Relationship between discharge and river plastics concentrations in a rural and an urban catchment

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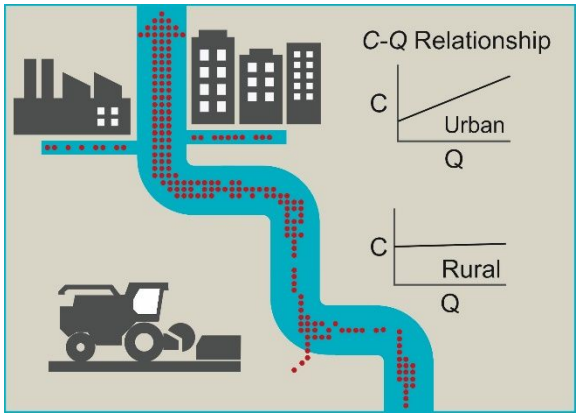
Abstract

Rivers play a major role in transport of plastic debris from inland sources like urban areas into the marine environment. The present study examines plastic particle concentrations and loads (> 500 µm) upstream and downstream of an urban subcatchment over 15 months and investigated the relationship between river water discharge (*Q*) and plastic concentration (*C*). The plastic particle concentration increases by 0.8 g/1000 m³ or 77 n/1000m³ from the rural to the urban subcatchment. In the rural subcatchment *C* does not increase with increasing *Q* (p=0.57), whereas a positive relationship between *C* and *Q* exists downstream of the urban catchment (p= 0.00003). Combined sewer overflows (CSOs) likely contribute additional plastic loads during high flow conditions. Based on the *C*-*Q* relationship, we estimate the total plastic export in 2016 from the entire catchment to be 3.0×10^6 n/year, or 2.6×10^4 n/(km² year) and 15 n/(cap year). Because of the positive *C*-*Q* relationship, 90% of the plastic load is transported during 20% of the time. The analysis of time-resolved plastic concentration data in rivers provides a data-driven tool to better estimate plastic loads and to better understand the catchment controls of plastic in rivers.

Graphical abstract



Introduction

Rivers are an essential pathway for land-based inputs of plastic debris into the sea.[1,2] They connect inland sources of plastic emission with marine environments. While the occurrence of plastic in the marine environment is well documented,[3,4] (and citations therein) only relatively few, yet an increasing number of studies provide data on plastic in rivers. These data comprise of either shoreline sampling[5,6] or sampling from the water column.[7–14] Shoreline samples indicate the composition of plastic debris present in the river systems, but concentrations and loads can only be derived from water column data.

It was demonstrated that plastic loads in rivers are positively related to the amount of plastic waste generated in the river catchment upstream of the observation point.[1,2] Waste generation is in turn related to human settlement; hence urban areas may be considered as an integral source for plastic emissions into rivers.[13,15,16] Emission pathways located in urban areas such as wastewater effluents,[17,18] combined sewer overflows (CSO), stormwater drain outlets,[19] and littering[20,21] are expected to contribute to plastic pollution of rivers. The composition of plastic pollution commonly observed in freshwater environments mirrors the production volumes of plastics; polypropylene (PP) and polyethylene (PE) are most often detected because they are the polymers with the highest production volumes worldwide.[11,12,22,23] However, observed plastic concentrations and loads in rivers do not only depend on the magnitude of emission but on instream processing including storage, remobilization, sorting and fragmentation.[21,24]

For solutes and particulate material, the temporal pattern of concentration and discharge (*C*-*Q* relationship) are helpful to characterize and classify the relation between hydrologic transport and the

characteristics of the source.[25–28] Temporal *C*-*Q* relationships can be classified into three archetypes: dilution, where *C* decreases with increasing *Q*; constant, where *C* shows little directional changes with *Q*; enrichment, where *C* increases with *Q*.[29] From these it is possible to infer whether loads are hydrologically controlled as implied by constant and enrichment archetype, or constant loads prevail as suggested by dilution pattern.

Moreover, the *C*-*Q* relationship can be used to estimate concentration and load based on river water discharge data and to generate reliable annual estimates as a basis to calculate per capita and area-specific loads of plastic particles. For suspended sediments, commonly a positive *C*-*Q* relationship is observed.[28] We hypothesize that plastic concentration increases with river water discharge as a result of remobilization from the riverbed and banks as well as the activation of additional inputs from stormwater drains and CSO. Presently available data on plastic concentration in rivers often report the conditions at one point in time. Only a few studies report time-resolved observations concerning plastic concentration and plastic load.[12,13,30] However, those studies were not explicitly designed to capture a range of discharge conditions. Nevertheless, the results indicate that concentrations tend to be higher at higher discharges e.g. due to rain events. No clear trend has been observed in estuaries. Previous studies reported elevated concentrations after flood events[10,30,31] but also no apparent differences after a stormwater event.[14,32] Plastic particle transport modeling suggests that plastic concentration is not only dependent on hydraulic conditions but on particle properties such as size.[33] Therefore, it is necessary to obtain *C*-*Q* relationships of individual particle size fractions.

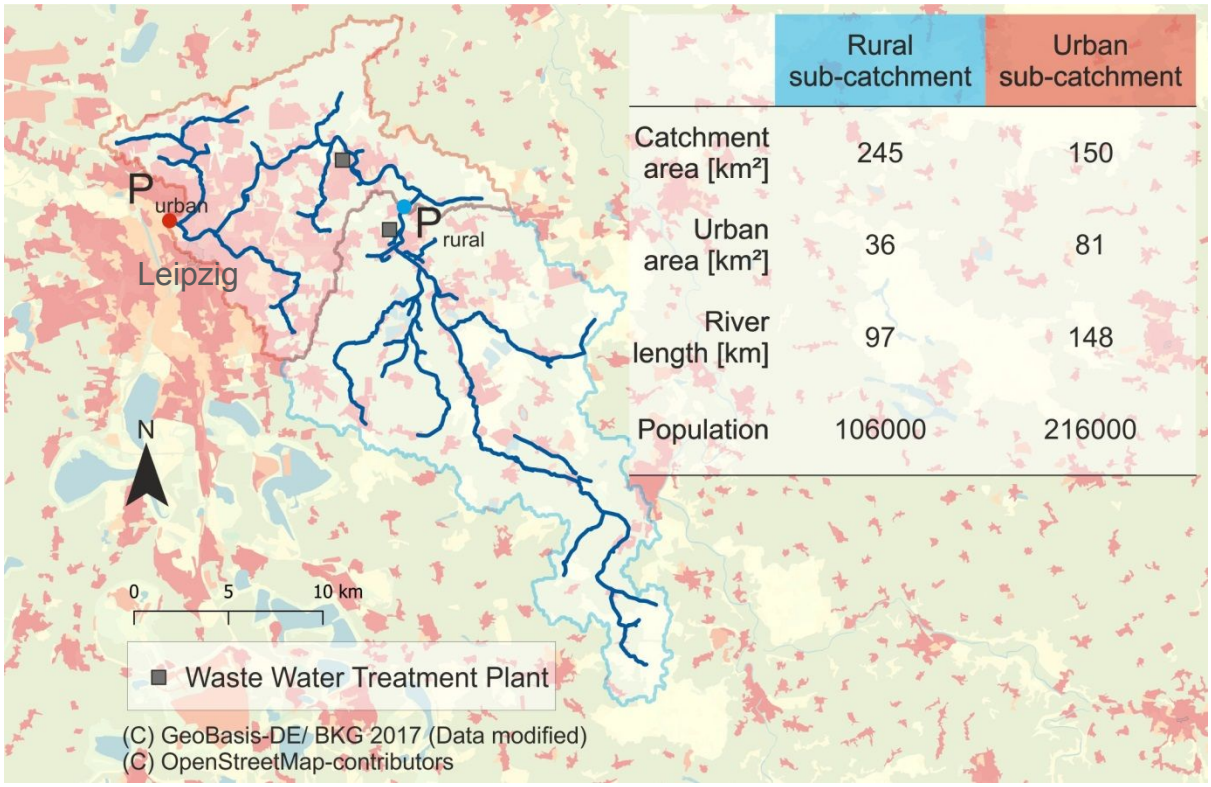
Robust analytical methods for sampling and quantification are an essential requirement for a comprehensive survey on plastic contamination.[34,35] Although standardized methodologies do not exist, it is possible to derive best practice rules for sampling, sample preparation and analysis of microplastic > 300 µm from existing studies of marine environments.[36] In this light, we applied an analytical methodology from literature to determine macro- and microplastic particle concentration at two stations along a river with a change in land use from rural to urban over a range of river discharge conditions in a time period of 15 months. Further, we investigated the plastic abundance and size distribution for plastic particles > 500 µm. We focused on the polymers with the highest production volume, polyethylene (PE), polypropylene (PP) and polystyrene (PS), because it was expected that these materials would show the highest abundance.[23]

