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DOI
10.1016/j.chemosphere.2015.05.040

Publication date
2015

Document Version
Final published version

Published in
Chemosphere

Chemosphere 138 (2015) 33–39

Contents lists available at ScienceDirect

Chemosphere

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

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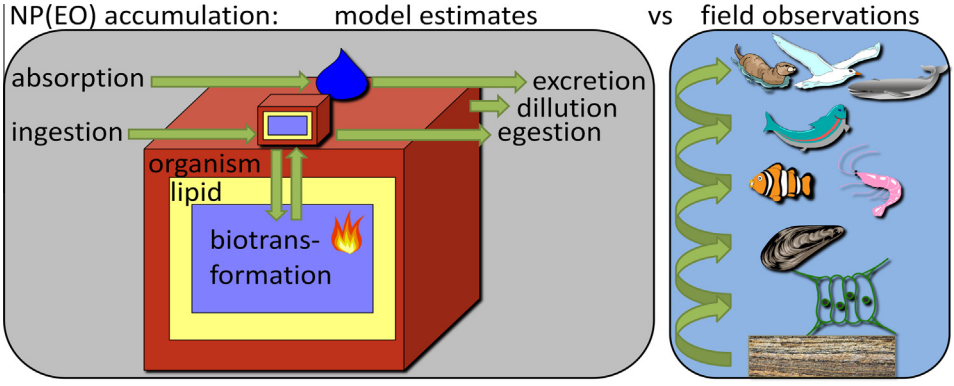
HIGHLIGHTS

- We modeled the trophic transfer of NP and NPEOs in an estuarine–marine food chain.
- Model estimates were compared to field and laboratory data.
- Modeled accumulation factors were within a factor of 5 of the observations.
- Estimated biota-sediment accumulation factors were lower than 1.
- Estimated biomagnification factors were close to 1.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 February 2015
Received in revised form 10 May 2015
Accepted 15 May 2015
Available online 27 May 2015

Keywords:
Uptake
Elimination
Biotransformation
Toxicokinetics
Western Scheldt estuary

ABSTRACT

There are several studies on bioaccumulation and biomagnification of nonylphenol (NP) and its ethoxylates (NPEOs), but their toxico-kinetic mechanisms remain unclear. In the present investigation, we explored the accumulation of NP and NPEOs in estuarine–marine food chains with a bioaccumulation model comprising five trophic levels. Using this model, we estimated uptake and elimination rate constants for NPEOs based on the organisms' weight and lipid content and the chemicals' K_{ow}. Further, we calculated accumulation factors for NP and NPEOs, including biota-sediment accumulation factors (BSAF) and biomagnification factors (BMF), and compared these to independent field measurements collected in the Western Scheldt estuary in The Netherlands and field data reported in the literature. The estimated BSAF values for NP and total NPEOs were below 1 for all trophic levels. The estimated BMF values were around 1 for all trophic levels except for the highest level (carnivorous mammals and birds). For this trophic level, the estimated BMF value varied between 0.1 and 2.4, depending on the biotransformation capacity. For all trophic levels, except primary producers, the accumulation estimates that accounted for biotransformation of NPEOs into NP were closer to the field data than model estimates that did not

Abbreviations: *E*, coefficient of efficiency; *i*, trophic level; NP, nonylphenol; NPEOs, nonylphenol ethoxylates; OMEGA, optimal modeling for ecotoxicological assessment.

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http://dx.doi.org/10.1016/j.chemosphere.2015.05.040

include biotransformation, indicating that NP formation by biotransformation of NPEOs might occur in organisms.

1. Introduction

Nonylphenol ethoxylates (NPEOs, where *s* represents the number of ethoxylate units) are non-ionic surfactants used in household and agricultural industrial products (Ying, 2006; Soares et al., 2008). After use, long-chain NPEOs are degraded to the more toxic nonylphenol (NP) and short-chain NPEOs (Giger et al., 1984). Various studies suggest that NP and NPEOs mimic natural estrogens and disrupt the endocrine systems of many species (Nimrod and Benson, 1996; Zhao et al., 2014). The toxicity of these substances and their synergistic toxic effects on aquatic organisms has been demonstrated in laboratory studies (Hu et al., 2014). Moreover, measured NP concentration in estuaries and seawaters in, for example, China, Singapore, Greek, The United Kingdom and The Netherlands were above the hazardous concentration for 5% of species (HC_5 of 0.84 μg L^{-1}), indicating an ecological risk for aquatic species (Diehl et al., 2012; Gao et al., 2014). Based on a log octanol–water partition coefficient ($\log K_{ow.}$) of 4.5 for NP and >3.7 for NPEOs, the substances are expected to have a high sorption affinity to sediment and high food chain accumulation potential (Ahel and Giger, 1993; Ying, 2006). Yet, only a few field studies have investigated whether NP and NPEOs accumulate in marine food chains (Hu et al., 2005; Diehl et al., 2012). Diehl et al. (2012) found biomagnification of NP in sea otters and staghorn sculpins collected in North American Pacific Coast estuaries. Conversely, Hu et al. (2005) found that NP and NPEOs exhibited trophic dilution in a marine food web from Bohai Bay in China. While several laboratory studies provided insight into the uptake, elimination and biotransformation processes that govern the accumulation and biomagnification of NP in aquatic organisms, such data are not available for NPEOs. In the present investigation, we explored the bioaccumulation and biomagnification of NP, $NPEO_1$, $NPEO_2$ $NPEO_{3-16}$ and total NPEOs ($NPEO_{1-16}$) in an estuarine–marine food chain and we assessed the role of biotransformation using a toxicokinetic model (Hendriks et al., 2001). We compared modeled uptake and elimination rate constants of NP and NPEOs with empirical rate constants from laboratory studies. Further, we compared modeled accumulation factors, including biota-sediment accumulation factors (BSAF) and biomagnification factors (BMF), to independent field data collected in the Western Scheldt estuary in The Netherlands and additional field data reported in the literature.

