



Modelling the transfer and accumulation of microplastics in a riverine freshwater food web

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ARTICLE INFO

Keywords:

Freshwater ecology
Trophic transfer
Food web modelling
Biomagnification
Plastic pollution

ABSTRACT

Microplastics are a pervasive pollutant of aquatic ecosystems and are reported to interact with a wide range of aquatic biota. The complexities of natural food webs means that the transfer and accumulation of microplastics is difficult to assess, and only a handful of studies have attempted to quantify trophic transfer in freshwater biota. Bioaccumulation models can provide a valuable tool to explore the transfer of microplastics along complex food webs, but such approaches have been rarely applied to freshwater ecosystems. Here, a food web accumulation model was implemented to assess the transfer, bioaccumulation and hence biomagnification potential of microplastics along a food web located in the River Slaney catchment in south-east Ireland. Literature feeding values and environmental field data were used to simulate microplastic uptake in benthic macroinvertebrates, with fish and Eurasian otter (*Lutra lutra* (Linnaeus, 1758)) comprising the higher trophic levels. Microplastic concentrations from the model were used to form a basis of comparison with empirical data for benthic macroinvertebrates and brown trout (*Salmo trutta* Linnaeus, 1758). Predicted concentrations were greatest in benthic macroinvertebrates and lowest in fish species such as European eel (*Anguilla anguilla* (Linnaeus, 1758)) and three-spined stickleback (*Gasterosteus aculeatus* (Linnaeus, 1758)). Biota magnification factors for fish and *L. lutra* indicate that microplastic accumulation between the specific predator-prey interactions are not expected. To better inform models such as this, and therefore improve their accuracy, it is important to gain a better understanding of microplastic retention times in biota and the interaction between microplastics and resources utilised by benthic macroinvertebrates and fish, such as plant material, allochthonous detritus as well as terrestrial and aerial prey.

Capsule: A bioaccumulation model, used to explore the transfer and possible accumulation of microplastics along a riverine food web, showed that microplastic are not expected to accumulate in the gastrointestinal tracts of higher level biota based on the predator-prey interactions specified.

Introduction

Microplastics (1 μm to 5 mm) are a pervasive pollutant of aquatic ecosystems (reviewed in Ajith et al. 2020, Li et al. 2020, Lusher 2015, Wong et al. 2020, Xu et al. 2020) encompassing a diverse array of morphology types, sizes and polymers (Rochman et al., 2019). The bioavailability and fate of microplastics in biota may be explained by

microplastic characteristics, species-specific ingestibility based on particle size constraints (e.g. mouth aperture in relation to microplastic length and width) (Koelmans et al., 2020; Rochman et al., 2019; Scherer et al., 2018; Wright et al., 2013), abiotic factors governing biotic interaction (e.g. microplastic exposure levels) (Collard et al., 2019; Krause et al., 2020) as well as organism physiology (e.g. gut morphology), which may influence particle retention, their likelihood of translocating

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<https://doi.org/10.1016/j.envadv.2022.100192>

Received 25 September 2021; Received in revised form 10 February 2022; Accepted 11 February 2022

Available online 12 February 2022

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to other tissues and transferring within food webs (Provencher et al., 2019; Roch et al., 2021). So far, microplastics have been reported in an extensive range of aquatic organisms, from aquatic invertebrates (e.g. Doyle et al. 2019) and fish (reviewed in Azevedo-Santos et al., 2019) to large marine mammals (e.g. Besseling et al. 2015). Growth in scientific literature pertaining to freshwaters has demonstrated that microplastics are just as prevalent in freshwater biota (reviewed in Azevedo-Santos et al. 2021, O'Connor et al. 2019, Parker et al. 2021). While the main pathways of exposure for many organisms are thought to be direct (Lusher, 2015; Ory et al., 2017; Roch et al., 2020), for predators it is assumed microplastics are primarily obtained through prey (i.e. secondary ingestion).

The capacity for microplastics to transfer between trophic levels and along simple food chains has been demonstrated in laboratory (e.g. Kim et al. 2018, Setälä et al. 2014) and semi-natural environments (Nelms et al., 2018). While in the field, microplastics recovered in piscivorous fish species, birds, and mammals are purported to have been derived primarily from prey items (Campbell et al., 2017; D'Souza et al., 2020; Eriksson and Burton, 2003; Hurt et al., 2020; Winkler et al., 2020). Secondary ingestion could suggest a potential mechanism for microplastics to bioaccumulate in freshwater biota, possibly resulting in biomagnification, but the inherent complexities of food webs are challenging to replicate in controlled environments. Furthermore, while microplastics may be ingested and egested by higher level organisms (e.g. Eurasian otter *Lutra lutra* (Linnaeus, 1758)) (O'Connor et al., 2022., in press; Smiroldo et al., 2019), the level that may be retained by an individual is not yet apparent. As a result, little is known about how microplastics may transfer and accumulate through different predator-prey combinations and so the potential for biomagnification is generally not yet well established (Krause et al., 2020). Food web bioaccumulation models can provide a valuable tool to explore the transfer of microplastics along food webs (Alava, 2020; Diepens and Koelmans, 2018).