The objectives of this study were to reveal the influence of an urbanization gradient from rural to urban on plastic emission pattern including 1) the abundance of plastics, 2) the characterization of polymer types, and 3) to explore if *C*-*Q* relationships exist and how they can be applied to characterize annual plastic loads. Our study demonstrates how the interpretation of time series data of plastic concentrations in rivers can enhance our understanding of the dominant controls of plastic export from river catchments.

Methods

Study catchment

The headwaters of the Parthe River are located south-east of the city of Leipzig, Germany. The river passes through the city and then discharges into the Weisse Elster in the northern part of the city (Figure 1). The study was conducted at two sampling locations at the Parthe River; P_{rural} and P_{urban}, representing two subcatchments. P_{rural} (N 51.362588, E 12.534989) is mainly characterized by rural and agricultural land use. It has an urban land use of 15%.[37] This subcatchment is upstream of the city of Leipzig and it is denoted as a rural subcatchment. The downstream location P_{urban} (N 51.356601, E 12.349401) is within the city of Leipzig and represents the outlet of the entire catchment. The subcatchment between the downstream (P_{urban}) and upstream sampling point (P_{rural}) is characterized by mainly urban land use (54% of the total area).[37] The urban area definition used in this study includes municipal green space such as parks. This allows for littering to be accounted for. The different degree in urbanization in both subcatchments is also reflected by the population density of 433 cap/km² and 1440 cap/km², respectively. There are no artificial barriers between P_{rural} and P_{urban} which may act as a sink for plastic particles. In each subcatchment one municipal wastewater treatment plant (WWTP) discharges treated effluents into the Parthe River (Figure 1). The WWTP in the rural subcatchment treats 2,800 x 10^3 m³/year (or 50,400 population equivalents, p.e.) and the one in the urban subcatchment 845 x 10^3 m³/year (15,400 p.e.). The major WWTP of the urban area is located downstream of the sampling site P_{urban} and therefore irrelevant for our study. CSOs may serve as an emission path for plastics debris in the urban subcatchment. However, data on the total number of combined sewer outlets was not available for this study. Due to the high proportion of combined sewer systems (CSSs) (80%) in the city of Leipzig, we expect a relevant number of combined sewer outlets (CSOs) in the urban subcatchment.



	Rural sub-catchment	Urban sub-catchment
Catchment area [km²]	245	150
Urban area [km²]	36	81
River length [km]	97	148
Population	106000	216000

Figure 1 River flow path through the rural and the urban catchment, sampling sites P_{rural} and P_{urban} (land use indicated by color code, red urban land-use, green yellow rural land-use, blue lakes and rivers), inset table provides attributes of the rural and the urban subcatchment including total area, urban area, river length and population

Sampling of suspended matter and river water

Sampling of suspended matter in the River Parthe was conducted between November 2015 and January 2016, and between October 2016 and February 2017. The sampling campaign did not include a spring and summer period. This may limit interpretation of data because potential seasonal variations of plastic loads may not be revealed. Sampling dates were chosen according to hydrological conditions covering low, medium and high river discharge. Our measurements cover discharges between 0.46 and 1.94 m³/s which represents 80% of the time of the year 2016. River discharge and the discharge through the sampling net was manually measured with a magnetic-inductive current meter (OTT MFpro, OTT Hydromet, Kempten, Germany) at the time of sampling or calculated to extrapolate for times not covered by the sampling from monitoring data of the gauging station located between P_{rural} and P_{urban} and measured discharge (see Table S.1; Table S.2; Figure S.1). In total,20 suspended matter samples were collected and analyzed, 10 samples from each site. Samples are denoted as P_{rural} or P_{urban} for the sampling site followed by sample number.

Samples were taken by stationary floating drift nets with a mesh size of 500 µm and an inlet opening of 30x30 cm. Thus, only particles between 500 µm and 30 cm could be quantitatively sampled. It must be noted, particles smaller than 500 µm can be bound to larger particles and thus also be sampled, but the concentration cannot be quantitatively determined. During each sampling, the net was deployed for 24 h at the thalweg of the river. The applied sampling strategy addressed floating and suspended material which was transported in the top 20 cm of the river during various flow conditions. However, bedload cannot be considered with this technique.

After sampling, the suspended solids were air dried and removed from the net, and the net was thoroughly cleaned with tap water to avoid material carry-over. All collected suspended solids were stored in glass bowls until further treatment. River water samples were taken in triplicates and independently of the suspended matter sampling at the same positions during low, medium and high river discharge conditions. River water samples were stored in glass vials and frozen at -20°C until analysis for caffeine as a wastewater indicator substance.

In order to compare two systems or values, parallel analyses are essential to derive measurement uncertainty. Without measurement uncertainty information judgment on event significance is not possible. In this study, we do not compare only two situations based on single measurements; rather we compare both subcatchments on a series of ten samplings. As the number of samples that could be analyzed in the laboratory was limited, we focused on the temporal variability at two sampling stations instead of obtaining technical replicates.

Sample preparation

Macroplastic particles larger than 5 mm and microplastic particles between 0.5 mm and 5 mm were separated from natural suspended matter in consecutive steps. First, all samples were dried at 60°C until a constant weight was obtained. After that four size fractions were differentiated by sieving using stainless steel sieves (Retsch GmbH, Haan, Germany): F1: ≥ 10 mm, F2: between 5 mm and 10 mm, F3: between 1 mm and 5 mm and F4: between 0.5 mm and 1 mm. Particulate matter in F1 was rinsed with tap water to detach smaller particles from surfaces (< 10 mm). Particulate material < 10 mm was further size-fractionated by sieving. All fractions were again dried at 60°C and weighed. Suspected plastic particles in F1, F2 and F3 were visually selected, removed and stored for later analysis in closed glass vessels under a clean-bench (Hera Safe, Heraeus Instruments, Hanau, Germany).

