



Research Paper

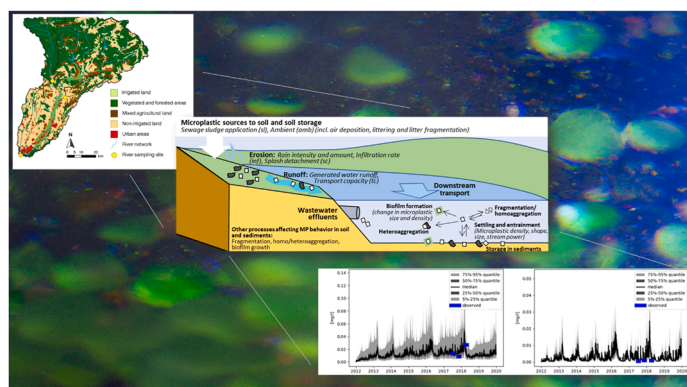
Retention efficiency for microplastic in a landscape estimated from empirically validated dynamic model predictions

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HIGHLIGHTS

- Microplastic fate model in terrestrial environment validated against empirical data.
- 20–50% Microplastic retention efficiency by landscape is estimated.
- Model predictions are within measurement uncertainty boundaries.
- Microplastic runoff from soil is an important source to the river.
- Sources of microplastic to terrestrial environment remain uncertain.

GRAPHICAL ABSTRACT



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ABSTRACT

Soils are recipients of microplastic that can be subsequently transferred to the sea. Land sources dominate inputs to the ocean, but knowledge gaps about microplastic retention by land hinder assessments of input rates. Here we present the first empirical evaluation of a dynamic microplastic fate model operating at landscape level. This mechanistic model accounts for hydrology, soil and sediment erosion, particle characteristics and behavior. We predict microplastic concentrations in water and sediments of the Henares river (Spain) within the measurement uncertainty boundaries (error factors below 2 and 10, respectively). Microplastic export from land and discharge by river fluctuates in a non-linear manner with precipitation and runoff variability. This indicates the need of accurate dynamic descriptions of soil and stream hydrology even when modeling microplastic fate and transport in generic scenarios and at low spatio-temporal resolution. A time-averaged landscape retention efficiency was

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calculated showing 20–50% of the microplastics added to the catchment over a multiannual period were retained. While the analysis reveals persistent uncertainties and knowledge gaps on microplastic sources to the catchment, these results contribute to the quantitative understanding of the role of terrestrial environments in accumulating microplastics, delaying their transport to the sea.

1. Introduction

Soils are the main recipients of microplastic pollution that is subsequently transferred to aquatic ecosystems [21,29,35,39,44]. Globally, it has been estimated that terrestrial sources contribute between 64% and 90% of the plastic debris in the oceans [40]. However knowledge gaps about their accumulation in soil, run-off and in-stream transport [4] has hindered robust assessments of these diffuse terrestrial source and their influence on regional and global distributions of microplastics [15,46, 47].

Models of microplastics fate and transport on land and stream water can be useful tools to address some of these gaps, by rigorously assimilate the complex behavior of these materials while accounting for environmental variability. Microplastics possess relatively low density, extremely wide shape and size distributions (ranging from the nanometer to the >cm scale) and can engage in interactions with other components of the environment such as soil water, soil natural particles and river sediments (among others), the stocks and flux of which can also vary in time [14,16,17,23,26,53]. Scarcity of harmonized holistic datasets useful to characterize both inputs and exposure of microplastics in specific landscapes and times, have represented a limitation on these models' development [22].

Landscape-scale, mechanistic models of microplastic fate and transport are needed to confront the scarcity of monitoring data, constrain fluxes to the marine environment and rigorously quantify environmental distributions. Unfortunately, only few prototypes of such models exist [13,2,31,49], and none have been tested against empirical data, so far. This limits the capacity to make rigorous assessment of microplastics fate and distribution and prioritize the pollution reduction actions called for by international governance and agreements [15,46,47].

Accumulation of microplastics in soils is likely associated to interactions with soil aggregates and storage in soil pores. Their mobilization from soil has been described as dependent on soil erosion

processes mainly through water runoff. Bioturbation may also influence microplastic fate [11,31,37,38,42]. Riverine transport of microplastics depends on flow characteristics (stream power and turbulence), interactions with river sediments (setting, entrainment, and burial in the river bed) and hetero-aggregation processes (i.e., binding of microplastics into natural sediment aggregates in the stream) [2,31,44,6,9] (Fig. 1). This framework however remains purely theoretical in absence of empirical validations. Fortunately, recent studies have provided seminal contributions to filling some of these lacunae enabling the definition of empirical relations between particle characteristics and transport rates [24,50,51]. Data that can help building holistic assessments of microplastics sources and distribution at landscape level [11, 35,43,48] have also become available and can be used for model training and assessment.

Here, we advance microplastic fate modelling by assembling and testing INCA-MP (Integrated Catchment model of MicroPlastics transport) (Fig. 1), a mechanistic system-dynamics model assimilating this state of the art [2,24,31,50,51]. INCA-MP describes landscape (catchment areas, river network structure, elevation and land use) and weather data (including daily time series of precipitation and air temperature). It also assimilates data of microplastic concentrations and sources to soils and streams (through application of sewage sludge to agricultural land and wastewater releases), and a generic ambient source (amb , $kg\ km^{-2}\ d^{-1}$) conceptually encompassing atmospheric deposition and other diffuse sources (e.g. from the fragmentation of litter, agricultural plastics, polymeric coatings degradation, wastewater irrigation etc.).

In this study we show the first calibration and performance assessment of INCA-MP in a configuration that describes the Henares, a Mediterranean river and catchment in Spain. This location choice was driven by the availability of observation (repeated in space and time) of microplastics in river water and sediments. Consistently collected data on microplastics concentrations in sewage sludge and wastewater,