2. Methods

2.1. The OMEGA model

The Optimal Modeling for Ecotoxicological Assessment (OMEGA) bioaccumulation model is a Microsoft Office Excel spreadsheet model developed for chemical risk assessment purposes. It combines mass balance and allometric theory in order to predict the accumulation of organic compounds and metals in aquatic or terrestrial organisms (Hendriks et al., 2001). The OMEGA model has been successfully applied to estimate the accumulation behavior of many chemicals, including organochlorines, polycyclic aromatic hydrocarbons and metals (Hendriks et al., 2001; Veltman et al., 2006; Stadnicka et al., 2012). Default values for parameters are obtained as a function of chemical properties (e.g., K_{ow}) and biological traits (e.g., body mass), to minimize empirical research that is severely limited by financial, practical, and ethical constraints. OMEGA calculates the equilibrium concentration of chemical residues in organisms as the sum of influx via water (absorption) and uptake from food (assimilation) divided by the total elimination rate, which comprises elimination via water ($j = 0$), feces ($j = 1$), growth dilution ($j = 2$) and biotransformation ($j = 3$). The concentration in an organism $C_{i,x}$ (μg kg^{-1} lipid weight) is thus calculated as (Hendriks et al., 2001)

$$C_{i,x} = \frac{\left(k_{0,x,in} \times C_{0w,x} + k_{1,x,in} \times C_{i-1,x}\right)}{\sum_{0}^{3} {}_{j} k_{j,x,out}} \quad (1)$$

where $k_{0,x,in}$ represents the rate constant for absorption (μg L^{-1}/μg kg^{-1} wet weight d^{-1}), $C_{0w,x}$ the dissolved concentration in water (μg L^{-1}), $k_{1,x,in}$ the rate constant for assimilation (μg kg^{-1} wet weight/μg kg^{-1} d^{-1}), $C_{i-1,x}$ the concentration in food (μg kg^{-1} wet weight) and $\sum k_{j,x,out}$ the sum of the rate constants for elimination (d^{-1}). Uptake rates and elimination rate constants pertaining to water, feces and growth dilution are calculated as functions of species' and chemical properties, according to relationships that have been calibrated on hundreds of rate constants from laboratory studies (Hendriks et al., 2001). For biotransformation, however, empirical rate constants have to be used, as it is currently not possible to estimate biotransformation rates directly from species' physiological characteristics and chemical properties (Van der Linde et al., 2001).

2.2. Modeling uptake and elimination rate constants

In principle, uptake and elimination were calculated as functions of the species' trophic level, weight and lipid content and the chemical's K_{ow}. The estuarine–marine food chain in OMEGA consists of five trophic levels (Hendriks et al., 2001; Veltman et al., 2006). The first trophic level ($i = 1$) consists of primary producers, such as aquatic plants, phytobenthos and phytoplankton. The second trophic level ($i = 2$) comprises herbi-detritivores and consists of molluscs, polychaetes and small crustaceans (i.e. zooplankton). The third trophic level ($i = 3$) consists of primary carnivores, such as small pelagic fish and large crustaceans (i.e. shrimps, crabs, lobsters). The fourth trophic level ($i = 3.5$) consists of primary–secondary carnivores, such as gadoids, perciforms and anadromous fish species. The highest trophic level ($i = 4$) consists of secondary carnivores, such as seabirds and mammals. The equations and parameter values used for calculating the absorption, assimilation and elimination rates, including the weight and lipid content of the different tropic levels and the chemicals' K_{ow} values, are provided in the Supporting Information (Text Section S1; Table S1).