Such models typically use a mass balance of uptake (e.g. dietary ingestion) and loss (e.g. egestion) rates to describe the bioaccumulation process of a pollutant in a specific organism. Mass balance models for individual organisms can be incorporated into larger descriptions of food webs in order to simulate bioaccumulation resulting from exposure to environmental media (e.g. water, sediment) and/or diet (Radomyski et al., 2018). Additional data for the pollutant and the specific organisms are required, such as information on feeding rates (Mackay and Fraser, 2000). Results obtained from the model, such as the predicted pollutant concentration in a specific organism, can be compared to empirical observations in order to assess model performance. While some food webs are modelled dynamically, and may account for temporal changes in biomass due to the immigration, emigration and mortality of species (e.g. Boyer et al. 2022, Ma and You 2021), most assume a steady state (i.e. time-averaged net result of uptake and loss processes), and do not reflect short-term seasonal and spatial variations (Herzke et al., 2016). Although previously applied to assess the movement of plastic pollution along marine food webs (e.g. Alava 2020, Diepens and Koelmans 2018), very few modelling approaches have been used in the context of freshwaters, with the exception of Ma and You (2021), who used a time-dynamic simulation model to explore the accumulation effect of microplastics through the food web of Baiyangdian Lake (China).

Therefore, the aim of the present study was to simulate the potential transfer, bioaccumulation and biomagnification of microplastics in a realistic food web using steady state solutions derived from a set of equations capable of accommodating microplastic uptake from multiple dietary components (Diepens and Koelmans, 2018). Here, terminology related to the fate of contaminants in food webs is used, with bioaccumulation referring to the progressive increase of microplastics in an organism over time due to the rate of ingestion exceeding the rate of egestion, and biomagnification referring to higher concentrations of microplastics being attained at higher trophic levels (Nordberg et al., 2009). The model was implemented for the River Slaney food web

located in south-east Ireland, which includes ecologically significant species such as brown trout (*Salmo trutta* Linnaeus, 1758) and *L. lutra*. Environmental concentrations obtained from the River Slaney were used to explore how microplastics transfer and potentially bioaccumulate in River Slaney biota and to what extent they may biomagnify through the food web.

Material and methods

Food web accumulation model

The model was adopted from the food web accumulation model (MICROWEB) developed and described by Diepens and Koelmans (2018), which studied the accumulation of plastics and associated contaminants (i.e. hydrophobic organic compounds (HOCs)) in biota from an Arctic food web. As the primary aim of the present study was to assess the potential food web transfer and biomagnification of microplastics themselves, only calculations pertaining to the first component of this model were implemented (Eq. (1)–(5)). That is the accumulation of microplastics in the gastrointestinal tract (GIT) of each taxon, with accumulation assumed to be a balance of uptake and loss processes (Diepens and Koelmans, 2018; Herzke et al., 2016). Uptake is restricted to the GIT, excluding microplastic accumulation in the tissue of the organism as well as adherence to surface anatomy (e.g. adherence to integument). Therefore, food web transfer refers to microplastic levels in the GIT only. According to Diepens and Koelmans (2018), the concentration of microplastics in biota can be modelled using the equation:

$$\frac{dC_{PLB,i}}{dt} = IR_i \sum_{j=1}^n (p_j C_{PLB,j}) - k_{loss,PL} C_{PLB,i} \quad (1)$$

The first term accounts for predator 'i' feeding on 'n' multiple food items 'j' with a species specific ingestion rate IR_i (g food g^{-1} biota d^{-1}). Dietary preferences ' p_j ' contribute to the diet as a fraction ($\sum p_j = 1$), each of which has a concentration of microplastic $C_{PLB,j}$ (g microplastics g^{-1} biota). The second term pertains to the loss rate constant of microplastics via egestion ($k_{loss,PL}$) (d^{-1}) and 't' is time. The steady state solution to Eq. (1) results in the microplastic concentration of species 'i':

$$C_{PLB,i} = \frac{IR_i \sum_{j=1}^n p_j (C_{PLB,j})}{k_{loss,PL}} \quad (2)$$

The first order loss rate constant ($k_{loss,PL}$) of microplastics can be calculated as the reciprocal of the gut retention time (GRT; d):

$$k_{Loss,PL} = \frac{1}{GRT, i} \quad (3)$$

Therefore Eq. (2) can be implemented in an alternate form (Diepens and Koelmans, 2018):

$$C_{PLB,i} = IR_i * GRT_i \sum_{j=1}^n (p_j C_{PLB,j}) \quad (4)$$

Microplastic uptake can be modelled once species specific ingestion rates, dietary preferences, microplastic fraction per dietary item (Eq. (5)) and either the loss rate constant of microplastics (i.e. $k_{loss,PL}$) (Eq. (2)) or the GRT of that organism (Eq. (4)) are known. The mass fraction of microplastics in an organism can be calculated as:

$$S_{PL,i} = \frac{M_{PL,i}}{(M_{PL,i} + M_{B,i})} \quad (5)$$

where $M_{PL,i}$ is the mass of microplastics in the organism and $M_{B,i}$ is the mass of that organism. This is mathematically equivalent to $S_{PL,i} = C_{PLB,i} / (1 + C_{PLB,i})$.

All modelling was performed in Excel 2016, and the model was verified by manually calculating all steps in the transfer of microplastics along a hypothetical 'dummy' food web (Supplementary Information

S2). Differences between the manual and excel C_{PLB} calculations were all less than 2.5%, although an 11% difference was observed in the biota magnification factor (BMF) for small fish. This is likely explained by the rounding of manual and excel calculations.

