthalates.

Volatile/semi-volatile organic contaminants in air are generally studied using active and passive sampling techniques. However, passive air samplers were used frequently due to its simplicity, cost-effectiveness, easy installation and operation without power source (Zhang et al., 2008; Net et al., 2015 and references there in). In order to trap the contaminants, the passive air sampling is done by using any one of the following, viz. polyurethane foam (PUF), XAD-Resin, semipermeable membrane devices and solid-phase extraction (SPE) disks/cartridges. Soxhlet and sonication are the common methods for extracting contaminants from the aforesaid sampling media and cleanup of extracts with sorbents (silica, florisil, alumina, etc.) is optional. Finally, analysis was mostly performed on instruments based on gas chromatography coupled to mass spectrometry (GC-MS and GC-MS/MS), whereas in rare cases liquid chromatography based instrument such as LC-MS and LC-MS/MS were also used (Xie and Ebinghaus, 2008; Net et al., 2015).

Recently, Saini et al. (2015) optimized passive air samplers for monitoring phthalates. Tran and Kannan (2015) reported phthalates in particulate and vapor phase (using PUF) of indoor air in Albany, USA. In India, phthalates in outdoor aerosols were reported from New Delhi (Li et al., 2014) and Chennai (Tamil Nadu) (Fu et al., 2010) only, using high volume air sampler. Therefore, to our knowledge no study has been performed to understand phthalate distribution at a regional scale in India.

Considering the above knowledge gap, an investigation was designed to (1) elucidate the spatial distribution and seasonal variation of phthalates in the atmosphere of Tamil Nadu along different transects like urban, suburban, coastal and agricultural; (2) ascertain the possible sources of phthalates, using principal component analysis (PCA); and (3) estimate the human inhalation exposure to phthalates from the atmospheric air of Tamil Nadu, India, and establish a baseline data.

2. Materials and methods

2.1. Study area and air sampling

The selected study area, Tamil Nadu (TN), has many significant features for being considered for this monitoring. Presently, TN is the sixth largest populous state with a population density of 555 persons per sq. km. The province is also one among the largest emerging economy in India with the second highest contribution (8.4%) for the Indian GDP (Silicon India, 2015). Four major Tier II cities in TN (Coimbatore, Salem, Tiruchirappalli and Madurai) contribute about 50% of its (State) economy's growth share (Taneja, 2016).

While considering the air pollution report of WHO (2016) based on the $PM_{2.5}$ levels, India houses 10 of the 20 most polluted cities in world. Further, the cities, Chennai, Tiruchirappalli and Coimbatore in TN ranked 314, 370 and 410, respectively (Gautham, 2016). Also, it is estimated that the ambient air pollution in India accounts for 3% of the total national burden of disease and are responsible for more than half a million (627 000) deaths (IHME, 2013; Balakrishnan et al., 2015), annually. Moreover, in Chennai where 33% of days showed severe to very poor air quality index during the first half of 2015, the air quality index was worse than in the country's capital, New Delhi (National, 2015). Meanwhile, the vehicle population is also increasing in TN with 10% growth in 2015–2016 (Government of Tamil Nadu, 2016).

Chennai, the capital of TN is the fourth-largest metropolitan city in India. The city extends over 1180 km^2, with a population of 4.6 million (Census of India, 2011), and it has more than 1400 small- to large-size industries. The major groups of industries are electronic, rubber, plastic manufacturing, petroleum processing, metal product manufacturing, etc. Coimbatore, the second-largest city in TN, is well known for its textile and iron foundry activities. Tiruchirappalli is the fourth-largest city in the state, famous for pilgrimage tourism, and it also houses more than 300-odd metal-fabricating industries, where about 1.5 lakhs tons of steel are being processed annually. The selected coastal locations, Pichavaram, Parangipettai and Muthupet, are small coastal towns situated on the southeast coast of India (Fig. 1).

Therefore, in order to understand the status of pollutants in air from Tamil Nadu, passive air samplers (PAS) were deployed at 31 urban, suburban, coastal and agricultural sites comprising locations at Chennai, Coimbatore, Tiruchirappalli, Muthupet, Parangipetai and Pichavaram (Fig. 1, SI Table 2 [Supplementary data]) during April 2009–January 2010. Sampling was performed during three