Preselection criteria were color, shape, and softness. Visual selection of potential polymer particles in fraction F4 was not possible. Therefore, a subsample of 0.25 g of fraction F4 was subjected to further treatment separating natural organic materials and plastic particles. Separation was achieved by temperature-controlled (60°C) dissolution of natural suspended organic matter in open glass vessels with 20 mL MilliQ water (Millipore, Direct-Q™ equipped with Millipak® Express 0.22 µm filter), 30 mL H_2SO_4 (95-97%, p.a., EMSURE, Merck, Germany) and H_2O_2 (30%, p.a., ROTIPURAN®, Roth, Germany).[38] H_2O_2 addition continued until gas bubble formation stopped. The dispersion was filtered through glass fiber filters (47 mm, GF6, Whatman, GE Healthcare Europe GmbH, Freiburg, Germany). The particulate material on the filter was rinsed with MilliQ water. In most cases, particle packing was sufficiently low at the filter surface to discriminate potential plastic particles from matrix particulate matter. In case of dense filter packing the remaining particulate material was subsequently re-dispersed in 1.2 kg/L NaCl solution (prepared from NaCl salt, > 99%, AppliChem, Panreac, Darmstadt, Germany) for density separation of plastic particles with a density < 1.2 kg/L from mineral particles.[39] The light fraction was collected on filters (47 mm, GF6, Whatman, GE Healthcare Europe GmbH, Freiburg, Germany), dried and stored at room temperature in covered glass vessels. Filters with fraction F4 were closely inspected by light microscopy (Leica, M205FA, Wetzlar, Germany) and particles which might be plastic according to the visual selection criteria were placed onto microscopy glass slides for further analysis by Raman spectroscopy.

Analysis and quantification of total suspended solids and plastic particles

Total particulate matter content in the samples was expressed as total suspended solids (TSS). TSS mass in each fraction F1 to F4 was determined after drying at 60°C until a constant weight was reached. TSS concentration was calculated based on dry mass and measured net discharge during each sampling campaign. All visually selected particles were analyzed by Raman spectroscopy (Witec alpha3000RA+, Witec, Ulm, Germany) equipped with a 532 nm laser to identify the polymer type of the plastic particle. Particles were individually analyzed using 10 replicate measurements with integration times between 1 and 10 s each depending on the intensity of the background fluorescence signal. The laser energy at the sample surface was adjusted between 6.5 and 7.5 mW. For polymer identification of particles, reference spectra of pristine polymer materials (polyethylene (PE), polypropylene (PP), and polystyrene (PS)) were recorded (Figure S.3) and compared with each

196 particle signal. For particles with high fluorescence background in fraction F1 to F3 the particle
197 surface was removed by scratching to gain access to the unaltered polymer material. Particle number,
198 particle mass and data on polymer type were recorded. Plastic particle mass of fraction F4 was not
199 determined due to a mass fraction of less than 1 % of the total mass.
200

201 ## Quantification of wastewater indicator substance caffeine in river water
202 ## samples

203 CSOs may occur during stormwater events and discharge untreated wastewater into the river. One
204 possibility to detect such CSOs is to monitor wastewater indicator substances. For this purpose, river
205 water samples were obtained at P_{rural} and P_{urban} for three different hydraulic conditions (low discharge,
206 medium discharge, high discharge). Each sample was taken by bailed sampling independently from
207 particle sampling. Water was stored in glass vials and frozen at -20°C until further analysis. River
208 water samples were analyzed by LC-MS/MS for caffeine concentration. A detailed method description
209 is provided in SI. 1.3.
210

211 ## Quality control, quantification and statistical analysis of the data

212 The analytical train of sample preparation was assessed by recovery experiments of different
213 polymers. Suspended matter from a mainly forested catchment from the River Selke in the Harz
214 Mountains, Germany (51°43'40.1"N 11°18'53.4"E) was spiked with known amounts of plastic particles
215 of various particle size fractions. Spiked and unspiked samples experienced the same procedure as
216 the ones from the Parthe River. Samples were handled and stored under the clean-bench to minimize
217 contamination with plastic particles.
218 Total plastic mass and plastic particle number in fractions F1, F2, F3 and F4 (only plastic particle
219 number) were converted into mass and number concentrations based on sampling time, measured
220 net discharge and river discharge, assuming uniform concentrations in the river cross-section. The
221 total plastic load was inferred from the plastic concentration (*C*) (particle mass and particle number)
222 and the river water discharge (*Q*). For calculation of plastic emission from the catchments, it was
223 assumed that i) the river is not a sink for the investigated polymer types, ii) constant discharge during
224 sampling and iii) homogeneous distribution of particulate matter in the river cross-section, i.e. a well-
225 mixed particle concentration. The latter assumption is required to calculate particle loads in the river

for each sub-catchment based on the *C*-*Q* relationship. It assumes that the sampling by the net is representative of the entire river cross-section. Since the *C*-*Q* relationships are based on multiple measurements at each sampling site, possible inhomogeneity of single data points are minimized by the data set. It should be noted that data uncertainty due to errors may not be discriminated from actual data variability without a careful error analysis. If measurement uncertainty (including sampling uncertainty) would be larger than the effects we interpret, no consistent pattern would be visible at all. We compare the (sub-) catchments by comparing their mean values. For these means, a standard deviation was calculated and a test on statistical significance was performed.

A mass balance approach was applied to calculate plastic export from both catchments. The data at sampling site P_{rural} represents the integral response on the plastic particle input in the rural subcatchment and enters the urban subcatchment via the river. The signal at P_{urban} is comprised of the input from the rural subcatchment via the river and urban subcatchment; it represents the outlet of the entire catchment. The difference between P_{urban} and P_{rural} (P_{urban}-P_{rural}) equals the plastic emission in the urban subcatchment.

Mean and median concentrations at P_{rural} and P_{urban} were calculated and compared using the two-sample t-test with a significance level of 0.05 to test for significant differences between both locations (OriginPro 2015, Sr2). A log-log linear regression described the C-Q relationship. All occasions in which no plastic items were sampled, i.e. concentration values were lower than the detection limit, were assigned random values in the range > 0 and < lowest plastic concentration. This was necessary because log-log relationships cannot account for zero values. The significance of the regression was tested with a 0.05 level. The uncertainty of the regression was analyzed by statistical simulation with 1000 replicates.[40] Regression and uncertainty analysis were performed using Matlab R2016b.