River Slaney food web and model parameters

The food web in question pertains to the River Slaney catchment, located in south-east Ireland, which was defined through microplastic studies of River Slaney biota (e.g. O'Connor et al. 2020; O'Connor et al., 2022, in press), subsequent dietary analysis from these studies, as well as information from a number of regulatory monitoring surveys that described community assemblages (e.g. Kelly et al. 2014, 2015). Three trophic levels (TL) were included that comprised benthic macroinvertebrates at the base of the food web, fish species such as Eurasian minnow (*Phoxinus phoxinus* (Linnaeus, 1758)) (TL: 3.2), three-spined stickleback (*Gasterosteus aculeatus* (Linnaeus, 1758)) (TL: 3.3), *S. trutta* (TL: 3.4) and European eel (*Anguilla anguilla* (Linnaeus, 1758)) (TL: 3.6) (Froese and Pauly, 2021), with *L. lutra* as a top predator (TL: \approx 3.8) (Mirzajani et al., 2021) (Fig. 1). Dietary preferences for *L. lutra* and *S. trutta* were verified using field data from earlier microplastic studies of the same catchment (O'Connor et al., 2020; O'Connor et al., 2022, in press), while the dietary preferences of *G. aculeatus* and *P. phoxinus* were estimated from frequency of occurrence data obtained from Roundwood Reservoir and the Vartry river in Co. Wicklow, Ireland (Dauod et al., 1985a, 1985b). Finally, dietary fractions of *A. anguilla* were derived from a study of the lower River Shannon (Ireland) (Cullen and McCarthy, 2007). Food ingestion rates and gut retention times (GRTs) for biota were obtained from the literature and ranges were supplied where available. Most parameters for fish were based on temperatures of

approximately 10–15 °C, which corresponds with the conditions under which field data were collected (i.e. August, September). Ingestion rates and GRTs for benthic macroinvertebrates were obtained to represent the main taxa reported in fish and *L. lutra* diets, which were also assessed for microplastics in the field. In some instances however, data were only available for taxa not presently found in Ireland, but which exhibit similar feeding characteristics (e.g. plecopteran shredders). Only macroinvertebrate taxa that contributed a fraction > 0.01 to the diet of fish or *L. lutra* were considered for modelling. Moreover, dietary preferences for which no microplastic data existed were grouped as 'other' (e.g. terrestrial invertebrates, winged adult insects). Ingestion rates and GRTs were expressed as a mean where two or three data points were found, or a geometric mean in the case of > 3 data points (Diepens and Koelmans, 2018). Furthermore, where taxa were represented by more than one family in the diet (e.g. Trichoptera), the mean value of both families was used. Where both the ingestion rate as well as the GRT were not available, data pertaining to similar taxa were used where possible (e.g. GRT for Lymnaeidae was used as values could not be found for Physidae). While the GRT of microplastics have been assessed for a select number of macroinvertebrate species (e.g. Scherer et al. 2017, Blarer and Burkhardt-Holm 2016), as well as fish (Roch et al., 2021), for many of the remaining taxa these were not known, and so in order to maintain consistency, only GRTs pertaining to food were used. The main invertebrate taxa included in the model comprised, *Gammarus* sp. (Amphipoda), Elmidae (Coleoptera), Chironomidae (Diptera), Ephemeroptera (e.g. Baetidae, Heptageniidae), Physidae (Gastropoda), Plecoptera (shredders) as well as Trichoptera (e.g. Hydropsychidae, Limnephilidae). A full list of the biological parameters and rates used to inform the model along with references are presented in Table S1.

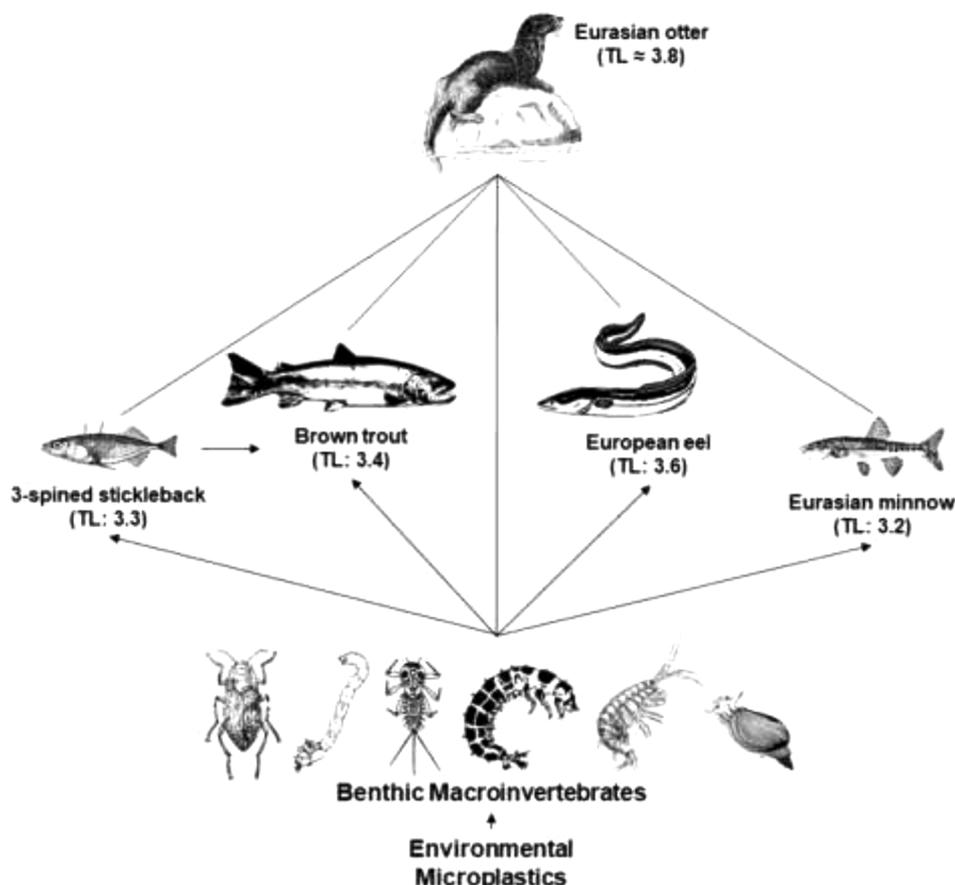


Fig. 1. Biota within the River Slaney food web along with specific predator-prey interactions as specified by dietary analysis and the literature. Microplastic uptake is simulated at the base of the food web through the feeding of benthic macroinvertebrates (TL: trophic level; all images were sourced from creative common archives).