2.3. Empirical biotransformation rates

Biotransformation appeared to be the predominant mechanism determining the fate of nonylphenolic compounds in aquatic organisms (Ahel et al., 1994). For example, NP can be metabolized in the liver and excreted through the bile of fish as NP-glucuronide or related hydroxylated compounds (Arukwe et al., 2000; Sundt et al., 2009). For biotransformation of NP by primary producers, we used a biotransformation rate of 0.1 d^{-1} based on algae

(*Cyclotella caspia*) (Liu et al., 2013). For herbi-detritivores, a biotransformation rate of 10.2 d^{-1} based on water fleas (*Daphnia magna*) was used (Preuss et al., 2008). Metabolic biotransformation half-lives ($t_{1/2,met}$) measured in multiple tissues of trout (*Oncorhynchus mykiss*) and salmon (*Salmo salar*) were converted to biotransformation rate constants according to $\ln(2)/t_{1/2,met}$, which in turn were used to calculate a geometric mean biotransformation rate constant of 0.3 d^{-1} for primary and primary–secondary carnivores (Coldham et al., 1998; Arukwe et al., 2000; Arnot et al., 2008). Unfortunately, no biotransformation data for strictly secondary carnivores were available. Therefore, we estimated biotransformation rates for secondary carnivores from the difference between experimentally derived elimination rate constants and the values predicted for physical–chemical elimination (Van der Linde et al., 2001). We calculated a biotransformation rate of 0.4 d^{-1} for secondary carnivores based on a whole body biological half-life of 1.5 d^{-1} measured in rats (*Rattus* sp.) administrated with NP and an elimination rate of 0.02 d^{-1} for secondary carnivores as calculated with OMEGA (Knaak et al., 1966). For NPEOs, only biotransformation data for bacteria were available (Kvestak and Ahel, 1995; Gu et al., 2010). Therefore, we used the biotransformation rate constants for NP also for NPEOs, assuming that the biotransformation rates for NPEOs were similar to those for NP.

2.4. Modeling accumulation factors

BMF values were calculated by dividing the concentration in the organism $C_{i,x}$ (lipid weight) by the concentration in its food $C_{i-1,x}$ (lipid weight). Concentrations were expressed on a lipid basis to avoid reflecting differences in storage capacity. For BSAF values, the concentration in the organism $C_{i,x}$ (lipid weight) was divided by the concentration in sediment $C_{0,x}$ (organic carbon). As some laboratory studies reported only bioconcentration factors (BCF) instead of uptake and elimination rate constants, we also calculated BCF values by dividing absorption by elimination (see Section 2.2) and compared these with empirical BCF values. The model was run with and without biotransformation rates to assess the effect of biotransformation on the accumulation of NP and NPEOs, yielding BSAF, BMF, BCF and elimination estimates with and without biotransformation. The residues of substances in species were calculated from dissolved water concentrations (Eq. 1). In order to calculate BSAF values with OMEGA, the dissolved concentration in water was derived from the chemical's concentration in sediment based on the solids–water partition coefficient K_d. At high aqueous concentrations, the molecules of non-ionic surfactants aggregate into micelles (Clunie and Ingram, 1983). The critical micelle concentrations of 5–13 mg L^{-1} for NP and 42 mg L^{-1} for NPEOs were more than three orders of magnitude higher than the aqueous NP and NPEOs concentrations measured at the locations included in the present study (see Section 2.5), indicating that micelle formation is not likely to occur (Brix et al., 2001; Ying, 2006). Therefore, the sorption of the NP and NPEOs to soil was calculated in the same way as sorption of neutral organic chemicals by relating the K_d to the organic carbon–water partition coefficient K_{oc} according to Karickhoff et al. (1979):

$$K_d = f_{oc} \cdot K_{oc} \quad (2)$$

with K_d representing the solids–water partition coefficient (L kg^1 dry weight), f_{oc} representing the fraction of the sediment as organic carbon (kg organic carbon/kg dry weight) and K_{oc} representing the organic carbon normalized partition coefficient (L kg^{-1} organic carbon). We used K_{oc} values from field measurements for the estimation of dissolved NP and NPEOs concentrations in water. Field-based $\log K_{oc}$ values ranged between 3.6 and 6.3 for NP, 5.5 and 5.6 for $NPEO_1$ and 5.2 and 6.4 for $NPEO_2$, corresponding with a geometric mean $\log K_{oc}$ value of 5.2 for NP, 5.5 for $NPEO_1$ and 5.7 for $NPEO_2$ (SI, Table S1). Following Van Vlaardingen et al. (2003), we calculated a $\log K_{oc}$ of 3.8 for $NPEO_{3-16}$.

