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Fate of nano- and microplastic in freshwater systems: A modeling study[★]



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ABSTRACT

Riverine transport to the marine environment is an important pathway for microplastic. However, information on fate and transport of nano- and microplastic in freshwater systems is lacking. Here we present scenario studies on the fate and transport of nano-to millimetre sized spherical particles like microbeads (100 nm-10 mm) with a state of the art spatiotemporally resolved hydrological model. The model accounts for advective transport, homo- and heteroaggregation, sedimentation-resuspension, polymer degradation, presence of biofilm and burial. Literature data were used to parameterize the model and additionally the attachment efficiency for heteroaggregation was determined experimentally. The attachment efficiency ranged from 0.004 to 0.2 for 70 nm and 1050 nm polystyrene particles aggregating with kaolin or bentonite clays in natural freshwater. Modeled effects of polymer density (1 -1.5 kg/L) and biofilm formation were not large, due to the fact that variations in polymer density are largely overwhelmed by excess mass of suspended solids that form heteroaggregates with microplastic. Particle size had a dramatic effect on the modeled fate and retention of microplastic and on the positioning of the accumulation hot spots in the sediment along the river. Remarkably, retention was lowest (18–25%) for intermediate sized particles of about 5 μ m, which implies that the smaller submicron particles as well as larger micro- and millimetre sized plastic are preferentially retained. Our results suggest that river hydrodynamics affect microplastic size distributions with profound implications for emissions to marine systems.

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1. Introduction

Land based sources are thought to make a large contribution to plastic debris in the oceans (European Environmental Agency, 2015; Jambeck et al., 2015). Plastic items come in a wide variety of sizes and types, with microplastic (<5 mm) being a size class of growing concern due to possible impacts on marine life. Indeed, microplastic can negatively affect organisms in freshwater and marine environments (Besseling et al., 2014b, 2013; Kühn et al., 2015; Lee et al., 2013; Wegner et al., 2012; Wright et al., 2013). Microplastic has been detected in the marine environment (Barnes et al., 2009; Browne et al., 2010; Claessens et al., 2011), and more

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recently, also in freshwater (Dubaish and Liebezeit, 2013; Eerkes-Medrano et al., 2015; Eriksen et al., 2013; Faure et al., 2012; Klein et al., 2015; Lechner et al., 2014). One major route for the occurrence of small plastic particles in the environment is expected to be wastewater, containing plastic particles from cosmetics and fibres from washing synthetic clothes (Browne et al., 2011). The other route is thought to be degradation of larger plastic items, which has the potential to release large numbers of microplastic particles (Zbyszewski et al., 2014).

To date, techniques for detecting microplastic particles in natural samples are still in their infancy. Although important progress is being made in the development of detection methods (Hidalgo-Ruz et al., 2012; Klein et al., 2015; Löder et al., 2015), present methods still are insufficiently distinguishing for some particle sizes and completely lacking for others (Song et al., 2015). The occurrence of nanoplastic is very plausible (Lambert and Wagner, 2016), however, current techniques are not yet capable of demonstrating their presence in the environment (Gigault et al., 2016;

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Koelmans et al., 2015). When microplastic from domestic sources passes wastewater treatment plants, or is formed by degradation of larger items, this leads to contamination of aquatic systems. It is generally hypothesized that once reaching surface water, plastic particles will be transported with the water, along rivers and into the sea. However, because of the limitations in standardized detection methods, the wide variability of plastic types and sizes. and insufficient knowledge on the mechanisms driving the fate of nanoplastic in rivers, support for this hypothesis is lacking. Therefore, there is a high need for the parallel development of tools that provide mechanism-based hypothesis on system behaviour that can be experimentally validated later on. This is similar to the development of nanoparticle models where first simple mass flow models evolved into validated spatiotemporal explicit models (Gottschalk et al., 2013). Fate models might also provide information on which particle sizes are retained in rivers, which in turn defines which size classes freshwater species are exposed to, and which size classes reach the marine environment. For instance, a relative lack of millimetre sized plastic was found in the plastic size distribution of the marine environment, which was hypothesized to be caused by size-selective oceanic sinks (Cózar et al., 2014). However, unexpected particle size distributions in marine ecosystems may be attributed to differential retention of plastic size categories in rivers.

We are not aware of earlier studies that use a fate model for plastic in rivers. Here, we simulate the transport of nano-, micro-, and millimetre sized spherical or near-spherical plastic particles in freshwater with a hydrodynamic model. The model simulates spatially and temporally explicit hydrodynamic particle behaviour, accounting for advective transport, particle aggregation, sedimentation, resuspension, polymer degradation and burial. We model polymer particles from 100 nm to 10 mm, and account for biofilm formation. For engineered nanomaterials, previous model studies showed that aggregation with suspended solids and subsequent sedimentation is the most likely removal process for these particles in water (Praetorius et al., 2012; Quik et al., 2015; 2011). The rates of these processes are important for microplastic as well, as they will determine the extent to which transport or transformation occurs.