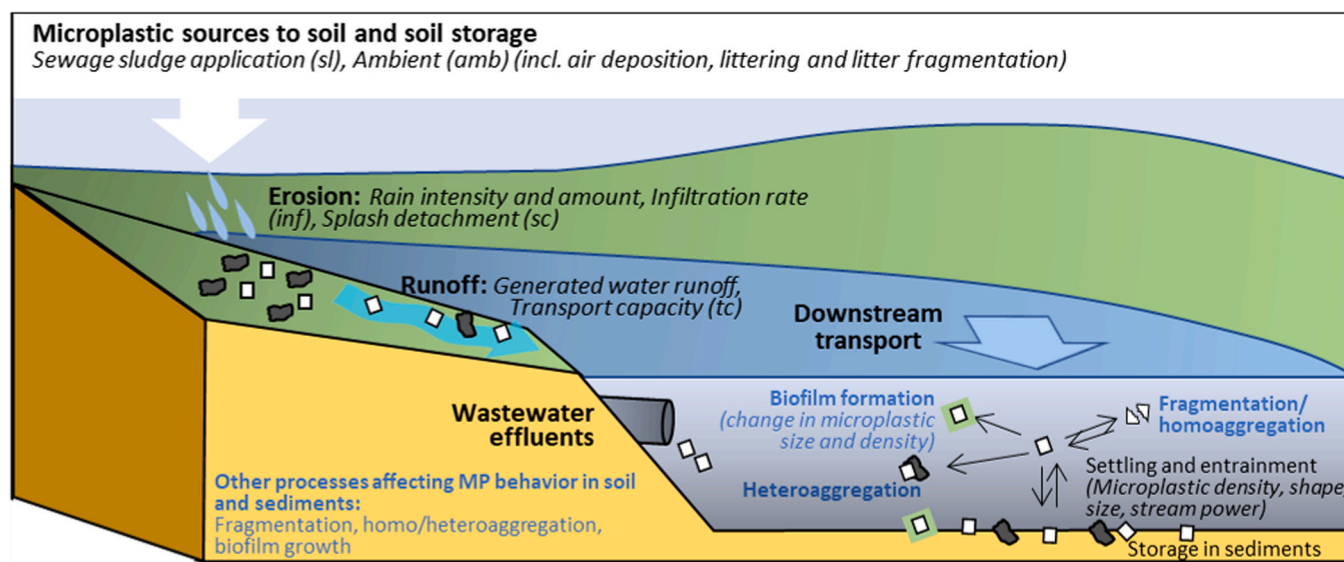


Fig. 1. : Depiction of the model frame with details on microplastics fate processes accounted for with their driving processes and/or parameters. White squares represent generic microplastics. Grey irregular shapes are natural sediments. The green corona surrounding some of the white squares represent biofouling. Abbreviation reported in parenthesis refer to the symbol of the relevant parameter included in the calibration. Processes reported in blue text refer to components of the model that were turned off in this specific application due limitations imposed by the resolution of the experimental dataset.

representing known important terrestrial and water-directed sources are also available for this site [42,43] and can be used to generate estimates of microplastic sources to the catchment. The scenario definition included information on estimated atmospheric deposition drawn from recent literature [8,57]. The aim of the study was to develop a first empirically constrained calibration and an external assessment of model predictivity. In addition, the calibrated model was used to develop a mechanistic assessment of microplastics storage and flows at the catchment scale and to estimate the average capacity of the landscape to delay microplastic transport to the marine environment.

2. Experimental

2.1. Model description

INCA-MP is a semi-distributed daily-timestep model in the INCA family [25,31,32]. It consists of a hydrology module that produces overland water and river flows and a microplastic module that uses these variables to simulate on-land and in-stream mobilization and transport of microplastic particles. The in-stream model solves its ordinary differential equations (ODE) using the Rosenbrock4 solver from boost:odeint [1]. Other ODEs are solved using an implementation of the Runge-Kutta 4 DASCUR solver [52]. The Model is built in the Mobius modelling framework [34].

The catchment is divided into sub-catchments. Each sub-catchment is divided into a set of landscape units (land use types) defined by the percentage of surface area they cover and by an individual set of soil characteristics, climate parameters (e.g. precipitation data) and microplastic inputs. Fluxes from land to the river are computed once per landscape unit and aggregated over each sub-catchment. In-stream processes are computed per river section whereby, in the current application we design one river section per sub-catchment. Water and suspended particles, including microplastic, are transported downstream in a (potentially branching) river network. The complete mathematical description of INCA-MP and the value of all parameters that were not included in the calibration are available in the [supplementary information](#).

2.2. Catchment description and microplastic sampling and analysis

The model was set up for the Henares River catchment (4144 km²) in Spain, which is located in the upper Tagus River Basin, the longest river in the Iberian Peninsula (Fig. S2). The area has a Mediterranean climate, with dry and hot summers and mild-to-cold winters. The upper part of the catchment is characterized by forests and extensive agriculture, while the lower part is prevalently agricultural but also receiving wastewater discharges from industrial and urban areas, including the cities of Guadalajara and Alcalá de Henares, which have approximately 90,000 and 200,000 inhabitants, respectively.

Microplastic monitoring data was obtained from three sampling sites, which were selected according to the degree of anthropogenic impact in the subcatchments described by the different prevalence of land-uses. Site 1-Sorbe was located downstream of forested and vegetated areas representing less than 10% of the total catchment, Site 2-Badiel was in a small sub-catchment influenced by agriculture and wastewater discharges from small villages representing less than 7% of the total catchment area and Site 3-Henares was located at the catchment outlet downstream of the cities and the industrial areas of Guadalajara and Alcalá de Henares and draining the entire catchment (Fig. S2, Table S1, S2, S7, S8). The sampling sites were located next to river flow gauging stations, from which data was obtained from the Centro de Estudios y Experimentación de Obras Públicas [7]. Daily values of air temperature and precipitation were obtained from the E-OBS gridded dataset.

Microplastics were monitored in stream water and river sediments, and in samples of sewage sludge applied to agricultural soils in the

catchment and in wastewater. River monitoring took place during three sampling dates, covering three different seasons (spring, summer, autumn; Table S2). The methods used for microplastic sampling as well as the results of the microplastic monitoring are described in [43]. Stream water (5–10 m³) was collected using a pump system and passed through a battery of nets (from 300 to 55 µm mesh) to volume reduce and size fractionate the samples. River sediment samples were taken using a core sampler to collect approximately 0.5 kg of material from a depth of 0–10 cm. Processed sewage sludge (representing the material applied to fields) was sampled directly from the sewage sludge hopper following standard processes for digestion and dehydration at the Waste Water Treatment Plants (WWTPs). In total, the study is based on 64 individual measurements of microplastics: 27 samples of sediments collected in 3 locations at 3 time points, 9 observations of stream water concentrations from integrative large volume samples, 10 and 18 observations of wastewater effluent and sewage sludge concentrations, respectively. For the sake of calibration and model assessment, model predictions were compared to the average of the replicated samples.

Microplastic particles were extracted from the respective sample matrices using approaches adapted to each sample type and comprising steps such as volume reduction, density separation and organic matter removal [20,43]. Stream water samples were handled according to their organic matter content. Some samples were sufficiently free from material to be directly vacuum filtered onto filter papers (Whatman GF/A, Ø 47 mm) for analysis. Samples with higher organic content were left to settle until the overlying liquid was clear. This was carefully decanted and filtered onto a filter paper and retained for analysis. The organic residue was treated using Fenton's reagent and filtered onto a filter paper for analysis. River sediment and sewage sludge samples were both subjected to an organic matter removal and density separation procedure following the procedure set out in [20]. Samples were treated using Fenton's reagent to reduce the organic content before a series of sequential density extractions at freshwater (1 g cm⁻³) and high (1.8 cm⁻³) density using filtered water and saturated sodium iodide solution, respectively. Each separation was filtered onto a filter paper and retained for analysis.

