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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

passage or gut retention times for cod can be found in the literature. Daan (1973) reported a GRT for normal food of 3.7 d (range 1–7 d) for North Sea cod. dos Santos and Jobling (1991) compared gastric emptying by cod of normal and indigestible food items including plastic particles. For herring as a regular prey item gastric emptying times of 1–7 d were found (dos Santos and Jobling, 1991), which agrees very well to the range provided by Daan (1973). For indigestible 0.5–0.7 mm plastic particles however, GRTs ranged up to 10 d, and for 2 mm plastic particles up to 20 d (dos Santos and Jobling, 1991). This means that gut passage of indigestible microplastics in fish can be substantially retarded, which will increase the exchange of chemicals between microplastic particles and biota lipids. Based on these data we used a microplastic GRT of 7 d in the model and in Eq (9), as a default value for North Sea cod, with a range of 3–20 d. From these values for M_{PL}, W and GRT an $IR_{PLASTIC}$ of 2.94×10^{-9} g/g WW $\times$ d^{-1} is calculated using Eq (9). With the IR_{FOOD} of 0.0126 g/g WW $\times$ d^{-1} for cod individuals of the same weight, this yields a value of $S_{PL} = IR_{PLASTIC}/IR_{FOOD}$ of 2.34×10^{-7}. This value for S_{PL} indicates that microplastic makes up a very low fraction of the mass ingested by cod.

2.2. Scenario studies

For the lugworm, scenario studies were calculated covering a wide range of microplastic mass fractions in the sediment (up to 10%), thus accounting for the observed spatial heterogeneity of plastic content of freshwater lakes, harbors, coastal areas, sea and ocean floor (Browne et al., 2011; Claessens et al., 2011; Reddy et al., 2006).

For North Sea cod, realistic internal plastic abundance data were available so these data based on actual habitat characteristics were used in the scenarios. Because for fish the plastic lipid exchange parameters (k_1, k_2) may be relatively uncertain, these parameters were varied.

Both scenario studies covered BPA and NP concentrations measured in marine plastics *in situ* as reported by Teuten et al. (2009), of 24.9–2660 μg/kg NP and 5–284 μg/kg BPA. These ranges are wide and the underlying data are conditional. However, it can be assumed that the concentrations relate to the polymer type and production process and therefore may be considered general and applicable to the North Sea as well. Still, one should realise that extreme values outside these ranges also have been reported, for instance >10,000 μg/kg of NP in field plastic pellets (Mato et al., 2001). Based on these ranges default values of 1000 μg/kg NP and 100 μg/kg BPA were used. To quantify the role of plastic as the source of these contaminants, the calculations did not include other sources or pathways of uptake. This implies C_{FOOD} and C_W (Eqs (1), (5) and (6)) were set to zero. As such the calculations show whether microplastic mediated transport alone may represent a hazard to aquatic organisms.

To account for parameter uncertainty, for biological variability and for variability in chemical release properties of a wide range of plastic types, probabilistic modeling was performed for the NP scenarios using Monte Carlo analysis. These analyses quantified the propagation of error originating from uncertainty in the main parameters by evaluating 10,000 random parameter value drawings from parameter space. To represent a wide range of worm lengths and feeding modes, for the worms a range of 2–5 h gut retention time was covered. To represent a wide variety of plastic particle sizes and types the plastic-lipid exchange coefficient k_1 was varied between 0.1 and 100 d^{-1}. Ranges and distributions of parameter uncertainty were based on literature or measurement error data as specified in Table S1. Results are presented as 5–95% percentiles of calculated model output values.

2.3. Model validation

A detailed model validation was beyond the scope of this study. The subprocesses however, have all been validated in the literature (see amongst others Teuten et al. 2009; Koelmans et al. 2013a,b; Hendriks et al. 2001) and the overall model was shown to be consistent with polychlorobiphenyl bioaccumulation data for *A. marina* in our previous study (Besseling et al., 2013). Furthermore, a dataset on NP accumulation from polyvinyl chloride (PVC) plastic to *A. marina* was recently published by Browne et al. (2013). Using their reported (very high) NP concentrations in PVC of 692 μg/g, the specific worm weight, plastic concentration of 5% and a specific NP partition coefficient for PVC (Atkinson and Duffull, 1991), their measured tissue concentrations of 4.4 ± 1.9 and 7.9 ± 3.1 could be reproduced assuming a k_1 of ~0.5 d^{-1}, which is within the aforementioned range of uncertainty for this parameter (0.1–100 d^{-1}) (details provided as Supporting Information, Table S2).

