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Leaching of plastic additives to marine organisms

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ABSTRACT

It is often assumed that ingestion of microplastics by aquatic species leads to increased exposure to plastic additives. However, experimental data or model based evidence is lacking. Here we assess the potential of leaching of nonylphenol (NP) and bisphenol A (BPA) in the intestinal tracts of *Arenicola marina* (lugworm) and *Gadus morhua* (North Sea cod). We use a biodynamic model that allows calculations of the relative contribution of plastic ingestion to total exposure of aquatic species to chemicals residing in the ingested plastic. Uncertainty in the most crucial parameters is accounted for by probabilistic modeling. Our conservative analysis shows that plastic ingestion by the lugworm yields NP and BPA concentrations that stay below the lower ends of global NP and BPA concentration ranges, and therefore are not likely to constitute a relevant exposure pathway. For cod, plastic ingestion appears to be a negligible pathway for exposure to NP and BPA.

1. Introduction

Pollution with plastic debris and microplastic fragments has been recognized as a major problem in fresh and marine water systems (Derraik, 2002; Andrady, 2011; Koelmans et al., 2014). Negative effects may relate to entanglement in plastic wires or nets, or to ingestion, which has been reported for benthic invertebrates, birds, fish, mammals and turtles (Laist, 1997; Besseling et al., 2013; Wegner et al., 2012; Foekema et al., 2013). It is generally assumed that microplastics may increase exposure of marine aquatic organisms to chemicals associated with the plastic, like persistent organic pollutants (POPs) or plastic additives (Gouin et al., 2011; Teuten et al., 2009; Hammer et al., 2012; Browne et al., 2013). In recent model analyses however, it was shown that the effects of plastic on bioaccumulation of POPs may be small, due to a lack of gradient between POPs in plastic and biota lipids, and that a cleaning mechanism is likely to dominate at higher Log K_{OW} values (Gouin et al., 2011; Koelmans et al., 2013a,b). For additives, monomers or oligomers of the component molecules of the plastics (hereafter referred to as 'additives') this issue has hardly been addressed. It is known that plasticizers may have biological effects already at low concentrations in the ng/L or μg/L range, especially for molluscs, crustaceans and amphibians (Oehlmann et al., 2009). It has been argued that one should expect low exposure to plastic additives because of the low diffusivities of chemicals like bisphenol A (BPA) or nonylphenol (NP) in plastics (Berens, 1997). For NP in polyvinyl chloride (PVC) and high-density polyethylene (HDPE) bottles, release half-lives to water of about 4–5 day were reported, albeit at elevated temperature (Loyo-Rosales et al., 2004). On the other hand, release rates may be higher for aged and brittle plastics (Koelmans et al., 2013; Artham and Doble, 2009; Sajiki and Yonekubo, 2003; Rochman et al., 2013) or in gastrointestinal gut fluids where high levels of DOC and surfactants facilitate exchange (Koelmans et al., 2013; Endo et al., 2013). For additives, plastic ingestion by marine organisms may be more relevant than for diffusely spread POPs because the plastic would still be a source of the additives (Teuten et al., 2009; Hammer et al., 2012; Koelmans et al., 2013a,b). Furthermore, compared to worms, leaching of additives may be more relevant for larger and longer living species, with longer gut retention times, such as fish. Interestingly, if microplastic ingestion would lead to increased bioaccumulation of plastic additives but to decreased bioaccumulation of traditional POPs at the same time (Gouin et al., 2011; Koelmans et al., 2013), there might be a trade-off between these positive and negative effects. We conclude that it is insufficiently clear whether additives should be a concern when addressing the impacts of marine plastics.

Aim of the present paper is twofold. First aim was to assess the plausibility of leaching of additives from plastic as a relevant exposure pathway for marine worms and fish. Second aim was to further elaborate a previously published biodynamic plastic-

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inclusive bioaccumulation model. To accomplish these aims, model scenario analyses were performed using an analytical solution to the previously published model. Steady state concentrations and time required to reach steady state were used as characteristic endpoints. Scenarios were calculated for two species, the polychaete worm *A. marina* and the fish *Gadus morhua*, henceforth referred to as lugworm and cod respectively. For lugworms in North Sea sediment, species and plastic ingestion data were taken from our previous bioaccumulation study (Besseling et al., 2013). For North Sea fish, species characteristics, plastic stomach content and plastic abundance frequencies were available for a range of species (Foekema et al., 2013), which allowed for estimation of average plastic ingestion rates. Two chemicals recognized as dominating in the leaching from plastic were selected; nonylphenol (NP) and bisphenol A (BPA) (Teuten et al., 2009; Hammer et al., 2012). Probabilistic modeling was applied to account for the impact of uncertainties.

2. Biodynamic model for leaching of chemicals from plastic

Koelmans et al. (2013) modeled bioaccumulation of hydrophobic chemicals ($dC_{B,t}/dt$; $\mu g \times g^{-1}\ d^{-1}$) from an environment containing plastic as a mass balance of uptake and loss processes:

$$\frac{dC_{B,t}}{dt} = k_{derm}C_W + IR(S_{FOOD}a_{FOOD}C_{FOOD} + S_{PL}C_{PLR,t}) - k_{loss}C_{B,t} \quad (1)$$

