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Recycling of plastic waste: Presence of phthalates in plastics from households and industry

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ABSTRACT

Plastics recycling has the potential to substitute virgin plastics partially as a source of raw materials in plastic product manufacturing. Plastic as a material may contain a variety of chemicals, some potentially hazardous. Phthalates, for instance, are a group of chemicals produced in large volumes and are commonly used as plasticisers in plastics manufacturing. Potential impacts on human health require restricted use in selected applications and a need for the closer monitoring of potential sources of human exposure. Although the presence of phthalates in a variety of plastics has been recognised, the influence of plastic recycling on phthalate content has been hypothesised but not well documented. In the present work we analysed selected phthalates (DMP, DEP, DPP, DiBP, DBP, BBzP, DEHP, DCHP and DnOP) in samples of waste plastics as well as recycled and virgin plastics. DBP, DiBP and DEHP had the highest frequency of detection in the samples analysed, with 360 μg/g, 460 μg/g and 2700 μg/g as the maximum measured concentrations, respectively. Among other, statistical analysis of the analytical results suggested that phthalates were potentially added in the later stages of plastic product manufacturing (labelling, gluing, etc.) and were not removed following recycling of household waste plastics. Furthermore, DEHP was identified as a potential indicator for phthalate contamination of plastics. Close monitoring of plastics intended for phthalates-sensitive applications is recommended if recycled plastics are to be used as raw material in production.

1. Introduction

Plastics are some of the most important materials for sustaining society and our current way of living (Andrady and Neal, 2009). Unfortunately, they are also associated with substantial environmental issues, as they are based primarily on non-renewable raw materials (e.g. oil), are commonly used in short-lived products (e.g. food packaging) and, once discarded, are predominantly landfilled or incinerated (Thompson et al., 2009). If not disposed of properly, waste plastics can end up in the oceans, thereby creating another environmental issue of growing concern (Jambeck et al., 2015). To tackle some of these issues, plastics recycling has been promoted within the European Union (EU). Recently proposed amendments to the directives on waste (EC, 2015a) and packaging waste (EC, 2015b) require 65% of municipal and 75% of packaging waste, including plastics, to be recycled by 2030. Nevertheless, the recycling of waste plastic is challenging due to heterogeneity of the material (e.g. polyethylene (PE), high-density polyethylene (HDPE), and polystyrene (PS)) and its chemical composition (Ignatyev et al., 2014).

Chemical composition can vary based on the plastic type (e.g. PE) or the intended use of such a product. Moreover, many hazardous chemicals can be potentially present in plastics, including phthalic acid esters, polycyclic aromatic hydrocarbons (PAHs), potentially toxic metals, etc. (NEA, 2013) Phthalic acid ethers, commonly known as 'phthalates', make up a group of industrial chemicals with high global production volumes. Phthalates are mostly used as plasticisers in plastics production, with polyvinyl chloride (PVC) incorporating the largest share of the market (Markarian, 2007). Although alternatives are available

Abbreviations: BBzP, butyl benzyl phthalate (CAS 85-68-7); DBP, dibutyl phthalate (CAS 84-74-2); DCHP, dicyclohexyl phthalate (CAS 84-61-7); DEHP, diethylhexyl phthalate (CAS 117-81-7); DEP, diethyl phthalate (CAS 84-66-2); DiBP, di-*iso*-butyl phthalate (CAS 84-69-5); DMP, dimethyl phthalate (CAS 131-11-3); DnOP, di-n-octylphthalate (CAS 117-84-0); DPP, dipropyl phthalate (CAS 131-16-8); HDPE, high-density polyethylene; HMW, high molecular weight; LOD, limit of detection; LWM, low molecular weight; MANOVA, multivariate analysis of variance; PE, polyethylene; PET, polyethylene terephthalate; PS, polystyrene; PVC, polyvinyl chloride; RHP, recycled household plastics; RIP, recycled industrial plastics; RWP, residual waste plastics; SSWP, source-segregated waste plastics; VP, virgin plastics.

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(Krauskopf, 2003; Markarian, 2007), phthalates still accounted for 70% of the plasticiser market in 2014, and they are forecast to account for 65% in 2019 (IHS, 2015). Phthalates can be divided into low molecular weight (LMW) and high molecular weight (HMW), whereby the former are used predominantly as solvents and in adhesives, waxes, inks, cosmetics, insecticides and pharmaceuticals, while HMW phthalates are produced in higher volumes and are used in construction materials, clothing, children's toys and household furnishing (BCERC, 2007). These two groups are commonly distinguished according to the alkyl group carbon chain length (R, Fig. 1). Examples of LMW (C_4—C_8) phthalates are diethyl phthalate (DEP), dibutyl phthalate (DBP), di-*iso*-butyl phthalate (DiBP) and diethylhexyl phthalate (DEHP), whereas diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), diundecyl phthalate (DUP) and ditridecyl phthalate (DTDP) are commonly referred to as HMW (C_9—C_{13}).