Modelling scenario and endpoints assessed

Microplastic uptake was simulated through the diet of benthic macroinvertebrates at the base of the food web, with no parallel uptake of microplastics at higher trophic levels (i.e. direct ingestion). This approach is justified as the primary aim of the study was to assess the potential transfer of microplastics along the food web. Uptake at the base of the food web was simulated assuming a maximum level of exposure for benthic macroinvertebrates, irrespective of dietary preferences. This was deemed appropriate as information pertaining to microplastic contamination in food items (e.g. leaf detritus, periphyton) is currently limited and thus there would have been a lot of uncertainty in deducing microplastic concentrations within dietary fractions.

Empirical data from the River Slaney were used to inform the environmental microplastic fractions of the model (Table 1), while measured concentrations of microplastics in benthic macroinvertebrates and *S. trutta* (O'Connor et al., 2020; O'Connor et al., 2022, in prep.) were used to form a basis of comparison with predicted microplastic concentrations (Table 2). Data pertaining to surface water samples, benthic macroinvertebrates and *S. trutta* were collated from six sites along the River Slaney for the months of August and September (2017 and 2018), while data for river shore sediments were collated for seven separate sites within the same catchment (August and September, 2018) (Table 1). The default modelling scenario was based on recorded environmental fractions, which enabled initial comparison between field observations for biota and model outputs. These parameters were then adjusted, and the model optimised in such a way that predicted microplastic concentrations were encompassed within all empirical ranges for biota (i.e. minimum, maximum concentrations) (scenario 2). Finally, differences between the predicted and maximum concentrations in *S. trutta* were minimised by increasing the environmental microplastic fraction. This was performed in order to assess the possible contribution of macroinvertebrate prey to the diet of *S. trutta*, and the potential level of microplastics transferred to *L. lutra* (scenario 3). Microplastic concentrations in biota (C_{PLB}) was the main output parameter of the model, which was then used to calculate the bioaccumulation metric, or biota magnification factor (BMF) for each predator-prey combination through the equation $C_{PLB,i} / (\sum_{j=1}^n P_j C_{PLB,j})$. BMF values > 1 indicate bioaccumulation while values < 1 indicate trophic dilution (Diepens and Koelmans, 2018).

Microplastic abundance to mass conversions

As the concentration of microplastics is modelled as the weight of microplastic ingested per unit mass of animal (e.g. g microplastics g⁻¹ biota), microplastic abundances from respective datasets (e.g. sediment, macroinvertebrates) were first converted to mass using information on particle type, size and density. Fibres are usually assumed to be cylindrical with respect to their primary shape (i.e. not coiled) (Kooi and Koelmans, 2019) and so fibre mass (M_{fibre}) was estimated through the following equation (Zheng et al., 2020):

$$M_{fibre} = \pi r^2 h \rho \tag{6}$$

where r is half the fibre width, h is the length of the fibre and ρ the polymer density (weighted average) (g cm³). The abundances of fragments and film were converted to volume (V) (Eq. (7)) assuming the length (L) to width (W) ratio of a fragment equates to the width to height ratio (L:W=W:H) (Koelmans et al., 2020), and the height of a film is 10 times smaller than that of a fragment (after Kooi and Koelmans, 2019). A Corey shape factor (CSF) was then calculated (CSF = H/√L x W) (Koelmans et al., 2020; Kooi and Koelmans, 2019; Waldschläger and Schüttrumpf, 2019) and the particle volume (mm³) determined using the equation described in Koelmans et al. (2020):

$$V = \frac{\pi}{6} L^3 \times CSF^2 \tag{7}$$

Fragment and film mass were determined by multiplying the volume of the particle by the polymer density (weighted average). The average mass of each particle type was then applied to corresponding abundances in each dataset.

Results and discussion

Transfer and accumulation of microplastics in the River Slaney food web

The MICROWEB accumulation model was employed to simulate microplastic uptake by benthic macroinvertebrates and resulted in varying steady state concentrations in macroinvertebrate biota. Predicted concentrations in macroinvertebrates were deemed to be low based on initial uptake from environmental media (combined mean fraction in water and sediment) and large discrepancies were observed between predicted and measured concentrations. Results were most comparable when applying the maximum fraction of microplastics in sediment (default scenario), resulting in a range of 2.58 × 10⁻⁷ – 7.30 × 10⁻⁶ g microplastics g⁻¹ biota. Diptera (i.e. Chironomidae) exhibited the highest microplastic concentration overall, which was consistent with observations from the field (Table 2) (O'Connor et al., 2022, in prep.). While predicted concentrations were still generally lower than empirical observations, many estimates were within measured ranges (i.e. minimum and maximum microplastic concentrations). Exceptions to this were Coleoptera and Ephemeroptera, which exhibited the lowest concentrations based on model calculations that were 61% and 57% below their respective minimum field concentrations (Table 2). This may be explained by the comparatively low ingestion rates and GRTs for Elmidae (Coleoptera) (Steedman and Anderson, 1985), coupled with the relatively rapid gut clearance times in grazing Ephemeroptera (e.g. Baetidae, Heptageniidae) (Cowan and Peckarsky, 1994; Pereira, 1980) (Table S1).

