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A qualitative screening and quantitative measurement of organic contaminants on different types of marine plastic debris

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HIGHLIGHTS

- Extensive list of organic compounds found on marine plastic debris identified.
- Validated method for PAH and PCB determination on beached pellets.
- Beached pellets reveal distinct pollutant pattern compared to sediment and biota.

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ABSTRACT

Chemical compounds present on plastic were characterised on different types of plastic litter and beached pellets, using a general GC–MS screening method. A variety of plastic related compounds, such as building blocks, antioxidants, additives and degradation products, were identified next to diverse environmental pollutants and biofilm compounds. A validated method for the analysis of PAHs and PCBs on beached pellets at the Belgian Coast, showed concentrations of $\sum$ 16 EPA-PAHs of 1076–3007 ng g^{-1} plastic, while the concentrations of $\sum$ 7 OSPAR-PCBs ranged from 31 to 236 ng g^{-1} plastic. The wide variety of plastic compounds retrieved in the general screening showed the importance of plastic as a potential source of contaminants and their degradation products.

1. Introduction

In the last decades, the occurrence of plastic in the marine environment gained increased interest from research scientists around the world (Ivar do Sul and Costa, 2014). In particular, microplastics, defined as plastics with a diameter <5 mm, have been researched in detail. Both 'primary' microplastics, such as industrial preproduction pellets and 'secondary' microplastics, derived from breakdown of larger plastic debris, are omnipresent in the marine environment (Arthur et al., 2009). Microscopic pieces of plastic are found ingested in a wide range of aquatic life, such as seabirds, mammals, fishes, bivalves, and crustaceans (Ryan, 2008; Boerger et al., 2010; Murray and Cowie, 2011. Rebolledo et al., 2013; De Witte et al., 2014) and have been observed in bottom sediments, in the water column and on beaches around the world (Thompson et al., 2004; Law et al., 2010; Liebezeit and Dubaish, 2012).

Plastic debris often acts as floating substrates through the marine environment. Bacteria, algae, bryozoan and mussels are only some of the alien species found colonising this new habitat. These species are transported by plastic and may become invasive (Barnes, 2002; Zettler et al., 2013; Goldstein et al., 2014). Plastic debris has been suggested to be a sink or vector for organic and inorganic contaminants in the marine environment (Mato et al., 2001; Hirai et al., 2011; Bakir et al., 2014). However, Zarfl and Matthies (2010), concluded that the transport fluxes of some organic components by plastic debris is relatively small compared to other fluxes. More and more types of contaminants, both environmental as plastic related, have been discovered on plastic debris, however a systematic overview of compounds is still lacking. Some of these contaminants can be related to the plastic production process, while other environmental contaminants have no clear association with plastic production process, but are related to other pollution sources, such as industrial activities and oil seeps. Alkylphenols, bisphenol A and polybrominated diphenyl ethers (PBDEs), commonly used as plastic additives, have been found at high concentrations in plastic fragments. In these plastic fragments, alkylphenols were identified at concentrations up to

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3940 ng g^{-1}, concentrations of bisphenol A were up to 35 ng/g with outliers up to 700 ng g^{-1}, whereas concentrations of PBDEs were found to be between 0.1 and 400 ng g^{-1} with outliers up to 9900 ng g^{-1} (Hirai et al., 2011; Rochman et al., 2014). These plastic additives were discovered on plastic fragments found both at remote and urban beaches as well as in the open ocean (Hirai et al., 2011). Polycyclic aromatic hydrocarbons (PAHs) on beached pellets and plastic fragments showed a mainly petrogenic signature, with total PAH concentrations up to 45,000 ng/g (Hirai et al., 2011; Antunes et al., 2013; Mizukawa et al., 2013). Polychlorinated biphenyls (PCBs) and organochloride pesticides (OCPs), mainly linked to legacy pollution, were found to have concentrations up to 450 ng/g and 200 ng/g, both in plastic fragments as beached pellets respectively (Hirai et al., 2011; Karapanagioti et al., 2011; Antunes et al., 2013; Mizukawa et al., 2013). Metals also shows a strong adsorption capacity to plastic with concentrations found up to 300 μg g^{-1} for Al, Fe, Cu, Pb and Zn and up to 80 ng g^{-1} for Cd, Cr, Co, Ni in beached pellets (Holmes et al., 2012).

This paper provides insights into the diversity of chemical compounds found on plastic debris. A general qualitative screening of organic compounds using gas chromatography–mass spectrometry (GC–MS) was performed on plastic litter fragments sampled from the Belgian Continental Shelf (BCS) and on beached pellets collected along the Belgian coastline. The compounds were grouped according to their presumed origin. In addition, a quantitative analysis of PAHs and PCBs, two groups of organic pollutants frequently detected on plastic, was performed on beached pellets collected along the Belgian coastline. Concentrations for individual compounds were calculated and critically evaluated.