The aim of this study is to analyse the theoretical fate and retention of plastic in a river using modeling, and to analyse the dependence of these endpoints on upstream initial microplastic concentration, particle size, polymer density and presence of biofilm. Following earlier nanoparticle study approaches (Praetorius et al., 2012; Quik et al., 2015; 2011) our aim was to model plastic fate mechanistically within uncertainty limits, but even more so to launch a concept that can trigger further development of models. Prospective modeling based on first principles can provide guidance for monitoring network design and for identifying priorities for the mitigation of plastic contaminated sites. Parameters were taken from the literature. Heteroaggregation, the aggregation of nano- and microplastic with suspended solids, is highly affected by the efficiency of attachment between these particles, α_{het} , a parameter which however is unknown for nano- and microplastic. This uncertainty was accounted for by scenario studies that used different values for α_{het} . To assess which of these scenarios for α_{het} may be more likely, values for α_{het} in natural water were experimentally determined and used as input in the model. The scenario studies were performed using hydrodynamic data of the Dommel river, which represents a realistic case study showing the spatiotemporal distribution of microplastics of different size, and which allows for the detection of accumulation hot spots. To cover the variety of (spherical) plastic particles, different scenarios are studied with a range of particle sizes, attachment efficiencies, with and without biofilm formation, several polymer densities and varying upstream concentrations.

2. Materials and methods

2.1. Experimental determination of the attachment efficiency (α_{het}) between nanoplastic, microplastic and clays

Heteroaggregation was studied in three experiments for two plastic particle sizes and two clay types representing suspended solids. These aggregation-sedimentation experiments of plastic with suspended solids were performed in 0.9 L glass columns (diameter 5 cm, height 43 cm) with natural lake water (Wageningen, Droevendaalsesteeg) filtered through 0.7 µm (Whatman, GF/F). The suspended solids kaolin clay (Fluka 60609) or bentonite clay (Sigma 285234) were dispersed at a concentration of 5 mg/L, which is a representative value for rivers with low discharge (Barton et al., 2014; Labille et al., 2015). Either 70 nm or 1050 nm polystyrene (Besseling et al., 2014b; Velzeboer et al., 2014) was mixed with the lake water at a concentration of 50 mg/L. These plastic concentrations were chosen to be higher than in the environment for accurate detection. This agrees to recent approaches to determine α_{het} for engineered nanomaterials (Labille et al., 2015; Quik et al., 2014b). Supernatants were sampled after settling times of 20 and 40 min, 1, 4 and 6 h and 1-3 days and directly measured by Dynamic Light Scattering (DLS), using a Cobolt Samba-300 DPSS laser at a wavelength of 532 nm, an ALV7002-USB as correlator and an ALV PM-15 as detector (Wegner et al., 2012), with linear calibration lines between 0 and 50 mg/L ($R^2 > 0.93$). Representative subsamples of the same supernatants were stored for 1 day in the refrigerator and analysed by spectrophotometry (DU® 730 Life Science UV/Vis Spectrophotometer A23616) at a wavelength of 310. 470 and 600 nm, with linear calibration lines between 20 and 100 mg/L ($R^2 > 0.98$). Values for α_{het} were calculated following the method of Barton et al. (2014) using the data obtained by both detection methods (calculation provided as Supporting Information).

2.2. Modeling the fate of spherical nanoplastic and microplastic

The fate of microplastic was modeled with the NanoDUFLOW model (Quik et al., 2015), parameterized for the investigation of plastic particle behaviour in riverine systems, including for the first time nano, micro- and millimetre sized plastic particles. Using traditional particle model concepts that were, amongst others, used for suspended solids, colloids and algae (Atteia, 1998; Burd and Jackson, 2009; Farley and Morel, 1986) and more recently in (nano-)particle transport models (Meesters et al., 2014; Praetorius et al., 2012; Quik et al., 2015; 2011; Sani-Kast et al., 2015), we described plastic particle behaviour as a function of the (plastic) particle related processes homo- and heteroaggregation, sedimentation based on Stokes settling theory, and degradation, dissolution, resuspension and burial. Homoaggregation, the mutual aggregation of particles, was included following a simplification as described by Quik et al. (2015). To be able to study the effect of microplastic particle size, scenarios were calculated for monodisperse plastic particles, so no mixture interactions between plastic particles of different sizes were included. Accordingly, heteroaggregation, the aggregation of plastic particles with suspended solids, was included by assuming five size classes of suspended solids interacting with one size class of plastic particles and four size classes of plastic homoaggregates. While theoretically more than one microplastic particle can attach to one suspended solid, it has been demonstrated for nanoparticles that the chance this happens is low (Labille et al., 2015; Praetorius et al., 2012; Quik et al., 2014a). This is caused by the excess number concentration of natural colloids and suspended solids in rivers, compared to that of nanoparticles, which also holds for micro- and nanoplastic (Table S2, Eerkes-Medrano et al., 2015; Lenz et al., 2016). Therefore, only primary heteroaggregates, that is, aggregates of a natural colloid with one plastic particle or one homoaggregate, were considered. This approach might be less suitable for shapes like fibres, that may aggregate through knotting and/or may exhibit non-Stokes settling behaviour.