Macroinvertebrate feeding ecology can vary depending on feeding strategy, resource availability and resource quality (i.e. nutritional value), as well as the nutrient assimilation efficiency of the organism. For instance, in a desert creek in Arizona, USA, Chironomidae were found to exhibit low assimilation efficiencies and very high ingestion rates, consuming up to four times their body weight per day (Fisher and Gray, 1983). Many shredders have been known to increase ingestion of low quality food in order to compensate for its decreased nutritional benefits (Cummins and Klug, 1979) and some scrapers (e.g. Gastropoda) with low nutrient assimilation efficiencies and high nutrient demands will also exhibit high ingestion rates in order to assimilate sufficient nutrients (Liess, 2014). As temperature exerts a direct influence on macroinvertebrate metabolism (Cummins and Klug, 1979) and gut clearance rates (Dam and Peterson, 1988), greater feeding intensity is expected under warmer conditions. Unlike many of the macroinvertebrate feeding studies that were available to parameterise the model, data pertaining to Ephemeroptera and Coleoptera (e.g. Cowan and Peckarsky 1994, Pereira 1980) were obtained under lower

Table 1

Environmental microplastic concentrations from the River Slaney used to determine the mass fraction of microplastics in surface water and sediment. Concentrations are expressed as g microplastics g⁻¹ sediment and g microplastics ml⁻¹ surface water.

Media	No. Sites	Mean	SE	Min	Max	Ref.
Water	6	2.81E-12	8.89E-13	2.96E-14	4.71E-11	O'Connor et al., unpublished
Sediment	7	1.44E-07	8.91E-08	1.58E-08	4.59E-06	Perich et al., unpublished
Combined		7.21E-08		7.92E-09	2.30E-06	

Table 2

Empirical and predicted microplastic concentrations in River Slaney biota (g microplastics g⁻¹ biota) along with biota magnification factors (BMF) following all adjustments of environmental microplastic fractions.

Group	Name	Empirical Concentrations (O'Connor et al., unpublished)				Model Predictions			BMF
		Mean	Median	Min	Max	Default ^a	Scenario 2 ^b	Scenario 3 ^c	
Inverts	Amphipoda	2.71E-05	3.18E-06	3.11E-07	2.83E-04	1.23E-06	3.19E-06	4.64E-05	
Inverts	Coleoptera	3.48E-05	6.19E-06	6.53E-07	3.00E-04	2.58E-07	6.70E-07	9.73E-06	
Inverts	Diptera	3.07E-04	2.67E-05	1.22E-06	2.07E-03	7.30E-06	1.90E-05	2.76E-04	
Inverts	Ephemeroptera	5.47E-05	1.82E-05	1.25E-06	3.63E-04	5.34E-07	1.39E-06	2.02E-05	
Inverts	Gastropoda	4.33E-06	8.85E-07	1.09E-07	1.81E-05	1.48E-06	3.86E-06	5.60E-05	
Inverts	Plecoptera	9.37E-05	2.00E-05	9.90E-07	1.93E-03	1.58E-06	4.12E-06	5.99E-05	
Inverts	Trichoptera	2.18E-05	5.10E-06	2.47E-07	3.42E-04	4.70E-07	1.22E-06	1.77E-05	
Fish	Minnow					5.72E-08	1.49E-07	2.16E-06	0.03
Fish	Stickleback					2.91E-08	7.56E-08	1.10E-06	0.02
Fish	Eel					2.15E-08	5.60E-08	8.14E-07	0.02
Fish	Brown trout ^d	3.56E-07	1.41E-08	3.45E-09	2.48E-06	6.54E-08	1.70E-07	2.47E-06	0.05
Mammal	Otter					3.07E-08	7.97E-08	1.16E-06	0.13

Predicted concentrations in River Slaney biota when:

^a The maximum microplastic fraction in environmental media is used (i.e. sediment).

^b Microplastic fraction in sediment is adjusted by a factor of 2.6 so as to match empirical ranges in macroinvertebrates.

^c The difference between the maximum and predicted concentration in *S. trutta* are reduced to 0.2% (factor of 37.8).

^d Empirical microplastic concentrations for *S. trutta* taken from O'Connor et al. (2020).

temperature ranges (e.g. 6–12 °C), and are possibly a better reflection of rates expected under field conditions. In the event of reduced temperatures, while similar trends may exist in terms of microplastic concentrations, differences in feeding rates between taxa would presumably be reduced (Cummins, 1973), and so microplastic intake is expected to be less. However, at lower temperatures GRTs would also be extended, which may increase the propensity for microplastics to accumulate in invertebrates. Nonetheless, it is clear that the data suggests discrepancies between the empirical and predicted concentrations in invertebrates based on the environmental microplastics levels used. In order to match all taxa with empirical ranges, it was necessary to increase microplastic fractions in sediment by a factor of 2.6 (scenario 2), which corresponds to a mass fraction of approximately 1.2×10^{-5} g microplastics g⁻¹ sediment (dry weight). Although all datasets were dominated by fibres, the presence of larger fragments in sediments, which are not bioavailable to biota (Koelmans et al., 2020), means that the discrepancies between empirical and model simulations for macroinvertebrates are likely to be greater than predicted. Sediment data were collected from separate sites to biota however, and only pertain to river shores (Perich et al., in prep), thus may not be reflective of conditions pertinent to the main river channel where the majority of macroinvertebrate kick samples originated. Although sediment samples were originally collected alongside biota (i.e. benthic macroinvertebrates) and surface water samples in the present investigation, they were not analysed for microplastics due to time and cost constraints within the wider project. Additionally, empirical concentrations observed in macroinvertebrates represent the entire organism, including adhering microplastic particles (i.e. external anatomy), and therefore differences may be expected given that predicted concentrations only reflect uptake in the GIT.

