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Phthalate occurrence in rivers and tap water from central Spain

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HIGHLIGHTS

- Phthalates were detected in river and tap water from Central Spain for first time.
- DBP was the major contributor to overall pollution in both rivers and tap water.
- DEHP was not found in both river and tap water because it is the most regulated.
- Phthalate concentration found does not represent an oestrogenic risk for organism.
- The risk assessment suggests a risk of phthalates in tap water acceptable.

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ABSTRACT

The aim of this study is to evaluate the presence and concentrations of the main phthalates in water from the Jarama and Manzanares rivers in the region of Madrid (RM, Central Spain), the most densely populated region of Spain, and to determine the possible oestrogenic activity based on found phthalate concentration. The presence of phthalates in major supply drinking water areas of the RM was also analysed, thus allowing a preliminary assessment of the health risks resulting from the concentrations obtained. The results of this study show the presence of the three (dimethyl phthalate (DMP), diethyl phthalate (DEP) di-n-butyl phthalate (DBP)) of five phthalates studied (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-(2-ethylhexyl) phthalate (DEHP), benzyl-butyl phthalate (BBP) and di-n-butyl phthalate (DBP)). The DBP was found in both river and tap water samplers, whereas DMP and DEP were found in only drinking water samples. The DBP was found to make the highest average contribution to pollution in both river and tap water. The DEHP was not found in both the river and tap water because it is one of the most regulated phthalates. The highest phthalate contamination was found in the Manzanares river and in those areas that receive treated water from the Tagus river. The phthalates found in river and tap water in the RM do not represent a potential oestrogenic risk for the aquatic environment or humans. A preliminary risk assessment suggested that the risk of exposure to phthalates from tap water in this study is acceptable, although continuous monitoring of the presence of these substances in both drinking and river water should be undertaken to detect possible increases in their concentrations. This is the first study to analyse the presence of phthalates in both rivers and drinking water of the centre of Spain.

1. Introduction

Endocrine disruptors (EDs) are chemical substances present in the environment that interfere with the normal function of the endocrine system in living beings and also produce an adverse effect in the organism or its offspring (Olea et al., 2002; Kim et al., 2007; Watanabe et al., 2007; Weiss, 2012; Plotan et al., 2013). Effects associated with these compounds, such as reduced fertility, feminisation, reproductive organ abnormalities or altered sexual behaviour, have been observed in mammals, fishes and benthonic organisms, etc. (Rivas et al., 2004). Interference with human male and female reproductive systems, where they provoke a series of disorders that may appear throughout an individual's life, including sexual precocity, hormone-related cancers (such as testicular and breast or ovarian cancer), reproductive tract

Abbreviations: BBP, butyl-benzyl phthalate; BW, body weight; CR, contact rate; DBP, di-n-butyl phthalate; DEHP, di-(2-ethylhexyl) phthalate; DEP, diethyl phthalate; DMP, dimethyl phthalate; DWSP, drinking water sampling point; DWTP, drinking water treatment plant; EC_{50}, effective concentration; ED, endocrine disruptor; EEQ, oestradiol equivalent; EF, exposure frequency; EI, exposure index; E2 equiv., relative oestrogenicity factor; E2, 17-β-Oestradiol; HQ, hazard quotient; LOD, limit of detection; RfD, reference dose; RM, region of Madrid; RSP, river sampling point; NE, north-east; NW, north-west; WWTP, wastewater treatment plant.

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abnormalities and infertility in males or endometriosis-related sterility in females, has also been observed (Rivas et al., 2004; Diamanti-Kandarakis et al., 2009). Moreover, some scientific articles published over the past few years have suggested that EDs may be implicated in the incidence of various metabolic disorders, including obesity and diabetes (Diamanti-Kandarakis et al., 2009).

The European Union has identified 553 substances that are able to alter the endocrine system, including dioxins, furans, polychlorinated biphenyls, surfactants (alkyl phenols), pesticides, herbicides, bactericides (parabens) or plasticisers (phthalates or bisphenol A), and has classified 194 of these in category 1 (clear evidence for endocrine disrupting effects in an intact organism) (ENC.D.4/ETU/2005/0028r) (European Commission, 2007). Some of these were already included in the list of priority hazardous substances in water (Directive, 2013/39/UE) (European Parliament and the Council, 2013), or are subject to review for subsequent inclusion (such as di-(2-ethylhexyl) phthalate (DEHP)). Although significant progress has been made in regulating such substances, many of them, such as the majority of chemical substances classified in the group of phthalates, are not even recorded on this list.

Phthalates (phthalic acid esters) are used to improve the plasticity of industrial polymers, thus meaning that they are commonly found in a wide range of products, such as food packaging, toys, paints or internal PVC coatings, construction materials, personal care articles and cosmetics (for example nail varnish), electronic and medical devices and paediatric articles (such as bags for intravenous fluids, breathing masks or umbilical catheters), among many others (Calafat et al., 2004; Kimber and Dearmen, 2010; Mankidy et al., 2013).