Heteroaggregation rates were calculated as the product of (a) the collision frequency in which orthokinetic, perikinetic and differential settling were accounted for (Eq. S5), and (b) the attachment efficiency (Quik et al., 2015) (Eq. S4). The modeled river system was a 40 km stretch of the river Dommel, a Dutch lowland river, with a flow velocity averaging 0.199 m s⁻¹ (Table S1). Water works present in the Dommel are a sediment settling area at 14.4 km flow distance and multiple weirs. A wastewater treatment plant (WWTP) in the city of Eindhoven discharges at the river Dommel (De Klein et al., 2016). A simulation time of 9 days was used. No storm, rain or other weather influences were investigated in this scenario study. The DUFLOW hydrological component for the Dommel has previously been validated (Langeveld et al., 2013). The NanoDUFLOW particle model has recently been validated for metal based submicron ($<0.45 \mu m$) particles (De Klein et al., 2016). A detailed description of the present implementation is provided as Supporting Information. R Studio software v0.98.976 (R Core Team, 2015) was used to control DUFLOW calculations and to process model output. Interpretation of NanoDUFLOW simulation results was assisted by modeling several particle specific sub-processes independent of the hydrological model, like modeling the collision rate and settling rates as a function of particle size according to Eqs. S5 and S8. NanoDUFLOW, including the equations, is described in detail in the Supporting Information.

2.3. Parameterization

2.3.1. Particle diameter

The modeled plastic particles were assumed to be spherical. The model was run for twenty-five microplastic diameters in the range from 100 nm to 10 mm. For all these particle diameter scenarios, the upstream microplastic input concentration was kept equal in mass, resulting in decreasing particle number concentrations with increasing diameter (Table S4C).

2.3.2. Collision frequencies

The collision frequencies were calculated according to Quik et al. (2015) (Eq. S5), following traditional approaches for non-nanoparticles (Atteia, 1998; Farley and Morel, 1986). This required inputs of particle radius and density, which could be taken directly from the defined scenarios.

2.3.3. Attachment efficiency

For the attachment efficiencies, α , for both homo- and heteroaggregation in freshwater, a default value of 0.01 was used (Barton et al., 2014; Xiao and Wiesner, 2013). We used literature values for nanoparticles as a proxy to motivate our default values as they comprise a broad range of suspended solid types. Due to the relatively low concentration of the spherical plastic particles compared to suspended solids, homoaggregation plays a negligible role compared to heteroaggregation (Labille et al., 2015; Quik et al., 2015; Therezien et al., 2014), which renders the model output insensitive to uncertainty in the attachment efficiency for homoaggregation. The importance and the uncertainty of the attachment efficiency for heteroaggregation (α_{het}) may be higher (Atteia, 1998; Barkmann et al., 2010; Barton et al., 2014; Praetorius et al., 2012; Quik et al., 2014a; Simon et al., 2002). Therefore, following Praetorius et al. (2012) the model's sensitivity to the magnitude of α_{het} was investigated by a scenario approach in which α_{het} was ranged from no ($\alpha_{het} = 0$) to complete ($\alpha_{het} = 1$) attachment. Additionally, α_{het} for nano- and microplastic was estimated from aggregation-sedimentation experiments as described above.

2.3.4. Biofilm

While part of the particles may have no biofilm (because they are freshly emitted or deposited from the atmosphere (Dris et al., 2015a, 2015b)), another fraction of plastic particles entering aquatic systems like river Dommel can be assumed to be already colonized by biofilms (Kiørboe et al., 2003; Lobelle and Cunliffe, 2011; McCormick et al., 2014; Xiao and Wiesner, 2013; Ye and Andrady, 1991; Zardus et al., 2008) and it is likely that this affects the hydrodynamics of the particle behaviour. We therefore provide simulations without as well as with biofilm. Biofilm formation is likely to alter the fate of microplastic by affecting diameter, overall density and attachment efficiency. Biofilm formation was included by adding on the particles a 0.4 µm thick biofilm layer, representing average bacteria width (Pernthaler et al., 1996), with a density of 1250 kg/m³, representing the density of organic matter (Avnimelech et al., 2001). Bacterial cell density can be lower (e.g. Godin et al., 2007), which implies that the modeled effect of biofilm can be seen as a maximum boundary. Attachment efficiencies are heterogeneous in nature, but previous work has shown that on the system level, average values can be used (De Klein et al., 2016; Meesters et al., 2014; Praetorius et al., 2012; Quik et al., 2015). Although being subject to uncertainty, biofilms have been found to increase the attachment efficiency of nanoparticles 2-3 times (Ouik et al., 2011: Xiao and Wiesner, 2013). Therefore, we explored the effect of increased attachment efficiencies of 0.02 and 0.03 for the biofilm scenarios.