Isolated particles were first subjected to a visual pre-selection of suspected microplastics using a Nikon SMZ 745 T stereomicroscope (20x magnification), which were subsequently photographed and characterized by size, morphology and color using an Infinity 1 camera accessory and the Infinity Analyze (v.6.5.4) software package. Suspected microplastics were identified following the protocol of [28].

Suspected microplastics were analyzed using Fourier Transform Infrared (FTIR) spectroscopy to confirm plastic composition. Larger microplastics (>300 µm) were analyzed using an Agilent Cary 630 FTIR with a diamond ATR accessory. Smaller particles and fibers were analyzed using a Perkin Elmer Spotlight 400 FTIR in µ-transmission mode. A diamond compression cell (Perkin Elmer, DC-3) was used to compress particles and improve spectral quality before loading onto the Spotlight FTIR. Four co-scans, taken at a spectral resolution of 4 cm⁻¹, were taken for each particle measurement on both FTIR instruments. For the larger particles, a background measurement was taken before each particle measurement. For the smaller particles, a new background was taken each time the diamond compression cell was loaded onto the machine every 1–10 particles. Each spectrum was compared to a series of commercial PerkinElmer Polymer library, Agilent Polymer library, open source [36] and in-house libraries and manually verified to confirm the polymer type. The size cutoff for microplastic detection was set to 50 µm.

During visual analysis, the length and width of each particle was measured using the Infinity Analyze software package. In addition to this, the depth of each particle was estimated. This facilitated an estimate of the volume of each particle. Microplastic mass estimates were then generated by combining the particle volume with a density value, based on the FTIR results for each particle. The full method, quality assurance measures and list of polymer densities used is provided in [43]

and [20].

Microplastic mass inputs into the Henares catchment via treated and untreated wastewater were estimated on the basis of measured microplastic concentrations in the inflows (untreated wastewater) and effluents (treated wastewater) of five selected WWTPs during two sampling events and the total wastewater volumes emitted over the course of the year, considering all discharge points (Fig. S2). Microplastic inputs into agricultural soils were estimated for each sub-catchment corresponding to Sites 1–3 based on land cover data and the sewage sludge application data provided by Council of Sustainable Development of Castilla la Mancha. For this, we first calculated the amount of sewage sludge from WWTP that was applied in each main crop (i.e., wheat, barley, corn) during the periods 2017–2019. We assigned wheat and barley as the main crops cultivated in mixed and non-irrigated agricultural lands, and corn as the main crop cultivated in irrigated agricultural lands. We estimated that approximately 1.5–2.7% of land dedicated to wheat and barley production had used sewage sludge as fertilizer at least once during that period, at a dose of 0.7–3.9 tons/ha dw; while about 2–15% of areas dedicated to corn production applied sewage sludge at least once at a dose of 2.5–4.6 tons/ha dw. By using this information and the amount of land dedicated to non-irrigated, mixed and irrigated agricultural production, we estimated that the total sewage sludge application to the sub-catchment dedicated to Sites 1, 2, and 3 were 36–77, 173–373 and 2557–16068 tons of sewage sludge dw during the period 2017–2019. The microplastic mass added to agricultural soils was determined on the basis of the concentrations measured in processed sewage sludge (after digestion and dehydration) of the three most relevant WWTPs in the watershed (WWTP 1, 4 and 5 from [43]).

2.3. Scope, limitations and main assumptions of the model application

The assumptions and boundaries associated to the modelling scenario are the following:

- i. The model scenario details input of microplastic (fragments and fibers) from known supposedly important sources such as: sewage sludge application to agricultural fields and wastewater effluents. An additional generic source (named ambient input (*amb*)) is also considered, encompassing the contribution of atmospheric deposition, inputs from fragmentation of litter in the catchment, contaminated water irrigation or any other uncharted source of fragments and fibers. In order to determine the amount of microplastic applied with sewage sludge to the fields, we multiplied the estimated concentration of microplastic in sewage sludge [42] with the amount of sewage sludge applied to agricultural lands of each sub-catchment every year. The sewage sludge was modeled as being applied in the August of each year, as this is typically the period of application in this region. Sewage sludge concentration was one of the parameters that was subject to variation in the Monte Carlo analysis. Since the analyses of different samples of sewage sludge provided variable results, the sewage sludge concentrations used in individual runs were estimated randomly drawing from a lognormal distribution fitted to the distribution of measured sewage sludge data (Table S1). Similarly, the representative concentrations of microplastic in wastewater effluents used in the model were drawn from a lognormal distribution fitted to the set of measured concentrations from different WWTPs discharging into the Henares River (Table S2). These fitted distribution represented the *priors* for modelling microplastics inputs to the catchment from these sources. Because no direct observations of *amb* exist, a homogeneous distribution was assumed as the *prior* for this parameter. We therefore considered a broad range (0–0.004 kg km⁻² d⁻¹) that contains and exceeds by one and a half order of magnitude the range of atmospheric depositions of microplastic measured in Europe (ranging 0.000005–0.0001 kg km⁻² d⁻¹) [8,57]. Any possible value of *amb* within this range was assumed to have the same probability.
- ii. The model scenario did not consider sources from tyre wear. The analytical method used to detect microplastic concentration was not suited or validated to detect these materials, especially in sewage sludge and river sediments. Suspected tyre wear particles were therefore excluded from the calibration and validation dataset. Accordingly, sources for these particles were not considered as model inputs. This approach represents an unavoidable narrowing of scope that fortunately does not invalidate the assessment and the conclusions of the study. Hence, there is no claim this study addresses the mass budget of all microplastic typologies in the system: it only addresses those that could be quantitatively analyzed in the environmental samples and for which the model could be reliably calibrated and assessed.
- iii. Simulations were conducted to predict masses of microplastics divided in two classes – namely, fibers and fragments. Accordingly, the experimental dataset used for calibration and model assessment were also grouped in this way. The class “fragment” included all individual microplastic observations data did not have the characteristic elongated shape of fibers (e.g. the ratio between the two main dimensions was higher than 100 and one dimension was below 20 μm). The fragment and fiber groups were not separated any further into size or density classes due to insufficient number of particles in the river sediment samples. All modelled microplastic were attributed a density value of 1.1. Considering the focus on such broad size classes, fragmentation processes, homoaggregation and ageing processing affecting particle density and size, were turned off during the model simulations (despite the model frame can detail them). This potentially represents a critical simplification. We argue that this was an unavoidable option given the lack of knowledge on the rate of these processes in soils and sediments. Their inclusion would have introduced the need of highly arbitrary assumptions and unquantifiable uncertainties.
- iv. In first approximation, all model parameters related to on-land sources, mobilization and transport of microplastics were set to be the same across all the landscape, regardless of land-use typologies. This is unrealistic, as erosion is probably higher in agricultural soils compared to pastures and forest soil, while primary sources and atmospheric depositions are higher in urban areas than, for example, in forests. However, considering the lack of sufficient information on spatial distribution of source intensity or other processes rates, and the focus of the model integrating across broader areas of the catchment, it is argued that the approach introduced here represented the minimalistic conservative assumption.
- v. While INCA-MP dynamically calculates pools and concentrations of microplastic in soil, no sufficient empirical data of microplastic concentrations in different soil types are yet available in this catchment, or elsewhere in Europe. We overcome this limitation by setting two conditions: first, we assumed an initial pool of 200 t of microplastics (fragments plus fibers) in the catchment topsoil layer (e.g. the part of the soil that can directly engage in microplastic exchange with the atmosphere and runoff water assumed to be 5 cm) at the beginning of the simulation period. This assumption was drawn from the few empirical evidences available to date: The assumed initial pool of soil microplastics is in fact equivalent to an average concentration of 0.00006% of total microplastics in soil, which is consistent with the range of observed soil concentration data available from different regions after averaging soil with different level of contamination (e.g. urban, agricultural, background soils) [10,12,18,19,27,41,45,48,54–56]. The second condition is that the annual average of the total pool of microplastics in soil $\bar{S}_{soil,y}$ increases with time (that is