2.5. Field and laboratory data acquisition and treatment

Independent field data pertaining to concentrations of NP and NPEOs measured in sediments ($n = 2$), algae ($n = 1$), common cockles (*Cerastoderma edule*) ($n = 1$), lugworms (*Arenicola marina*) ($n = 2$), mysid shrimps (*Mysis* sp.) ($n = 2$), brown shrimps (*Crangon crangon*) ($n = 2$), sprats (*Sprattus sprattus*) ($n = 2$), soles (*Solea solea*) ($n = 2$), European eels *Anguilla anguilla* ($n = 4$) and common terns (*Sterna hirundo*) ($n = 1$) were obtained from a monitoring program carried out in the Western Scheldt estuary nearby Terneuzen in The Netherlands in 2005. Sampling and analysis of NPEOs were carried out according to methods reported elsewhere (Zhao et al., 1999; De Voogt et al., 2000). Measured concentrations that were below the detection limit were set to half the detection limit and we assessed the influence of different methods for handling non-detects on the field-based accumulation values by setting the non-detects at the same value as the corresponding detection limit and at zero. Additional NP and NPEOs data were obtained from other field and laboratory studies reported in the literature. To facilitate comparison, we assigned all species from the field and laboratory dataset to the trophic levels used for the OMEGA calculations. Trophic levels were allocated based on feeding preferences reported in the literature and databases (Pauly et al., 1998; Fishbase, 2015). A BSAF value was calculated from each sediment–organism pair, which consisted of the measured concentrations in one sediment and one organism sample taken at the same location and during the same sampling event. Similarly, a BMF value was calculated from reported predator–prey pairs as specified in the particular study, which consisted of organism samples taken at the same location and during the same sampling event. Concentrations from replicate samples were geometrically averaged before calculating the accumulation factors. Concentrations in sediments and organisms were converted to an organic carbon dry weight basis and lipid weight basis, respectively. If reported, we took the organic carbon and lipid fractions from the original study. If the organic carbon fraction or lipid fraction was not given, we obtained area- or species-specific values from other studies. We collected 44 sediment–organism pairs and 24 predator–prey pairs from seven field studies for NP and 27 sediment–organism pairs and 13 predator–prey pairs from five field studies for NPEOs, respectively. The reported predator–prey pairs consist of a predator that was one trophic level above its prey, except for four secondary carnivores that were two or three trophic levels above their prey. The BMFs of these predator–prey pairs were excluded from the dataset and interpreted separately. As the accumulation factors are based on equilibrium partitioning between the sediment organic carbon content and/or the species' lipid content(s), the BSAF and BMF values are theoretically independent of sediment type or species (Wong et al., 2001). Therefore, we calculated for each trophic level an overall geometric mean BSAF and BMF value based on the BSAF and BMF values from all individual data pairs that belong to the same trophic level. Empirical uptake and elimination rate constants and BCF values of 14 species from 15 laboratory studies were compared to model predictions. This was done for NP only, because we did not find empirical uptake and elimination rate constants and empirical BCF values for NPEOs in the literature. The collected field and laboratory data with allocated trophic levels and predator–prey relations are provided in the SI (Table S2).

2.6. Model performance evaluation

The performance of OMEGA was evaluated by comparing model estimates with field-based accumulation values and laboratory-derived rate constants. The coefficient of efficiency E (dimensionless) was calculated to assess the model performance (Legates and McCabe, 1999). E was calculated for each substance based on all available trophic levels according to

$$E = 1 - \frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(O_i - \overline{O})^2} \quad (3)$$

where O_i represents the log-transformed observed value for each sediment–organism pair, predator–prey pair or individual rate constant, P_i the log-transformed estimated value for each data pair or rate constant, $\overline{O}$ the log-transformed mean of the observed values and n the number of observed values. E ranges from minus infinity to 1, with a value of 1 indicating perfect model estimation. A positive E indicates that the model estimates are more accurate than the mean of the observed values.

3. Results

3.1. Estimated accumulation factors compared to field data

The estimated BSAF values for NP and total NPEOs were below 1 for all trophic levels (Fig. 1). The estimated BMF values for NP and total NPEOs were around 1 for all trophic levels, except for secondary carnivores. For this trophic level, the BMF values estimated with and without biotransformation were 0.1 and 2.4, respectively. The estimated accumulation patterns for $NPEO_1$, $NPEO_2$ and $NPEO_{3-16}$ were similar to those of total NPEOs (SI, Fig. S1).

For NP and total NPEOs, the difference between accumulation estimates and average field-based accumulation factors were less than a factor of 5 for most trophic levels. Exceptions were found for NP, where estimates with biotransformation underestimated average field-based accumulation factors for primary–secondary and secondary carnivores up to a factor of 6 and 150, respectively. Conversely, the estimates of total NPEOs without biotransformation overestimated average field-based accumulation factors for secondary carnivores up to a factor of 50. In addition, the averaged field-based BSAF and BMF values of NP for primary producers were more than 1 order of magnitude underestimated and overestimated, respectively. For total NPEOs, the averaged field-based BMF value for primary producers was more than 1 order of magnitude overestimated. The coefficients of efficiency calculated for NP and total NPEOs ranged from 0.1 to −1.4, indicating that the model estimates were similar to or slightly less accurate than the mean of the measurements.

