A systems approach to understand microplastic occurrence and variability in Dutch riverine surface waters


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A systems approach to understand microplastic occurrence and variability in Dutch riverine surface waters


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ABSTRACT

Assessment methods on data quality and environmental variability are lacking for microplastics (MP). Here we assess occurrence and variability of MP number concentrations in two Dutch rivers. Strict QA/QC procedures were applied to identify MP using Fourier-transform infrared (FTIR) microscopy followed by state of the art automated image analysis. For a series of randomly selected, yet ever smaller subareas of filters, we assessed how accurately MP numbers and polymer types are represented during partial filter analysis. Levels of uncertainty were acceptable when analysing 50% of a filter during chemical mapping, and when identifying at least a subset of 50 individual particles with attenuated total reflection (ATR)-FTIR. Applying these guidelines, MP number concentrations between 67 and 11532 MP m⁻³ were detected in Dutch riverine surface waters. Spatial differences caused MP number concentrations to vary by two orders of magnitude. Temporal differences were lower and induced a maximum variation of one order of magnitude. In total, 26 polymer types were identified, the most common were polyethylene (23%), polypropylene (19.7%) and ethylene propylene diene monomer rubber (18.3%). The highest diversity of polymer types was found for small MPs, whereas MP larger than 1 mm was scarce and almost exclusively made of polyethylene or polypropylene. Virtually all sampling locations revealed MP number concentrations that are considerably below known effect thresholds for anticipated adverse ecological effects.

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1. Introduction

Microplastics (MP) have been detected globally across all major environmental compartments. It is expected that most of the plastic litter originates from land based sources and is relocated by e.g. urban runoff or riverine transport towards the marine environment (Hurley and Nizzetto, 2018; Rochman, 2018). The latter has been confirmed recently by Lorenz et al. (2019) who examined the MP distribution in the southern North Sea and found highest concentrations in surface waters where riverine input of the Thames and Rhine occurs. Although awareness of the relevance of this transport route is rising, knowledge on MP in rivers is still scattered. MP have been reported in various river systems, in sediment (Hurley et al., 2018; Mani et al., 2019), water (Cheung et al., 2018; Kataoka et al., 2019; Koelmans et al., 2019) or biota samples (Roch et al., 2019), with reported concentrations varying by several orders of magnitude (Adam et al., 2019; Koelmans et al., 2019).

Various large and small scale processes affect MP concentrations and its distribution within a river system. Higher MP concentrations in surface waters have been linked to the vicinity to urbanized areas (Kataoka et al., 2019; Mani et al., 2015), or higher flow velocities during rain events (Cheung et al., 2018) that cause settled MP to be released from sediments. Flow conditions can thus substantially change the spatial distribution of MP in a river (Eo et al., 2019; Hurley et al., 2018; Kooi et al., 2018) and can strongly vary over the seasons. Yet only a few studies considered this and

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identified higher MP concentrations in surface waters during low flow conditions in summer, and Eo et al. (2019) found highest MP abundances during the dry and wet season while concentrations were significantly lower during a moderate season. Further insights on seasonal variations are needed.

Discharges of waste water treatment plants (WWTPs) are expected to be an important point source for MP, thereby affecting the distribution of MP in a river (Boucher et al., 2019). The presence of MP in WWTP effluents has been confirmed by multiple studies (Mintenig et al., 2017; Simon et al., 2018; Talvitie et al., 2017), though reported concentrations vary considerably (Koelmans et al., 2019). These variations in observed MP concentrations may exist due to when and where samples were taken and thus reflect the variability on a WWTP or system’s level. These variations, however, can also depend on how the samples were taken or how MP were extracted and analysed (Connors et al., 2017; Filella, 2015). To be able to distinguish between system level variability and procedural uncertainty it is required to follow strict quality assurance/quality control (QA/QC) procedures. Recently, Hermsen et al. (2018) and Koelmans et al. (2019) assessed the reliability of studies by evaluating a set of defined QA/QC criteria. Only four out of 50 reviewed studies that examined MP in aqueous samples were found to fulfill all proposed quality criteria (Koelmans et al., 2019), which indicates limitations with respect to the reliability of studies, and increases the uncertainty around generated data. One of the proposed criteria describes the need to identify the particles’ chemical nature for a sufficient amount of particles. Numerous studies did not include any polymer identification step, but purely relied on a visual selection of particles. Confirming the presence of specific polymer types is essential to be able to see patterns, to point out potential sources and to properly link results of exposure and effect studies (Kooi and Koelmans, 2019; Potthoff et al., 2017). The more recent studies do identify the particles’ chemical nature (Lorenz et al., 2019; Mani et al., 2019). Due to long analysis times this is frequently done for a part of a sample only (Lorenz et al., 2019; Mintenig et al., 2017; Simon et al., 2018). Peeken et al. (2018) applied chemical imaging on three subareas of a filter by which they found that MP were distributed unevenly on a filter. Analysing small subareas of filters with Fourier-transform Infrared (FTIR) or Raman spectroscopy might thus considerably under- or overestimate actual MP abundances. Still, the uncertainty introduced by partial filter analysis or by identifying a subset of particles using attenuated total reflectance (ATR)-FTIR has not yet been quantified. We argue that it is needed to systematically assess the trade-off between shortening the analysis time, and the loss of information and accuracy on MP numbers and polymer types. As sample handling and MP analysis are laborious, finding the balance between a doable analysis time and an acceptable level of analytically introduced uncertainty constitutes a major step forward.

