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Determination of selected organophosphate esters in the aquatic environment of Austria

Elena Martínez-Carballo, Carmen González-Barreiro,
Andrea Sitka, Sigrid Scharf, Oliver Gans *

Department of Organic Analysis, Umweltbundesamt GmbH (Austrian Federal Environment Agency), Spittelauer Lände 5, A-1090, Vienna, Austria

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Abstract

Organophosphate esters are used in multitude of applications such as flame retardants, plasticizers and lubricants. In recent years concerns have been raised in regards to the environmental impact of some of the more commonly used phosphoric acid triesters, because many of them are toxic and persistent. Liquid–liquid extraction and ultrasound-assisted solvent extraction followed by liquid chromatography coupled to tandem mass spectrometry detection (LC−MS/MS) were used for the determination of nine priority organophosphate esters in waste and surface water, as well as in sediment samples for first time in Austria. Recoveries ranged from 63% to 94% in water and from 74 to 104% in sediment with estimated quantification limits between 2.6 and 7.9 ng/l in surface water, 4.1 and 13 ng/l in effluent waste water, and between 0.48 and 11 μg/kg in sediment. The validated method was applied to determine the occurrence of the selected organophosphorus flame retardants (OPFRs) and plasticizers in the aquatic environment of Austria. The impact of the discharge of waste water treatment plants into the receiving water bodies was also studied.

Keywords: Organophosphate esters; Organophosphorus flame retardants; Plasticizers; Effluent water; Surface water; Sediment; Liquid chromatography–tandem mass spectrometry

1. Introduction

Organophosphate esters have been used since decades as flame retardants and plasticizers due to their technical characteristics.

According to the European Flame Retardant Association (EFRA), flame retardants are additives that can be added or applied as a treatment to organic materials such as plastics, textiles and timber. Alternatively, they can be used during the production process as a chemical modifier of some plastic materials (EFRA, 2006). In essence, they are compounds which, when integrated into or coated over the surface of a fibre or material, will provide a flame retardant barrier and so protect against fire.

Fire continues to be a major cause of death, injury and property loss around the world. Flame retardants supply the most effective method available of protecting a wide range of materials including textiles, cables, building materials and insulation, electrical equipment, wood and timber products, lighting, toys, etc.

Global demand for flame retardants is forecasted to grow 4.4% per year to 2.1 million metric tons in 2009. Growth will be largely driven by gains in developing

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* Corresponding author. Organische Analytik/Organic Analysis, Umweltbundesamt GmbH, Spittelauer Lände 5, 1090 Vienna, Austria. Tel.: +43 1 313 04 / 5212; fax: +43 1 313 04 / 5222.

E-mail address: oliver.gans@umweltbundesamt.at (O. Gans).

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countries in Asia (in particular, China), Latin America and Eastern Europe (Green, 2003).

However, many of them are toxic and have been directly linked to health problems; thus, their benefits must be weighed against exposure to chemicals that are potentially harmful to human health and the environment. For example, triphenyl phosphate (TPP) and tributyl phosphate (*n*-isomer: T*n*BP), are suspected to be neurotoxic (WHO, 1991a,b), while others like *tris*-(2-chloroethyl)phosphate (TCEP), *tris*-(1,3-dichloro*iso*propyl) phosphate (TDCP) and *tris*-(2-chloro*iso*propyl)phosphate (TCPP) are carcinogenic for animals (Mattews et al., 1990; European Commission, 2001).

Several previous studies have demonstrated that the discharge of treated waste water into the receiving rivers is an important source of organophosphate esters in the aquatic environment (Meyer and Bester, 2004; Marklund et al., 2005b; Rodil et al., 2005; Rodríguez et al., 2006) and, therefore, it is crucial to obtain information about the concentration levels of these substances in such environmental aqueous matrixes. Nevertheless, their occurrence in surface water has been reported in the literature only in few studies from Germany (Fries and Püttmann, 2001; Fries and Püttmann, 2003; Andresen et al., 2004) during this decade. In USA they were determined together with numerous organic pollutants (Kolpin et al., 2002; Glassmeyer et al., 2005). So far, little is known about their presence in sediment samples (Kawagoshi et al., 1999). Comparable data for Austria are not yet supplied.