2. Materials and methodology

A general qualitative screening of contaminants was performed on plastic litter and beached pellets, sampled along the BCS and the beach of Oostende (Belgium). The plastic litter was defined as the different types of plastic recovered during sampling at open sea. Samples were Soxhlet-extracted using hexane:dichloromethane (1:1) as a solvent. Fractionation was done by a silica column according to the polarity of the organic compounds, based on the scheme of Schwarzbauer et al. (2000). Hereafter, samples were analysed using a GC–MS. Chromatographic peaks were putative identified based on a GC–MS library search, after which the peaks underwent a quality check, which insures a strong and trustworthy list of compounds. Details on the samples, the sampling method, the analysis method and the data analysis can be found in the Supplementary data, Section 1.

Black beached pellets (weathered and unweathered) and visually yellowing transparent beached pellets were collected along the Belgian coast. Following collection of beached pellets, the samples were analysed for PAH and PCB. Beached pellets were soaked for 3 days in hexane. The organic extracts were fractionated over a silica column. PAHs were analysed on a GC–MS, while PCBs were analysed on a gas chromatography – electron capture detector (GC-ECD). Validation of both PAH and PCB analytical methods was performed by analysing virgin polystyrene (PS) and polyethylene (PE) pellets. Details on the samples, sampling method, analysis method and validation can be found in the Supplementary data, section 1.

3. Results

3.1. General screening of organic compounds

Based on the source, a general screening of organic compounds on plastic litter and beached pellets resulted in the identification of a broad range of compounds, which were divided into 7 types: (a) plastic related compounds, (b) PAHs and their derivatives, (c) alkylated phenyl benzenes, (d) oxygen containing aliphatic compounds, (e) biofilm and algae compounds, (f) miscellaneous compounds and (g) compounds with unknown source. The complete list can be found in Table 1. Compounds of type A, plastic related compounds, can be related to the plastic production process. These compounds are known to be added intentionally to the plastic or are degradation products hereof, although some compounds may be derived from other sources.

A large variety of plastic related contaminants were detected both on plastic litter as on beached pellets. Plastic building blocks, such as (branched) alkanes and alkenes were found on all types of plastic. Antioxidants, like 3,5-di-tert-butyl-4-hydroxybenzalde hyde and butylated hydroxytoluene (BHT), and degraded antioxidants, such as 3,5-di-tert-butyl-4-hydroxyphenyl-propionic acid and 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione, were also commonly found on both plastic litter and beached pellets. In comparison, a variety of other antioxidants and degradation products were identified only on plastic litter or solely on beached pellets. The antioxidant 2,2-methylenebis (6(1,1-dimethyle thyl))-4-methyl-phenol and a degradation product 4,4′-ethylene bis(2,6-di-tert-butyl-phenol) were present on plastic litter, whereas the antioxidant thiobis-alkyl-phenol and a degraded antioxidant 3,5-di-tert-butyl-4-hydroxybenzoic acid were determined from beached pellets. Other types of additives were also typical for certain types of plastic. The surfactant glycerol monostereate and an impurity or degradation product glycerol were only present on beached pellets, whereas the plasticizers tributylacetyl-citrate and trimethyl benzaldehyde were only found on plastic litter. In addition, the UV-absorber 2-(3,5-di-tert-butyl-2-hydroxy phenyl)-5-chloro-2H-benzotriazole was found exclusively on plastic litter. The stabilizer octabenzone, however, was present both on plastic litter and beached pellets. Degradation products of plastic were detected both on plastic litter and beached pellets, although the products differed: benzoic acid, isopropenyl acetophenone, isophthalic acid and phthalic acid were found on beached pellets, whereas 1-methyl-10,18-bisnorabieta-8,11,13-triene was determined from plastic litter. Next to plastic related compounds, PAHs were omnipresent on both plastic litter and beached pellets. Oxygenated and/or alkylated PAHs were also present on both plastic litter and on beached pellets, although a larger variety of these PAH derivatives were found on beached pellets. Alkylated phenyl benzenes, such as butylidenebis-benzene and methyl-propanediyl-bis-benzene, were present both on plastic litter and beached pellets, although the individual compounds differed per plastic. Oxygen containing aliphatic compounds, such as alcohols, dicarboxylic acids, and fatty acids can be related to plastic itself, as building blocks, impurities or degradation products, or can be associated to biofilms. Other biofilm and algae compounds were found on both plastic litter and beached pellets. The biofilm compounds found on plastic litter showed a distinctly different composition than those found on beached pellets. Monoterpenes and sesquiterpenes were only present on beached pellets. Miscellaneous compounds predominantly determined from beached pellets were cosmetics related compounds, such as sunscreens and fragrances, as well as rubber related compounds. A degradation product of the pesticide dichloro-benzenamide was present only on beached pellets. Finally, some compounds with an unclear or unknown origin were also detected on plastic litter or beached pellets.

3.2. Validation of the PAH and PCB analytical method

A quantitative method was developed and applied for the determination of PAHs and PCBs (see Supplementary data, Section 1d). A limited validation was set up to estimate accuracy, precision and