This study aimed to assess the occurrence of MP and to explore its variability in surface waters of two Dutch river systems. Strict QA/QC procedures (Hermsen et al., 2018; Koelmans et al., 2019) were followed to identify MP down to 20 μm using FTIR microscopy followed by an automated image analysis (Pprimke et al., 2019). Sampling locations were chosen (1) with a high spatial resolution and at different flow velocities in the river Dommel to assess the spatial variability of MP within one river, (2) with two locations where the sampling was repeated to assess the seasonal and daily variation of MP occurrences, and (3) included WWTP effluents, as well as an up- and downstream sampling location of their discharging points to assess the relative contribution of WWTPs to the total riverine MP load. A secondary aim was to assess the introduced uncertainty through partial filter analysis and the analysis of a subset of particles by comparing generated MP data for a series of randomly selected, yet ever smaller fractions on their accurate representation of MP numbers and polymer types. Finally, generated MP data are discussed in the context of previously reported concentrations and of anticipated risks for aquatic biota.

2. Material and methods

2.1. Study area

MP were identified and quantified in surface waters of the Dutch part of the Meuse river basin. One of its tributaries is the Dommel that originates in Belgium and flows over a length of 80 km through the Netherlands. Flow velocities of the Dommel vary over the river length and over the seasons (0.001–0.98 m s⁻¹, mean 0.28 m s⁻¹ with a mean discharge of 3.1 m³ s⁻¹). The Dommel is fed by the discharges of three WWTPs, as well as by several smaller tributaries and combined sewer overflows (de Klein et al., 2016). The Dommel is well studied and described in a temporal and spatial explicit model (NanoDUFLOW), which is based on hydrological data of the Dommel and has been applied to study transport of metal-based nanoparticles (de Klein et al., 2016) and nano- and microplastics (Besseling et al., 2017).

The Meuse has an average width of about 100 m and an average discharge of 350 m³ s⁻¹. The Meuse is mostly rain fed, resulting in strong differences between summer and winter flow regimes. The Dutch part of the river basin is characterized by a high number of inhabitants, intensive agriculture and industry. At the same time the Meuse is used as a source for drinking water production. Three subsequent basins, built in the 1970s in the national park ‘De Biesbosch’, enable water storage and sedimentation processes to improve water quality.

Surface water samples were taken in the Dutch part and over the lengths of both rivers, the Meuse (N = 12) and the Dommel (N = 20) (Fig. 2). Locations included the sedimentation basins and the effluents of five WWTPs discharging directly or indirectly into the two rivers were sampled. The majority of samples was taken in autumn 2017. The sampling was repeated at two sites during different seasons in 2018 (Table S1).

2.2. Sampling

A centrifugal water pump (Leo 4xCm 120C, China) was used to filter surface water over stacked stainless steel sieves with mesh sizes of 300 μm, 100 μm and 20 μm (ø 20 cm, ThermoFisher Scientific, USA). The inlet tube (polyvinyl chloride, PVC) was equipped with a metal cap (opening 2 cm) and mounted on a wooden pallet. This enabled sampling the upper 5 cm of the water column, and an upstream orientation of the tube. Before sampling, tubes and pump were primed for 5 min, and the sieves rinsed with filtered surface water. The sample volume was determined by a connected water meter. Between 1.3 and 8 m³ were filtered with a flow rate of approximately 2 m³ h⁻¹ over the two bigger sieves. The sample volume depended on the amount of suspended matter. Regularly the flow was lowered and the 20 μm sieve placed underneath the other sieves. By doing so 0.03–2.25 m³ water were filtered over the 20 μm sieve, which on average represented 15% of the total sample volume (Table S1). The residues were rinsed into individual glass bottles that were closed with aluminium foil and stored at 4 °C until further processing in the laboratory. Materials retained on the sieves, or MP enclosed in aggregates, resulted in capturing also MP smaller than the respective mesh sizes. During sampling care was taken that the outlet tube discharged the filtered water down-stream of the sampling location. Airborne contamination was abated by covering the upper sieve with a metal lid in which the inlet tube was hung.
2.3. Sample preparation

Sample preparation to extract MP retained on the 20 and 100 μm sampling sieves was done at KWR Watercycle Research Institute (The Netherlands). The sorting of MP > 300 μm and all FTIR analyses were conducted in the laboratories of Wageningen University and Research (The Netherlands). During sample preparation quality criteria as presented by Koelmans et al. (2019) were followed. Before starting to handle environmental samples, the susceptibility to contamination and the achievability of a good MP recovery were tested for three working places used in literature, namely a normal lab bench (Dris et al., 2015; Mintenig et al., 2017), a glove box (Torre et al., 2016) and a laminar flow hood (Lorenz et al., 2019; Peeken et al., 2018). To do so samples of 1 L of Milli-Q water underwent the same steps as environmental samples. For further details on these pre-tests, contamination mitigation and quality assurance we refer to the Supplementary Information (Paragraph S1).