Microplastic uptake was simulated irrespective of dietary preferences in macroinvertebrates assuming maximum exposure to environmental microplastics. Although a rather simplistic exposure route, it was considered necessary as it would have been difficult to disseminate microplastic levels by food type, given that microplastic levels for these food items are not generally known. However, as microplastics have been observed interacting with plant material in aquatic environments (Castrop et al., 2020; Seng et al., 2020), and transfer of microplastics from plants to invertebrates has been demonstrated at laboratory level (e.g. Mateos-Cárdenas et al. 2019), it is likely that transfer from plant material serves as an important exposure pathway (Kalčíková, 2020). Stable isotope analysis by García et al. (2021) demonstrated that microplastic ingestion was generally higher in fish consuming a larger proportion of allochthonous carbon, which could be attributed to

predation on invertebrates consuming leaf detritus (e.g. shredders). It is possible therefore, that microplastics are adhering to leaf litter and periphyton, presenting a greater exposure pathway to benthic fauna than sediments alone.

Steady state microplastic concentrations in fish ranged from 2.15×10^{-8} for *A. anguilla* to 6.54×10^{-8} g microplastics g⁻¹ biota for *S. trutta* based on the default modelling scenario (i.e. maximum environmental fraction), and predicted concentrations were also within empirical ranges for *S. trutta* (Table 2). When the maximum microplastic fraction in sediment was increased by a factor of 37.8 (scenario 3), the simulated and maximum concentrations in *S. trutta* were reduced to a difference of 0.2% (Table 2). Interestingly, following this adjustment predicted concentrations in preferred invertebrate prey such as Diptera (i.e. Chironomidae) and Trichoptera, were most comparable to empirical mean values (difference: 11% and 19%, respectively), while prey rarely taken (e.g. Coleoptera, Ephemeroptera) showed some of the greatest differences (Table 2). On the other hand however, predicted concentrations in Gastropoda, which also form an important component of *S. trutta* diet, exceeded all empirical values following adjustments for scenario 3. The low selectivity of taxa like Coleoptera, Ephemeroptera and Plecoptera in the diet of *S. trutta* (dietary fractions: 0.05, 0.02, 0.01, respectively) reflects a preference for larger sized prey, such as Trichoptera, which are easier to detect and have a higher energetic value (Cochran-Biederman and Vondracek, 2017; Meissner and Muotka, 2006; Oscoz et al., 2005). Thus, it is expected that microplastic levels observed in these smaller sized taxa are unlikely to be transferred to *S. trutta*. As opportunistic foragers (Cochran-Biederman and Vondracek, 2017; Syrjänen et al., 2011), *S. trutta* are also known to consume terrestrial invertebrates as well as winged adult insects within the River Slaney catchment (O'Connor et al., 2020; Ryan and Kelly-Quinn, 2015), and while little is known regarding the microplastic levels in these prey items or what they might contribute in terms of dietary transfer, interactions with microplastics have been observed (e.g. Maaß et al. 2017, Rillig et al. 2017). As with microplastic assessments of GITs, dietary analysis of fish only provides a snapshot of the conditions at the time of sampling and inferences regarding microplastic concentrations in prey and fish should be interpreted carefully. This is particularly true given that significant relationships have not been observed between dietary composition and microplastic abundances (O'Connor et al., 2020).

Microplastic concentrations among fish species followed a similar pattern when environmental fractions were adjusted (Table 2). BMF values of 0.05 for *S. trutta*, 0.03 for *P. phoxinus* and 0.02 for *A. anguilla* and *G. aculeatus*, respectively, indicate that there is unlikely to be sufficient microplastic accumulation occurring between fish and their prey

that could lead to biomagnification of microplastics. This is accordance with the literature, which has found that biomagnification of microplastics is unlikely to occur in the GIT of fish, at least for the main microplastic size ranges reported ($> 100 \mu\text{m}$) (Covernton et al., 2021). Like invertebrates, differences in concentrations between fish may be explained by ingestion rates and GRTs, but also, the dietary composition specified for each species. There may be uncertainties associated with fish diets, particularly *P. phoxinus* and *G. aculeatus*, which were determined from frequency of occurrence data collected in a nearby system (i.e. Roundwood, Co. Wicklow) (Dauod et al., 1985a, 1985b), that may have overestimated the contribution of small prey, due to all items being assigned the same importance irrespective of their mass (Ahlbeck et al., 2012). Furthermore, as certain dietary information were only specified to Phylum level (e.g. Mollusca) within these studies (i.e. Dauod et al., 1985a, 1985b), the importance of items like Gastropoda may be overestimated in the model. However, it is noted that gastropods (e.g. Hydrobiidae, Physidae) were recovered in the diet of both *P. phoxinus* and *G. aculeatus*. Most parameters for fish were available for temperature ranges akin to field conditions (e.g. 10–15 °C) and so these were used where possible. Temperature affects the maximum rate of consumption in fish through its effects on gastric evacuation, and at low temperatures fish may cease to feed (Wootton, 2012). Concentrations in *A. anguilla*, which were the lowest in the context of the entire food web, are reflective of lower ingestion rates for a species, which is highly temperature dependent (Baras et al., 1998) and known to reduce feeding activity during colder months (Cullen and McCarthy, 2007). Though literature values for *A. anguilla* ranged between 0.02 - 0.04 g food g⁻¹ biota d⁻¹ (Schulze et al., 2004), the water temperatures for which these were estimated ($> 17^\circ\text{C}$) are likely higher than those anticipated based on the modelling conditions specified, and so the lower limit was used (Table S1). Furthermore, limited information regarding gut clearance times for the species creates some uncertainty surrounding the GRT which may be underestimated in this instance. This is also the case for *P. phoxinus*, which as a cyprinid species, does not contain a 'true' distinct stomach (Russell and Wootton, 1993; Wilson and Castro, 2010), and so the GRT only pertains to the foregut of the species. However, it is expected that contents in the hindgut would also be negligible at the time of foregut evacuation.