2.3.5. Polymer density

By default, microplastic was assigned a density of 1040 kg/m³, which is the average of polymer densities found in the marine environment (Andrady, 2011). Furthermore, polymer density was varied from 1000 to 1500 kg/m³, representing a wide range of polymer types and with 1000 kg/m³ also representing non-settling plastic. For the scenarios with different polymer densities, the upstream plastic input concentration was kept constant on a volume basis.

2.3.6. Upstream concentration

A default upstream plastic mass concentration of 1 ng/L was used. This concentration represents the average order of magnitude of published concentrations of microplastic in freshwater (Table S2) (Besseling et al., 2014a; Eriksen et al., 2013; Faure et al., 2012; Lechner et al., 2014). Besides this 'realistic' simulation, we performed simulations that studied the proportionality of predicted concentrations to the initial concentration, because initial concentration might as such affect the fate of particles (Quik et al., 2015). Hence, additional scenarios were analysed with upstream input concentrations varying by a factor of 10⁶, i.e. a factor 10² lower and a factor 10⁴ higher than the default upstream concentration.

2.3.7. Burial and degradation

Burial to lower sediment layers was included with a rate of $3.17 \times 10^{-9} \, \mathrm{s}^{-1}$ (Koelmans et al., 2009). Plastic degradation and abrasion in water and sediment were modeled as first order removal processes. The first order removal rate constant for biodegradation was set at $6.81 \times 10^{-9} \, \mathrm{s}^{-1}$ based on a maximum biodegradation of 1.75% per month observed by Harshvardhan and Jha (2013). Whereas degradation and abrasion processes may play a role at very long time scales, the estimated kinetic constants are too low to affect transport and retention given the present flowtimes

for the river Dommel. This also renders the model output insensitive to uncertainty in the parameters for degradation. Further parameterization was as specified in the Supporting Information (Tables S1 and S5).

3. Results and discussion

3.1. Attachment efficiencies (α_{het}) for heteroaggregation of nanoplastic and microplastic with suspended solids

There are several published methods to estimate α_{het} values from experimental aggregation data (Barton et al., 2014; Labille et al., 2015; Praetorius et al., 2014; Quik et al., 2014b), the discussion of which is beyond the scope of this hydrological modeling paper. Here, we pragmatically estimated α_{het} values for two near-spherical plastic particle sizes with two clay types in three combinations in natural freshwater following a procedure previously applied to nanoparticles (Barton et al., 2014). For 70 nm polystyrene with kaolin clay the average α_{het} for triplicates each measured by two detection methods (see below) was 0.04 (range 0.004-0.07) and with bentonite clay 0.1 (range 0.09-0.1). For 1050 nm polystyrene with bentonite clay α_{het} was on average 0.09 (range 0.06–0.2) (Table S6). As far as we know, these are the first aggregation data reported for nano- and microplastic in natural lake water. The type of suspended solids (i.e. kaolin vs. bentonite) slightly affected α_{het} , which confirms earlier findings that attachment efficiencies in the environment partly depend on the characteristics of suspended solids (Labille et al., 2015). The two detection methods DLS and spectrophotometry gave very comparable outcomes in particle numbers. The experimentally determined values ranged between 0.004 and 0.2 and thus are close to the values that were taken from the literature to motivate our default values (Barton et al., 2014; Xiao and Wiesner, 2013) and therefore support using these values in the modeling, as discussed further in the next sections. At the same time, we emphasise that our experiments are the first that use nano- and microplastic particles for hetero-aggregation experiments and that they will not apply equally to plastic particles of all shapes, like for instance fibres. To fully understand the aggregation characteristics of the wide variety of nano- and microplastic particles in the aquatic environment, more research is recommended.

