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Evaluating the contribution of ingested oil droplets to the bioaccumulation of oil components — A modeling approach

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HIGHLIGHTS

- Without oil droplet uptake, 75% of the PAH body burdens were predicted accurately.
- $\sum$PAH body burdens were predicted within a factor of five deviation.
- Oil droplets increased model accuracy only for the filter feeder *Mytilus edulis*.
- For non-filter feeders, oil droplet uptake could be neglected.

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ABSTRACT

The dietary uptake of oil droplets by aquatic organisms has been suggested as a possible exposure pathway for oil-related chemicals. We confronted two bioaccumulation models, one including and one neglecting oil droplet uptake, with measured polycyclic aromatic hydrocarbon (PAH) body burdens of five marine species. The model without oil droplet uptake was able to predict 75% of the observations within one order of magnitude. Total PAH body burdens were predicted within a factor of five. For most species, inclusion of oil droplet uptake did not improve model accuracy, suggesting a negligible contribution of oil droplet uptake to PAH bioaccumulation. Only for *Mytilus edulis*, model accuracy improved (up to five times) after the inclusion of oil droplet uptake. Our findings suggest filter feeding as a determinant for the PAH uptake via oil droplets, but more research is needed to test this hypothesis.

1. Introduction

During oil spills, the marine pelagic ecosystem is exposed to the water accommodated fraction (WAF) of oil (French-McCay, 2004). This WAF consists of the water soluble fraction (WSF) and dispersed oil droplets (Ramachandran et al., 2004). Oil droplets form naturally by physical processes e.g. mixing by wind and waves, but their formation can also be enhanced by applying chemical oil dispersants (Ramachandran et al., 2004). For aquatic organisms living in the water column, bioaccumulation and toxicity of oil components have mainly been ascribed to the WSF (French-McCay, 2004). However, the size range of oil droplets that do not resurface (<20 μm) typically overlaps with the size range of food items for certain aquatic organisms e.g. copepods (Hansen et al., 2009; Nordtug et al., 2011a) or can attach to food (Olsvik et al., 2011). Therefore, ingested droplets have been suggested as an additional uptake route for oil components (Baussant et al., 2001; Hansen et al., 2009; Nordtug et al., 2011b). For the impact assessment of oil spills, it is important to quantify how ingestion of oil droplets affects the bioaccumulation of oil components (De Laender et al., 2011b). However, the contribution of the ingested oil droplets to the body burdens of oil components is at present unclear. A few studies compared the toxicity of dispersed oil with and without droplets to actively feeding organisms and found a negligible effect of droplets on the studied endpoints (Hansen et al., 2009, 2012; Nordtug et al., 2011b). However, these studies considered short exposure periods only and focused on toxicity while bioaccumulation was not assessed.

It can be expected that the contribution of ingested oil droplets to the body burdens of oil components depends on the feeding type of the organism, on the partitioning of oil components between water and oil and on the capacity of the organism to eliminate oil components. Depending on the available food concentrations, filter-feeding organisms can filter large volumes of water (Bayne et al., 1993) and these species are probably exposed to a higher number of oil droplets compared to,

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for example, actively hunting predators. Also, while water soluble components will mainly partition to the water, less water soluble components e.g. polycyclic aromatic hydrocarbons (PAHs) will remain in the oil droplets when dispersed in water (Payne and Driskell, 2003; Redman et al., 2012). Especially for the less water soluble components, ingestion of oil droplets could serve as an additional exposure pathway.

In this study, we assess to what extent oil droplets contribute to the body burden of PAHs in aquatic species using a bioaccumulation model. For this purpose, we extended an existing bioaccumulation model (Hendriks et al., 2001) with the ingestion of oil droplets and tested if this extension increased model accuracy. We used data from four published studies to evaluate model accuracy (Aas et al., 2000; Baussant et al., 2001; Bechmann et al., 2010; Song et al., 2012), representing a total of 98 measured concentrations of 27 PAHs in five aquatic species. Finally, we interpret our results based on the oil–water partitioning of the oil components and the feeding type of the species.

2. Materials & methods

2.1. The bioaccumulation model

The bioaccumulation model used in this study is based on classical fugacity theory and on allometry, i.e. rate constants for influx and efflux scale with body size (Hendriks et al., 2001). Accumulation kinetics are modeled as a function of the octanol–water partition of the organic chemical and of the weight, lipid content and trophic level of the species considered.

The bioaccumulation model (Eq. (1)) considers uptake via water and food and elimination via water and food, by growth dilution and by biotransformation. This model has been tested for various groups of organic chemicals and taxa (Hendriks et al., 2001; De Laender et al., 2009, 2010, 2011a; Baert et al., 2013). Symbols used in the equations are listed in Table 1.

$$\frac{dC_i}{dt} = k_{0,x,in} \cdot C_{0,w} + k_{1,x,in} \cdot C_{i-1} - \sum_{j=0}^{j=3} k_{j,x,out} \cdot C_i \quad (1)$$