Following *A. anguilla* and *G. aculeatus*, the lowest microplastic concentration was predicted for *L. lutra*, and this was consistent following all adjustments of environmental microplastic levels (Table 2). Despite possessing the highest BMF value in the food web (BMF: 0.13), realistic biological ingestion and egestion data suggest that there is no bioaccumulation of microplastics in this top predator. Therefore, there is unlikely to be any biomagnification of microplastics in the River Slaney food web, based on the predator-prey interactions, parameters specified and the size range of the microplastics assessed. Although GRT times of 1 d (i.e. 24 h) were found to be the main length of time required to pass prey remains, it is acknowledged that some remains may take longer to evacuate, with scales of yellow perch *Perca fluviatilis* Linnaeus, 1758 being observed in spraints (i.e. faeces) up to 10 d following feeding of individuals in captivity (Carss and Parkinson, 1996). Moreover, while the daily food requirement of an adult *L. lutra* is estimated to be 0.13 g food g⁻¹ biota d⁻¹ (Kruuk et al., 1993, cited in Ruiz-Olmo et al., 2005), one study of a lactating female along the Shetland coast (Scotland, UK) calculated intake to be approximately 0.28 g food g⁻¹ biota d⁻¹ (Nolet and Kruuk, 1994). Thus, in a worst case scenario, should microplastics be retained in the GIT for such a duration, it is possible that biomagnification could occur, with BMF predictions of 1.30 in the case of 0.13 g food g⁻¹ biota d⁻¹ and 2.80 in the case of a lactating female.

The dietary preferences of *L. lutra* were informed from analysis of spraints collected from the River Slaney following isolation of microplastics (O'Connor et al., 2022., in press). As the primary aim of that study was to assess microplastic exposure, some dietary remains were damaged and could not be quantified, and therefore dietary results were expressed as frequency of occurrence. As with the diet of *P. phoxinus* and

G. aculeatus, dietary fractions were estimated from these data, and so there may be some inaccuracies with respect to dietary proportions and the importance of items such as benthic macroinvertebrates. Furthermore, as it was not possible to distinguish the vertebrae of salmonids (i.e. *S. trutta*, Atlantic salmon *Salmo salar* Linnaeus, 1758) through dietary analysis, all remains indicative of this family were assumed to represent *S. trutta* for the purposes of modelling. Lastly, though all cyprinids remains were grouped by family (i.e. Cyprinidae), vertebrate sizes coupled with diagnostic features of the asterisci (i.e. otoliths), meant that these remains most likely belonged to *P. phoxinus*.

Implications and recommendations

The simulation of microplastic transfer within the River Slaney food web, agrees with recent work, suggesting that biomagnification of microplastics within aquatic food webs is not currently predicted for the main size ranges reported in biota ($> 100 \mu\text{m}$) (Alava, 2020; Covernton et al., 2021; Diepens and Koelmans, 2018; Gouin, 2020; Walkinshaw et al., 2020). Moreover, bioaccumulation of microplastics is not expected between any of the predator-prey relationships defined within the River Slaney, which is unlike Diepens and Koelmans (2018) as well as Alava (2020), who reported microplastic accumulation between seal-Atlantic cod and humpback whale-zooplankton, respectively. Findings within the present study may be largely due to the transitory throughput of plastics in the predators defined (D'Souza et al., 2020), which would mitigate accumulation.

The microplastic concentrations reported here are merely a reflection of the balance between ingestion, gut retention and egestion (Diepens and Koelmans, 2018), and do not consider accumulation in tissues or organs, nor do they account for direct ingestion among fish, which is considered a significant pathway (Roch et al., 2020). It is noted however, that an extension of the present model has been recently applied to account for microplastic uptake in humans derived from consumption of, amongst others, fish tissue (Mohamed Nor et al., 2021). GRT is an important parameter in determining bioaccumulation of microplastics, and may be explained by organism physiology (e.g. GIT morphology) (Provencher et al., 2019). Roch et al. (2021) found that retention of microplastic particles in fish species was particle size-dependent, with a greater retention time for smaller particles in species like rainbow trout (*Oncorhynchus mykiss* (Walbaum, 1792)). Recent studies suggest that particle concentrations exponentially increase with decreasing size (Kooi and Koelmans, 2019; Roch et al., 2019), but are often overlooked in the environment due to detection limitations (Brander et al., 2020). This is particularly important in the context of bioaccumulation given the proclivity for these particle sizes to translocate to the surrounding tissues of organisms such as fish (e.g. $< 100 \mu\text{m}$) (Barboza et al., 2019). Therefore, as data used to inform the current model did not consider these size ranges ($< 100 \mu\text{m}$), the same conclusions regarding biomagnification may not necessarily apply to smaller microplastics or particles in the submicron range. However, correction procedures described by Koelmans et al. (2020) and Kooi et al. (2021) (see Supplementary Information S3), offer a correction factor (CF) to translate particle number concentrations within a measured size range to any default size range once the particle size distribution is known. In this case, the CF required to translate particle number concentrations from the measured size range (100 μm to 5 mm) to the default size range (1 μm to 5 mm) is $\text{CF} = 1909$. By applying a CF to the measured size range and calculating the ratio between the microplastic concentrations in the muscle and GIT of fish, Mohamed Nor et al. (2021) were able to probabilistically simulate the uptake of smaller particles (1–10 μm) in humans from consumption of fish tissue. While the excretion of microplastics in macroinvertebrates is reported to be rapid (Blarer and Burkhardt-Holm, 2016; López-Rojo et al., 2020) rates were shown to be size dependent (Weber et al., 2021) and so egestion of larger particles may take longer. It is noted however, that while Scherer et al. (2017) did not observe complete evacuation of spherical particles in Chironomidae (48