3.2. Modeling the fate of nano- and microplastic in water and sediment of the Dommel river

3.2.1. Simulated concentrations of nano- and microplastic

To study the effect of microplastic particle size on spatial distribution, transport in the river Dommel was modeled for 25 microplastic size classes separately. Within 5 days of simulation time, microplastic concentrations in the water reached steady state over the entire 40 km river stretch, thus confirming the sufficiency of a 9 days simulation period for all size classes (Fig. S5A). For the sediment, however, steady state is not reached within the 9 days simulation period (Figs. S5B-D). The locations of peak concentrations in sediment are mainly related to the emission scenario and spatial properties of the river Dommel. The height of these peak concentrations largely depended on particle size of either plastic (Pl) or natural (SS) particles (Fig. 1). Particles <5 μm reached their highest concentrations in the sedimentation area 14 km downstream, whereas bigger particles settled earlier upstream (Fig. 1D, F, H, Fig. 2). Within the 9 days simulation period, peak concentrations in sediment of (a) up to 13 μ g/kg were reached within 1 km from the source (Fig. 1J, plastic particle diameter $> 500 \mu m$), (b) up to $0.1 \mu g/kg$ in the sedimentation area 14 km downstream (Fig. S1R, plastic particle diameter 50 μ m) and (c) up to 0.01 μ g/kg at the end of the 40 km river stretch (Fig. S1 A, C, E, N, P, plastic particle diameter < 500 nm and $10-20 \mu m$). The settling of plastic particles to the sediment phase resulted in a linear increase in sediment concentrations with a maximum rate of 1.5 µg kg⁻¹ day⁻¹ for the >500 µm particles within 1 km from the source, a maximum of $1.2 \times 10^{-2} \ \mu g \ kg^{-1} \ day^{-1}$ for the ~50 μm sized particles in the sedimentation area and a maximum of 1.5 ng kg⁻¹ day⁻¹ for the nano and 10-20 um sized particles at the end of the river system (Table S3, Fig. S5B-D). By combining these accumulation rates with the loss rates from the sediment by burial, steady state concentrations can be calculated (Koelmans et al., 2009; Quik et al., 2014a). The maximum steady state concentration in the river stretch was 5 mg/kg, which was reached for >1 mm particles at < 1 km from the source (Fig. 2, Table S3). However, for most other sizes and locations the steady state concentrations were a factor 2 to 15 lower. The calculated steady state concentrations within 1 km from the source (Fig. 2) correspond with concentrations of microplastic found by Wagner et al. (2014) in sediment in Europe of 34-64 particles/kg, which, with a size of 10^2-10^3 µm based on their figures and a particle weight of 5 µg per particle (Van Cauwenberghe et al., 2013), would be around 0.25 mg/kg.

3.2.2. Spatial distribution of nano- and microplastic

The concentration profiles of nano- and microplastic in the water and sediment were clearly related to the spatial characteristics of the river section and the size of plastic particles (Fig. 1). Here, spatial characteristics relate to differences in river width, depth and flow rate (Table S1) resulting in net sedimentation and resuspension areas (Ouik et al., 2015). The 100 nm singular nanoplastic particles (Pl₁) show a gradual decrease in concentration in the water phase, coupled to an increase in concentration of heteroaggregates (Fig. 1A). There is no sharp decrease in 100 nm nanoplastic concentration at the sedimentation area after 14.4 km, which implies that their removal from the water column is by aggregation with suspended solids and barely by direct settling. With increasing size of the plastic particles (Fig. 1, Fig. S1), removal of singular particles from the water phase occurs earlier, i.e. within a shorter flow distance. This can be explained from the dependence of the various sub-processes with particle size. First, the rates of direct Stokes settling increase substantially with size (Fig. S6A, Table S4B). Whereas settling of smaller plastic particles is dependent on their aggregation with suspended solids (governed by α_{het} in Fig. 3A), larger plastic particles settle at a rate which is independent of the heteroaggregation rate. Second, the frequencies of the collisions between plastic particles and suspended solids depend on the relative sizes of plastic particles and suspended solids due to altered orthokinetic aggregation and differential settling resulting in formation of heteroaggregates (Fig. S6E-F, Table S4D). Heteroaggregation rates depend on particle number concentrations, which are highest for the smallest size class (Eq. S4, Fig. S6B, Table S4C). Initially, heteroaggregate concentrations in the water phase increased for all particle sizes and subsequently decreased due to settling of the heteroaggregates, which occurred predominantly within 1 km from the input source for particles \geq 5 µm, and at the sedimentation area at 14 km for particles <5 µm (Fig. 1, Fig. S1). This corresponds well with peak concentrations in the sediment, as mentioned above. Homoaggregation played a minor role compared to heteroaggregation due to lower collision frequencies (Fig. S7, Table S4B) (Quik et al., 2015), causing that homoaggregate concentrations are not visible in Fig. 1.