$S_{soil,y} - \bar{S}_{soil,y-1} \geq 0$). This is consistent with evidences from a range of studies [10,12,55,56].

2.4. Parameter calibration, uncertainty analysis and model assessment

A lack of harmonized holistic observations of microplastics in source matrixes (such as sewage sludge and wastewater samples) and environmental compartments (e.g. sediments and stream water) consistently sampled and analyzed in specific locations and times has so far represented a major hindrance to the assessment of models and the effort of reducing uncertainties in their parameters. Exploiting the new observation dataset, a calibration algorithm was developed based on a Monte Carlo run of the model, where each run utilizes a set of parameters randomly sampled from a-priori distributions drawn from empirical observations or, when these were absent, from uniform distribution defined from conservative assumptions on their expected ranges (as described in the previous section). A success score (mathematically described below) was attributed to each model run based on the fit to observed concentration data. The output of the analysis was the posterior distribution of the parameter set and predicted microplastic concentration, obviously encompassing an estimation of the parameters' and outputs' most likely values. Such an approach allows consider the empirical information and its associated variability and uncertainty in a fully objective way. No arbitrary manual tuning of parameters' values was in fact operated in this study to achieve high predictive performance.

The first step to set up the model scenario for microplastic fate prediction is the description of the catchment hydrology. INCA-MP achieve this mechanistically starting from meteorological data. Calibration against hydrological data was implemented by tuning the parameters of the hydrological module as described elsewhere [32], in order to maximize the fit between river flow predictions at the control points and respective observations. INCA-MP satisfactorily reproduces stream water flow (Fig. S1, Table S3) at two points: the Sorbe and Henares. Predictions for the Badiel point were unfortunately unsatisfactory, likely due to the small agricultural area drained by this first-order reach in combination with the daily temporal resolution of the model. In these conditions, even a single unmapped water extraction and/or recharge points can significantly affect river water flows. In order to avoid further propagating such an uncertainty, Badiel data were excluded from the analysis.

The observations dataset of "fragments" was considered during parameter calibration, owing to the broader density of data available for this class and their larger morphological and physical heterogeneity. The dataset of "fibers" was instead used as external validation set. While the data of fibers originated from the same samples in which also the fragments were determined, the two subsets can be treated as independent. In fact: i) fragments and fibers have distinct sources ii) they are transported with different efficiency within soil, river sediments and stream water; and iii) the model utilizes different sets of equations and parameters for fragments and fibers [24,50,51]. The independence of these two subsets of data is ultimately demonstrated by the lack of correlation in measured concentrations of fibers and fragments in all analyzed matrices.

Table S7 (supplementary information) lists the parameter set included in the calibration. These parameters were chosen for being the most sensitive ones in determining changes in stream water predicted concentrations of microplastic (e.g. the result of an initial sensitivity analysis run through the "hold other parameter constant" approach). Such a preselection was necessary to keep sampling space dimension computationally manageable. Other parameters were either set to reflect the assumptions given above or were available from literature [24,50,51].

We run the model from 2012 to 2019 (inclusive). This period was initialized with a 5 years "warm-up" period preceding the year of the

monitoring. In the Monte Carlo simulation, parameter sets were sampled based on a Latin Hypercubes strategy, with prior distributions given in Table. The Monte Carlo simulation was scripted using the Python wrapper that is available for all Mobius models. The number of sampled parameter sets was 10000. We follow a GLUE-like methodology [3], and assign a likelihood value Li (unitless) to each parameter set, based on the yielded model fitness. Li is used as a weight when determining the posterior distribution of the parameters and the distribution of model outcomes, and was calculated as:

$$Li = 0.3 \bullet NNSE(m_{henares,sim}, m_{henares,obs}) + 0.2 \bullet NNSE(m_{sorbe,sim}, m_{sorbe,obs}) + 0.3 \bullet NNSE(c_{henares,sim}, c_{henares,obs}) + 0.2 \bullet NNSE(c_{sorbe,sim}, c_{sorbe,obs}) \quad (1)$$

Where $m = m_{bed,frag}$ is the mass of bed fragments, $c = c_{susp,frag}$ is the concentration of suspended fragments, and $NNSE$ is a normalized Nash-Sutcliffe efficiency given by

$$NNSE(sim, obs) = \frac{1}{\sum_t (1 - \frac{obs_t - sim_t}{sim_t})^2} \quad (2)$$

\sum_t includes all the individual time steps in which there is an observation of fragments in stream water or river sediments. The numerical coefficients attribute arbitrary weights for the likelihood calculation. Results from Henares were given a slightly higher weight (0.3) compared to Sorbe (0.2) due to the lower stream order and the larger catchment. While the Henares datasets represented over 95% of the total empirically-derived information, the choices of these arbitrary coefficients allowed maintaining a level of influence in the calibration also for the smaller catchment Sorbe. Model results from the Badiel sampling point were disregarded due to flow conditions that were difficult to model. This had little impact on the study as Badiel represented less than 7% of the total agricultural area of the whole Henares catchment. The results from Henares were given a slightly higher weight due to the larger catchment size.

