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Threat of plastic ageing in marine environment. Adsorption/desorption of micropollutants

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ABSTRACT

Ageing of various plastics in marine environment was monitored after immersion of two synthetic (polyvinylchloride, PVC, and polyethylene terephthalate, PET) and one biodegradable (poly(butylene adipate co-terephtalate), PBAT) plastics for 502 days in the bay of Lorient (Brittany, France). Data analysis indicates that aged PVC rapidly releases estrogenic compounds in seawater with a later adsorption of heavy metals; PET undergoes a low weakening of the surface whereas no estrogenic activity is detected; PBAT ages faster in marine environment than PVC. Aged PBAT exhibits heterogeneous surface with some cavities likely containing clay minerals from the chlorite group. Besides, this degraded material occasionally shows a high estrogenic activity. Overall, this study reports, for the first time, that some aged plastics, without being cytotoxic, can release estrogenic compounds in marine environment.

1. Introduction

Due to their physical properties, such as high resistance to mechanical shocks and to chemicals, plastics are found in a large range of manufactured products. Production of plastics, intended for packaging, building, or medical devices, has greatly increased during the second half of the 20th century (PlasticsEurope, 2013, 2015, 2016). Unfortunately, it is now well known that some of these synthetic plastics induce significant adverse effects on wildlife and human health.

Plastic formulation includes polymers, thermosets or thermoplastics, and also other ingredients required to improve the physical properties of materials. Polyethylene, polypropylene, polystyrene, polyvinylchloride (PVC), polyamide, polyethylene terephthalate (PET), polyvinyl alcohol are the most commonly used synthetic polymers (Kedzierski et al., 2017; PlasticsEurope, 2016). Biodegradable polymers are also used such as the poly(butylene adipate co-terephtalate), designed as PBAT. This flexible polyester exhibits similar mechanical properties to those of polyethylene (Oliveira et al., 2017). Plasticizers (such as phtalates and adipates), metals (such as antimony, lead), antioxidants (such as phenolic and phosphite compounds), UV stabilizers (such as benzotriazole and titanium dioxide), fillers (such as calcium carbonate), dyes (such as titanium dioxide) and antimicrobial ingredients (such as Triclosan, silver) are the additives mixed with various polymers.

Today, it is well recognized that some additives can migrate from the polymeric matrix towards the surrounding environment. Unfortunately, some of them are known to be harmful to the marine ecosystem and to human health (Avio et al., 2017). This is the case, for example, for some phthalates, such as butyl benzyl and dibutyl phthalates, which are estrogenic endocrine disruptors (Benjamin et al., 2017). Thus, these molecules may cause dysfunctions of the immune and reproductive systems, cancers and neurodegenerative disorders (Benjamin et al., 2017). Plastics may also contain metal ions such as iron (Fe), copper (Cu) and chromium (Cr). These ions are involved, at low concentration, in molecules transport and cell signaling pathways, hence controlling essential cellular processes in all living organisms (Jakimska et al., 2011). However, an excess of these ions can induce adverse effects such as enzymatic activity alteration or oxidative stress generating free radicals responsible for DNA damage and membrane's lipid peroxidation. Other metal ions such as silver (Ag) and aluminum (Al), through their direct interaction with DNA, may also lead to cellular apoptosis. Therefore, the degradation of ageing plastics in aquatic environment, associated with the delivery of these additives, is an environmental threat.

In aquatic environment, the different micropollutants discharged mainly by wastewater treatment plants, agricultural farms, industries and hospitals include heavy metals and endocrine disruptors (Boutrup et al., 2009; Le Grand et al., 2017; Tchounwou et al., 2012). Some

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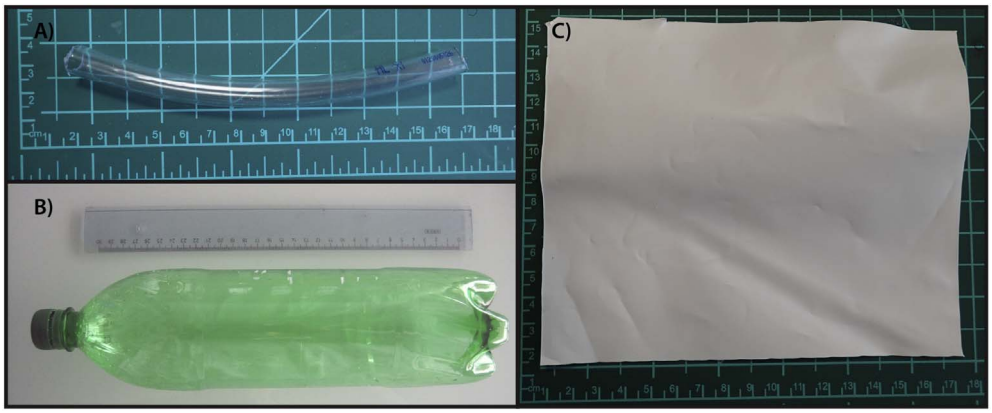