3.2.3. Retention of microplastic with implications for transport to sea

Using the data from the default scenario presented in Fig. 1, the retention of microplastic in the 40 km river stretch was calculated

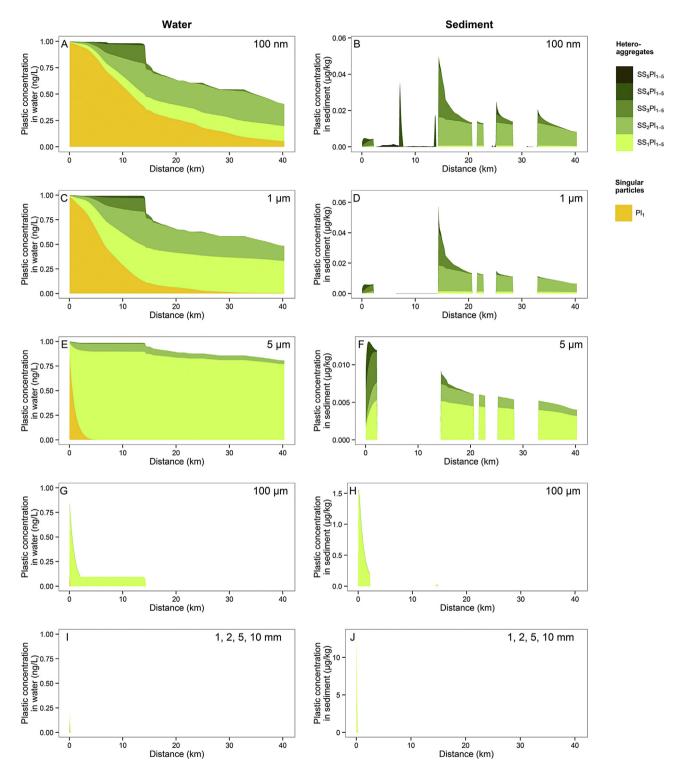


Fig. 1. Spatial distribution of plastic over a 40 km river stretch. Plastic concentrations are given for the water column (left-sided panels) and for sediment (right-sided panels). These concentrations are reached after nine days of plastic input into the river, representing steady state concentrations for the water column and intermediate state for the sediment. Different sections along the river are characterized by either net sedimentation or net resuspension, sections with net resuspension show no accumulation of plastic in the sediment. From top to bottom panels are ordered based on the order of increasing initial plastic particle size. The simulations used default settings with an average density of 1040 kg/m³, which is similar to that of polystyrene. The upper curves in the panels indicate the total concentration of microplastic, whereas the coloured areas indicate how plastic particles in singular form (Pl_1) and plastic in heteroaggregates ($Sl_{1-5}Pl_{1-5}$) with suspended solids of different size classes (Sl_{1-5}), contribute to the total concentration. Homoaggregate (Pl_{2-5}) concentrations were negligible and therefore not visible in the figure. Heteroaggregate concentrations are plotted as sum for Sl_xPl_{1-5} , though are mainly composed of Sl_xPl_{1-5} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

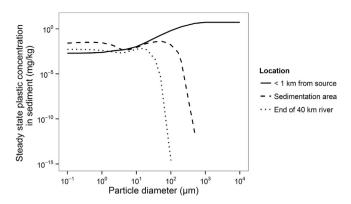


Fig. 2. Steady state plastic concentrations in sediment at a distance within 1 km from the input source, at the main sedimentation area 14.4 km downstream and at the end of the 40 km river stretch. Steady state concentrations based on linear increase rates by aggregation and sedimentation, and loss due to burial (Table S3).

as the percentage of the upstream microplastic input concentration that remained within the sediment of the 40 km river stretch. Remarkably, the relationship of retention with microplastic particle size was not monotonous but showed two maxima, up to 60% for plastic particles $\leq 1~\mu m$ and up to 100% for plastic particles $\geq 50~\mu m$, with a clear minimum in between where retention was only 18% for particles of ~4 μm (Fig. 3A). This typical pattern in retention for particles with increasing diameter was caused by a trade-off between sedimentation of heteroaggregates (driven by the larger size and higher density of the suspended solids), and sedimentation of the plastic particles. For plastic particles between 100 nm and 2 μm , increasing the diameter resulted in a reduced sedimentation rate of the heteroaggregates and for bigger plastic particles a larger diameter resulted in an increased sedimentation rate of the heteroaggregates (Table S4B).

If we know the percentage of microplastic retained in the 40 km river stretch, we can calculate how many stretches i.e. what distance is needed to retain 99% of the microplastic in the sediment of a river (RD99). This assumes that on average, retention percentages will be roughly similar across river stretches of this length, an assumption the validity of which of course is highly dependent on river morphology. The rationale for extrapolating to such a percentage is that discharges further from sea than the RD99, can be assumed to mainly contribute to plastic pollution in freshwater, whereas discharges within the RD99 will contribute to plastic pollution in both the fresh and marine environment. The RD99 was calculated by linear interpolation where this distance lied within 40 km and by exponential extrapolation where this distance lied further away than 40 km. Highly depending on particle size, the RD99 was calculated to be around 200 km for nanoplastic and reaches up to >900 km for microplastic, whereas millimetre sized plastic retained within a few kilometres (Fig. 3B). These calculations thus imply that for river morphologies like that of the Dommel, the intermediate size class of microplastic is preferentially transported downstream.