3. Results and discussion

3.1. Modeled concentrations due to ingestion of microplastic

3.1.1. Leaching of NP and BPA to the lugworm

For NP, model calculations show that time to steady state t_{SS} is about one day if the default plastic-lipid exchange rate coefficient k_1 of 10 d^{-1} is used (Fig. 1). An increase in plastic content of the sediment up to 10% reduces the time to steady state from 1.5 to 0.8 d, which is explained from the fact that S_{PL} increases the time constant in Eq (7).

Ingestion of plastic with 1000 μg/kg NP translates into a lipid-based concentration of similar magnitude, up to about 1500 μg/kg NP for 10% plastic in the sediment (Fig. 2). However, the highest plastic concentration in natural sediment has been reported to be 81 mg/kg, i.e. $S_{PL} = 8.1 \times 10^{-5}$ (Reddy et al., 2006), for which a steady state concentration of 250 μg/kg NP in worm lipids is calculated. This lower bioaccumulation is not proportional to the 10/0.0081 factor decrease in sediment plastic content S_{PL}, and the related NP concentration. This is primarily explained from the fact that S_{PL} appears in the numerator as well as the denominator of Eq (6). A lower S_{PL} reduces the 'carrier' component as well as the 'cleaning' component of the plastic effect, which limits the sensitivity of the model outcome to a change in S_{PL}.

Accounting for random variability in gut retention times (between 2 and 5 h) and plastic chemical release properties ($0.1 < k_1 < 100$ d^{-1}) shows that 90% of the model predictions are

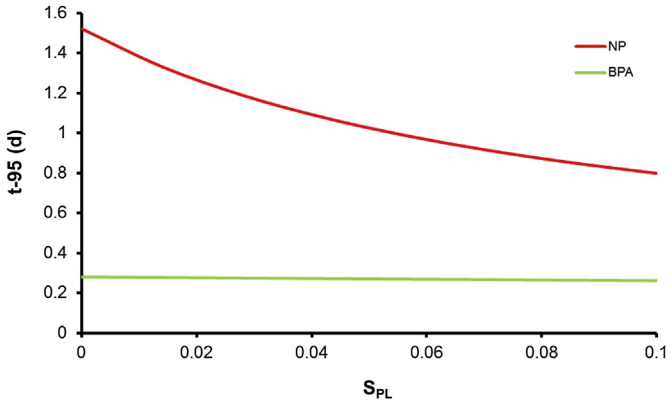

Fig. 1. Time required to reach 95% of steady state (*t*-95) in the lugworm for NP and BPA as a function of PE mass fraction (S_{PL}) in the sediment.

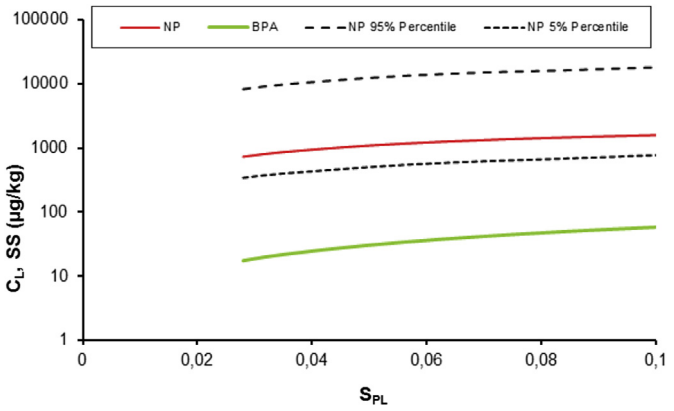

Fig. 2. Lipid normalized steady state concentrations of NP and BPA in the lugworm (C_L^{SS}; µg/kg lipids) as a function of PE mass fraction (S_{PL}) in the sediment. Dashed lines indicate the upper and lower bounds of the range of uncertainty in modeled NP concentrations, defined as 5% and 95% of the modeled concentrations, respectively.