We extended this model with uptake and elimination rates via ingested oil droplets, $k_{oil,x,in}$ and $k_{oil,x,out}$ respectively (Eqs. (2)–(4)):

$$\frac{dC_i}{dt} = k_{0,x,in} \cdot C_{0,w} + k_{1,x,in} \cdot C_{i-1} + k_{oil,x,in} \cdot C_{oil} - \sum_{j=0}^{j=3} k_{j,x,out} \cdot C_i - k_{oil,x,out} \cdot C_i \quad (2)$$

$$k_{oil,x,in} = \frac{p_{oil}}{1-p_{oil}} \cdot \frac{1}{p_{CH_2,oil} \cdot (K_{ow}-1)+1} \cdot \frac{w^{-\kappa}}{\rho_{H_2O,oil} + \frac{\rho_{CH_2,oil}}{q_{T:c} \cdot K_{ow}} + \frac{1}{p_{CH_2,oil} \cdot K_{ow} \cdot (1-p_{oil}) \cdot q_{T:c} \cdot \gamma_{oil}}} \quad (3)$$

$$k_{oil,x,out} = \frac{1}{p_{CH_2,i} \cdot (K_{ow}-1)+1} \cdot \frac{w^{-\kappa}}{\rho_{H_2O,oil} + \frac{\rho_{CH_2,oil}}{q_{T:c} \cdot K_{ow}} + \frac{1}{p_{CH_2,oil} \cdot K_{ow} \cdot (1-p_{oil}) \cdot q_{T:c} \cdot \gamma_1}} \quad (4)$$

2.2. Model testing

To evaluate if the extension with oil droplets resulted in more accurate model predictions, we compared measured body burdens of oil components with predictions by the model without (Eq. (1)) and with (Eq. (2)) oil droplets. The body burdens were calculated assuming equilibrium between the compartments (water, oil, biota, and food) and Eqs. (1) and (2) were rewritten to reflect steady state conditions (Eqs. (5) and (6), symbols in Table 1).

$$C_i = \frac{k_{0,x,in} \cdot C_{0,w} + k_{1,x,in} \cdot C_{i-1}}{\sum_{j=0}^{j=3} k_{j,x,out} \cdot C_i} \quad (5)$$

$$C_i = \frac{k_{0,x,in} \cdot C_{0,w} + k_{1,x,in} \cdot C_{i-1} + k_{oil,x,in} \cdot C_{oil}}{\sum_{j=0}^{j=3} k_{j,x,out} \cdot C_i + k_{oil,x,out} \cdot C_i} \quad (6)$$

We focused on PAHs because: (i) they are the best studied group of oil components (Kennedy and Farrell, 2005) and (ii) the bioaccumulation model has been shown to predict body burdens for these substances reasonably well (Hendriks, 1999; De Laender et al., 2011a). We acknowledge that the number of suitable oil-related studies is limited (Olsen et al., 2013b) but we were still able to find four suitable studies. In these studies, biota were exposed to mechanically dispersed oil i.e. without use of a chemical dispersant and PAH concentrations in the oil, in the WAF and in the biota were reported. These studies reported PAH body burdens in five species: three fish species (*Gadus morhua* (Aas et al., 2000), *Paralichthys olivaceus* (Song et al., 2012) and *Scophthalmus maximus* (Baussant et al., 2001)), one mollusk (*Mytilus edulis* (Baussant et al., 2001)) and *Pandalus borealis* (Bechmann et al., 2010), a crustacean (Table 2). All studies except the *P. olivaceus* study used a continuous flow system (Sanni et al., 1998) to prepare the oil dispersions.

PAH-specific values needed for the model were the K_{ow}, used to calculate most rate constants (Table S1, Hendriks et al., 2001), and the biotransformation rate constant $k_{3,x,out}$. Physicochemical parameters, including K_{ow}, were obtained from the PETROTOX model (CONCAWE, 2011). For fish, the minimum and maximum biotransformation rates of individual PAHs were based on previous studies (Arnot et al., 2008; De Laender et al., 2011a). Shellfish and invertebrates have a less efficient PAH metabolism than vertebrates and PAH biotransformation rates for *M. edulis* and *P. borealis* were assumed to be between 10% of the minimum and maximum PAH biotransformation rates for fish (Livingstone, 1998; Hendriks et al., 2001).

We assumed that the ingestion coefficient of oil droplets (γ_{oil}) was equal to the ingestion coefficient of food (γ_1). Three model parameters related to oil droplets were unknown: the fraction of ingested oil droplets assimilated by the organism (p_{oil}), the water layer diffusion resistance associated with oil droplets ($\rho_{H_2O,oil}$) and the lipid layer permeation resistance associated with oil droplets ($\rho_{CH_2,oil}$). The latter two parameters have been calibrated before for ingested food particles (Hendriks et al., 2001). However, it is unknown if the uptake mechanism of substances from oil droplets is comparable to the uptake mechanism from food particles and thus if the resistances associated with food uptake are also applicable for the uptake from oil droplets. Therefore, we assumed that the uptake of substances from oil droplets followed the same mechanism as the uptake of substances from food (Hendriks et al., 2001): only substances of assimilated oil i.e. oil that passes the intestine wall, were considered taken up. For p_{oil}, quantitative data were lacking. Egestion of oil droplets has been observed e.g. in the fecal pellets of copepods (Olsen et al., 2013a) but no information about the proportion of egested to ingested oil droplets was given. These three oil droplet related parameters were thus accompanied by a large uncertainty (Table 1).

Measured water concentrations of PAHs often represent the sum of the truly dissolved PAHs ($C_{0,w}$) and PAHs present in microscopic oil droplets (C_{oil}, Redman et al., 2012). In order to predict body burdens with the bioaccumulation model, these two fractions needed to be inferred from the measured total water concentrations. Both fractions were calculated based on the solubility of the components, as described elsewhere (Redman et al., 2012). Solubility values were obtained from the PETROTOX model (CONCAWE, 2011). PAH oil concentrations were