MP > 300 μm The residues of the 300 μm sampling sieve were visually inspected using a stereomicroscope (Nikon Stereo SMZ2T, Japan). The sorting of potential MP particles was facilitated using a Bogorov chamber (Poly methyl–methacrylate, PMMA 70 ml, HydroBioS Germany). All particles with a bright or transparent colour, no cellular structures and certain bending properties were isolated, photographed (Euromex CMEX 5 MP, The Netherlands) and measured at their longest and shortest dimension. At the same time their shape and colour were noted.

MP < 300 μm Multiple steps were taken to reduce natural organic and inorganic sample components when extracting MP retained on the 20 and 100 μm sampling sieves (Figure S 1). Puriﬁcation started with the addition of sodium dodecyl sulphate (SDS, 5%, Serva Electrophoresis GmbH, Germany), after which potassium hydroxide (KOH, 10%, Carl Roth GmbH, Germany) and hydrogen peroxide (H2O2, 32%, Carl Roth GmbH, Germany) were added. Before adding the subsequent chemical, samples were ﬁltered over a stainless steel 20 μm mesh placed in a stainless steel ﬁlter capsule. Further required were a vacuum pump (ME1C, Dijkstra Vereenigde, The Netherlands) and a Teflon tube attached to the ﬁlter capsule. The sample residues on the 20 μm meshes were transferred into beakers and the subsequent chemical was added. During all steps an incubation temperature of 35 °C was kept for which samples were placed in an oven. Inorganic particles were removed by performing a density separation using a zinc chloride (ZnCl2, Carl Roth GmbH, Germany) solution with a density of 1.6 g cm−3. From the 20 μm mesh, residues were rinsed with the ZnCl2 solution into separation funnels and were left to settle for 24 h. Materials with a density above 1.6 g cm−3 settled to the bottom and were removed by regularly and slowly turning the outlet valve. All lighter materials were ﬁltered one more time over the 20 μm mesh, then onto 0.2 μm aluminium oxide ﬁlters (anodisc 25 mm, Whatman, U.K.,) for which a ﬁltration funnel with an inner diameter of 15 mm was used. These ﬁlters were placed into slightly opened glass petri dishes and dried at 35 °C for ﬁve days.

During sample preparation, cross-contamination was minimized by always using the same 20 μm steel mesh and glass beaker for individual samples. In parallel to actual samples, procedural blanks were treated and analysed and their results were considered when analysing MP in environmental samples (Paragraph S1).

2.4. MP identiﬁcation and quantiﬁcation

MP > 300 μm – ATR-FTIR Sorted, potentially synthetic, particles larger than 300 μm were identiﬁed using ATR-FTIR (Varian 1000 FT-IR, Agilent USA). Particles were placed individually onto the ATR crystal, polymer types were identiﬁed based on the recorded spectra (600- 4000 cm−1) with the aid of the ‘Hummel Polymer and FTIR Spectral Library’ (ThermoFisher Scientiﬁc, USA). If the number of sorted particles was <50, all particles were analysed. A subset of 50 randomly chosen particles (32–76%) was identiﬁed for eight samples with numbers of sorted particles > 50 (Koelmans et al., 2019). To assess the loss of accuracy when analysing only a subset of pre-sorted particles all particles (73–123) were analysed for further three samples (section 2.6).

MP < 300 μm – Micro-FTIR To identify MP < 300 μm, an FTIR microscope equipped with an ultrafast motorized stage and a single mercury cadmium telluride (MCT) detector (Nicolet iN10, ThermoFisher Scientiﬁc, USA) was used. The anodisc ﬁlters with sample residues were placed on a calcium ﬂuoride (CaF2) crystal (EdmundOptics, Germany) to avoid the ﬁlter from bending. Chemical mapping of these samples was conducted in transmission mode for pre-deﬁned ﬁlter areas (Loder et al., 2015; Mintenig et al., 2017, 2018). MP from the 100 μm sampling sieve was analysed on a ﬁlter area of approximately 12 × 16 mm (66% of the total ﬁlter area). IR spectra were recorded with a spatial pixel resolution of 30 μm and in a wavenumber range of 1250–3200 cm−1. The aperture size was set as 50 × 50 μm controlling the energy amount presented to the sample, the spectral resolution was set as 16 cm−1, and 1 scan per pixel was conducted. For MP analysis retained on the 20 μm sampling sieve two areas (both approximately 88 mm2, and together 62% of the ﬁlter area) were mapped with a spatial pixel resolution of 20 μm, with remaining settings kept unchanged. The loss of accuracy by partial analysis of the ﬁlter area was quantiﬁed separately (section 2.6).