Observed data (obs) were derived from the measurements of microplastic occurrence by converting information on individual particles size, shape, and density at each point into an aggregated mass value. For converting the observed concentrations in the river sediment from $kg(MP)/kg(sediment)$ to $kg(MP)/m^2$ we assumed that microplastics accumulate in the top 15cm of the sediment bed (this is the length of the sampling cylinders) and that the density of the sediment is $2g/cm^3$, which is representative of what was measured.

2.5. Calculation of average landscape retention efficiency

In order to define a measurement that quantify the tendency of a catchment to retain microplastics emitted over land or in the catchment stream we introduce the Retention Efficiency Index (eff) representing a measure of the fraction of the microplastic total mass added to the system that tend to remain in catchment soils and river sediments, over time. It is calculated as the median of the time variability of the instantaneous retention efficiency eff_T , whereby:

$$eff_T = \frac{S_{c,T}}{S_{c,T} + E_T} * 100 \quad (3)$$

Here, $S_{c,T}$ (kg) is the total storage of microplastics present at any given time step T in the soil and sediments of the catchment, minus the total storage assumed at the beginning of the simulation (i.e. $S_{c,T} = (S_{soil,T} + S_{sediment,T}) - (S_{soil,t0} + S_{sediment,t0})$).

E_T (kg) is the total export of microplastic from the catchment exiting the main river mouth integrated between $t0$ and T.

eff_T is strongly dependent on meteorological and hydrological conditions, varying strongly over time with a skewed distribution. This is

because both the export of microplastics from soil, sediments and the river mouth are driven by meteorological conditions and are maximized during unfrequent (in time) high flow events. Since the focus here is to describe a general retention efficiency, we calculate $\overline{\text{eff}}$ as the median of the values taken by eff_T over time throughout multiple years of simulations (from 2012 to 2019). Calculations for $\overline{\text{eff}}$ were reiterated (as done for any other parameters) through the Monte Carlo analysis to keep track of uncertainties in model parameterization.

3. Results

3.1. Model Calibration

Model calibration focused on obtaining informative posterior distributions of all parameters defining microplastic fate, including those for which measurement are not yet available. Concerning parameters with constrainable priors, calibration yielded posterior distributions for sewage sludge and wastewater microplastic concentrations (used to define inputs to the system) reflecting the distribution of measurements (Fig. 3). Higher likelihood values for the generic ambient input *amb* (for which no detailed information was available) tended instead to level out in the high range of the conservatively assumed homogeneous prior distribution (Fig. 3) suggesting sources other than sewage sludge and wastewater could have a very important role.

Once fed with the best set of parameters from the calibration, the model converged to good precision (i.e. the breadth of the model confidence boundaries obtained from the Monte Carlo analysis) and accuracy (i.e. the distance between the median of the model predictions from the observed data) (Fig. 2). Stream water concentrations of fragments were all within the model prediction confidence boundaries with the median of the predictions typically differing less than a factor of 2 from the observations.

Concerning river sediments, for the Henares main stream, calibration yielded prediction confidence boundaries for fragments that contained experimental observations and that differed by less than a factor of 2 from the measurements (Fig. 2). In the case of Sorbe, however the model tended to systematically overestimate fragment concentrations in sediments (in the worst case by a factor of 5), which is also in the range of the boundaries of measurement uncertainty [30].

The discrepancy between the model performance in estimating fragments in the river sediments of the Henares and Sorbe is explainable by the minimalistic assumptions introduced on microplastic sources (assumption iv of Section 2.3). In absence of specific evidence, the value of generic ambient source *amb* was in fact set to be the same in any point of the river catchment. This leads to overestimating inputs for Sorbe, which, unlike most of the remaining Henares catchment area, is a forested subcatchment with a low anthropic presence. For the sake of objectivity, however the introduction of arbitrary adjustments in the parameters were avoided, even when they could make sense.

The model exhaustively captured the differences in microplastic levels observed at the two sub-catchments, both in stream water and river sediments. At the Henares points, fragment concentrations were measured to be at least one order of magnitude higher than at the Sorbe point, which was also precisely reflected by the model estimates. The ability of describing temporal variability could instead not be systematically assessed given that the difference between consequent measurements at a given point was in most cases non-significant (considering the uncertainties inherent to concentration measurements in water and sediments [5,30]).

Calibration enabled constraining uncertainties of many, yet not all, the model parameters included in the analysis (Fig. 3). For example, best estimates for *entrainment* (a parameter controlling erosion and settling of particles in the river sediments) successfully converged within the range 0.5–1 d N m⁻². Large uncertainties however persist on the value of the parameters controlling microplastic erosion and storage in soil, with

posterior distributions not dissimilar to the uniform prior. This is likely driven by the high degree of freedom imposed by the assumption of uniform prior distributions applied to all these interrelated parameters. Such a situation can in fact prevent convergence to a more defined domain without additional empirical insights. The predictive ability of the model, in spite of the residual uncertainty on the parameterization of the microplastic land erosion module, suggests that this part of the theoretical frame can potentially be further simplified if measurements of specific parameters will not become available. Alternatively, focused study on the dynamic of microplastics in the water column will be needed to increase confidence in this mechanistic frame. This could be the focus of a future application of the model.

Despite these limitation and residual uncertainties on parameterization, the calibration of INCA-MP yielded meaningful predictions with relatively narrow precision boundaries.

3.2. Assessment of model predictive ability

Following calibration with the fragment dataset, we challenged the model to externally predict the microfiber dataset for the same case study. Predicted fiber concentrations had similar accuracy and precision to the fragment calibration (Fig. 2), demonstrating an ability of capturing the large spatial variability observed between the two monitoring locations. In the case of stream water, INCA-MP yielded prediction boundaries for fiber concentrations that included experimental data and with median of predictions being within a factor of two from measurements. The prediction of fiber concentrations in river sediments, too, reflected the performance achieved with the calibration dataset with a tendency to overestimate. In this case an outlier was observed in the Henares datasets that was a factor of 10 higher from the median of predictions. This observation was likely a measurement outlier, exceeding by a factor > 10 the value of other measurements conducted at the same point.

Considering the confidence boundaries for measurements of microplastic in river sediments (estimated to vary by a factor of 3 below and above the mean of replicate measurements - meaning significant variability can be measured when differences between two observations are in the range or above a factor of 10) [5,30], these results can be considered as satisfactory.

3.3. Dynamic assessment of microplastic flows and stocks in the catchment

Following model calibration and evaluation, we analyzed the fluxes and budget of microplastics in the catchment calculated by the model. The model simulation captures the effects of baseline flow and high flow events in the accumulation and release of microplastics from river sediments. Baseline flow results in a gradual accumulation of microplastics in the river sediments (Fig. 2). Low water flow and low runoff coincide with relatively constant level of microplastic in the stream (mostly fed by wastewater effluents). With baseline precipitation conditions, stream water concentrations increase partly contributed by land runoff. High flow (such as that observed in early 2018) depletes the stream bed reservoir generating a peak in microplastic stream water concentrations (Fig. 2). The post flood phase is then characterized by low concentrations in both river sediments and stream water, as the terrestrial and in-stream stocks of readily mobile microplastics (i.e. the top soil and sediment pools) are depleted.

