Chemosphere 132 (2015) 114–119

Contents lists available at ScienceDirect

Chemosphere

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

Toxicity of leachate from weathering plastics: An exploratory screening study with *Nitocra spinipes*

Sofia Bejgarn [a], Matthew MacLeod [a], Christian Bogdal [a,b], Magnus Breitholtz [a,*]

[a] Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Svante Arrhenius väg 8, SE 114 18 Stockholm, Sweden
[b] Institute for Chemical and Bioengineering, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland

HIGHLIGHTS

- Plastics were repeatedly leached and irradiated with artificial sunlight.
- 8 of 21 plastics produced leachates causing acute toxicity to *Nitocra spinipes*.
- Both increases and decreases in toxicity were observed after irradiation.
- No consistent trend was seen among different materials.
- Chemical screening showed no evidence of PVC oligomers from the polymer backbone.

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 27 February 2015
Accepted 6 March 2015
Available online 29 March 2015

Handling Editor: Tamara S. Galloway

Keywords:
Plastic litter
Microplastic
Marine
Leachate
Toxicity
Nitocra spinipes

ABSTRACT

Between 60% and 80% of all marine litter is plastic. Leachate from plastics has previously been shown to cause acute toxicity in the freshwater species *Daphnia magna*. Here, we present an initial screening of the marine environmental hazard properties of leachates from weathering plastics to the marine harpacticoid copepod [Crustacea] *Nitocra spinipes*. Twenty-one plastic products made of different polymeric materials were leached and irradiated with artificial sunlight. Eight of the twenty-one plastics (38%) produced leachates that caused acute toxicity. Differences in toxicity were seen for different plastic products, and depending on the duration of irradiation. There was no consistent trend in how toxicity of leachate from plastics changed as a function of irradiation time. Leachate from four plastics became significantly more toxic after irradiation, two became significantly less toxic and two did not change significantly. Analysis of leachates from polyvinyl chloride (PVC) by liquid chromatography coupled to a full-scan high-resolution mass spectrometer showed that the leachates were a mixture of substances, but did not show evidence of degradation of the polymer backbone. This screening study demonstrates that leachates from different plastics differ in toxicity to *N. spinipes* and that the toxicity varies under simulated weathering.

1. Introduction

Globally, approximately 288 million tons of plastics were produced in 2012 (PlasticsEurope, 2013), predominantly from petroleum and natural gas (Edshammar, 2002). Between 60% and 80% of all marine litter consist of plastics (Derraik, 2002), but the total amount of plastic litter in marine environments is uncertain and highly variable (Ryan et al., 2009; Lambert et al., 2014). The mass of plastic particles has been found to be approximately six times higher than of plankton in a study at the North Pacific gyre (Moore et al., 2001). Other estimations include 18 000 pieces of plastic litter floating on every square kilometer of ocean surface (UNEP, 2006). Recently, Cózar et al. (2014) confirmed the ubiquitous presence of plastic debris in the open ocean and identified a broad size distribution of floating plastic debris on a large scale. Although it is believed that only about 15% of marine debris is washed to shore, monitoring at Baltic Sea beaches found an average of 130 pieces of litter per 100 m of beachfront, whereof 56% was plastic (Marlin Baltic Marine Litter, 2014). Hundreds of animal species worldwide have been affected by entanglement or ingestion of plastics (Laist, 1997). Additionally, microplastics can transfer between trophic levels (Farrell and Nelson, 2013; Wright et al., 2013) and potentially modulate uptake of persistent organic pollutants (POPs) in marine food webs (Besseling et al., 2012).

The time required for plastics to degrade in the environment is estimated to be on the order of hundreds to thousands of years

* Corresponding author. Tel.: +46 8 674 7241, mobile: +46 70 600 2686.
E-mail addresses: sofia.bejgarn@aces.su.se (S. Bejgarn), matthew.macleod@aces.su.se (M. MacLeod), christian.bogdal@chem.ethz.ch (C. Bogdal), magnus.breitholtz@aces.su.se (M. Breitholtz).

http://dx.doi.org/10.1016/j.chemosphere.2015.03.010
0045-6535/

(Barnes et al., 2009). Photo-oxidation by ultraviolet (UV) light is the primary degradation pathway for plastics (Hammer et al., 2012). In marine environments, decreased sun exposure due to shading by water and fouling might increase the persistence of plastic (O'Brine and Thompson, 2010; Hammer et al., 2012). Furthermore, UV-stabilizers and other chemical additives are often added to plastics (Edshammar, 2002). Plastic additives have been shown to be released; for example, plasticizers can be found in leachate from landfills (Asakura et al., 2004).

The extent of leaching of additives from plastic and leachate composition is influenced by both the properties of the additive substance and the properties of the plastic polymer, such as the degree of amorphous or crystalline structure (Hansen et al., 2012). Also important is whether or not additives are chemically bound to the polymer (Bibi et al., 2012). Several studies on toxicity of individual plastic additives exist (Lambert et al., 2014), as well as studies concerning human health and migration into food or water from plastic materials (e.g. Wagner and Oehlmann, 2009; Cheng et al., 2010). Plastic leachate into freshwater has previously been found to cause acute toxicity to *Daphnia magna* (Lithner, 2011). However, we are not aware of any studies of the aquatic toxicity of leachates from plastic in marine environments during simulated weathering of plastics.