Results and discussion

Study design and quality control

This study aims to identify plastic emission patterns from catchments with different land use. Plastic emission patterns may be reflected by average plastic concentrations, polymer type and the relation between plastic concentration (*c*) and river discharge (*Q*). These measures were derived from multiple samplings at two locations under various discharge conditions. Uncertainty of these data due to

255 systematic errors in sampling, sample preparation and subsequent analysis may result in
256 misinterpretation. Therefore several precautionary steps have been taken to reduce data uncertainty.
257 First, data uncertainty due to unrepresentative sampling (heterogeneous distribution of plastic in the
258 river) was reduced with high sample volumes (> 340 m³, Table S.1 and S.2) which were obtained
259 during 24-h sampling campaigns. Second, average data was compared from ten individual samplings
260 in each subcatchment rather than comparing individual pairs of samples from both subcatchments.
261 To account for uncertainty introduced by sample preparation, we tested the stability of PE, PP and PS
262 as well as the dissolution of the matrix during sample clean-up. The following reagents were tested:
263 H_2O_2(30%); H_2O_2(30%)+HNO_3(65%); H_2O_2(30%)+$FeSO_4$(0.05M) and H_2O_2(30%)+H_2SO_4(96%). We
264 observed incomplete dissolution of the matrix after the addition of H_2O_2 as well as H_2O_2+$FeSO_4$, and
265 dissolution of PS after the addition of H_2O_2+HNO_3. The best results, i.e. complete matrix dissolution
266 and no visible changes of the polymers, were obtained for a combination of H_2O_2 and H_2SO_4. This
267 combination was applied in our study. Our observation agrees well to previous reports, such as Tagg
268 et al. (2015).[41]
269 A known number of plastic particles (PP, PS) with different particle sizes (3 mm and 0.8 mm) were
270 spiked into total suspended matter obtained from the Selke River (environmental background sample)
271 and subsequently separated and analyzed by the established procedure. Recoveries after sample
272 preparation, including pre-separation, clean-up and density separation followed by Raman analysis
273 revealed average mass recovery of 89% of spiked plastic material (PP, PS) of 3 mm and 800 µm size
274 (min.: 73%; max.: 100%) (Table 1). The data indicates that recoveries were slightly lower for smaller
275 particles. However, it is assumed that there is no selective loss of smaller particles in the investigated
276 particle size range (> 500 µm). Particle size-selective loss is likely to occur for smaller particle size
277 fractions, which were not in the focus of the present study. The procedure was applicable for the
278 extraction of PS (density 1.05 g/cm³) and PP (density 0.90 to 0.915 g/cm³) from the suspended matter
279 fraction. Recovery of PE was not tested separately because of similar density to the tested material
280 compared to PE (0.91 and 0.97 g/cm³).

281 **Table 1: Average plastic particle recovery determined in spiking experiments with PP and PS of 3 mm**
282 **and 0.8 mm particle size (n=2), in each recovery experiment 5 to 10 particles were spiked**

Polymer type	Size [mm]	Mass-recovery [%]	Number-recovery [%]
PP	3	99%	100%
	0.8	73%	60%
PS	3	100%	100%
	0.8	100%	100%

283

Polymer particle size, concentration and load

Polymer abundance, particle size, particle counts and total particle mass concentration may serve as a first indication of different plastic type emission pattern upstream and downstream of the urban subcatchment.

The plastic particle concentration changes from upstream to downstream of the urban subcatchment by 0.8 g/1000 m³ or 77 n/1000m³. Due to the high variability, this change is statistically not significant (Table 2). A similar increase is found for size fractions F1 and F2, while the concentration of fraction F3 decreases in mass and the finest fraction (F4) decreases in number between P_{rural} and P_{urban} (Table 2). High standard deviation is not due to limited precision of the analytical method, as visible from the results of spiking experiments (Table 1) but due to the highly dynamic nature of the plastic concentration in the river. Similar high measurement uncertainties of plastic concentrations in rivers were reported in previous studies.[12,13] Nevertheless the moderate increase in particle mass concentration from the rural to the urban catchment is not only visible for the mean and median data (Table 2), but holds true for most of the individual samplings (Table S.5 and Table S.6).

Larger particles were less abundant than smaller ones at both sites (Table 2). The smallest particle fraction (F4) comprised more than 50% of the total plastic particle number concentration whereas its contribution to the total plastic particle mass was negligible. Based on an estimation (assuming spherical shaped particles with a density of 1 g/cm³ in all fractions, and similar particle numbers in F1 to F3) particle counts in fraction F4 have to be approximately 900 times higher compared to the sum of particle counts in fraction F1 to F3 which contribute to 10% of the total mass. Particle mass concentration was thus controlled by particles > 1 mm which is in accordance with previous studies.[7,13,42] Plastic particle numbers may further increase for particle sizes below 500 µm.[43,44] However, it is assumed that these particles may only have a minor contribution to the total particle mass studied herein. The environmental relevance of plastic particles of different sizes is a matter of debate. Smaller particles may exhibit higher mobility in rivers[33] and might be more effectively ingested by and translocated in organisms such as mussels[45] and show elevated release of plastic additives or absorbed pollutants due to the high surface to volume ratio.[46,47]

The plastic concentration upstream and downstream of the urban area is generally within the range of plastic concentrations in rivers of similar size (discharge < 10 m³/s). For example, the Los Angeles and San Gabriel River are heavily impacted by urban land-use and show plastic concentration > 10^4

n/1000 m³,[9] microplastic concentrations for estuarine rivers were also significantly higher in a densely populated catchment (Patapsco River: 1637 km², 900,000 cap.) than in rural and suburban dominated catchments (Magothy River, Rhode River, Corsica River each < 100 km², < 35,000 cap).[10] Transport of plastic in urban areas towards the river may be more efficient, meaning faster and therefore undergo less mass loss as compared to rural areas. The more efficient transport in urban areas compared to rural areas may be a consequence of higher connectivity due to higher degree of surface sealing as well as the presence of channels discharging treated and untreated wastewater into the rivers.[48]

Table 2 Plastic particle and total suspended solids (TSS) concentration and loads as well as plastic concentrations and loads for fraction F1, F2, F3, and F4 at P_{rural} and P_{urban} as well as for (P_{urban}-P_{rural}); statistically significant (p=0.05) changes between P_{rural} and P_{urban} are indicated by *); light gray fields indicate an increase from the rural to the urban subcatchment

	fraction		unit	Rural catchment, (P_{rural})			Urban+rural catchment, (P_{urban})			urban catchtment, $\Delta(P_{urban}$-$P_{rural})$	
				mean	median	stdev	mean	median	stdev	mean	median
Mass concentration											
TSS	all	> 0.5 mm	mg/m³	56	40	38	79	90	51	95	135
plastic	F1-F3	> 1 mm	mg/m³	0.2	0.018	0.3	0.54	0.25	0.60	0.80	0.40
	F1	> 10 mm	mg/m³	0.0*	0.000	0.0	0.38*	0.19	0.46	0.6	0.32
	F2	5-10 mm	mg/m³	0.02	0.000	0.05	0.06	0.05	0.13	0.1	0.08
	F3	1-5 mm	mg/m³	0.2	0.012	0.3	0.06	0.04	0.06	0.00	0.06
Number concentration											
plastic	all	> 0.5 mm	10^{-3} n/m³	66	60	41	74	56	67	79	53
	F1	> 10 mm	10^{-3} n/m³	0.3*	0.0	0.6	2*	1	2	2	2
	F2	5-10 mm	10^{-3} n/m³	0.8	0.0	1.8	3	2	5	5	3
	F3	1-5 mm	10^{-3} n/m³	12	2	28	27	16	33	37	26
	F4	0. 5-1 mm	10^{-3} n/m³	53	45	33	42	24	48	35	10
Mass load											
TSS	all	> 0. 5 mm	g/h	90	55	28	321	380	89	232	324
plastic	all	> 0. 5 mm	g/h	0.3	0.02	0.2	2.2	1.04	1.0	1.9	1.0
Number load											
plastic	all	> 0. 5 mm	n/h	105	82	29	300	237	116	195	155

[a] NOTE: change in concentration was corrected for the difference in discharge, for calculation see section methods

The mean water discharge between the two sampling points of the Parthe River increases by a factor of ~2.5, due to the increase in catchment size and a higher specific discharge in the urban subcatchment (Table S.3). Correspondingly, the instantaneous plastic load in the river markedly increases by a factor of 7.3 (mass, F1-F3) and 2.9 (number (F1-F4) from the P_{rural} to P_{urban}. The median plastic load added in the urban subcatchment (P_{urban}-P_{rural}) is approximately 1.0 g/h or 155 n/h.