h period), a shorter GRT was observed in the presence of food. However, as this is only known for a select few taxa, further laboratory studies that assess the uptake and accumulation of microplastics in experiments with increased realism, would assist in improving the accuracy of the current model, which may have underestimated the true retention time of microplastics.

The discrepancies between predicted and empirical concentrations in invertebrate taxa, using realistic environmental microplastic fractions, suggests that the environmental microplastic data used here may not represent the true extent of microplastics exposure for biota. As noted earlier however, while surface water samples were collected from the same sampling sites as biota, sediments were not, nor were they collected from the main river channel and therefore do not provide a direct indication of microplastic levels for benthic macroinvertebrates. It is also possible that many smaller sized particles were overlooked in water and sediment samples due to the isolation methodologies employed, and so microplastics which are bioavailable to biota may not have been effectively recovered. This is reflected in the microplastic size classes isolated from these matrices, which were dominated by particles in the 350 µm to 5 mm category (water: 90%; sediment: 96%). One way to reduce methodological bias between biotic and abiotic samples in the future is to match the isolation and characterisation methods as close as possible (Kukkola et al., 2021). Additional explanations for the discrepancies observed in macroinvertebrates may be related to the microplastic exposure pathways for these biota. Garcia et al. (2021) reported that fish species with a higher proportion of allochthonous carbon also contained higher numbers of microplastics, which may imply that microplastics are being ingested either through terrestrial invertebrates or through ingestion of aquatic invertebrates consuming allochthonous detritus (e.g. shredders). As river food webs are closely coupled with the terrestrial environment (Allan and Johnson, 1997; Woodward and Hildrew, 2002), it is important that a better understanding of the possible microplastics inputs associated with these resources (e.g. leaf litter) is attained. Furthermore, while it is acknowledged that plants may represent a viable pathway for microplastics to enter aquatic food webs (Kalčíková, 2020), the extent to which they interact with microplastics in river ecosystems is still understudied. Additional information on these aspects, may allow for incorporation of microplastics through fractions of macroinvertebrate diet, improving upon the uptake pathway used in the current version of the model, but also inform additional pathways for fish.

Conclusions

This study implemented a food web accumulation model to simulate the transfer of microplastics through the River Slaney food web (Ireland), being one of the first to apply such an approach to a freshwater food web of this complexity. Model predictions showed that microplastic concentrations were highest in benthic macroinvertebrates, following uptake from environmental media, and lowest in fish species such as *A. anguilla* and *G. aculeatus* based on the feeding parameters and dietary preferences specified. BMF values for fish and *L. lutra* (< 1) indicate that accumulation between specific predator-prey interactions are not expected based on realistic ingestion and egestion data, and therefore biomagnification of microplastics is not predicted for this food web. These observations were consistent throughout all adjustments of environmental microplastic fractions, and are in agreement with the literature, which suggests that biomagnification is currently unlikely to occur in aquatic food webs. However, as microplastic accumulation was confined to the GIT only, translocation of particles to tissue or organs was not considered. Moreover, implementation of the model in this instance did not account for parallel uptake of microplastics in fish (i.e. direct ingestion). GRTs, as informed from the literature, only pertained to food and did not consider microplastic retention times, mainly due to a limited number of studies being available, and so true microplastic retention times may have been underestimated. As the GRT of

microplastics is considered especially important for the accumulation, translocation as well as dietary transfer of microplastics, it is imperative that further research is conducted so as to inform accumulation models like this, which are a valuable tool for exploring the transfer of microplastics in complex food webs. Moreover, information on microplastic interactions with additional dietary sources (e.g. plants, terrestrial resources) would assist in incorporating these items as part of invertebrate and fish diets, thus allowing for a more realistic assessment.

CRediT authorship contribution statement

James D. O'Connor: Conceptualization, Investigation, Validation, Writing – original draft, Visualization. **Heather T. Lally:** Conceptualization, Writing – review & editing, Supervision. **Albert A. Koelmans:** Conceptualization, Methodology, Validation, Writing – review & editing. **Anne Marie Mahon:** Supervision. **Ian O'Connor:** Project administration. **Róisín Nash:** Project administration, Writing – review & editing. **John J. O'Sullivan:** Writing – review & editing. **Michael Bruen:** Writing – review & editing. **Linda Heerey:** Writing – review & editing. **Sinéad Murphy:** Conceptualization, Validation, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was funded under the Irish Environmental Protection Agency (EPA) research program 2014 – 2020, through the research project “Sources, Pathways and Environmental Fate of Microplastics in Freshwater Systems (2016-W-LS-10)”. The EPA research program is a Government of Ireland initiative funded by the Department of Communications, Climate Action and Environment. It is administered by the EPA, which has the statutory function of coordinating and promoting environmental research.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2022.100192.

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