3.2. Uptake and elimination rate constants

For NP, the estimated absorption and elimination rate constants without biotransformation decreased with each trophic level by a factor of 10–15, except for secondary carnivores (Fig. 2A and B). The absorption rate for this trophic level was a factor of 500 lower compared to primary–secondary carnivores. The BCF estimates without biotransformation increased with each trophic level by a factor of 1.5 (Fig. 2C), with the exception of secondary carnivores. The estimates with biotransformation were comparable to those without biotransformation, except for secondary carnivores. For this trophic level, the elimination and BCF estimates with biotransformation were a factor 30 higher and lower, respectively, than estimates without biotransformation. The estimated uptake and elimination rates for $NPEO_1$, $NPEO_2$ and $NPEO_{3-16}$ were comparable to those for NP (SI, Table S3).

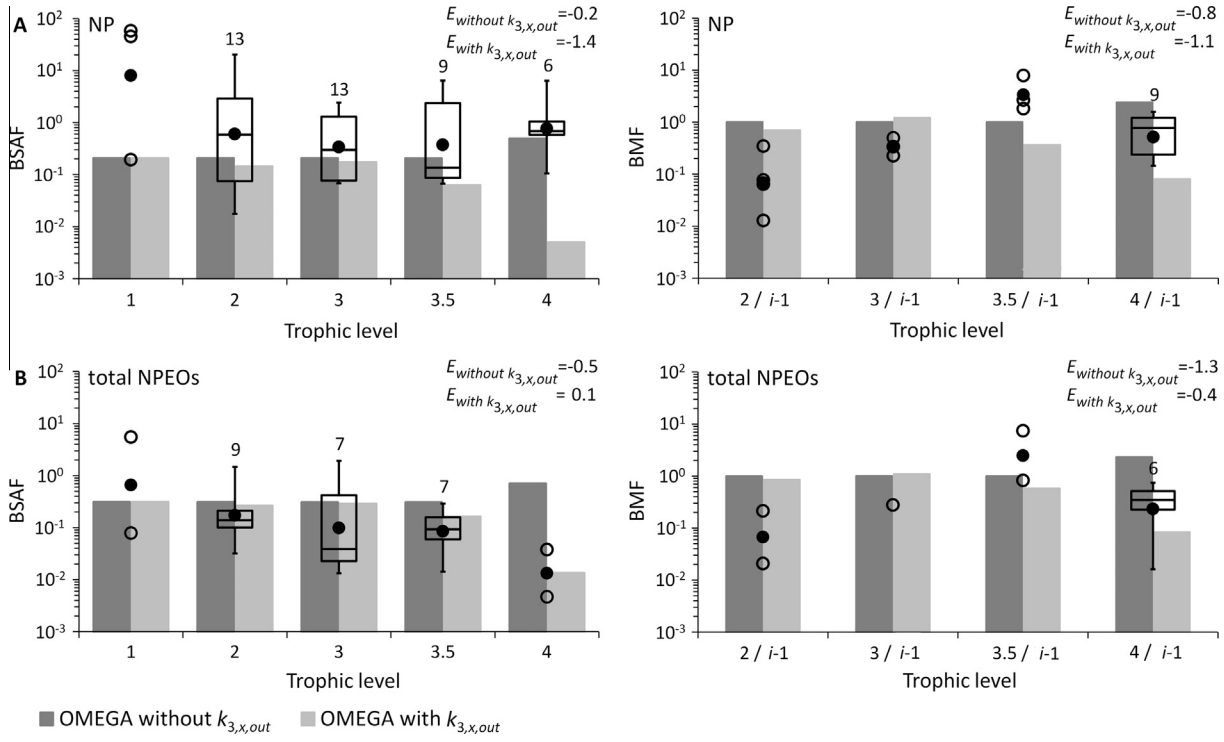

Fig. 1. Biota-sediment accumulation factors (BSAF) (lipid weight carbon weight^{-1}) and biomagnification factors (BMF) (lipid weight lipid weight^{-1}) modeled with and without biotransformation rate $k_{3,x,out}$ (d^{-1}) of (A) NP and (B) total NPEOs ($NPEO_{1-16}$) compared to geometric mean field-based values (closed circles). Parameter E represents the coefficient of efficiency. Spear-style box plots show the distribution of the values obtained from field studies. The number on top of each box plot is the number of data pairs for that trophic level. When the number of data pairs was small ($n < 5$), the box plots were replaced by the individual values (open circles).