Fig. 4 shows the temporal variability of microplastic inputs to river, inclusive of confidence intervals of the estimates. Input from land to river are in the order of 1000–4000 t y⁻¹. Wastewater effluents are an important source to the river too, roughly representing an equivalent input when considering the skewed distribution of these estimates. When comparing the median of the estimates wastewater instead represents one fifth of the inputs from land.

Fig. 5A-C illustrates the temporal trends of fragments accumulation

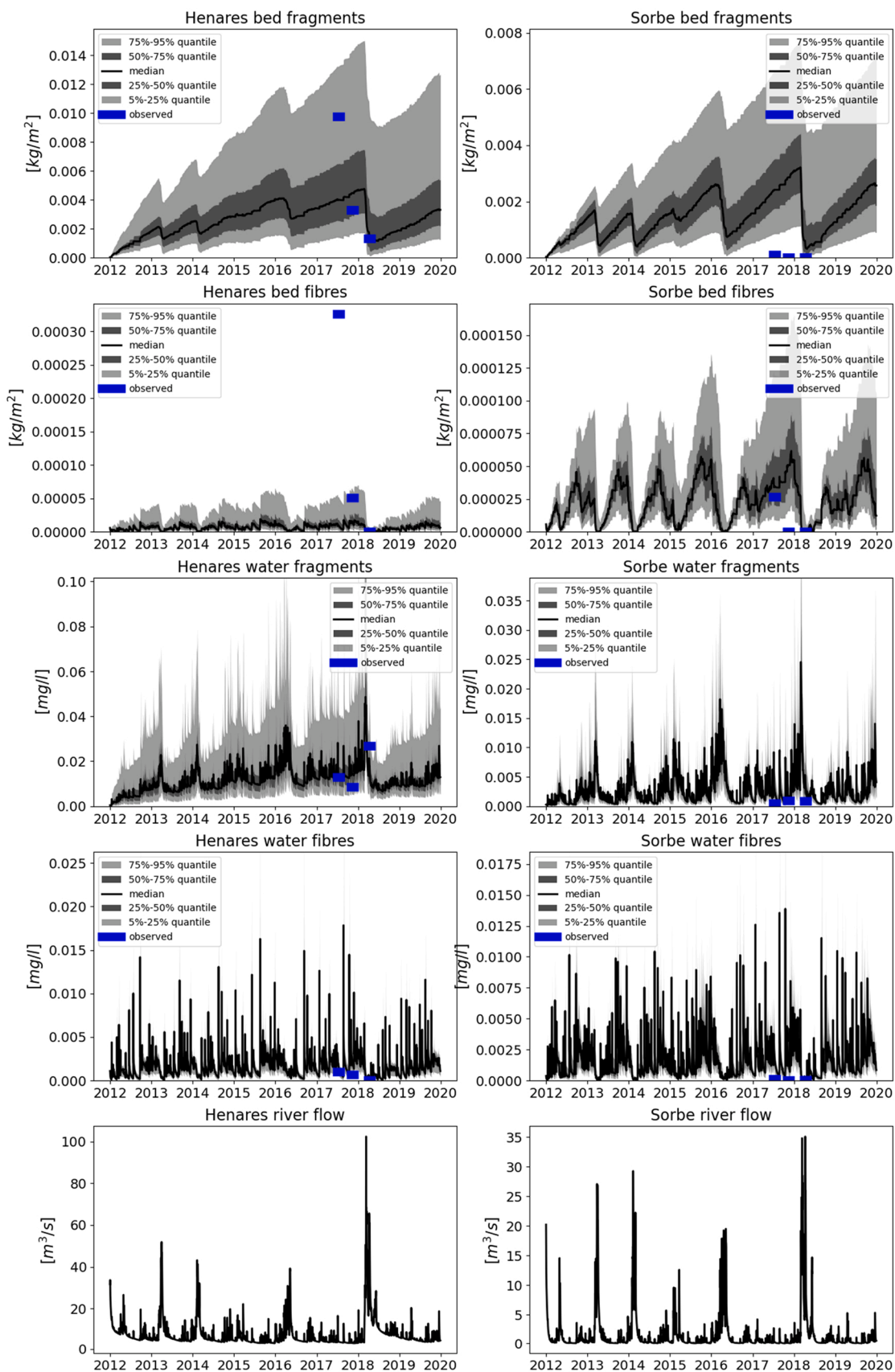


Fig. 2. : Weighted quantiles of selected time series results of modeled and observed values of microplastics masses and concentrations in the riverbed and flowing water of the Henares and Sorbe reaches of the Henares River catchment. The quantiles are based on the ensemble of results from the Monte Carlo run, weighted by the performance parameter Li given in Eq. 1.