As a result of their widespread use by the general population, and as they are a common waste product of industrial activity (Kimber and Dearmen, 2010), phthalates do not need to be persistent to be found in the environment, thus meaning that they are continually present (Olea et al., 2002). In 1999 the European Union attempted to ban the use of six phthalates (di-(2-ethylhexyl) phthalate (DEHP), butylbenzyl phthalate (BBP), di-n-butyl phthalate (DBP), di-isononyl phthalate (DINP), di-isodecyl phthalate (DIDP) and din-octyl phthalate (DNOP)) in toys and paediatric articles that could be introduced into the mouth of children younger than three years of age (Decision 1999/815/EC of the Commission in the framework of Directive 92/59/EEC of the Council), although it was not until 2005 that the sale and use of phthalates in such articles was finally banned (Directive 2005/84/EC) (European Parliament and the Council, 2005). The European Union has recently considered DEHP to be a priority hazardous substance (Directive, 2013/39/UE) (European Parliament and the Council, 2013) and the USA, which had already catalogued it as such, has established a maximum allowable concentration in continental surface waters of 1.3 μg/L. Also the WHO guideline for DEHP in drinking water (WHO/SDE/WSH/03.04/68) and the USEPA (US EPA, 2012) has established a maximum allowable concentration in drinking water of 8 μg/L and 6 μg/L respectively above which the well-being of aquatic organisms and human health may be endangered.

There are very few studies concerning the presence of phthalates in water. Some international studies have detected these compounds in wastewater (Olujimi et al., 2012), river water (He et al., 2011; Zhang et al., 2011; Tang et al., 2012; Liu et al., 2013), seawater (Martí et al., 2011) and even in sediments (Bastos et al., 2012), and they have occasionally been detected in drinking water (Al-Saleh et al., 2011; Amiridou and Voutsa, 2011; Tang et al., 2012; Dévier et al., 2013; Blanchard et al., 2013). In the few studies published in Spain, phthalates have been analysed in wastewater, seawater and sediments (Chaler et al., 2004; Bartolomé et al., 2005; Sánchez-Avila et al., 2009; Sánchez-Avila et al., 2011; Sánchez-Avila et al., 2012), as well as in river and drinking water (tap or bottled) (Regueiro et al., 2008; Sánchez-Avila et al., 2011; Bono-Blay et al., 2012; Sánchez-Avila et al., 2012), with most such studies concentrating on the NE Mediterranean region. None of the aforementioned studies have analysed the presence of phthalates in rivers in central Spain, which have a heavy pollutant burden due to the fact that this is the most densely populated region in the country with significant industrial activity (INE base, 2012).

The aim of this study is to evaluate the presence and concentration of the main phthalates in water samples from Jarama and Manzanares rivers (central Spain); and to determine the possible oestrogenic activity based on found phthalate concentration. Likewise, the presence of phthalates in the main drinking water supply areas for the Region of Madrid (RM) will also be analysed; and the risk quotients were calculated in order to estimate possible health risk through consumption of phthalates from drinking water.

2. Materials and methods

2.1. Description of the sampling location

With a surface area of only 8028 km^2 (1.6% of Spain as a whole), the Region of Madrid (RM) is the Spanish region with the third highest number of inhabitants (6,498,560). This number represents 14% of the entire Spanish population. As a result, this region is the most densely populated in Spain, and Madrid is one of the most densely populated cities in Europe (676 inhabitants per km^2). Around 50% of the population is concentrated in the urban agglomeration of the city of Madrid (3,233,527 inhabitants), with a further 23% living in the towns in the metropolitan area (1,496,379 inhabitants). Moreover, the region has a mean industrial production index of 75% (mean for 2012), which is very close to the national value of 77% (INE base, 2012), thereby reflecting the large number of industries located in the centre of the region (Fig. 1).

2.1.1. River water sampling

A single sampling, in which samples were collected at 100 m from the discharge points of the seven main WWTPs in the RM, was selected on the basis of their equivalent population and nearby industry. The WWTPs selected discharge into the main rivers of the RM, namely the Manzanares, which crosses the city of Madrid (RSP-1, RSP-5, RSP-6 and RSP-7), and the Jarama (RSP-2, RSP-3 and RSP-4), which passes through the SE of the region (Fig. 1; Table S1). The sampling was performed in the third week of February 2012 because in this month the maximum flow rate for both rivers is recorded (a peak flow rate of (T = 3.95 years): 85 m^3/ s for the Manzanares River and a peak flow rate of (T = 3.95 years): 138 m^3/s for the Jarama river) (Spanish Hydrological Plan of the Tagus River Basin (2009–2015 Planning Cycle)). Mornings were cold but sunny, with temperatures near 5 °C, and afternoons were much warmer, with temperatures near 20 °C. Samples were collected from 9 am to 5 pm in pre-rinsed opaque bottles phthalate-free (500 mL) and were stored frozen for subsequent transport and analysis.

2.1.2. Drinking water sampling

A one-off composite sampling is one in which seven samples were collected from the main drinking water supply areas in the RM. Samples were collected from taps in private residences (Fig. 2; Table S2). The sampling was conducted in the second week of December 2012. Being indoors temperatures are around 22 °C. These samples were collected from 8 am to 12 pm (150 mL every 8 h) in pre-rinsed opaque bottles phthalate-free (500 mL). 60 μL of sodium thiosulfate with a concentration of 0.75 g/mL was added to each sample to block the chlorine typically contained in drinking water and prevent it from interfering with the analysis. They were stored frozen for subsequent transport and analysis.

2.2. Analytical method

The analytical method is based on that described by Bono-Blay et al. (2012) and was performed by the external laboratory IDEA-CSIC.