The median of instantaneous plastic load is normalized to the urban area equaling $0.06x10^{-2}$ g/(km² h) and $1.2x10^{-2}$ g/(km² h) in the in the rural and urban subcatchment, respectively. These results are in the range of global estimates which vary between ~$1.9x10^{-6}$ g/(km² h) and $18,300x10^{-2}$ g/(km² h) depending on the catchment.[2] With approximately $0.2x10^{-6}$ g/(cap h) and $4.7x10^{-6}$ g/(cap h) the median instantaneous mass load per capita is one order of magnitude higher in the urban compared to the rural subcatchments (Table S.9). Per capita emissions should be interpreted as a metric to compare among different rivers and are not directly linked to the behavior of individuals but also depend on commercial and construction activities. Per capita plastic emission for a water channel in Vietnam (Nhiue Loc- Thi Nghe canal) are higher and ranged between $170x10^{-5}$ g/(cap h) and $3,300x10^{-5}$ g/(cap h).[42] The difference between the study in Vietnam and our study may be attributed to different source strengths, i.e. number of plastic users/manufacturers and additional emission pathways.

Polymer abundance

The polymer distribution at both sampling sites differed between the particle size fractions F1 to F4: while the finest fraction (F4, 500 µm - <= 1mm) was a mix of all three polymer types, the coarser fractions (F1 – F3) almost exclusively consisted of PS (Figure 2). At both sampling locations, the average concentration of PS, PP, and PE increased with decreasing particle size. Due to the high variability of the data we did not observe an increase in PS, PP and PE downstream of the urban subcatchment compared to the rural subcatchment (Table S7 and Table S.8). For instance, the average PS concentration in the rural subcatchment was strongly controlled by one sample which showed very high particle number concentrations in F3 (Table S.5, P_{rural}_S10). There was also no change observed in the relative composition of the three polymers with increasing discharge with exception to this high PS concentration in F3. A recent review on occurrence of polymer types by Koelmanns et al. revealed PE, PP and PS as the most frequently found polymers in freshwaters.[23] Other studies reported either PE or PP to be the most abundant polymer type in rivers such as the Antua River, Portugal[11], in several urban rivers in Illinois, USA[49] and in the Teltow Channel, Berlin, Germany.[12] However, PS was also detected in freshwater samples and are reported to dominate microplastic particles.[9] The polymer composition may vary among different locations in the same river and across different rivers depending on local sources.[7] In our study, the dominating polystyrene beads had the typical shape and morphology of expanded polystyrene insulation material (Figure

S.3). We attribute this high PS abundance to building construction projects during the sampling period, particularly low-energy modernization and construction with extensive use of PS building insulation material. Similar findings were reported earlier by Moore et al. (2011) who identified PS particle as insulation material.[9] A current survey on plastic pollution in German rivers observed PS dominating portions of the total plastic content as well.[22]. Our study only takes PE, PP and PS particles into account and therefore it is not possible to deduce the absolute total plastic particle concentration.

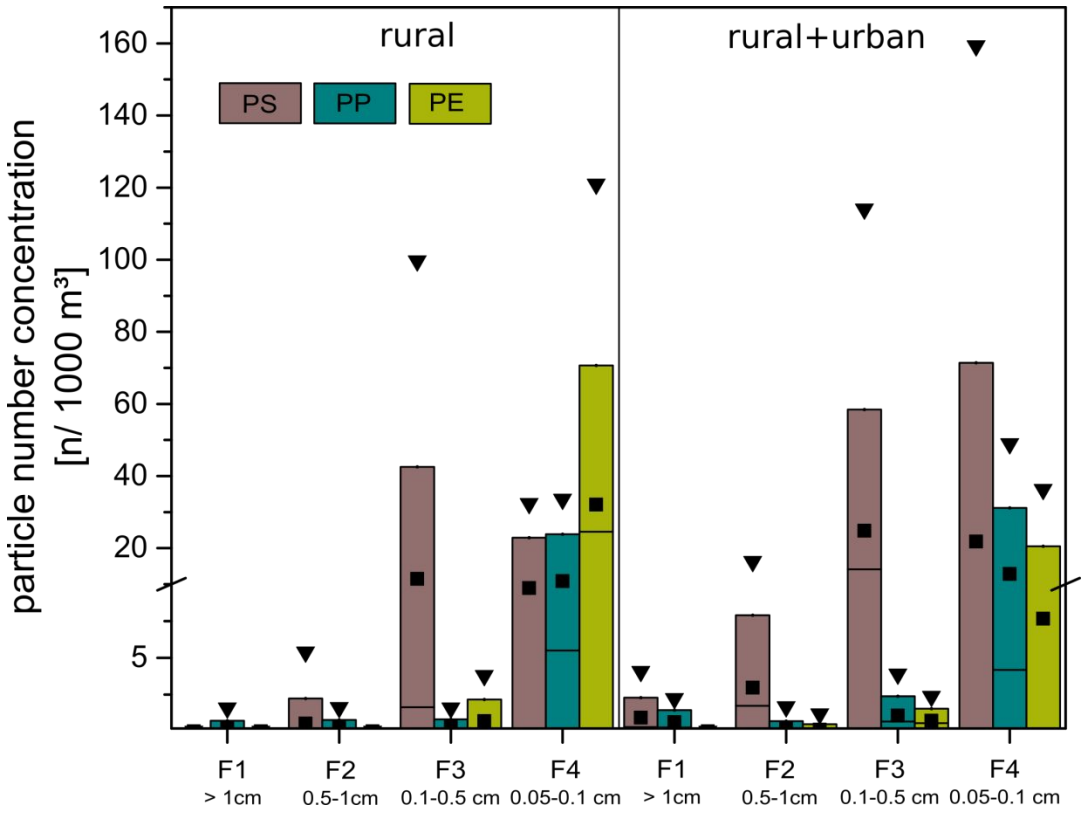


Figure 2: Polymer concentration [n/1000 m³] in the rural subcatchment and downstream of the urban subcatchment, mean value (solid rectangle), median value (horizontal solid line), standard deviation (colored box), maximum value (solid triangle), note: axis with particle number concentration has a break at 10 n/1000m³

Relationship between plastic concentration and river discharge (*C-Q* relationship)

Plastic concentrations and loads are the combined result of source characteristics, and instream transport and retention. Characterizing these *C-Q* relationships can provide insight into the underlying controls of plastic export from river catchments. The *C-Q* relationships for the plastic particles at the two sampling sites of the Parthe River (P_{rural} (rural subcatchment) and P_{urban},(total catchment)) are shown in Figure 3. In the rural subcatchment, the plastic particle concentration is not significantly

related to discharge, neither for total plastic (Figure 3 b, c) nor for its size fractions (Figure S.4 d-g). It is noted here, that no *C*-*Q* relationship was calculated for F1 and F2 at P_{rural} because of the low number of plastic items found in these fractions (Figure S.4 d, e). There was also no positive *C*-*Q* relationship for total suspended solids (Figure 3 a). Little directional changes in *C* with *Q* are typical for geogenic solutes and suggest a widespread, diffuse source.[29] The rural subcatchment receives treated wastewater from a WWTP (population equivalents 55 000) which potentially contributes to the load of microplastics. However, if WWTP effluents would be dominating factor, one would expect a dilution pattern in *C*.[32] This effect might not be evident in our study because of the lower particle size cutoff. It is known that plastic particles < 250 µm may increase downstream of a wastewater treatment plant.[49–51] However, this particle size range was not included in the present study.