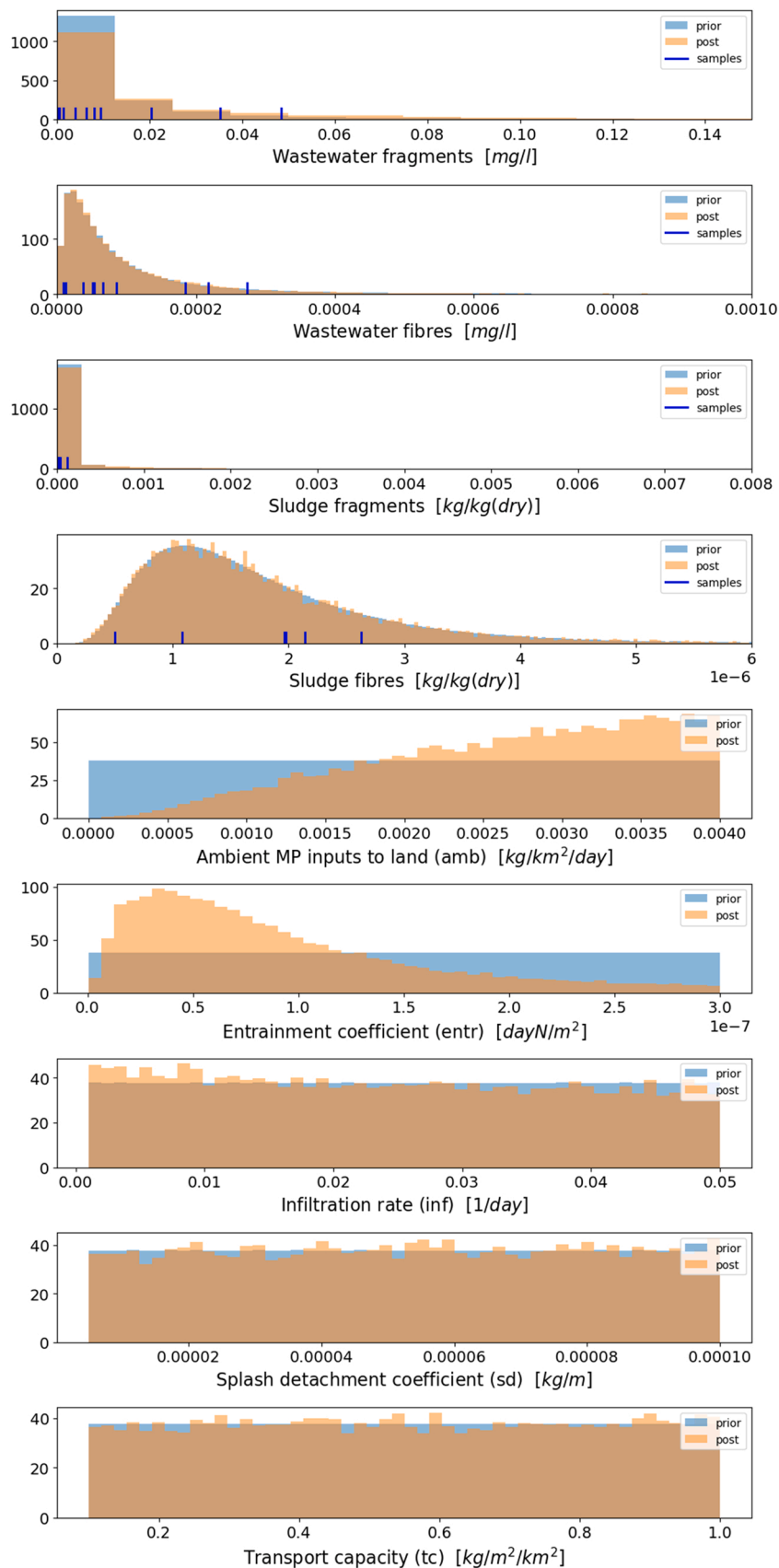


Fig. 3. : Prior and posterior distributions of the randomly drawn parameters. The x axes are the scale of the parameter values explored by the model to attain best predictions. The y axis is a weighted frequency where the weight in the posterior is the model performance measure L_i given in Eq. 1.. “Samples” refer to the measured concentrations in sludge and wastewater given in Table S1 and Table S2.

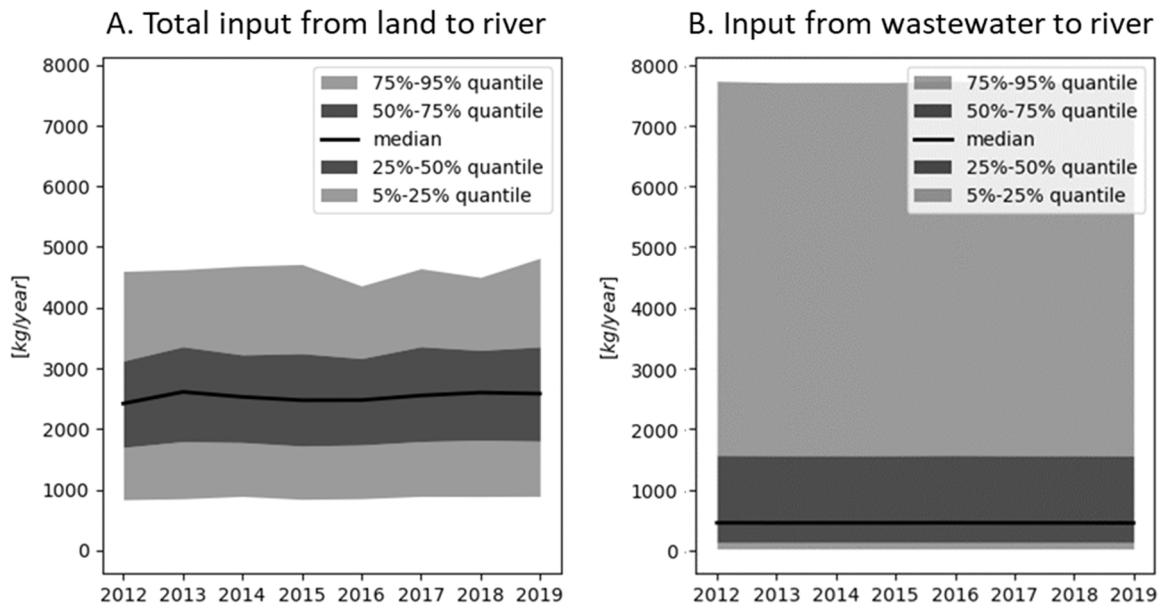


Fig. 4. : Inputs of microplastic to the Henares stream. A. Total yearly microplastic transfer from land to river (sum of all the catchment). B. Estimated inputs of microplastic to river from wastewater effluents. The quantile distributions are computed in the same way as in the analysis in Figure. Wastewater flows are set as constant value, randomly extracted (at each iteration of the model run) from the distribution of empirical data.

in the catchment in relation to the total river outflow, as predicted by the model. Repeated treatments with sewage sludge and other inputs from diffuse sources (represented by *amb*) drives to the multiannual accumulation of microplastic in soil. The addition of microplastics through

sludge application is shown by the step-like increases occurring during the summer months of each year (Fig. 5A). Following these spikes, the model predicts periods in which the soil temporarily tends to dissipate part of its microplastic pool (this is the case of at least over 25% of the