Growing concern about phthalates is related to their toxicity, in particular to their endocrine-disrupting activity (Matsumoto et al., 2008). Studies suggest that human exposure to e.g. DEHP may lead to serious effects on reproduction and development (Caldwell, 2012; Heudorf et al., 2007). Although adverse effects of high phthalate doses are relatively well documented (Martino-Andrade and Chahoud, 2010), epidemiological studies (Jurewicz and Hanke, 2011) and integrated approaches to toxicity (Kovacic, 2010) suggest potential adverse effects of even low-dose phthalate exposure and call for more data. Due to their low molecular weight, LMW phthalates are susceptible to migration from plastics, and hence they are more relevant to human toxicity (Heudorf et al., 2007). Thus, the majority of LMW phthalates are classified as substances of very high concern (SVHC) in Europe, and certain restrictions on their use and applications may apply (EC, 2007, 2005; EU, 2015). Similarly, US EPA issued an action plan to prioritise eight phthalates, the majority of which are LMW (USEPA, 2012).

The human population can be exposed to phthalates from a variety of sources, with medical devices, ingestion with food and dust constituting the major sources (Latini, 2005). As the most recent data on human exposure come from biomonitoring studies (a bottom-up approach reporting concentrations in, for example, human blood), there is still uncertainty in accounting for all the potential exposure routes and their importance to their total exposure to the population (Latini, 2005; Wittassek et al., 2011). From a risk assessment perspective, this calls for better data on the presence of phthalates in potential exposure sources.

Although phthalate plasticisers are predominantly used in PVC (Markarian, 2007), their potential use or contamination in a variety of polymers has been previously suggested (Ionas et al., 2014; Jaworek and Czaplicka, 2014; Shen, 2005). Shen (2005) looked into a variety of polymers, including PE, PS, PVC, as well as PE laminates and cellulose-based polymers, and identified phthalates in 24 out of the 25 plastics samples analysed. Polyethylene terephthalate

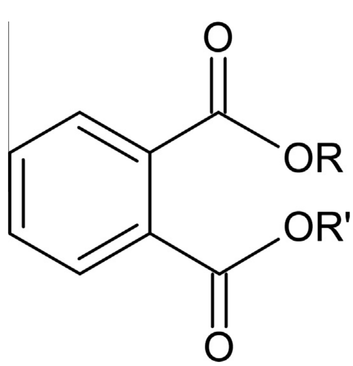

Fig. 1. Common structure of a phthalate molecule. R and R′ denote alkyl (or aryl) group.

(PET) has been shown to leach endocrine-disrupting chemicals (EDCs), including phthalates, into water contained in PET bottles (Amiridou and Voutsa, 2011; Casajuana and Lacorte, 2003; Keresztes et al., 2013; Montuori et al., 2008; Sax, 2010; Wagner and Oehlmann, 2011). When compared to PET bottles made of virgin plastics, Keresztes et al. (2013) clearly showed higher concentrations of phthalates in water bottled in PET potentially containing 20–30% (w/w) of recycled PET, thus suggesting recycling of plastics as a source of phthalate contamination. The abundance of phthalates has also been identified in a number of foods coming from a variety of geographical areas (Fankhauser-Noti et al., 2006; Fierens et al., 2012; Poças et al., 2010; Schecter et al., 2013). Although packaging was identified as one source (Fankhauser-Noti et al., 2006; Wormuth et al., 2006), contamination during food preparation and packaging usually cannot be ruled out, either (Tsumura et al., 2001). Additionally, use of recycled plastics and paper for food packaging was connected to possible increase in childhood exposure to selected phthalates (Lee et al., 2014). Finally, only a few studies have discussed the potential impact of plastics recycling on phthalate content, and so whether or not recycling can lead to plastic contamination and the increased presence of phthalates remains unclear.

The aim of the present work was to quantify selected LMW phthalates (DMP, DEP, DPP, DiBP, DBP, BBzP, DEHP, DCHP and DnOP) in samples of household waste plastics, as well as recycled and virgin plastics. Based on a consistent and comprehensive statistical data analysis methodology, the aim was further to evaluate whether the source (i.e. waste, recycled or virgin plastics) had a significant influence on phthalate content in the collected samples. Finally, the importance of plastics recycling for phthalate contamination was discussed.

2. Materials and methods

2.1. Sample collection

Samples of residual (RWP) and source-segregated (SSWP) waste plastics were collected from a municipality in Southern Denmark in April 2013. The sampling campaign covered 100 single-family households for a period of two weeks. Further details of the residual waste sampling are available in an earlier publication (Edjabou et al., 2015), while the same temporal and geographical scopes were applicable to the source-segregated waste samples collected. Waste samples were sorted manually in accordance to polymer resin identification codes (e.g. 1 – PET, 2 – HDPE, etc.) provided on individual plastic items. Identification codes specify of what the main polymer plastic products are made, without taking into account the presence of other materials (e.g. plastic 'sleeves' or labels on packaging) or chemicals (e.g. glue) in the final product. To supplement the waste plastic samples obtained from households, samples of processed plastics were obtained from industry. Samples of recycled household (RHP) and industrial (RIP) as well as virgin (VP) plastics were collected directly from recyclers and producers. RHP, RIP and VP samples were obtained from China, Denmark, Germany and the Netherlands, in order to illustrate potential variations in the source and quality of the material, which could result in different phthalate contents. In total, 20 waste (13 for RWP and seven for SSWP) and 28 recycled (nine for RHP and 11 for RIP) and eight virgin plastic (VP) samples were collected and analysed. An overview of the samples used in the present study is provided in Table S1 (Supplementary material). In the case of recycled and virgin plastics samples, neither the precise source (apart from a general distinction between household (i.e. post-consumer) and industrial (i.e. pre-consumer)) nor the exact intended use of the final plastic product (packaging, transportation, food-contact materials, etc.)