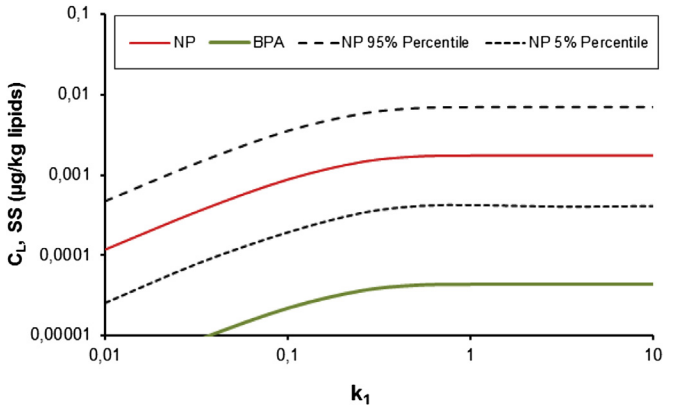

Fig. 3. Lipid normalized steady state concentrations of NP and BPA in North Sea cod (C_L^{SS}; µg/kg lipids) as a function of the plastic-lipids exchange coefficient (k_1) governing NP and BPA exchange kinetics in the fish gastrointestinal tract. Dashed lines indicate the upper and lower bounds of the range of uncertainty in modeled NP concentrations, defined as 5% and 95% of the modeled concentrations, respectively.

between 0.5 and 10 times the predictions for the default parameter set (Fig. 2). The high bound values would relate to fast release, for instance from very small particles such as micrometer sized fibers or particles.

For BPA, the main differences with the NP scenarios are that order of magnitude lower concentrations in plastics were used and that BPA has a ten times lower K_{OW} value. Molecular weights and polymer diffusivities, however, are similar for BPA and NP (Berens, 1997; Touze-Foltz et al., 2012), which implies that the same default values and ranges for k_1 can be used. Steady state concentrations are reached in about 6.5 h (Fig. 1) and range from 0.05 µg/kg worm lipids at a realistic sediment plastic content of 81 mg/kg to about 60 µg/kg worm lipids for the scenario with 10% plastic (Fig. 2).

3.1.2. Leaching of NP and BPA to fish

For the realistic cod scenario, the plastic content in the food was kept at actual values inferred from data for North Sea cod, but the plastic-lipid exchange parameter k_1 was varied between 0.01 and 10 d^{-1} to account for variability in chemical release properties from microplastic. It appears that reaching steady state requires fifteen days (not shown), irrespective of the magnitude of the plastic-lipid exchange parameters k_1 and k_2. The insensitivity to these rate parameters follows from the low plastic ingestion rates (low S_{PL}) calculated for cod. Consequently, the S_{PL} term in the denominator of Eq (8) is negligible compared to k_{loss}, so that k_{loss} determines the time required to reach steady state.

Continuous ingestion of plastic containing 1000 µg/kg NP at realistic ingestion rates yields a low steady state NP concentration of 1.7 ng/kg lipids (Fig. 3). Because of the longer gut retention times in cod, all k_1 values higher than 0.5 d^{-1} lead to equilibrium at the end of gut passage. This explains that bioaccumulation does not increase further at higher k_1 values (Fig. 3). It is highly plausible that desorption rate constants to gut fluids are between 1 and 10 d^{-1} (Koelmans et al., 2013), which means that 1.7 ng/kg lipids can be considered a realistic estimate.

Accounting for variability in GRT and IR resulted in a factor of three uncertainty in each direction (Fig. 3), leading to an interquartile (IQR) range of modeled NP steady state concentrations of 0.6–5 ng/kg lipids.

For BPA, steady state concentrations in fish are reached in about 3.75 h (not shown). This time to reach steady state was four times lower than for NP, because the parameter value for k_{loss} was 4 times higher. As mentioned above, for the fish scenarios k_{loss} in fact determined the modeled time to steady state, because the S_{PL} term in the denominator of Eq (8) was negligible compared to k_{loss}.

Continuous ingestion of plastic with 100 µg/kg BPA by uncontaminated fish would lead to a very low steady state concentration of 0.044 ng/kg. For BPA no uncertainty analyses were performed. However, because the Monte Carlo analyses for fish addressed uncertainty in GRT and IR, the relative uncertainty for BPA will be the same as for NP. This means that uncertainty in the steady state concentration for BPA, expressed as IQR range, also is a factor of three in both directions, giving a total range of 0.015–0.13 ng/kg.

3.2. Present NP and BPA concentrations in lugworm and cod in the field, compared to the modeled concentrations due to ingestion of microplastic

In the above sections estimates for steady state NP and BPA concentrations due to ingestion of microplastics were presented, for *A. marina* and *G. morhua*. The next question is whether these concentrations are substantial compared to NP and BPA concentrations in lugworms and fish individuals collected from the field. The latter concentrations would reflect the actual chemical uptake or release by all pathways, that is, from water, food and plastic. We argue that if the values calculated based on plastic ingestion are negligible compared to concentrations observed in the field, the impact of plastic ingestion may be assumed to be unimportant. The estimated concentrations in biota can also be compared to literature values for effect thresholds. Concentrations in biota in the field can be calculated either from environmental concentrations in sediment and water using biota-sediment or biota-water concentrations factors, or can be taken directly from the literature.