The generated FTIR data were automatically analysed using two software tools, MPHunter (Liu et al., 2019) and MPAPP (Primpke et al., 2019), in combination with the reference database presented by Primpke et al. (2018). These software tools were later transferred into siMPle, a freeware which can be downloaded via https://simple-plastics.eu/. Within the software all recorded spectra are compared against the spectra of a reference library, this is done for the raw spectrum and for its ﬁrst derivative. The resulting hits are afterwards evaluated as described by Primpke et al. (2017b) followed by an image analysis using MPAPP. This analysis uses ﬁrst a pixel hole closing mechanism prior to a particle/ﬁbre recognition with set parameters (Primpke et al., 2019) and yields in numbers and polymer types for MP particles and ﬁbres, including the longest and shortest dimension for individual MP. Based on criteria presented by Primpke et al. (2018) polymer speciﬁc threshold values were determined by evaluating the spectra of ﬁve samples manually (Table S 2).

Based on the MP two-dimensional shapes the mass per MP, and subsequently per sample, was estimated. To do so, we followed the approach by Simon et al. (2018) and calculated the ratio of the shortest and longest dimension of all identiﬁed particles, which on average was 0.56 with a standard deviation (SD) of 0.19. For particles it was assumed that this ratio would be the same for a particle’s height and its shorter dimension. For ﬁbres the individual lengths were given while a ﬁxed diameter of 15 μm was assumed (Napper and Thompson, 2016; Pirc et al., 2016). The mass was calculated from the MP volume and the density of its material. As exact particle densities cannot be determined during analysis, the mean polymer densities indicated in literature were used (Table S 2).

2.5. Statistical analysis

The Shapiro-Wilk normality test was used to test if MP number concentrations were normally distributed amongst WWTPs and river systems. A non-parametric Kruskal-Wallis rank sum test was used to compare MP in grouped locations. The Dunn test resulted in an adjusted p-value based on the Benjamini–Hochberg method.
which was used to compare differences between individual groups. All tests were performed using the software RStudio (v.1.1.463).

2.6. Assessment of data reliability

Based on generated MP data we assessed how randomly selected, yet ever smaller sample fractions being analysed can impact final results and when levels of introduced uncertainties become unacceptable. This was done for the partial analysis of a filter during chemical mapping, and for the identification of only a subset of pre-sorted particles >300 μm using ATR-FTIR. For both analyses five samples with varying MP abundances were selected. These were assessed in regard to an accurate representation of (i) MP number concentrations and polymer types during chemical mapping and (ii) polymer types for ATR-FTIR analysis. MP abundances varied for the environmental samples from 157 to 2928 per filter during chemical mapping (Fig. 1) that were detected when analysing 66% of the filter. For ATR-FTIR analysis the MP abundances varied between 18 and 123 per sample (Figure S 3). Using Microsoft Excel, randomly 10 filter areas, subsets of particles respectively, were generated representing 75, 50, 25, 10, 5, 1 and 0.5% of the total sample. Within these sample fractions the representation of polymer types and MP number concentrations was assessed and their coefficient of variation calculated. A coefficient of variation ≤1 indicates an acceptable variance and was set as threshold to provide sufficiently robust data on MP numbers and respective polymer types.

3. Results and discussion

3.1. Assessment of data reliability

This study was conducted by following the QA/QC recommendations by Koelmans et al. (2019) which have also been adopted in recent reports (UKWIR, 2019; WHO, 2019). Based on the provided quality criteria this study would score 17 out of 18 points and data would thus be assessed as ‘reliable’. One point was subtracted as sample preparation was not done under clean air conditions. The overall score is higher than the average scores from studies on surface waters (4–15, mean 7.9) and on WWTP effluents (3–13, mean 7.3) (Koelmans et al., 2019).

Generated data will still inhere a certain degree of uncertainty introduced during sampling, sample handling and analysis of parts of a sample only. The latter was assessed for an accurate representation of MP number concentrations (Fig. 1A) and polymer types after micro-FTIR analysis (Fig. 1B, Figure S 2) as well as polymer types after ATR-FTIR analysis (Figure S 3).