Fig. 1. Plastic samples used for ageing tests. A) PVC flexible tube. B) Green PET bottle. The samples placed in the marine environment are opened on both sides to let water circulation inside the bottle. C) PBAT sheet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

heavy metals can be adsorbed by plastics (Ashton et al., 2010; Brennecke et al., 2016; Holmes et al., 2012, 2014) such as cadmium and lead (Boucher et al., 2016; Nakashima et al., 2016). Furthermore, due to their hydrophobic surface, plastics can be contaminated by hydrophobic organic molecules (Rios et al., 2007). Among them, persistent organic pollutants (POPs) are commonly observed such as dichlorodiphenyltrichloroethane (DDT), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) (Antunes et al., 2013; Kwon et al., 2015; Rios et al., 2007). DDT, one of the most widely used insecticides in the world, has already been detected in certain plastic particles collected in the environment (Frias et al., 2010; Rios et al., 2007). DDT bioaccumulates in fish and along the food chain (Ogata et al. 2009; Sun et al., 2017). PCBs, extensively used for their electric insulating properties, are also present in plastic particles (Frias et al., 2010). Some of these molecules are carcinogens and/or endocrine disruptors. PAHs, poorly soluble in water and less bioavailable for degradation by microorganisms (bacteria, fungi and algae), can be adsorbed to plastics (Fisner et al., 2013a; Fisner et al., 2013b; Frias et al., 2010). These molecules come from incomplete combustion of organic matter and can be toxic, carcinogenic and mutagenic. The study of organisms subjected to both plastic particles (polyethylene) and PAH (pyrene) showed the existence of harmful combined toxic effects (Oliveira et al., 2012; Oliveira et al., 2013).

In the oceans, fragmentation of plastics generates debris called microplastics due to their size below 5 mm. Even if abiotic and biotic degradations of plastics are now well recognized, the rate of these events depends on the plastic chemical nature, the fillers, the hydrophilicity of their surfaces, and also their environmental conditions (Shah et al., 2008; Restrepo-Flórez et al., 2014). Any abiotic factor that promotes oxidation of the material will allow a better microbiological degradation since microorganism attachment is facilitated with a more oxidized surface (Restrepo-Flórez et al., 2014). Increased oxidized moieties have already been monitored by Fourier Transform Infra-Red spectroscopy, during plastic weathering process (ter Halle et al., 2017).

Microplastics found in marine environment, accumulate in sediments or float on the sea surface. They can be considered as vectors that transfer pollution from one site to another (Nakashima et al., 2016). Therefore, they can contaminate ecosystems still untouched by pollution (Bouwman et al., 2016; Cole et al., 2011) such as the Arctic ocean, where plastic drift appears to be an additional way to transport and disperse PAHs (Zarfl and Matthies, 2010). When ingested, microplastics play the role of a “Trojan horse” allowing certain toxic molecules to enter living organisms. It has been shown that under simulated gut conditions, micropollutants desorption can be 30 times faster than in seawater (Bakir et al., 2014). Without being the main route of contamination (Bakir et al., 2016), ingestion of microplastics could be an additional way to contaminate the food chains with additives, heavy metals (Boucher et al., 2016; Fife et al., 2015) or POPs (Colabuono et al., 2010).

Nevertheless, the interactions between plastics, additives and micropollutants during ageing in the marine environment remain little understood and the potential toxicity of plastic debris is poorly documented. In this context, the present study aims to compare the degradation, weakening and fragmentation of three thermoplastics immersed in seawater; two plastics with a same density, namely PVC (1.20–1.45 g/cm^3) and PET (around 1.38 g/cm^3) and, one biodegradable polymer, PBAT (around 1.26 g/cm^3). The plastic ageing process follow-up was performed for 502 days in Lorient's harbor. Changes of the surface topography over time were analyzed by scanning electron microscopy (SEM) and the inorganic composition by SEM coupled with energy-dispersive X-ray spectroscopy (EDX). In parallel, cytotoxicity and estrogenic risk evaluation of ageing plastics were performed using well-characterized human models. The first one was primary differentiated human endothelial cells (HUVEC) exposed to plastic extracts as mammalian and fish cells can equally well predict cytotoxicity (Castaño and Gómez-Lechón, 2005). The endothelium is a key target in aquatic species whose alterations may be associated with developmental defects and in vertebrate adults, with inflammation, edema and compromised immune system (species more sensitive to pathogen exposition). The second one was yeast estrogen screening (YES) assay, consisting of genetically modified yeast over-expressing human estrogen receptor that allows a better detection of estrogenic endocrine compounds than fish estrogen receptor (Le Grand et al., 2015; Dang et al., 2011).

2. Material and methods

2.1. Plastic samples

Three kinds of plastics were tested: polyvinyl chloride (PVC), polyethylene terephthalate (PET) and polybutyrate adipate terephthalate (PBAT).

PVC that is polymerized using vinyl chloride monomers (C_2H_3Cl) can be found in rigid and flexible forms. Flexible PVC can be obtained with the addition of plasticizers to the polymeric matrix such as phthalate esters. In the present study, 18 cm long commercial flexible and translucent PVC tubes were used (Fig. 1A). Parts with ink were not used for the tests. Due to specific properties such as resistance to impact or glass-like transparency, PET is frequently used to manufacture bottles for drinking water. Manufactured green PET bottles were used in the experiment (Fig. 1B). Parts with glue residues were excluded from the tests (Bejgarn et al., 2015). PBAT is a well-known biodegradable biopolymer. White sheets of 15 × 18 cm with a thickness of 150 µm were used for the experiments (Fig. 1C).

2.2. Plastic ageing experimental design

Plastic samples were placed in Kernevel harbor (GPS coordinates: 47.7173, − 3.3666; France) located in the Bay of Lorient, at 3 km south