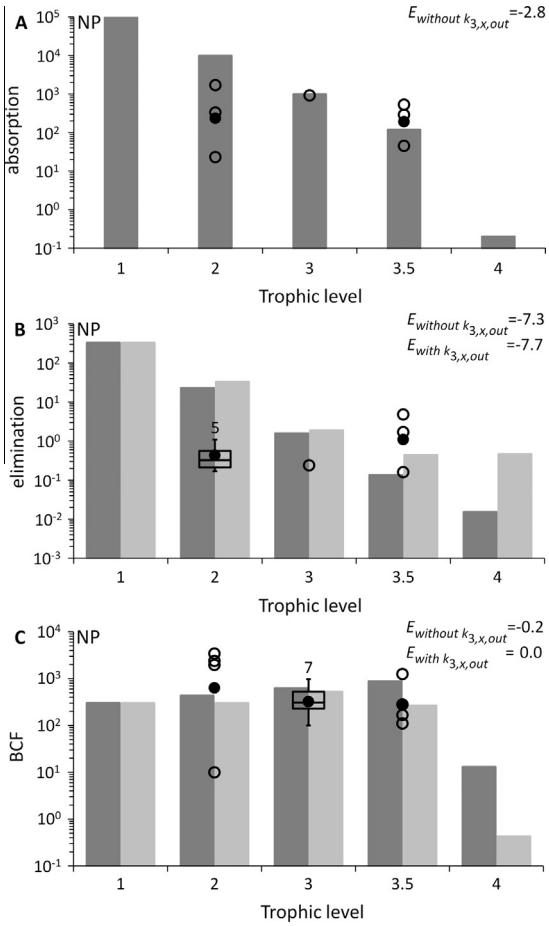

Fig. 2. Modeled (A) absorption (μg kg^{-1} wet weight/μg L^{-1} d^{-1}) without biotransformation rate $k_{3,x,out}$ (d^{-1}), (B) elimination (sum of excretion, egestion, and growth dilution) (d^{-1}) and (C) bioconcentration factors (BCF) (μg kg^{-1} wet weight/μg L^{-1}) with and without biotransformation rate $k_{3,x,out}$ (d^{-1}) compared to geometric mean empirical values (closed circles). See Fig. 1 for further captions.

The estimated absorption rate constants and BCF values for primary carnivores and primary–secondary carnivores were within a factor of 3 from the mean empirical values. Both empirical absorption and elimination rate constants for herbi-detritivores were overestimated by one order of magnitude or more. However, the difference between estimated and average empirical BCF values was less than a factor of 2 for this trophic level (Fig. 2C). The coefficients of efficiency for BCF with and without biotransformation were 0.0 and −0.2, respectively.

4. Discussion

4.1. Model assumptions and uncertainties

In the OMEGA model, residues of substances in species were calculated from dissolved water concentrations. The dissolved chemical concentration in water was predicted from the chemical concentration in sediment based on the K_d and K_{oc}. Karickhoff et al. (1979) observed a good relationship between K_d and K_{oc} values, but noted deviations for sediments having an organic carbon content lower than 0.1%. The organic carbon content of the sediment samples used in the present study ranged from 0.2% to 10%, indicating that the model approach to sorption (Eq. 2) should be representative. We used K_{oc} values from field measurements for the estimation of dissolved NP and NPEOs concentrations in water, because K_{oc} values from laboratory studies were not available and K_{oc} values of NPEOs estimated with quantitative structure–activity relationships (QSAR) and K_{ow} values were found to be one to two orders of magnitude lower than the field-based K_{oc} values (Karickhoff et al., 1979; EPI Suite, 2012; Table S2). K_{oc} predictions from QSARs and K_{ow} are designed for and based on properties of uniformly hydrophobic organic compounds and might be less successful for estimating K_{oc} values for amphiphilic surfactants such as NPEOs (Van Vlaardingen et al., 2003). This might explain the differences between the field-based and QSAR- and K_{ow}-based K_{oc} values for NPEOs. For NP, the QSAR-based logK_{oc} value of 4.5 obtained from EPI Suite and the K_{ow}-based logK_{oc} value of 4.3 were one order of magnitude lower than the mean field-based logK_{oc} value (text Section 2.4). The QSAR- and K_{ow}-based logK_{oc} values for $NPEO_1$ and $NPEO_2$ were 3.1 and 3.9, and 3.4 and 4.0, respectively. For $NPEO_{3-16}$, QSAR-based values were not available and the K_{ow}-based logK_{oc} value of 3.5 was comparable with the field K_{oc} value. A sensitivity analysis with OMEGA revealed that the BSAF values for NP modeled with K_{ow}-based K_{oc} values overestimated most field-based BSAF values with a factor of 2–5 (SI, Fig. S2). The model performance increased for the estimates with biotransformation (E increased with 1) and decreased without biotransformation (E decreased with 0.2). For total NPEOs, this analysis showed that the BSAF estimates for most trophic levels were at least one order of magnitude higher than the field-based BSAF values (E decreased with 1.6–2.3). These findings indicate that the BSAF estimates are sensitive to K_{oc} values and that K_{oc} values must be selected with care for amphiphilic surfactants. However, the BMF and BCF values and the rate constants were insensitive to changes in K_{oc} values.