Here, we report an initial screening of the marine environmental hazard properties of leachates from weathering plastics. Plastics from commercially available products were repeatedly leached and weathered by artificial sunlight. Leachates were screened for acute toxicity with the micro-crustacean *Nitocra spinipes*. Our hypotheses were that leachates from common plastic materials would show different toxicity towards *N. spinipes*, and that the toxicity would change as the plastic material was weathered by artificial sunlight.

2. Material and methods

2.1. Materials

For this initial screening survey we selected plastics from products that are commercially available in department stores in Stockholm, Sweden, and that are likely to be common in Swedish households (Table 1). The range of selected plastics represent: (1) Examples of six common plastics that account for 80% of European plastic demand: Polyethylene, (PE), Polypropylene (PP), Polyvinyl chloride (PVC), Polystyrene (PS), Polyethylene terephthalate (PET) and Polyurethane (PUR) (PlasticsEurope, 2012); (2) The largest application sector in Europe, i.e. packaging (PlasticsEurope, 2013); and (3) The common plastics found on the beaches of the Baltic Sea, i.e. packaging and short-term usage plastic (Marlin Baltic Marine Litter, 2014). Packaging with recycling labels was tested to ensure that different types of plastics were covered, however, some examples of unlabeled packaging and products were also selected for study.

In addition, three bioplastics were included. Bioplastics are biodegradable and/or made from renewable resources (European Bioplastics, 2014). Many of the selected plastics were thin films. Only one plastic, the toothbrush at 1.3 cm, was thicker than approximately 5 mm. For descriptions of each plastic material, see Supplementary Material (SM). Leachate from tires has been shown to be toxic in other studies (e.g. Gualtieri et al., 2005; Wik and Dave, 2006), hence pieces of a used (washed) car tire were included as a positive control.

2.2. Preparation of plastics for leaching and aging

All labels were removed from the plastic material and parts with glue residues were not used. Dust was wiped off, but the plastic was only washed if necessary, e.g. for containers of soap and the used tire. These were washed with hand dishwashing liquid and rinsed in deionized water.

To facilitate leaching and increase the surface area available for exposure to artificial sunlight we used a variety of methods to grind the plastics into powders. Grinding techniques included mechanical cryogenic grinding, manual grinding in liquid nitrogen and grinding in a Blendtec HP3A blender. For the mechanical cryogenic grinding, a Retsch CryoMill with 50 mL cells and a 2 cm diameter steel ball were used. The cell was filled to $\leqslant 1/3$ with plastic material that had been cut with clean stainless steel scissors or pliers. Each plastic was ground for approximately 2 min, with 4 min precooling. Several sets of grindings per sample were necessary to yield approximately 10 g of ground material. The cells were wiped clean with disposable cellulose tissues or washed between the different materials. Materials that resisted both types of cryogenic grinding were ground in the Blendtec blender, see SM. None of the grinding techniques were effective for PET, Bio-PET and the EN 13432 compliant biodegradable garbage bag, hence approximately 1 cm^2 pieces cut with scissors were used for leaching and weathering experiments. When necessary, the ground plastic materials were stored in sealed glass containers in a refrigerator at 4 °C.

The particle size of the ground plastics was assessed by sieving through two nets, with 1 and 0.3 mm mesh size, respectively. If sieving was not possible, the grain size was assessed using an optical microscope. For size distributions and pictures, see SM. One plastic product (PS-cups) was duplicated throughout the study.

2.3. Leaching

Leaching was performed according to the Swedish standard 12457:2003 "*Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 L* kg^{-1} *for materials with particle size below 4 mm*" (SIS, 2003), with some modifications. First, the leaching time was increased from 24 h to 72 h. Second, natural brackish water from the Baltic Sea was used. Third, no moisture content was determined since moisture content is generally very low in plastics (Bruder, 2011).

The leaching was accomplished by mixing approximately 10 g of each plastic with natural brackish water to obtain a liquid-to-solid-ratio (L/S) of 10. The salinity of the water was 7‰ (±0.2) and the pH 7.9 (±0.25). The water had previously been filtered (Munktell v5 filter) and heated to 80 °C, and been allowed to cool to room-temperature for at least 24 h. Samples 1–8 were leached in darkness in round bottom flasks on a rotary mixer (Labianco, model 256) at 6 rotations per minute (rpm). Due to a malfunction the first leaching (corresponding to 0 h of artificial sunlight) of samples 1–8 were not rotated during approximately 24 h, and were therefore left rotating an additional 24 h, making the total water exposure time 92 h. The mixer was replaced for samples 9–22 with a Heidolph elektro KG Kelheim type RZR E60 with a speed of 21 rpm.

The liquid and solids were separated by suction filtration, using a PALL 45 µm membrane filter (Supor 450 standard, 47 mm). Leachate pH was accepted within the range of 6–9 (which is the acceptable pH range for acute toxicity tests with *N. spinipes*), and was adjusted with sodium hydroxide or hydrochloric acid if necessary (for pH of leachates, see SM) to approximately 7–8. Filtrated leachates were stored in a refrigerator at 4 °C for a maximum of 72 h prior the ecotoxicological testing.

2.4. Test species and ecotoxicological test

The acute toxicity tests were performed according to the Swedish standard 028 106 "Determination of acute lethal toxicity