Nonylphenol – If equilibrium partitioning would apply to the uptake of NP from sediment organic matter (OM) to *A. marina* lipids, and if sediment organic matter and worm lipid contents would be of similar magnitude, i.e. about 5%, normalized biota sediment accumulation factors (BSAFs) of chemicals of medium hydrophobicity for benthic invertebrates would be close to one (Selck et al., 2012). However, Besseling et al. (2013) found much higher values for polychlorobiphenyl accumulation in *A. marina*. Furthermore, normalized BSAFs for NP for several marine invertebrate species ranged from 5 to 55, with a median value of 15 (Literature summary provided as Supporting Information, Table S3). In their recent meta-analysis of global NP concentration data, Bergé et al. (2012) reported a range of (0.02–120) × 10^3 µg/kg in suspended solids based on 10 studies, and a

range of (0.02–72) × 10^3 μg/kg in sediments based on 35 studies. Assuming an OM content of about 5%, OM normalized concentrations would be a factor of 20 higher. Using a BSAF of 15, lipid based worm concentrations would be another factor 15 higher, that is, (6–21600) × 10^3 μg/kg lipid based on suspended solids, which may well represent sediment top layers, and (6–36000) × 10^3 μg/kg lipid, based on sediments. Literature values for NP concentrations directly measured in benthic invertebrates are scarce and fragmentary, yet agree to the lowest end of the aforementioned range. For instance, Takahashi et al., 2003 reported a range of 8–140 μg/kg WW, which translates to ~320–6000 μg/kg lipid. The above model calculations showed that ingestion of microplastic at a high yet realistic concentration can explain NP concentrations in the lugworm of 250 μg/kg worm lipids, which is much lower than the lower end of the NP concentration ranges of about 6000 μg/kg estimated to occur in the field. The Monte Carlo modeling however, showed an order of magnitude uncertainty at the higher end, with concomitant worm concentrations up to ~2500 μg/kg lipids. We conclude that only in environments with NP concentrations at the lower ends of the reported concentration ranges, leaching of NP to worms by ingestion of plastic may constitute a relevant exposure pathway. Because of these low NP concentrations however, actual risks of NP would still be limited in these environments.

In the same meta-analysis of NP concentration data, Bergé et al. (2012) reported a range of 0.01–45 μg/L in surface waters (median 0.33 μg/L) based on 41 studies including river, estuarine, bay, lagoon and sea water systems across all continents. Furthermore, the US EPA provides a summary of bioaccumulation and effect data for NP (Brooke and Thursby, 2005), from which a median lipid normalized bioconcentration factor (BCF) of 100,000 can be calculated (range 4000–200,000), based on 19 values from four studies. Combining the lower boundaries of the ranges in aqueous concentration and BCF data would give a lower boundary value of 0.01 × 4000 = 40 μg/kg lipids. The meaning of this value is that given the levels of NP contamination on a global scale, an arbitrary fish sample is likely to show a NP concentration of at least 40 μg/kg lipids. Literature values for NP concentrations directly measured in fish tissue are scarce and fragmentary, yet fall within the aforementioned range (eg., 3.3–29.1 μg/kg WW, Kannan et al., 2003), which translates to ~130–1200 μg/kg lipids). The value of 40 μg/kg lipids is about a factor of 10,000 higher than the range of modeled NP steady state concentrations of 0.6–5 ng/kg lipids due to ingestion of microplastics. Even if we use a factor of three higher NP concentration due to ingestion by plastic as indicated by the Monte Carlo analysis, present environmental NP concentrations still are much higher. This means that ingestion of microplastic seems to provide a negligible contribution to exposure observed in the field. Based on toxicity data, the EPA provides NP final chronic effect threshold values of 6.6 and 1.6 μg/L for fresh and salt water species respectively (Brooke and Thursby, 2005). Using the same lowest estimate of BCF of 4000 these values would relate to chronic lipid based concentrations in fish of 26,400 and 6400 μg/kg lipids, values that are at least roughly a factor (1–4) × 10^6 higher than the concentrations due to ingestion of microplastic containing 1000 μg/kg NP. Based on these data we conclude that it is highly unlikely that ingestion of microplastic by cod as a representative example of marine fish would lead to negative effects of exposure to NP.