The *C*-*Q* relationship is clearly different downstream of the urban subcatchment (Figure 3). All particle fractions show increasing concentration with increasing discharge (Figure S.4, positive slope b of the regression). The *C*-*Q* relationship is significant for the particle fractions F3 and F4 and, as these have the largest share in the total particle number concentration, also for the total particle number concentration. These significant enrichment patterns suggest a preferential mobilization and or emission of particles between 0.5 mm and 5 mm with increasing discharge. As TSS shows a similar *C*-*Q* relationship than plastic (Table S.10), the ratio between plastic and TSS concentration is relatively constant (~ 0.6%) independently from river water discharge.

A major pathway that connects urban areas to rivers is the sewer system. In separate sewer systems surface-runoff is discharged into surface waters after some physical pretreatment (often settling basins). The studied catchment predominantly comprises a CSS that directs surface runoff together with the sanitary wastewater into the WWTPs. Intense rainfall can exceed the capacity of the sewer network and the WWTP and, then, CSO is directly discharged into rivers without any treatment. We qualitatively confirmed the presence of untreated domestic wastewater at high river discharge by detecting increased levels of caffeine, a compound which is usually well eliminated in WWTPs[52] and therefore only present in the river in case of direct discharge (Table S.4). We conclude that CSO events at least partially drive the observed enrichment pattern. As WWTPs retain ~ 99% of the incoming plastic load,[53] efforts to reduce CSO events e.g. by increasing retention space in the sewer network would reduce plastic emissions from urban catchments into rivers. As long as CSOs are

avoided, CSSs are advantageous as all surface runoff is treated in a WWTP compared to separate sewer systems where particles can enter rivers via stormwater drains.

Beyond additional inputs during rain events, remobilization of plastic particles from the banks and bed of the river can lead to increased concentration. However, the maximum discharge of 1.94 m³/s at P_{urban} was below bankfull discharge and too low to induce bed load transport. Large flow events however, have been shown to mobilize plastic from the river networks.[21] Seasonal flow variations and the resulting *C-Q* relationship have been observed to show a dilution pattern in the Gallatin catchment in the Northwestern US which suggests rather constant plastic source strength.[14]

Our results indicate that there is no universal increase of plastic concentrations with increasing discharge. An increased urban land use and CSO likely cause the shift in the *C-Q* relationship from a constant to an enrichment pattern on the course from the rural subcatchment to the total catchment.

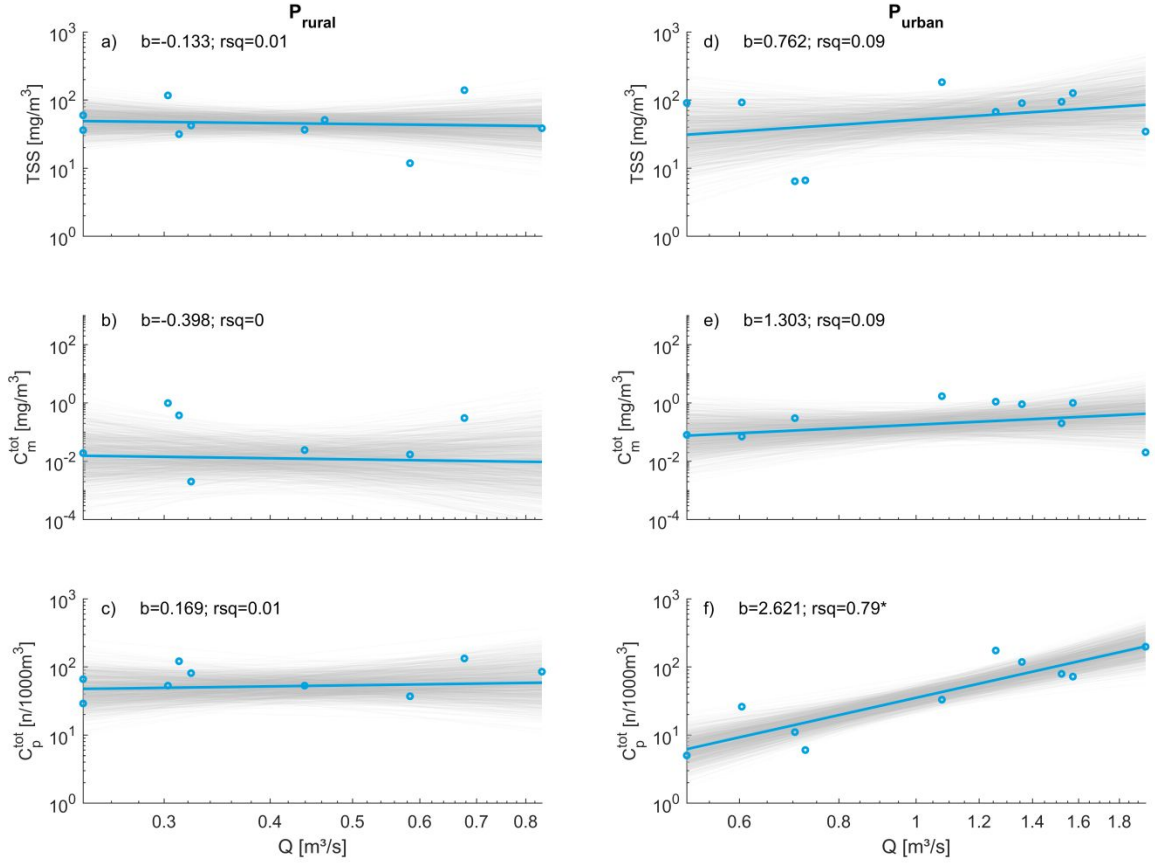


Figure 3: Relationship of total suspended solids and plastic concentration (mass and number) with river discharge (*Q*) at P_{rural} (a-c) and P_{urban} (d-f); statistically significant relations are indicated by "*"; b slope and rsq (R^2) correlation coefficient

Prediction of annual plastic loads based on *C-Q* relationships

The regression equation derived from the data shown in Figure 3 for *Q* and *C* can be used to estimate plastic number concentrations based on river water discharge (Figure 4a). We calculated the temporal pattern of plastic export for the whole catchment in 2016 (Figure 4b). Accordingly the mean and the median annual particle load (F1-F4) was ~3.5×10^6 and 3.0×10^6 n/year, with 10 and 90% prediction bounds of 1.5×10^6 and 6.0×10^6 n/year. These annual loads are similar to average instantaneous loads (calculated from Table S.9). However, *C*-*Q* based loads provide additional insight into the temporal variability of plastic export from the studied catchment, highlighting the importance of high discharge periods for the overall export.