Independently of varying MP abundances, MP number concentrations were represented with an acceptable coefficient of variation (≤1) when mapping 50 and 75% of the filter area. The same applied for 25% if several thousand MP were concentrated on a filter. Lower MP abundances and especially a partial analysis of

Fig. 1. Uncertainties expressed as coefficient of variance (CV) of identified (A) total MP number concentrations, and (B) polymer types during partial filter analysis with micro-FTIR. In orange (A) total MP abundances per filter are given for five individual samples, while in (B) relative abundances of polymer types are indicated for the samples with the lowest and highest MP abundances (see Fig. S2 for the remaining three samples). The CV was calculated for individual samples based on 10 randomly selected filter areas of specified size (0.5–75%). Areas that miss a CV and are coloured in dark grey indicate that this polymer type was not identified in any of the generated 10 filter areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Fig. 2. Sampling locations in the river catchments of the Meuse (A) and the Dommel (B). Sampled WWTP effluents are written in bold, surface water was examined upstream (US) and downstream (DS) of the WWTPs’ discharging points. The detected MP concentrations (MP m$^{-3}$) are indicated with respect to the different polymer types identified.
10% or less of a filter considerably increased uncertainties (Fig. 1A). The five samples contained 9 to 15 polymer types, all were presented with an acceptable level of uncertainty (coefficient of variation 0.02–0.53) when analysing 75% of a filter (Fig. 1B, Fig. S2). The same applied for the most common polymer types, e.g. polyethylene (PE), polypropylene (PP) or rubber type 3, when analysing at least 5% of the filter. The correct representation of more rare polymer types by analysing ever smaller filter areas depends on original MP abundances (Fig. 1B, Figure S 2). However, these rare polymer types are likely overlooked when analysing <5% of a filter, and represented inaccurately for a partial filter analysis of 10–50% depending on MP abundances.

Combining these two aspects, it is thus recommended to map at least 50% of a filter using micro-FTIR. If a filter contains several thousand MP it might also be sufficient to analyse 10–25% of a filter. Analysing 5% or less of a filter should certainly be avoided, otherwise data on MP numbers and polymer types will entail high uncertainty levels. This becomes even more important considering that MP are not distributed evenly on a filter (Peeken et al., 2018). However, there are further restrictions during chemical mapping as the correct identification of MP can be hampered by a thick filter cake (Loder et al., 2015; Lorenz et al., 2019). To generate accurate results high sample volumes and a good sample preparation with a high MP extraction efficiency should be strived for (Lorenz et al., 2019).

We also assessed the accurate representation of polymer types when analysing ever smaller subsets of pre-sorted particles with ATR-FTIR. Independently of the samples’ total number of sorted particles, the presence of polymer types was depicted accurately when analysing 75% of all particles (Figure S 3). Rare polymers were overlooked and uncertainties around presented polymer distributions became unacceptably high when analysing 10–25% of the particles, which corresponds to approximately 10–20 particles. In agreement with the recommendations by Koelmans et al. (2019), analysing all, or at least 50 of the pre-sorted, potential synthetic particles, will depict abundances of different polymer types with an acceptable level of uncertainty.

3.2. MP in riverine surface waters

MP concentrations MP particles and fibres down to a detection limit of 20 μm were detected in all samples. Number concentrations varied between 67 and 11532 (median 862) MP m⁻³ (Figs. 2 and 4). MP in surface waters of the Meuse have been assessed by one earlier study, the results, however, are not comparable due to different methodologies and reportage of results (Leslie et al., 2017). Globally, between 0 and 1.3 × 10⁴ MP m⁻³ (median 2.75 MP m⁻³) were reported in riverine surface waters (Koelmans et al., 2019). The here presented numbers are at the higher ends of this range. This could be explained by studies targeting different MP sizes. The current size limit is lower compared to studies that sampled with a 333 μm neuston net and reported lower number concentrations (Baldwin et al., 2016; Hoellein et al., 2017). Further, the majority of studies reported on a few polymer types only (Koelmans et al., 2019), while in the present study 26 different polymer types were identified (Figure S 4). The here applied automated image analysis of FTIR data is a major step forward as it circumvents human bias and automatically compares spectra against a standardized database of common polymer types (Primpke et al., 2018). In this way rare polymer types, or very small MP are not overseen but identified correctly (Mani et al., 2019). Remarkably, several types of rubbers were highly abundant, which has not yet been reported for riverine surface waters in earlier studies.

Data on MP in environmental samples constitute merely a snapshot of the environmental situation and the processes taking place. Until now only a few studies examined individual rivers over their length in detail (Ding et al., 2019; Hurley et al., 2018; Mani et al., 2015). To better understand the MP distribution on a systems’ level the sampling was restricted to two river systems, reducing the number of variables that need to be taken into account when comparing generated data. The snapshot character of data was reduced by choosing sampling locations at a high spatial resolution, and by assessing temporal variations.

Slight differences in regard to MP number concentrations were found for the two river systems. In the Meuse, the concentrations ranged from 177 to 1381 (median 867) MP m⁻³ (Fig. 2A), while concentrations in the Dommel and its tributaries were in the range of 160 to 11,532 (median 654) MP m⁻³ (Fig. 2B). Although the discharges of Dommel and Meuse differ by a factor of 100, MP concentrations are rather similar. In both rivers MP abundances did not increase continuously over the river length.