Bisphenol A – In their recent review, Flint et al. (2012) provide global ranges for BPA concentrations in surface waters, sediments and biota. Concentrations in sediments and suspended solids range from 0.7 to 56 μg/kg, with a range of 5.6–56 μg/kg for marine waters in The Netherlands (Flint et al., 2012; Vethaak et al., 2005). Again assuming an increased BSAF of about 15 for polar chemicals like BPA, this would translate to a range of about 20–1700 μg/kg on a lipid basis. We are aware of only one study that actually measured BPA in river benthos: Takahashi et al. (2003) reported a range of 0.3–12 μg/kg wet weight for the Tama river, a range that is about two orders of magnitude higher (i.e. ~30–1200 μg/kg worm lipids) when corrected for dry weight and lipid content assuming a DW/WW ratio of 0.2 and a lipid fraction of 0.05. This range agrees very well with the range of 20–1700 μg/kg that was calculated from published concentrations in sediments and estimates of BSAF. In the previous section we modeled a steady state concentration of 0.05 μg/kg worm lipids at a high but realistic sediment plastic content of 81 mg/kg ($S_{PL} = 8.1 \times 10^{-5}$) and a steady state concentration of about 60 μg/kg for a sediment plastic content of 10% sediment ($S_{PL} = 0.1$). The latter steady state concentration thus fairly agrees to the lower end of the range of concentrations often encountered in the environment. This implies that plastic ingestion can explain such concentrations. However, this only occurs if the plastic concentration is very high, i.e. 3–10%, if the environmental concentrations are at this lower end of the range and if the ingested plastic is the dominant or only source of BPA and has a relatively high BPA concentration.

For BPA many surface water concentration data are available including specific values for the North Sea to which also the cod plastic ingestion data relate. For global surface waters the data fall in the range of 0.0005–21 μg/L, with detected values of 0.014–0.33 μg/L specifically for marine water locations in The Netherlands (Belfroid et al., 2002). BCF data for BPA are scarce, but published values range from 5 to 68 (Flint et al., 2012; Staples et al., 1998), implying that BPA is not considered a bioaccumulative compound. Combination of the lower boundaries of BCF and concentration data and normalizing on 5% lipids would yield BPA concentrations in fish of at least 0.05 μg/kg lipids for global waters and 1.4 μg/kg for marine waters in The Netherlands, like the North Sea. The concentrations resulting from BPA leaching from ingested plastic were calculated to range between 0.015 and 0.13 ng/kg, which is three orders of magnitude lower. Consequently, we conclude that exposure of fish by plastic ingestion makes a negligible contribution compared to uptake from ambient water and common prey items.

4. Summarizing discussion

In the above sections we showed that ingestion of microplastic by the lugworm may constitute a substantial exposure pathway, but that the combination of required conditions reflects an unlikely scenario and that risks still would be limited because of the low environmental NP and BPA concentrations required. Ingestion of microplastic by cod is expected to result in a marginal contribution to NP and BPA exposure, which therefore is irrelevant too, even considering the uncertainty in the modeled concentrations and the variability of environmental concentrations.

By our neglect of biotransformation, use of relatively high plastic concentrations and rather high chemical exchange coefficient k_1, the present conclusions may be considered conservative, implying that the contribution by plastic ingestion will be negligible in general. This assessment already accounted for the main factors of uncertainty such as worm length, feeding mode, gut retention time and plastic to water exchange kinetics. However, our present assessment concerned direct exposure and did not address secondary poisoning of for instance benthivorous fish, by consumption of benthic invertebrates that are exposed through microplastic ingestion. Therefore, modeling secondary poisoning and experimental validation of prognostic model based conclusions is recommended. Further, it should be noted that the anticipated limited relevance of chemical leaching after ingestion by fish, does not imply that leaching from marine plastics as such is irrelevant for aquatic species. After all, NP and BPA releases from consumer products and waste water treatment are known to be substantial.

We reviewed global ranges of NP and BPA concentrations in water and sediments, which already cause considerable exposure to these chemicals. Additives are known to be leached directly into fresh and marine waters due to the natural breakdown of plastic in the environment (Flint et al., 2012) and plastic thus contributes to these concentrations. Finally, we emphasize that the present conclusions rely on prognostic modeling and that validation by experimental data and field data is to be recommended.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.12.013.

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