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Atmospheric fate of phthalate esters in an urban area (Paris-France)

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Abstract

The atmospheric fate of six phthalate esters was investigated in the urban area of Paris (France). Total atmospheric levels (ng m^{-3}) were as follows: DMP, 0.5; DEP, 10.7; DnBP, 22.2; BBP, 4.6; DEHP, 18.9; and DnOP, 0.5 ng m^{-3}, showing a predominance of DnBP and next, DEHP. They are mainly present in the vapour phase, from 93.8% to 64.9%, particularly for the esters with alkyl chain length of less than six C. An inverse correlation was found between the vapour phase concentrations and the molecular weight and also a direct correlation between the vapour phase concentrations and the log [vapour pressure] of the compounds. Seasonal variations were displayed by principal component analysis (PCA), due to significant correlation between phthalate concentrations and air temperature. Rain water concentrations (ng L^{-1}) were as follows: DMP, 116; DEP, 333; DnBP, 592; BBP, 81; DEHP, 423; and DnOP, 10. PCA analysis showed a seasonal variation of these concentrations correlated to the air temperature. The experimental water/air scavenging ratio was calculated and was in accordance with the theoretical one obtained from the vapour pressure and the Henry's law constant for each phthalate ester. The global trend was a decrease of the washout coefficient in relation with the rise of alkyl chain length. Yearly balances for rainwater and bulk deposition allowed the estimation of dry deposits that represented about half of total. Our findings highlight the major part played by particles in atmospheric deposition processes.

Keywords: Phthalate esters; Atmosphere; Bulk deposition; Rain water; Physico-chemical parameters

1. Introduction

Phthalate esters are produced in extremely large volumes and are represented in the different compartments of our environment to which they are released during their manufacture, utilization and waste disposal. They are widely used, particularly in plastic matter industry, as important additives which impart flexibility to polyvinylchloride resins (PVC) and also to other polymers such as polyethylene terephthalate (PET), polyvinyl acetates, cellulosics and polyurethanes (Staples et al., 1997). Plasticizers are present in building materials, home furnishings, clothing, food packaging. Di-*n*-butyl phthalate (DnBP) is used in epoxy resins, cellulose esters and special adhesive formulations. Dimethyl phthalate (DMP) and diethyl

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phthalate (DEP) are present in cellulose ester-based plastics such as cellulose acetate and butyrate. Di(2-ethylhexyl)phthalate (DEHP) is found in medical disposals and in a number of medicine coatings.

Their world production increased from 1.8 million tons in 1975 to 3 million tons in 2001, the quarter being represented by the DEHP (Hervé-Bazin et al., 2001). In 1997, European consumptions were 500 to 600 thousand tons per year for DEHP, 20 to 50 thousand tons per year for butylbenzyl phthalate (BBP) and DnBP, and lastly, 10 to 20 thousands tons per year for DMP plus DEP (Harris et al., 1997).

Besides, the worldwide yearly production of PVC averages 20 million tons. It is needed for packaging (15%) and for construction materials (>50%). The PVC waste amounts were estimated to 4.1 million tons in 1999 and a rise of that waste is likely to occur (up to 30% in 2010 and 80% in 2020). Consequently, the environmental contamination level will be enhanced, as phthalates are the main additives used in plastic industry. At the present time, they are detected in different compartments of the environment at concentrations ranging from 0.3 to 77 ng m^{-3} in the atmosphere, from 0.3 to 98 μg L^{-1} in surface water, from 0.2 to 8.4 mg kg^{-1} dw in sediment and from 28 to 154 mg kg^{-1} dw in sewage sludge (Giam et al., 1978; Staples et al., 1997; Fromme et al., 2002).

Since the 1990s, these compounds have been suspected to be involved in endocrine disruption such as anti-oestrogen effects, especially in Rodents (Sultan et al., 2001) and also in carcinogenic processes and mutagen induction (Moore et al., 2002). Particularly, the DEHP was listed among the 33 hazardous substances in water, by the European community (Decision no. 2455/2001/CE of November 20, 2001). Moreover, a scientific committee on toxicity, ecotoxicity and the environment (CSTEE) of the European Commission on Health and Consumer Protection was delivered on the human risk assessment of DEHP, in January 2002. Consumer exposure to DEHP may arise from toys and child-care articles, building materials and home furnishing, car interiors, clothing and via medical devices and food contact materials (CSTEE, 2002). The DEHP exposure was estimated from the biomonitoring data based on urinary metabolites (5MEHP, 5OH-MEHP and 5oxo-MEHP). Recently, a no adverse effect level (NOAEL) of 4.8 mg kg^{-1} bw/day for testicular toxicity was determined from a three-generation reproductive study in rats (CSTEE, 2004).

Their opportunity of being released into the environment may occur by the manufacturing steps and by leaching from final products. After their service life, the phthalate containing products may be landfilled. A study in Germany showed that more than 90% of total phthalates present in household waste materials collected from waste managements was represented by DEHP, the main PVC plasticizer (Bauer and Herrmann, 1997).

After entering the atmospheric compartment, phthalate esters are redistributed between gas and particle phases and removal mechanisms such as oxidative or photolytic reactions may occur, followed by wet and dry deposition processes. Both volatilization and deposition occur simultaneously and their balance is determined by different factors such as wind speed, temperature and physico-chemical properties of the compounds: vapour pressure, water pressure and water solubility (Staples et al., 1997). In bulk deposition, phthlate esters originate both from wet processes and dry settling. During precipitation, pollutants may be removed from air by: (1) rain-in which is a dissolving of vapour compounds in cloud aerosols; (2) washout, corresponding to raindrops formation when clouds turn to precipitation which also washes down atmospheric particles (Gill and Graedel, 1983). In order to estimate deposition due to atmospheric loadings, it appeared essential to consider both wet and dry depositions.

Atmospheric contamination is a very important issue and a number of international organizations and programmes are currently involved in its assessment (UNEP: United Nations Environment Programme, IMO: International maritime organisation ECE-EMEP: European Monitoring and Evaluation Programme of the Economic Commission for Europe, OSPAR: Convention for the Protection of the Marine Environment of the North-East Atlantic, IADN Integrated Atmospheric Deposition Network). Atmospheric levels of phthalates represent an actual exposure hazard by inhalation as shown by similarities between diesters distribution in indoor air and human urines with prevailing DEP and DnBP (Rudel et al., 2003).

Our study was performed over a 1-year period, in urban area (Paris-France). First, we estimated the atmospheric levels of six phthalate esters and their