Highest concentrations were detected in the downstream part of the Dommel close to the cities Eindhoven (8450 MP m⁻³) and StOedenrode (11532 MP m⁻³). This is in line with the findings of Kataoka et al. (2019) and Mani et al. (2015) who could link higher MP abundances to the vicinity to urban areas. In contrast, the more rural part of the Domeml, including all locations that lie upstream of Eindhoven, revealed much lower MP concentrations (median 309 MP m⁻³) (Fig. 2B). The Shapiro–Wilk normality tests indicated that MP number concentrations were non-normally distributed amongst WWTP effluents and river systems. Thus a non-parametric Kruskal- Wallis rank sum test was conducted revealing significant differences between the upstream and downstream locations of the Dommel (p-value = 0.0032) which was also confirmed by the Dunn test (adjusted p-value of 0.0024). No significant differences were found between these locations and the samples from the Meuse or the WWTP effluents.

To reduce levels of suspended matter the Dommel passes the Klotputten, a wide basin with low flow velocities (0.002 m s⁻¹ on average) that facilitates sedimentation processes. Surface water was sampled at the upstream and downstream end of this basin. Contrary to expectations, MP concentrations did not decrease, and were even slightly higher at the downstream location (587 compared to 460 MP m⁻³) (Fig. 2B). In contrast, the sampled sedimentation basins of ‘De Biesbosch’ revealed a considerable decrease of MP from surface waters due to low flow velocities. This might be explained by the much longer residence times. At Drimmel, water from the Meuse is pumped into the basins to facilitate the settling of natural suspended matter. MP also settled resulting in decreasing MP concentrations from 789 MP m⁻³ (Drimmelen) to 607 MP m⁻³ (Biesbosch1) and 67 MP m⁻³ (Biesbosch2) (Fig. 2A). Similar polymer types were present in the three samples, however their numbers and proportions changed. Compared to the inlet water, surface water in the first sedimentation pond contained less particles made from PP and the Acrylates/Polyurethanes/Varnish cluster. The lower MP numbers in the second pond can be explained by the strong decline of PE and Rubber type 3 particles in comparison to the first pond (Fig. 2A).

The discharges of WWTPs are expected to influence the distribution of MP in a river. MP concentrations in the effluents ranged from 941 to 1741 (median 1024) MP m⁻³ (Fig. 2Aa&B). They were thus higher than MP detected in the upstream regions of the Dommel, but comparable to the ones reported for the downstream locations. Riverine surface water was sampled up- and downstream of these effluents’ discharging points. The upstream locations in StOedenrode and Roermond revealed a higher contamination than the effluents or the downstream locations. The MP concentration in the effluent of the WWTP Eindhoven was lower than the one identified in the upstream location and can thus not explain the
concentration increase in the Dommel from 2678 to 8450 MP m\(^{-3}\) (Fig. 2B). Although WWTPs continuously add MP to the river systems we could not see a general increase in MP abundances at the sampled downstream locations. Higher MP concentrations might rather be linked to diffuse sources (Hurley and Nizzetto, 2018) or other riverine dynamics and processes.

One of these processes could also be weather induced variations. These were assessed at WWTP effluents when examining the effluents of two smaller WWTPs (Maasbommel and Oijen) for MP > 300 µm for which concentrations of 46 and 1494 MP m\(^{-3}\) were observed (Fig. S5). The latter was recorded at the WWTP Oijen when sampling the effluent during a strong rain event with an effluent discharge of 10560 m\(^3\) h\(^{-1}\) which was considerably higher than the monthly average of 1,550 m\(^3\) h\(^{-1}\). Two weeks later, the same effluent was sampled again three subsequent times under normal weather conditions (Table S1). Lower concentrations of 211, 279 and 711 MP m\(^{-3}\) were detected. Still, MP abundances were much higher than determined in the effluents of the other four WWTPs where a mean concentration of 77 (SD 44) MP m\(^{-3}\) was retained on the 300 µm sieve. These data confirm findings that MP number concentrations can vary between WWTP effluents (Mintenig et al., 2017; Simon et al., 2018), and that this strongly depends on weather and rain conditions (Pirimpek et al., 2017a; Wolff et al., 2019). This not just holds true for WWTP samples, but environmental samples in general where an increase of MP in surface water has been linked to higher flow regimes (Cheung et al., 2018; Hurley et al., 2018; Watkins et al., 2019). MP concentrations in the Dommel were linked to respective flow velocities (Table S1, Fig. S6). The critical shear stress equation (Waldschläger and Schüttrumpf, 2019) indicates a critical flow velocity of 0.275 m s\(^{-1}\) that led to an increase of MP in surface waters. At flow velocities higher than that concentrations above 6800 MP m\(^{-3}\) were detected for MP > 20 µm around Eindhoven and StOedenrode. These concentrations are considerably higher than at lower flow velocities, where we found a mean concentration of 924 (SD 722) MP m\(^{-3}\).