The mean and median population specific annual plastic particle loads for the urban subcatchment are 19 and 15 n/(cap year), respectively. Similarly, the mean and median area specific plastic particle load exported from the urban subcatchment are 3.0×10^4 and 2.6×10^4 n/(km² year). Plastic particle loads in the Parthe River are determined for particle sizes > 500 µm. As it is expected that particle number increases with decreasing particle size, number loads are presumably higher for particle size ranges < 500 µm.[44]

As concentrations increase with discharge, loads are particularly high during high flow periods. The relative cumulative plastic load distribution (Figure 4c) during one year shows that 90% of the plastic loads would be transported out of the urban catchment in 20% of the year. The range of discharges throughout 2016 has been moderate with peaks around 4 m³/s.

C-*Q* relationships can provide a useful tool to estimate plastic loads based on a limited number of determinations of the plastic load and of the discharge. *C*-*Q* relationships for the plastic particles should be established for a larger number of catchments to explore to which extent they are transferable from one site to another and to broaden the database for assessing riverine plastic discharges on a broader scale. They might become particularly useful if regular monitoring programs would be established for assessing the pollution of rivers with plastic particles. Since the determination of plastic concentration in surface water is labor-intensive and requires extensive analytical equipment, *C*-*Q*-relationships may provide a simple proxy to estimate plastic loads and concentrations based on observations of river discharge. However, our results suggest that there is no general functional relationship between *C* and *Q*, but in the urban settings we found strong indications that such a functional relation exists. It is possible to infer potential controls and source patterns and to classify the plastic export behavior of different catchments.

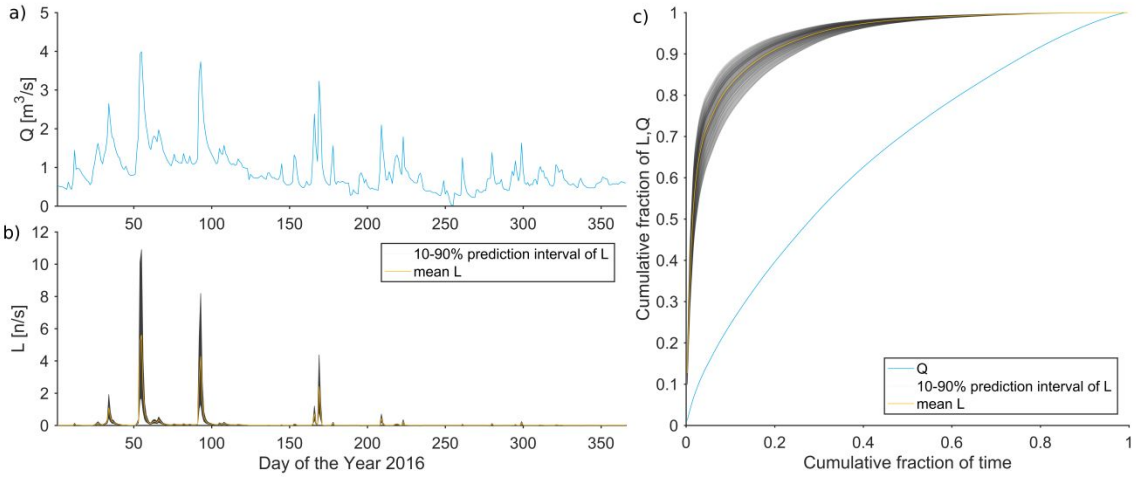


Figure 4: a) Temporal pattern of river discharge in 2016, b) estimated temporal pattern of median plastic load calculated with the *C-Q* relationship shown in Figure 3f and c) comparison of plastic load (*L*) and river water discharge (*Q*) as cumulative fraction of *L* and *Q* versus cumulative fraction of time of the Parthe River at P_{urban}

Supporting Information

Data on river discharge calculation, Raman reference spectra, an analytical method for caffeine analysis, river discharge and caffeine loads, particle concentration data at both sites, specific particle loads, C-Q relationships for plastic and total suspended solid concentrations

Acknowledgment

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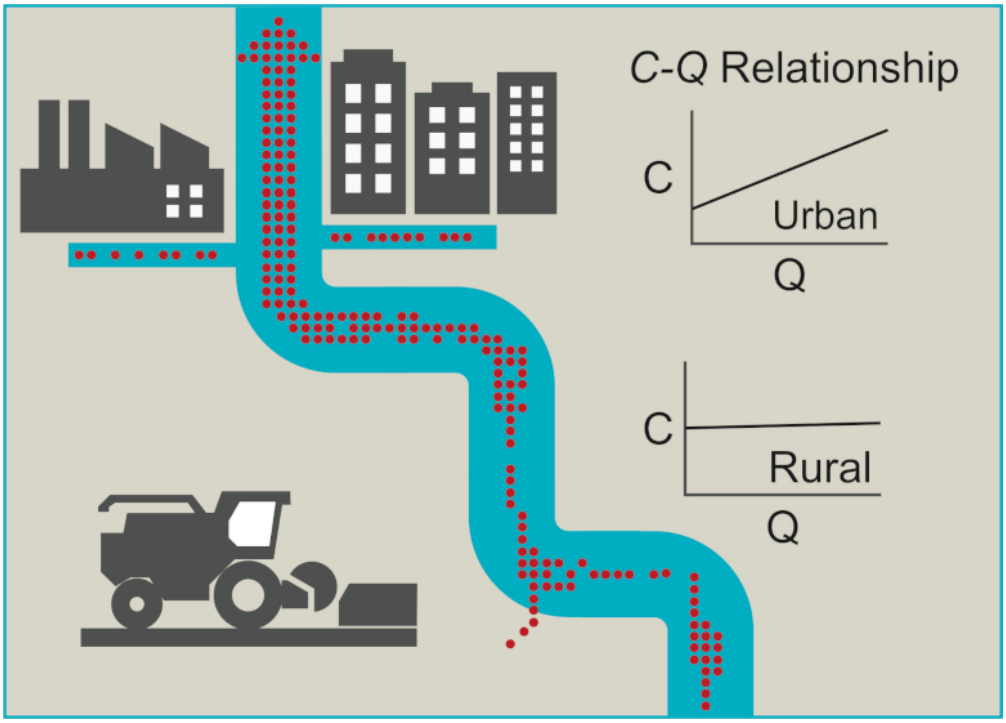