The first term in Eq. (1) quantifies dermal (including gills) uptake from ambient water. The second term quantifies uptake from ingested food and exchange with plastic particles. The third term quantifies overall loss due to elimination and egestion. The first and third term are parameterized following traditional approaches with C_W (μg/L) is the concentration in the ambient water and k_{derm} ($L \times g \times d^{-1}$) and k_{loss} (d^{-1}) are first order rate constants for dermal uptake and overall loss through elimination and egestion. Following Hendriks et al. (2001), k_{loss} is a minimum value, excluding possible biotransformation. In the second term, IR_t ($g \times g^{-1} \times d^{-1}$) represents the mass of food ingested per unit of time and organism dry weight, a_{FOOD} is the absorption efficiency from food, S_{FOOD} and S_{PL} are the mass fractions of food and plastic in ingested material respectively ($S_{FOOD} + S_{PL} = 1$) and C_{FOOD} is the chemical concentration in food. The product $a_{FOOD} \times C_{FOOD}$ quantifies the contaminant concentration that is transferred from food, i.e. prey species, to the organism during gut passage. Note that for species like fish, weight usually is expressed as wet weight (WW), in which case IR_t also is based on wet weight. The transferred concentration from plastic during gut passage (GP), $C_{PLR,t}$, (μg/g) is calculated using (see Koelmans et al., 2013a,b, for detailed derivation):

$$C_{PLR,t} = \frac{k_1 C_{PL} - k_2 C_{L,t}}{k_1 + \frac{M_{PL}}{M_L}k_2}\left(1 - e^{-\left(k_1 + \frac{M_{PL}}{M_L}k_2\right)GRT}\right) \quad (2)$$

In which k_1 and k_2 (d^{-1}) are forward and backward first order rate constants describing the transport between plastic and biota lipids, GRT is gut residence time (d), C_{PL} and $C_{L,t}$ (μg/g) are the chemical concentrations in the ingested plastic particle and the biota lipids at the moment of ingestion (i.e. $C_{L,t} = C_{B,t}/f_{lip}$, μg/g), and M_{PL} and M_L are the mass of plastic and lipids in the organism respectively (g). Eq. (2) can be rewritten as:

$$C_{PLR,t} = A_{PL}k_1 C_{PL} - A_{PL}k_2 C_{L,t} \quad (3)$$

in which

$$A_{PL} = \frac{1 - e^{-\left(k_1 + \frac{M_{PL}}{M_L}k_2\right)GRT_t}}{k_1 + \frac{M_{PL}}{M_L}k_2} \quad (4)$$

If GRT is constant, also A_{PL} is constant over time. Combination of Eqs (1), (3) and (4) and using $C_{L,t} = C_{B,t}/f_{lip}$, yields the mass balance equation for bioaccumulation:

$$\frac{dC_{B,t}}{dt} = k_{derm}C_W + IR \times S_{FOOD}a_{FOOD}C_{FOOD} + IR \times S_{PL}A_{PL}k_1 C_{PL} - \left(IR \times S_{PL}A_{PL}k_2/f_{lip} + k_{loss}\right)C_{B,t} \quad (5)$$

for which the following steady state solution (body burden at steady state, C_B^{SS}) can be calculated:

$$C_B^{SS} = \frac{k_{derm}C_W + IR(S_{FOOD}a_{FOOD}C_{FOOD} + S_{PL}k_1 C_{PL}A_{PL})}{IRS_{PL}k_2A_{PL}/f_{lip} + k_{loss}} \quad (6)$$

The steady state concentration thus reflects the balance between rates for dermal uptake, uptake by food and uptake by plastic ('carrier') all in the numerator, versus 'cleaning' by plastic ingestion and chemical loss, which are covered by the denominator. The analytical solution to Eq. (5) is:

$$C_{B,t} = \left(C_{B,t=0} - C_B^{SS}\right) \times \left(e^{-(IR\ S_{PL}k_2A_{PL}/f_{lip} + k_{loss})t}\right) + C_B^{SS} \quad (7)$$

The time required to reach 95% of steady state (t_{SS}) can be approximated as three times the time constant of the system ($1\text{-}e^{-3}$):

$$t_{SS} = 3 \Big/ \left(IR\frac{S_{PL}k_2A_{PL}}{f_{lip}} + k_{loss}\right) \quad (8)$$

2.1. Parameters

Lugworm – Biological parameters for the lugworm were taken from the literature and are provided as Supporting Information (Table S1). Compared to the previous model implementation for bioaccumulation of PCBs (Koelmans et al., 2013a,b), the chemical parameters, i.e. for BPA and NP, are different, with generally much lower Log K_{OW} values than for the PCBs. Polyethylene was taken as model for marine plastic (Table S1).

Fish. Cod was selected as a representative species of North Sea fish, for which also sufficient data on biological parameters are available from the literature (Table S1). Greenstreet (1995) reports a food ingestion rate IR of 0.0126 g/g WW $\times$ d^{-1} for North Sea cod individuals of 3300 g WW and a length of 66.3 cm. Plastic ingestion rates and S_{PL} values for cod in the North Sea were calculated as follows. The mass of plastic in fish intestines (M_{PL}, g) can be calculated from $M_{PL} = IR \times S_{PL} \times GRT \times W$, in which W is the wet weight of the fish. Consequently, the plastic ingestion rate $IR_{PLASTIC} = IR_{FOOD}S_{PL}$ (g plastic ingested per g wet weight of cod, per d) by cod equates to:

$$IR_{PLASTIC} = M_{PL}/(GRT \times W) \quad (9)$$

Foekema et al. (2013) dissected 80 individuals of cod caught across the North Sea, and found one plastic particle of about 1 mm diameter in 10 of the 80 fish individuals. Assuming a density of plastic of ~1 kg/L this translates into an *average* value of $M_{PL} = 6.8 \times 10^{-5}$ g plastic per cod individual. The average weight W of the 80 individuals was 3312 g WW. Data for gut