One of the study aims was to interpret data in respect to the system scale behaviour. Thus, we assessed if the variability of detected MP concentrations would be influenced more by spatial than by temporal aspects. Within three weeks in autumn 2017, 13 locations in the Dommel were sampled under very similar weather conditions. The sampling was repeated at StOedenrode for another five times in 2018 (Table S1, Fig. 3).

The Kruskal- Wallis rank sum test revealed no significant differences (p-value = 0.1346) between spatial, seasonal or daily variability (Fig. 3). Differences within the Dommel only become significant if differentiating again between the rural and urban areas (p-value = 0.0157). While spatial differences caused MP number concentrations to vary by two orders of magnitude, temporal variations were lower and induced a maximum variation of one order of magnitude. This confirms that spatial differences, like geographical and demographic differences or the inputs of WWTPs, induce larger variations in a system compared to the temporal variations at one location due to e.g. differences in flow or wind conditions. Also within a day the determined MP concentrations varied, however, differences were comparably low and varied by a factor of 1.4 in StOedenrode (Fig. 3, Table S3), and 3.4 in the effluents of the WWTP Oijen where MP > 300 µm was identified (Figure S3, Table S3).

**MP sizes and shapes** in all samples more particles than fibres were detected. Fibres accounted for 1.4–34% (median 12.9%) of the total MP numbers in surface water, and for 12.5–22.9% (median 12.4%) in WWTP effluent samples. On average, fibres were 300 µm long. Their width was approximately 15 µm which is in accordance to other studies (Napper and Thompson, 2016; Pirc et al., 2016).

At all locations increasing abundances with decreasing MP sizes were detected. In total, 67.1% of all MP was smaller than 100 µm (Fig. 4A), with 26.3% being smaller than 25 µm, and 18.5% of the MP having their longest dimension between 25 and 50 µm. Only 6.7% were longer than 300 µm, and 1.1% longer than 1 mm respectively. The fitted power law resulted in an exponent x = 2.79 with an R² of 0.93 (Figure S7) which is comparable to the ones found in literature (Kooi and Koelmans, 2019). The mesh size during sampling and sample handling was 20 µm. Smaller MP could have been retained when filters started clogging. However, small MP particles or fibres might also have passed sieves vertically or might not have been detected during micro-FTIR analysis. As such, number concentrations of MP of approximately 20 µm are likely to even be higher.

**Polymer types** in total 26 different polymer types were identified (Figure S4). The samples from the Meuse contained on average 13 (SD 2) different polymer types, while 12 (SD 3) were detected in the Dommel, and 15 (SD 2) in the WWTP effluents respectively. Most abundant polymer types were PE, PP, rubber type 3, nitrite rubber and acrylates/polyurethanes/varnish which together represented 81% of all identified MP particles and fibres (Fig. 2, Figure S4). PE (23%) and PP (19.7%) were detected most frequently. Both polymer types have been reported in high concentrations earlier. Rubber type 3 (18.3%), which is ethylene propylene diene monomer (EPDM) rubber, was the third most abundant polymer type identified. EPDM is commonly used as sealing material, for tubes, car doors, but also in building and roof constructions. Until now it was rarely detected in the environment. This might be explained by the identification methods used, as recent studies that also applied micro-FTIR with automated image analysis were able to identify EPDM and other types of rubber in considerable concentrations (Haave et al., 2019; Mani et al., 2019). As knowledge on rubber particles in the environment is very limited, these data are of particular interest. This especially holds true for the abrasion of car tyres which are considered a major source of MP to the environment (Boucher et al., 2019; Hurley and Nizzetto, 2018), however no data are yet available to verify emission statistics (Kole et al., 2017). As already indicated by Haave et al. (2019) it is difficult to assess car tyre abrasives. High contents of Carbon Black hampers the identification by micro-FTIR of one of its main components, styrene butadiene rubber (SBR). Further, its density is higher than the commonly used ZnCl₂ solution (1.6 g cm⁻³). Therefore, other sample preparation and identification methods than used in the current study are required to estimate abrasions of car tyres in the environment. Also remaining rubber
types, such as Nitrile rubber, cannot solely be linked to traffic activities as their fields of application are so diverse.

The different MP sizes also reflect differences in relative abundances of polymer types: MP larger than 1 mm were almost exclusively made from PE or PP. Smaller MP had a much higher polymer diversity (Fig. 4A). The same conclusions were drawn by recent studies which also applied micro-FTIR with automated image analysis (Haave et al., 2019; Lorenz et al., 2019; Mani et al., 2019). This emphasizes the importance of examining these small MP to correctly depict occurrences and distributions of polymer types in the environment.

**MP mass concentrations** For all samples taken in the Dommel and in the Meuse, the total MP mass concentration was estimated as described in section 2.4. The mass based concentration varied between 51 and 7270 (median 670) μg m⁻³. In general, samples with low MP number concentrations also revealed low mass concentrations. Samples taken in the Haringvliet and StOedenrode (first replicate taken on 21.8.2018) revealed comparably low mass concentrations which, however, could not be explained by particularly high numbers of small particles (Table S3).