As biotransformation appeared to be the predominant mechanism determining the fate of nonylphenolic compounds in aquatic organisms (Ahel et al., 1994), we included biotransformation rate constants in OMEGA. The biotransformation rate constants of NP for the different trophic levels are considered to be indicative because the values were based on a limited number of species. The biotransformation rate constants of NPEOs were assumed to be similar to those of NP. However, a laboratory study with bacteria showed that the biotransformation rates of longer-chain NPEOs ($s \geqslant 5$) were higher than those of short-chain NPEOs ($s \leqslant 4$) (Kvestak and Ahel, 1995). In addition, Jonkers et al. (2005), found that the biodegradation rates of NPEOs (0.06–0.07 d^{-1}) were higher than of NP (0.03 d^{-1}) in surface waters. A sensitivity analysis with twice the biotransformation rates of NPEOs revealed only minor changes in accumulation factors, with model performance slightly improving for BSAF (E increased with 0.1), but not for BMF (E decreased with 0.4). These findings indicate that the model is insensitive to small changes in NPEOs biotransformation rate constants (SI, Fig. S3).

The biotransformation rate constant for secondary carnivores was lower than or comparable to those for the other trophic levels. Yet, the impact of biotransformation on the accumulation in secondary carnivores appeared to be much larger compared to the other trophic levels (Fig. 2). This could be explained by the fact that both the absorption and elimination rate constants decreased with increasing trophic level (Hendriks et al., 2001), so the relative contribution of biotransformation to the total elimination increased with trophic level. This is particularly the case for secondary carnivores, because the uptake and elimination rate constants via water were two orders of magnitude lower than those for the other trophic levels.

As the modeled BMF values pertained to predators that are one trophic level above their respective prey, the field-based BMF values for predator–prey pairs consisting of a predator that was two or three trophic levels above its prey were excluded from the dataset. However, the BMF values for these predator–prey pairs were in the same range as the BMF values for predators that were one

trophic level above their prey. Exceptions were found for NP where Diehl et al. (2012) reported a field-based BMF value of 10.9 for otters (*Enhydra lutrisnereis*) feeding on mussels (*Mytilus californianus*). For total NPEOs, Hu et al. (2005) reported a field-based BMF value of 2.2 for herring gulls (*Larus argentatus*) feeding on mullets (*Liza so-iuy*). Including the BMF values for secondary carnivores that were two to three trophic levels above their prey increased the overall field-based BMF value for secondary carnivores with 0.2 for NP and 0.1 for total NPEOs, suggesting that the exclusion of these predator–prey pairs played no major role in our study.

Measured concentrations of 13 samples in the Western Scheldt estuary were below the detection limit. The concentrations of these samples were set to half the detection limit. Statistical estimates of the concentration below the detection limit are generally preferred, provided that the proportion of detects per analyte is higher than 50% (Helsel, 1990). We were unable to use statistical methods because the detection limits in the present study varied with analyte and sample intake, yielding an insufficient proportion of detects per analyte. This analysis revealed no changes in the accumulation factors for NP and NPEOs (SI, Fig. S4). For the individual oligomers, however, some field-based accumulation factors varied with the method for handling non-detects, in particular the BSAF and BMF for $NPEO_1$ and $NPEO_2$. These accumulation factors should be interpreted with caution because they are entirely based on data pairs with one or two non-detects.

The OMEGA model assumes that chemical concentrations are uniformly distributed within an organism's body. Yet, NP and NPEOs might accumulate to varying concentrations in different tissues of organisms. For example, the NP concentrations in bile and feces of trout (*O. mykiss*) were a factor of 2–15 higher than in liver after 144 h of dosing (Coldham et al., 1998). Unfortunately, we did not find data needed to convert NP and NPEOs concentrations measured in specific tissues to whole-body concentrations, such as partition coefficients between tissues or tissue weights. The comparability of measurements and model estimates of NP and NPEOs body burdens might be improved by using more complex multi-compartment models which includes the movement of chemicals among different organs or tissues. However, although multi-compartment models may outperform one-compartment models, they require more physiological data (Stadnicka et al., 2012).