graphical abstract

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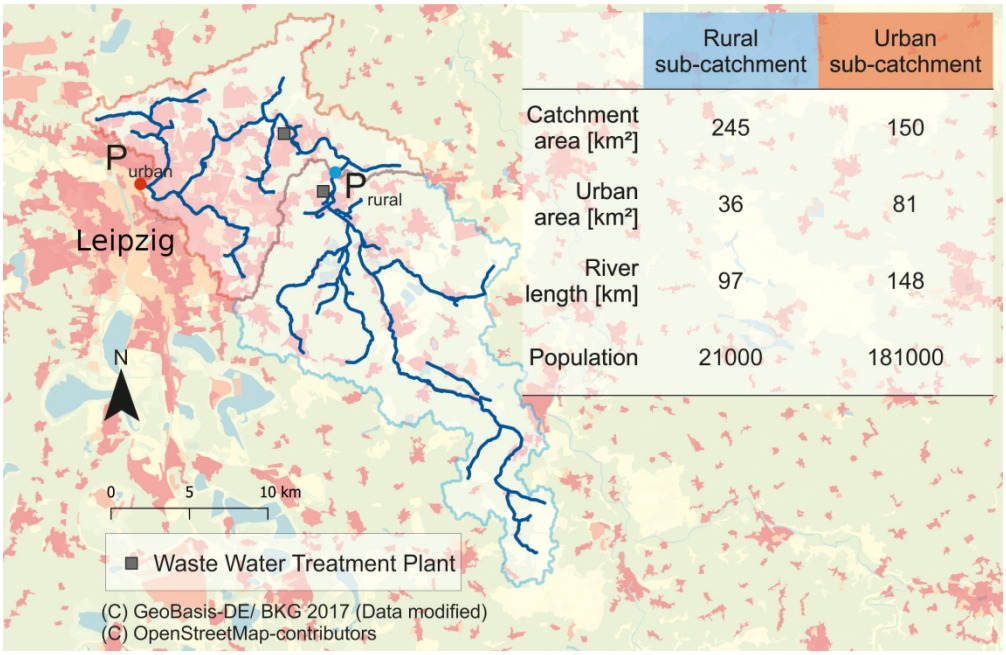

Figure 1 River flow path through the rural and the urban catchment, sampling sites P_{rural} and P_{urban} (land use indicated by color code, red urban land-use, green yellow rural land-use, blue lakes and rivers), inset table provides attributes of the rural and the urban subcatchment including total area, urban area, river length and population

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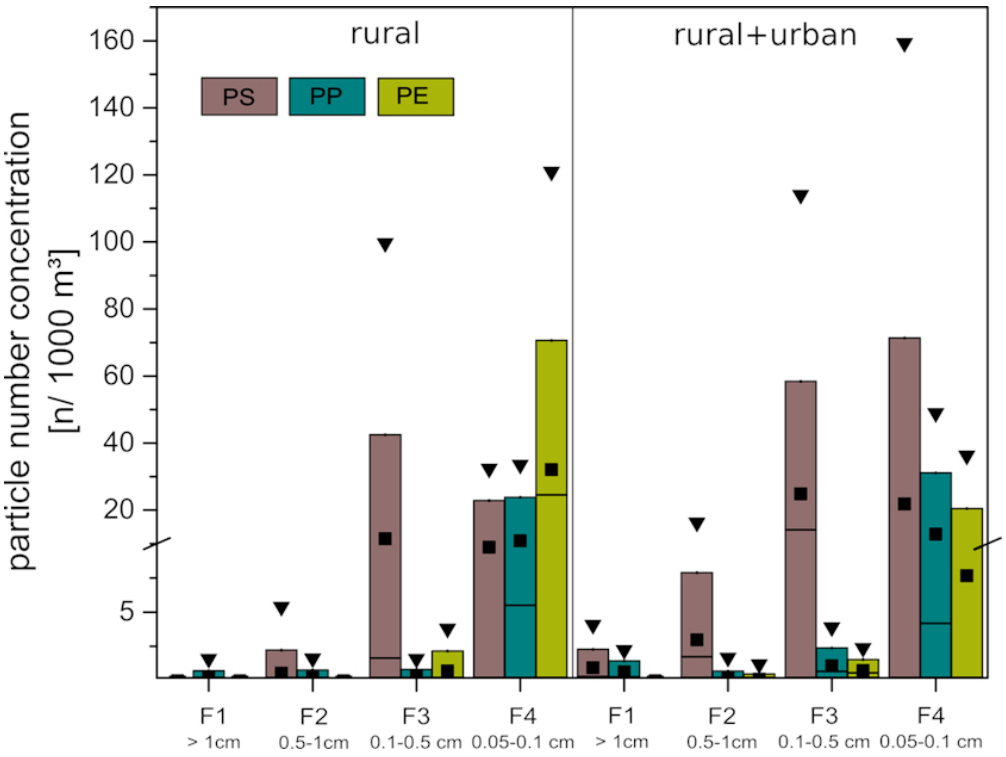

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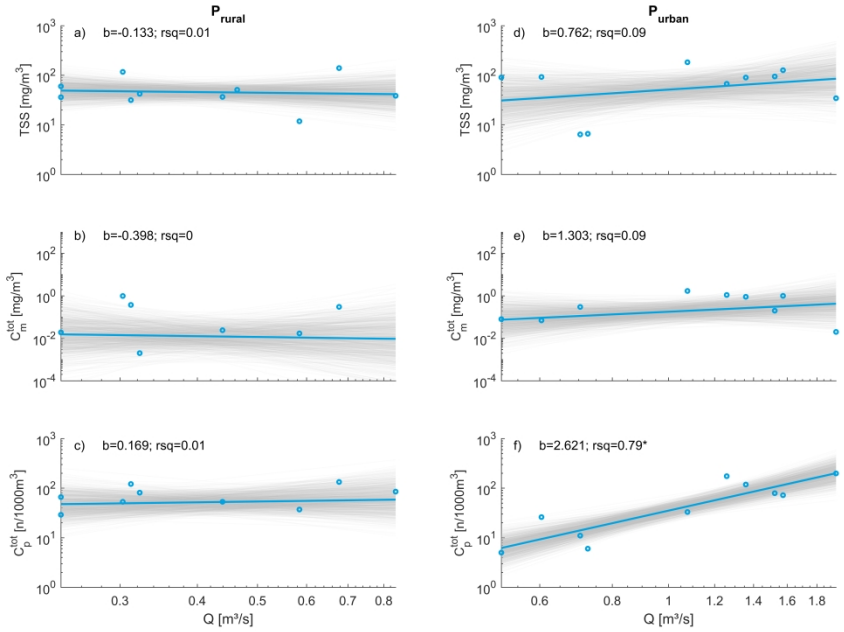

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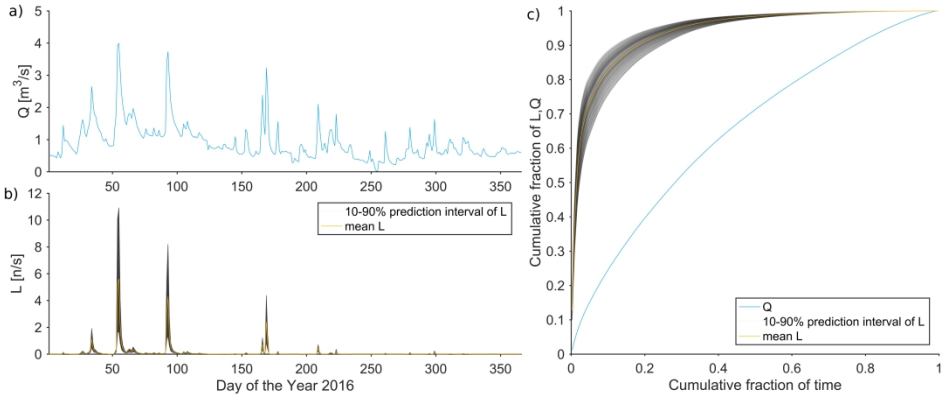

Figure 4: a) Temporal pattern of river discharge in 2016, b) estimated temporal pattern of median plastic load calculated with the C-Q relationship shown in Figure 3f and c) comparison of plastic load (L) and river water discharge (Q) as cumulative fraction of L and Q versus cumulative fraction of time of the Parthe River at P_{urban}

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