3.2.4. Effect of attachment efficiency, biofilm formation, polymer density and input concentration on retention

3.2.4.1. Attachment efficiency. We used a default attachment efficiency for heteroaggregation α_{het} of 0.01, whereas we showed experimentally that the attachment efficiency is very similar within error limits, i.e. 0.004–0.2 (Table S6). To be able to evaluate the relevance of such variations, we calculated all spatial profiles for a range of lower and higher attachment efficiencies (Fig. 3A). Increasing the attachment efficiency above 0.01 affected the overall

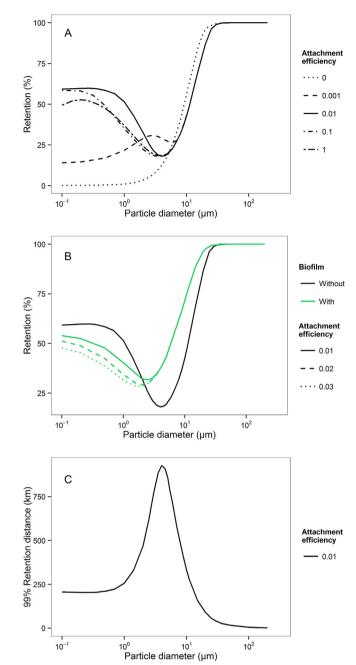


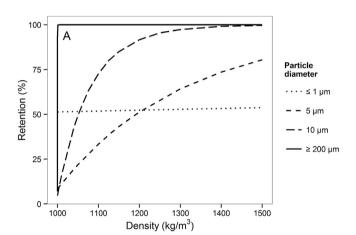
Fig. 3. Retention and 99% retention distance of microplastic with a density of 1040 kg/m³ as a function of particle size in a 40 km river stretch. Panel A: effects of attachment efficiency (α_{het}) on retention. Panel B: effects of biofilm and α_{het} on retention. Panel C: 99% retention distance for the default value of α_{het} (0.01).

retention by a factor 0.72-1.03. Of this change in overall retention, a decrease by a factor 0.72-0.99 is seen in the lower size range, whereas the retention is not affected by more than 1% for particles $\geq 4~\mu m$ (factor 1-1.03). Consequently, the range and variability observed between the default literature value of 0.01 and the experimentally determined average α_{het} values of about 0.04-0.1 (range 0.004-0.2, Table S6) also had negligible impact on the observed profiles and retention, which shows the robustness of the modeling results and the adequacy of the default value. However, reducing the attachment efficiencies to 0 (no aggregation at all) or 0.001 (very low aggregation) resulted in a reduction of retention for small particles down till 0%, whereas for the middle and bigger sized particles this enhanced retention by up to a factor 1.6 (4 μ m

sized particles) (Fig. 3A). Given the literature values and experimentally determined values it is not likely that α_{het} was in fact smaller than 0.01.

3.2.4.2. Biofilm formation. The previous simulations did not consider fouling or presence of biofilm, as explained above. Simulating the presence of a biofilm by changes in particle density and size did not change the overall qualitative trends and patterns in the behaviour of the particles, as can be seen by comparing Fig. 1 and Fig. S3. More quantitatively, this presence of biofilm on the plastic particles resulted in some size dependent changes in retention (Fig. 3). For particles \geq 50 µm, which represent a major fraction of the microplastic particles in the environment, no effect of biofilm on retention was calculated. For particles ≤2 µm retention decreased from around 60-50% down to 50-40%, which was caused by a faster formation of heteroaggregates through reduced settling of these heteroaggregates. In the middle part of Fig. 3 increases in retention from around 40% up to 70% were calculated, due to an increase in the settling of heteroaggregates (Fig. 3B, Figs. S6-7). When also accounting for the effect of biofilm on the attachment efficiency (i.e. an increase of α_{het} by a factor 2 to 3), the retention of particles $\leq 2 \mu m$ is further reduced to about 50–30% (Fig. 3B).

3.2.4.3. Polymer density. For plastic particles ≥200 µm retention in the 40 km river stretch was calculated to be high, approaching



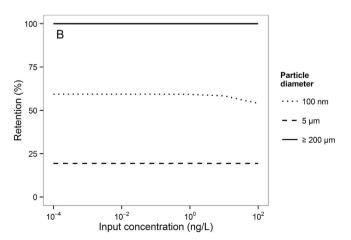


Fig. 4. Panel A: Influence of polymer density on retention for different particle diameters with a default value of α_{het} (0.01) and input concentration (1 ng/L). Panel B: Influence of input concentration on retention for different particle diameters with a default value of α_{het} (0.01) and polymer density (1040 kg/m³).