The current trend in the analysis of these compounds in water environmental compartments shows the use of liquid–liquid extraction (LLE) (Andresen et al., 2004; Marklund et al., 2005a,b; Andresen and Bester, 2006), solid-phase extraction (SPE) (Fries and Püttmann, 2001, 2003; Meyer and Bester, 2004; Rodil et al., 2005; Quintana et al., 2006), and, more recently, solid-phase microextraction (SPME) (Rodríguez et al., 2006) or membrane-assisted solvent extraction (MAE) (Quintana and Reemtsma, 2006), followed, in general, by gas chromatography–mass spectrometry (GC−MS) (Fries and Püttmann, 2001, 2003; Andresen et al., 2004; Meyer and Bester, 2004) or gas chromatography-nitrogen phosphorus detection (Marklund et al., 2005a,b; Rodríguez et al., 2006) and, in less extension, by liquid chromatography–tandem mass spectrometry (LC−MS/MS) (Rodil et al., 2005; Quintana and Reemtsma, 2006; Quintana et al., 2006).

The purposes of this work were to develop reliable analytical methods to evaluate 9 priority OPFRs and plasticizers for first time in the aquatic environment of Austria (i.e. waste water, river water and sediment samples). The impact of the discharge of waste water treatment plants into the receiving water bodies is studied. Furthermore, the distribution of the selected analytes between the water and solid (sediment) phases is shown. The analytical methods are based on LLE for water samples, ultrasound-assisted solvent extraction for sediment samples and liquid chromatography coupled to tandem electrospray mass spectrometry (LC−ESI−MS/MS) for identification of the analytes.

2. Experimental

2.1. Chemicals and standards

Tris-(2-butoxyethyl)phosphate (TBEP, 94%), *tris*-(2-chloroethyl)phosphate (TCEP, >97%), tributyl phosphate (TBP, >99%), triphenyl phosphate (TPhP, >99%), triethyl phosphate (TEP, >99%) and tritolyl phosphate (TCP, >90%) (technical mixture of isomers) were obtained from Sigma-Aldrich (Vienna, Austria). *Tris*-(1,3-dichloro-2-propyl)phosphate (TDCP, >98.5%) and *tris*-(2-ethylhexyl)phosphate (TEHP, >99%) were purchased by Fluka (Vienna, Austria). *Tris*-(2-chloropropyl) phosphate (TCPP, >99.5%) was delivered by Dr. Ehrenstorfer (Augsburg, Germany) and the surrogate TBP-d_{27} (98–99%) was supplied by Cambridge Isotope Laboratories (Andover, MA, USA).

All organic solvents used for sample preparation were residue analysis grade or better. HPLC grade solvents were used for work related to liquid chromatography.

Individual stock solutions (10,000 mg/l) of the analytes were prepared in acetonitrile (ACN). Standard solutions were stored at −20 °C in amber vials and were freshly prepared every 3 months. Working standard mixtures of 1 mg/l were prepared in ACN by dilution from the stocks and stored at 4 °C. These mixed standards were used for fortification in recovery experiments and for preparation of calibration standards.

2.2. Cleaning and pre-treatment of laboratory glassware

Due to organophosphate esters are common indoor air pollutants, all glassware was cleaned with acetone and baked at 250 °C for at least 10 h before its use.

2.3. Sampling

Sixteen grab samples of effluents from different municipal waste water treatment plants (WWTPs) as well as 4 water and 4 sediment samples from 3 Austrian rivers were collected in summer 2005.

Water samples were collected and stored in sampling bottles (aluminium 1.2 l; Bürkle, Germany). Many