MP smaller than 100 μm were most frequent by numbers, however, their individual weight was so low that they contributed only for approximately 2% to the total MP mass concentration (Fig. 4B). Total mass was largely determined by the presence of MP > 2 mm. As these MP are almost exclusively made of PE and PP, it is not surprising that the two polymer types constitute the largest share in terms of MP mass concentration (Fig. 4B, Table S3).

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Fig. 4. Relative distribution of (A) MP numbers and (B) mass concentrations in relation to MP sizes, and (C) the cumulative frequency distribution of total MP number concentrations identified in the Dommel and the Dutch part of the Meuse, vertical lines represent predicted no effect concentrations (PNEC by Everaert et al. (2018): 6.7 × 10⁴ MP m⁻³ (purple), Besseling et al. (2019): 2.0 × 10⁵ MP m⁻³ (yellow), Adam et al. (2019): 7.4 × 10⁵ MP m⁻³ (blue), Burns and Boxall (2018): 1.3 × 10⁶ MP m⁻³ (red)). Acr/PUR: acrylates/polyurethanes/varnish cluster, PA: polyamide, PC: polycarbonate, PE: polyethylene, PEST: polyester, PP: polypropylene, PS: polystyrene, PVC: polyvinyl chloride. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
3.3. General discussion

Until now only a few studies have focused on examining the spatial distribution of MP in individual rivers in detail (Ding et al., 2019; Mani et al., 2015). Only five studies identified MP with a detection limit of approximately 50 μm, but all selected particles for further identification and did not include chemical mapping (Koelmans et al., 2019). This is the first study assessing the spatial and temporal variability of MP down to a size of 20 μm using FTIR microscopy followed by an automated image analysis (Primpke et al., 2019). As such, the results provide a valuable insight into the presence and distribution of various polymer types in riverine surface waters and WWTP effluents.

Several studies have discussed the need to implement standardized QA/QC criteria to generate reliable and comparable data (Filella, 2015; Hermsen et al., 2018). Koelmans et al. (2019) provided guidelines for nine criteria for the analysis of MP in aqueous samples, one of them recommends that at least 25% of a filter should be analysed during chemical mapping. Based on here presented data we favour that at least 50% of a filter should be mapped to accurately assess MP number concentrations and polymer types. This also reduces the risk of data misinterpretation due to the uneven distribution of MP. In filters (Peeken et al., 2018). Further aspects that should be considered are high original sample volumes and efficient MP extraction steps to increase actual numbers of identified particles. Further, the analysis of at least 50 pre-sorted particles with ATR-FTIR showed that different polymer types were presented with an acceptable level of uncertainty. In this study, care was taken that the complete sample after MP extraction was concentrated on one or more anodic filter, and that of each filter at least 60% were chemically mapped. For MP > 300 μm a visual pre-selection of potentially synthetic particles was unavoidable from which a minimum of 50 particles (32–76% of the sorted particles) was analysed with ATR-FTIR. As such, we consider our data to reflect actual MP numbers and polymer types relatively accurate. However, we might have underestimated concentrations of MP of around 20 μm which would imply that levels of MP pollution are higher than concluded here.

The cumulative frequency distribution of detected MP number concentrations covers a range from 67 to 11532 MP m⁻³ (Fig. 4C). Samples were taken from different representative water system types that are typical for the Netherlands, including small ditches, the rural and urban parts of an intermediate river and a big international waterway. Therefore, we argue that this distribution of MP concentrations represents that of all Dutch riverine surface waters reasonably well, enabling a generic assessment of risks for aquatic biota. To do so, one needs to combine exposure and effect concentrations (Koelmans et al., 2017). Until now, four studies presented an environmental risk assessment of MP with estimates for the Predicted No Effect Concentration (PNEC), which is the threshold concentration at which no adverse effects are expected to occur (Adam et al., 2019; Besseling et al., 2019; Burns and Boxall, 2018; Everaert et al., 2018). The PNEC estimates do not differentiate between MP sizes or polymer types, therefore neither does the frequency distribution of MP number concentrations from Dommel and Meuse. The majority of locations revealed MP concentrations that are below, or even considerably below, the determined PNEC concentrations (Fig. 4C).

In two Dutch river systems, between 67 and 11532 MP m⁻³ were identified. Virtually all of these concentrations are considerably below known effect thresholds. Thus, based on the current knowledge, MP associated risks for aquatic biota are not likely to be anticipated in Dutch riverine surface waters. The three locations with MP number concentrations above one of the PNECs were in the vicinity to big cities, if risks are to be expected, they will most likely be highest in highly urbanized and polluted areas.

Authors agreement

SMM and MK designed the study together with SCD, AAK and APVV. SMM, MK and MWE performed the field work. SMM and MWE prepared the samples and performed µFTIR measurements together with MK and PERH. SP conducted the polymer identification. SMM wrote the article with substantial contributions from and final approval of all authors.

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.

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