Journal of Environmental Management 204 (2017) 50–60

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Detection of bisphenol A, cumylphenol and parabens in surface waters of Greater Poland Voivodeship

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ARTICLE INFO

Article history:
Received 31 March 2017
Received in revised form
18 August 2017
Accepted 22 August 2017
Available online 29 August 2017

Keywords:
Bisphenol A
Cumylphenol
Paraben
River
Lake
LC-MS/MS

ABSTRACT

Amounts of bisphenol A (BPA), 4-cumylphenol (CP) and 5 parabens – methylparaben (MP), ethylparaben (EP), propylparaben (PP), butylparaben (BP) and benzylparaben (BzP) in Greater Poland Voivodeship's surface waters are reported. The water samples were collected from selected 15 locations in 2015–2016 at seven different time points: in March, June, August, and October 2015 and March, June, and September 2016. MP was found in every tested sample with typical concentration at several dozen nanograms per liter and the highest level almost 1600 ng L^{-1} in a sample collected from the Warta River in October 2015. The other four parabens were determined at considerably lower concentrations than MP at levels not exceeding 100 ng L^{-1} with PP found at the highest and BzP at the lowest levels. BPA was determined at similar concentration level to parabens – between 5 ng L^{-1} and 95 ng L^{-1} and CP was found only in a limited number of samples. Noticeable seasonal changes of paraben concentrations were found showing that for these compounds the pollutant release factor dominates both the biodegradation factor and the water volume factor. These seasonal changes were not observed for BPA and CP. Out of all determined parabens only MP was found at considerably higher concentrations than BPA. However, MP's endocrine properties are much lower than those of BPA posing a lower environmental impact potential than BPA. Influence of other (more endocrine disrupting) parabens is also relatively weak in comparison to BPA due to their considerably lower concentrations in the environment.

1. Introduction

Progress of human civilization in the last two centuries was connected with very fast industrialization and growing production of many products including thousands of chemicals. As a result many toxic compounds were released to the environment. Therefore, its protection became of utmost importance to save plants, animals and humans. Worldwide concern about the environment led to ban on usage of some toxic compounds in the second half of the 20th century. However, apart from toxicity another important aspect of chemicals was found to play a very important role in the last years – their endocrine disrupting properties. It was proved that among many compounds widely used for years some were able to mimic hormones or block their activity. Therefore, endocrine disrupting compounds can negatively influence living organisms even at very low concentrations (Diamanti-Kandarakis et al., 2009; Schug et al., 2011).

Among different endocrine disrupting (ED) compounds bisphenol A (BPA) is one of the most widely studied because of its influence on many organisms and widespread usage. BPA is an analogue of estrogen which can interact with its receptor and affect the reproductive behavior (Bonefeld-Jørgensen et al., 2007; Matsushima et al., 2007; Krishnan et al., 1993) and it was found in human blood, breast milk, amniotic fluid and placental tissue (Vandenberg et al., 2007). BPA has also showed low estrogenic activity confirmed by *in vitro* proliferation of MCF-7 human breast cancer cells (Perez et al., 1998). Meanwhile, a structurally similar compound 4-cumylphenol (CP) was less extensively studied even though it has about 12 times higher estrogenic activity than BPA (Terasaki et al., 2005).

Abbreviations: BPA, bisphenol A; CP, 4-cumylphenol; MP, methylparaben; EP, ethylparaben; PP, propylparaben; BP, butylparaben; BzP, benzylparaben; ED, endocrine disruptor; PC, polycarbonate.

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http://dx.doi.org/10.1016/j.jenvman.2017.08.034
0301-4797/

BPA is one of the highest production volume chemicals delivered worldwide at the level of three million tons per year (Zhang et al., 2013). It is used mostly to produce polycarbonate (PC) plastics and as a precursor to manufacturing monomers of epoxy resins (SUBSPORT – bisphenol A, 2013). It is also a material used in medical devices like implants or tubing so concerns about releasing BPA during everyday use are noticeable (Usman and Ahmad, 2016; Darbre, 2015; SCENIHR, 2015). CP is used mainly in production of PC plastics, surfactants, fungicides and preservatives (Chiha et al., 2011). These compounds have been regulated or banned in many countries but they are still in use in large amounts e.g. in China, as well as in other Asian countries (Wang et al., 2012).

Annual production of bisphenol A is estimated to a few millions tonnes (SUBSPORT – bisphenol A, 2013; Geueke, 2014). Human exposure to BPA is connected mostly to its usage in food packaging. BPA can leach from the protective internal layer of epoxy resin of canned food or from polycarbonate bottles and storage containers. However, absorption through skin is also important e.g. by contact with sales strips made of thermal paper (SUBSPORT – bisphenol A, 2013; Geueke, 2014). Some reports suggest that diet and thermal paper are equally responsible for human internal exposure (SCENIHR, 2015). Moreover, it was found that in many countries almost entire human population i.e. between 91% and 99% has detectable BPA in their urine (SCENIHR, 2015; Calafat et al., 2005).