100%. For particles 100 nm-1 μm retention was low; about 50%, which was nearly independent of polymer density. However, for the size classes in-between (1–200 μm), retention is highly determined by the polymer type at hand, namely strongly increasing with increasing polymer density (Fig. 4A, Fig. S2). A special case exists for nano- and micrometre sized polymers that have a density equal or slightly lower than that of water, like for instance polyethylene and polypropylene. It is often assumed that such polymer particles will float and show low retention in water systems. However, for such plastic particles, dispersion into the water column will still occur due to common mixing and shear or due to wind induced mixing of surface water (Kukulka et al., 2012), after which they will rapidly heteroaggregate with suspended solids. Alternatively, the low density polymers (<1000 kg/m³) are likely to aggregate with natural or anthropogenic non-polymer particles in the surface microlayer (SML), where particle concentrations are high (Song et al., 2014). For low density microplastic ≤ 1 µm, the density and numbers of suspended solids overwhelm that of the microplastic, such that the settling of heteroaggregates virtually is determined by that of the suspended solids, leading to a retention of about 50% (Fig. 4A). However, for low density microplastic particles larger than a few μm , retention of heteroaggregates is largely dependent on polymer density, leading to zero retention (Fig. 4A). Consequently, these low density microplastic particles, those remaining in singular form or those newly settling on the water surface, are expected to be transported further downstream and have longer RD99.

3.2.4.4. Input concentration. In our default scenarios, the particle number concentration was highest for the smallest particles, as input concentration was kept constant for all particle sizes. Because in our environmentally realistic scenarios the particle number concentration of microplastic was relatively low compared to the suspended solids, homoaggregation played a negligible role compared to heteroaggregation. Although peak concentrations in water and sediment varied with input concentration, the overall retention (%) remained unaffected by input concentration at input concentrations < 1 ng/L (Fig. 4B).

4. General discussion and implications

Rivers are often viewed simply as sources of plastic from terrestrial to marine ecosystems, but our modeling results indicate that part of the nano- and microplastic fraction can be efficiently retained in river systems. Therefore, emissions of microplastic to freshwater will not just result in 'down the drain' transport to coastal areas and the oceans. The strong dependence of retention on size in the 1-50 µm range (Fig. 3A) can be evaluated with respect to know sizes of microplastic being emitted to freshwater. Tyre dust, abrasion and shedding from polymer based textiles (Sundt et al., 2014), or personal care products (PCPs) (Gouin et al., 2015) are often mentioned with respect to emissions to sea. The size of tyre dust is reported to range 60-80 μm, which may imply substantial retention in freshwater, based on the present simulations. Concentrations of black carbon in freshwater sediments indeed have been shown to be high, i.e. median black carbon contents as a fraction of total organic carbon are 9% for sediments (Cornelissen et al., 2005). Microplastic particles in personal care products are reported to range between 1 and 800 μm (Sundt et al., 2014). Whereas the lower end of this range thus would be rather mobile in freshwater, particles at the higher end of this range would be retained efficiently in aquatic sediments, implying a potential risk to sediment dwelling organisms. We showed that especially nanoplastic and millimetre sized plastic are likely to be retained in rivers to a relatively high extent, which may define implications for species with specific feeding traits and sensitivities to these size fractions. The other side of the coin is that it suggests that especially micrometre sized particles are transported by rivers, resulting in exposure of marine and coastal areas to micrometre sized particles. Furthermore, it can be speculated that the preferential river retention of millimetre sized plastics may contribute to the lack of millimetre sized plastic as observed recently in the marine environment (Cózar et al., 2014), compared to the expected particle size distribution.

Our model shows that based on initial waste sources and downstream distance, exposure concentrations can be predicted. Recently, the occurrence of microplastic in freshwater sediments has been experimentally confirmed (Corcoran et al., 2015; Wagner et al., 2014). This calls for a thorough model validation and risk assessment for microplastic in freshwater systems. As mentioned, we did not aim to provide a fully validated model that can simulate all types of plastic particles with certainty. Still, the model is valid with respect to its conformance to known theory and parameter constraints, whereas its adequacy to simulate measured concentrations for other types of particles has been demonstrated recently (De Klein et al., 2016). The present implementation was designed for (near-)spherical particles, and effects of particle shape need to be assessed before the model can be applied to more diverging types of plastic particles such as single fibres or thin sheets. For fibres, knotting may be more important than attachment, leading to effectively higher attachment efficiencies. Aggregates of knotted fibres would eventually approach sphericity implying they could be accommodated by the model once size and density would be known, or otherwise by including shape correction factors for sedimentation. Furthermore, uncertainty with respect to fouling, aggregation and sedimentation would affect absolute concentrations, but probably not the general trends with respect to location of hot spots. After all, model analysis showed that biofilm formation would not have large effects on particle fate. In that sense, the model provides a generalised tool that can be implemented for other catchments as well, and that can help in the design of optimum sampling grids and frequencies, based on a priori prospective simulations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.10.001.

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