4.2. Model estimates compared to field- and lab-based data

The field-based accumulation factors differed within a trophic level (Fig. 1), in particular for NP. The variation of accumulation values within the same trophic level might be attributed to different feeding selectivity and feeding locations of species (Burkhard, 2003). For example, the BSAF value of NP based on demersal seabreams (*Acanthopagrus schlegel*) was higher compared to benthopelagic fish species (Zhang et al., 2011; Fishbase, 2015). In the Morro Bay, the highest accumulation values of NP were determined for otters (*E. lutrisnereis*), which feed on species that are likely residents of the estuary (Diehl et al., 2012). The accumulation factors for other marine mammals collected in Morro Bay were lower than those for otters, possibly due to a weaker link to the estuarine trophic chain. Judged from these two examples and the negative coefficients of efficiency *E* (Fig. 1), it might be worth to include different food chains in OMEGA, such as a benthic, an intermediate hyper-benthic and a pelagic food chain (Veltman et al., 2006), provided that sufficient field-based accumulation values are available for comparing model estimates with field data. Another explanation for the variation in field-based accumulation factors might be found in temporal variation in biotransformation rates. Kvestak and Ahel (1995) found that the biotransformation of $NPEO_{1-16}$ by bacteria was a factor of 2.5 higher at 23 °C than at 13 °C. Therefore, temperature might play a large role in the bioaccumulation of NPEOs. Temperature-dependent biotransformation rate constants could not be included in the model, because of insufficient data to establish quantitative relationships between biotransformation rate constants and temperature.

NP appeared to be biotransformed in many aquatic organisms (Ahel et al., 1994; Sundt et al., 2009), but the accumulation factors for NP with biotransformation were less accurate than the estimates without biotransformation (Fig. 1). This was particularly the case for (primary-)secondary carnivores for which the field accumulation factors were underestimated by a factor 6–150. We tested whether the formation of NP by biotransformation of NPEOs might cause the elevated NP concentration in (primary-)secondary carnivores by modeling the accumulation of NP including biotransformation of NPEOs into NP. This was done assuming that organisms produce NP by biotransformation of NPEOs, that the biotransformation rates for NPEOs are similar to those for NP, and that NP produced by biotransformation of NPEOs is eliminated from the organisms according to the elimination rate constants for NP. This test resulted in NP estimates within a factor of 1–5 from the field data. The coefficients of efficiency were $E = -0.2$ for BSAF and -1.0 for BMF (SI, Text Section S2; Fig. S5), thus suggesting an improvement of the model fit compared to the NP model with biotransformation of NPEOs into NP ($E = -1.4$ for BSAF and -1.1 for BMF). This indicates that NP formation by biotransformation of NPEOs might occur in organisms. Yet, these results should be interpreted with caution as biotransformation of $NPEO_2$ in salmon (*O. mykiss*) did not produce NP, but $NPEO_2$-glucuronide (Cravedi et al., 2001). Whether other fish species or birds and mammals can metabolize ethoxylated NPs into NPs and the fate of NPEOs metabolites in organisms are to be determined.

For primary producers, the field-based BSAF value of NP was underestimated by one order of magnitude and the BMF values for NP and NPEOs were overestimated by one order of magnitude (Fig. 1). These misfits can partly be attributed to the low lipid fraction of the plankton/detritus samples of 0.06% (Diehl et al., 2012) compared to the lipid fraction of 1% as used in OMEGA. Another explanation might be that the uptake of substances in proteins might become an important accumulation mechanism in organisms with a low lipid fraction (<1%) (Hendriks et al., 2005), such as some algae species. Therefore, the estimations of algal accumulation might be improved by including protein–water distribution coefficients in OMEGA.

5. Conclusions

In the present study, we estimated uptake and elimination rate constants and accumulation factors of NP, $NPEO_1$, $NPEO_2$, $NPEO_{3-16}$, and total NPEOs for five trophic levels in estuarine–marine food chains with the OMEGA model. Such toxicokinetic parameters are extensively used in environmental risk assessment. For example, BSAF and BMF values or uptake and elimination rate constants are frequently used for predicting chemical residues of hydrophobic chemicals in organisms, assessing toxicity risks associated with contaminated sediments and developing water or sediment quality criteria for the protection of wildlife and human health. The inherent gaps in accumulation data for new or relative unknown substances, such as NP and NPEOs, can potentially be filled by toxicokinetic models like OMEGA. The estimated BSAF values for NP and total NPEOs were below 1 for all trophic levels. The estimated BMF values were around 1 for all trophic levels, except for secondary carnivores. For this trophic level, the estimated BMF value varied between 0.1 and 2.4, depending on the

biotransformation capacity assumed (Fig. 1). For all trophic levels, except primary producers, the accumulation estimates that accounted for biotransformation of NPEOs into NP were closer to the field data than model estimates that did not include biotransformation, indicating that NP formation by biotransformation of NPEOs might occur in organisms (SI, Fig. S5). The model estimates for NP and NPEOs might be improved by modeling different food chains in OMEGA, such as a benthic, intermediate hyper-benthic and pelagic food chain, provided that sufficient field-based accumulation values are available for comparing model estimates with field data.

Acknowledgments

We thank Prof. Dr. Mark A.J. Huijbregts and the anonymous reviewers for their comments and suggestions which have improved the quality of this manuscript.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.05.040.

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