Parabens are esters of *p*-hydroxybenzoic acid. These compounds just like BPA and CP have been used for decades. They include methylparaben (MP), ethylparaben (EP), propylparaben (PP), butylparaben (BP), benzylparaben (BzP) and other esters of *p*-hydroxybenzoic acid which are mostly used as preservatives in cosmetics (like lotions or sunscreens), pharmaceuticals or in a limited range in food products. These compounds are widely used because of their low price and broad antimicrobial properties (Liao et al., 2013). The antimicrobial effect rises with increasing length of the ester chain group and simultaneous decrease of solubility in water (Błędzka et al., 2014; Andersen, 2008). Parabens were found to influence endocrine system and gained much attention although, apart from publications presenting their endocrine disrupting properties (Routledge et al., 1998; Miller et al., 2001; Okubo et al., 2001) readers can find papers describing their safety (Golden et al., 2005; Pugazhendhi et al., 2007). However, there is also some evidence that parabens may increase the risk of cancer (especially breast cancer) due to the fact that they were found in breast tumor cells (Harvey and Darbre, 2004; Darbre et al., 2004; Shanmugam et al., 2010). As endocrine disruptors parabens were measured in male urine to relate their levels to infertility and semen quality. No evidence was found for connection between concentrations of parabens and quality of semen or hormone levels, however butylparaben was associated with sperm DNA damage (Meeker et al., 2011). Also estrogenic activity of parabens is much lower in comparison to natural hormones. Routledge et al. (1998) compared activity of different parabens with that of 17β-estradiol. It was dependent on alkyl chain length with MP, EP, PP and BP being 2,500,000-fold, 150,000-fold, 30,000-fold and 10,000-fold less potent than 17β-estradiol, respectively. Similar results were found by Miller et al. (2001) with potencies of parabens relative to 17β-estradiol equal to 1/3,000,000, 1/200,000, 1/30,000, 1/8000 and 1/4000 for MP, EP, PP, BP and BzP, respectively.

As a result of many concerns and studies the European Union set allowable concentration of parabens in cosmetics. For MP and EP the limit of 0.4% as acid was set and for the sum of PP and BP as acids it is 0.19%. The sum of parabens is limited to 0.8% level as acid (Regulation, 2009; Commission Regulation, 2014). Other parabens including benzylparaben, isopropylparaben, isobutylparaben and pentylparaben were banned (Commission Regulation, 2014). Nevertheless, demand for parabens is still very high. According to the European Chemical Substances Information System annual production of MP is between 1000 and 10,000 tonnes, whereas the demand for EP and PP is lower and their production is 10–1000 tonnes per year. BP is delivered at less than 10 tonnes per year (SUBSPORT – parabens, 2013). As a result of their widespread usage parabens can be found in surface water, sediment, sludge from waste water treatment plants or living organisms (Liao et al., 2013). There is a growing number of research studies and published results on this emerging group of environmental contaminants but are more focused on new analytical procedures about paraben determination. Furthermore, most of these publications show one time-point observations and a simplified view of the problem. Thus, little is known about the magnitude of endocrine disruptor contamination of surface waters all over the world.

In our previous study (Zgoła-Grześkowiak et al., 2016) on parabens it was found that their concentrations in the environment depended on sampling time. Higher contamination in the summer season suggested more intensive usage of cosmetics (including sunscreens and antiperspirants) in that time. However, the study contained results only from 3 time points that could allow us to hypothesize on seasonal changes in concentrations of parabens. Therefore, it was decided to continue the studies for a longer period of time to test our hypothesis.

The aim of the study was to detect the amount of BPA, CP and 5 parabens in Wielkopolska Voivodeship's surface water samples using liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) detection. The results gathered from the 18-month long study will help in assessment of concentration ranges in surface waters of the European country after introduction of law regulations on parabens. It will be also possible to check if seasonal changes in concentrations are present. Moreover, comparison of concentrations calculated for parabens with these obtained for BPA and CP will enable to assess the risk connected with the use of parabens.

2. Materials and methods

2.1. Chemicals

Standards of methylparaben, ethylparaben, propylparaben, butylparaben, benzylparaben, bisphenol A, 4-cumylphenol, bisphenol A - d_{16}, and methylparaben - $^{13}C_6$, purchased from Sigma-Aldrich (St. Louis, MO, USA) were all at least 99% purity each. The MS-grade acetonitrile and methanol were from POCh (Gliwice, Poland). Ammonium acetate used as mobile phase additive was purchased from Sigma-Aldrich. The HPLC-grade water was prepared by reverse osmosis in a Demiwa system from Watek (Ledec nad Sazavou, Czech Republic), followed by double distillation from a quartz apparatus.

2.2. Sample collection and handling

The water samples were collected from rivers and lakes in Wielkopolska Voivodeship, Poland. The collection of water samples from selected 15 locations was done in 2015–2016 at seven different time points: in March, June, August, and October 2015 and March, June, and September 2016. Locations of sampling points are presented in Fig. 1. The lakes are located: in the Lake District of Poznań (Lusowskie, Śremskie, Pamiątkowskie and Bytyńskie), the Września Plain (Bnińskie) and the Lake District of Gniezno (Wierzbiczańskie) that is 5–70 km from Poznań – the capital city of Wielkopolska Voivodeship (population 550,000). No sewage disposal is present in this area. The Samica Stęszewska (Krosinko