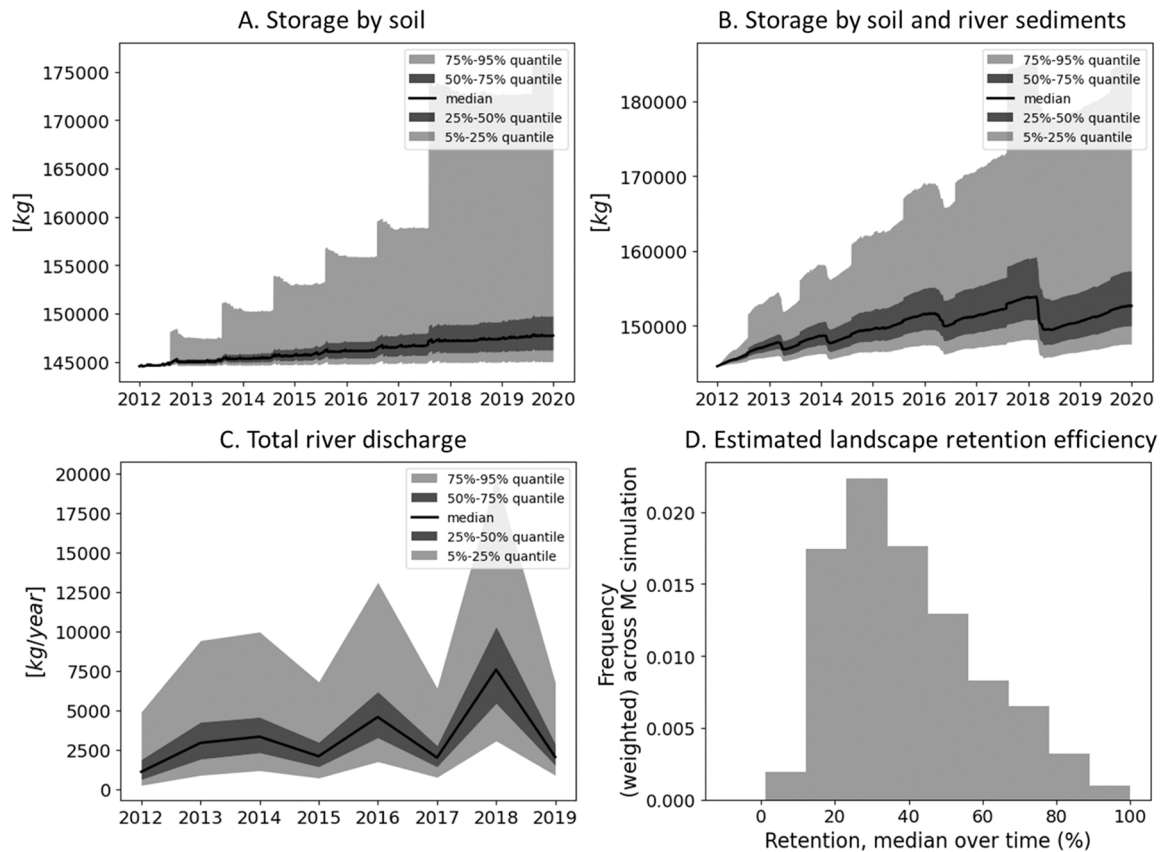


Fig. 5. : Dynamics of stocks and fluxes of microplastics in the catchment. A. Temporal variability of the storage of fragments by the catchment soil. B. Temporal variability of the microplastic storage by soil and river sediments. C. Annually integrated discharge of microplastics by the Henares river. D. Estimate of the catchment retention efficiency index \bar{eff} . The quantile distributions in all these figures are computed in the same way as in the analysis in Figure.

parameter sets tested during the Monte Carlo analysis). With more conservative assumptions on microplastic mobilization from land, soil could still release particles to the stream water during more intense precipitation events. This was basically observed with all parameters sets.

Over the 8 years of the simulation, the fragment pool in soil increases 1.3–20% (depending on the parameter set). This is generally consistent with available evidences from other studies and locations [10,12,55,56].

Fig. 5B shows the total storage of fragments by the catchment summing the pool of soil and sediments. At any given moment soil hosts the majority of microplastics in the catchment (over 90%). This is because soil acts as a long-term capacitor while river sediments, according to the model predictions, can easily release during floods a large part of the accumulated microplastics. During one of these events (like the one in early 2018) the catchment can dissipate even 4–7.5 t ($1\text{--}1.8 \text{ kg km}^{-2} \text{ y}^{-1}$, scaled to the catchment area) of microplastics in few days. Annually, the Henares discharges from its mouth between 1.3 and 7.5 t y^{-1} ($0.3\text{--}1.8 \text{ kg km}^{-2} \text{ y}^{-1}$) of microplastics (median of estimates) depending on year, and up to 19 t y^{-1} ($4.6 \text{ kg km}^{-2} \text{ y}^{-1}$) when considering less conservative estimates (Fig. 5C).

3.4. Landscape efficiency to retain microplastics

In order to give a better representation of this catchment ability to retain or delay transfer of microplastic to the downstream and their export through the river mouth, we integrated microplastic fluxes, and averaged soil and sediment microplastic storages, over time. Fig. 6 depicts the generalized and time-averaged catchment-scale mass budget. In order to justify levels of microplastics measured in stream water and river sediments, substantial runoff needs to be generated from land. Estimated release of microplastic from wastewater directly to the river, accounts only for 10–50% (median = 25%) of the total inputs of microplastics to the river. The magnitude of ambient diffuse sources on land (*amb*) is estimated to be 10–100 times higher than the input from sewage sludge applications. This is needed to justify substantial runoff to feed the river storage and runoff, while preventing the depletion of the soil storage (which is assumed to increase over time according to evidences)[10,12,55,56]. This may appear surprising since sewage sludge application has been generally considered as a main source of microplastics for soils[10,33]. On the other hand, dropping the assumption on

the increase of soil storage over time leads to a lower estimate of *amb* relative to sewage sludge inputs, but also to a rapid and unlikely depletion of the soil storage.

In summary, this analysis suggests that about 75% of the total input of microplastics to the catchments and stream derive from undefined sources (accounted here for by the *amb* parameter). These are contributed by atmospheric depositions, littering, and other diffuse sources. In order to further consolidate understanding of the mass budget of these pollutants in landscapes, further effort should be placed in the identification of sources and assessment of their intensity.

Next, we used modelled data on microplastic storage and discharge to calculate the index of catchment retention efficiency \overline{eff} . Because the index is integrating over multiple years it represents the typical fraction of microplastics added to the catchment that tend to remain in the catchment soils or sediments, averaging the highly dynamic nature of microplastic flows and budget described in Fig. 5A-C. Fig. 5C shows the probabilistic distribution of estimated \overline{eff} values (calculated for the period 2012–2019). The interquartile of the estimates varied between 20%–50%, with a mode at 30%, indicating a higher likelihood that the catchment retain, in average and on the long-term, a slight minority of the total load of microplastics added to the system.

4. Discussion

This first application and empirical assessment of a dynamic model of microplastic fate at catchment scale demonstrates the possibility of obtaining reliable mechanistic predictions. This study exploited one of the most detailed measurement datasets [43] describing microplastic inputs to and loads within the catchment and river consistently obtained from harmonized measurements. Once fed with inputs estimated from the measurements of sewage sludge and wastewater effluents the model yielded satisfactory predictions of microplastics concentrations in stream water and river sediments at the effluent points of the main river reaches with observations repeated over time.

While this monitoring effort was sufficient to obtain satisfactory model accuracy and precision, substantially denser datasets, encompassing both environmental concentration data and quantitative information on microplastic sources to the landscape and waterscape, are needed to improve some model parameters, especially those concerning

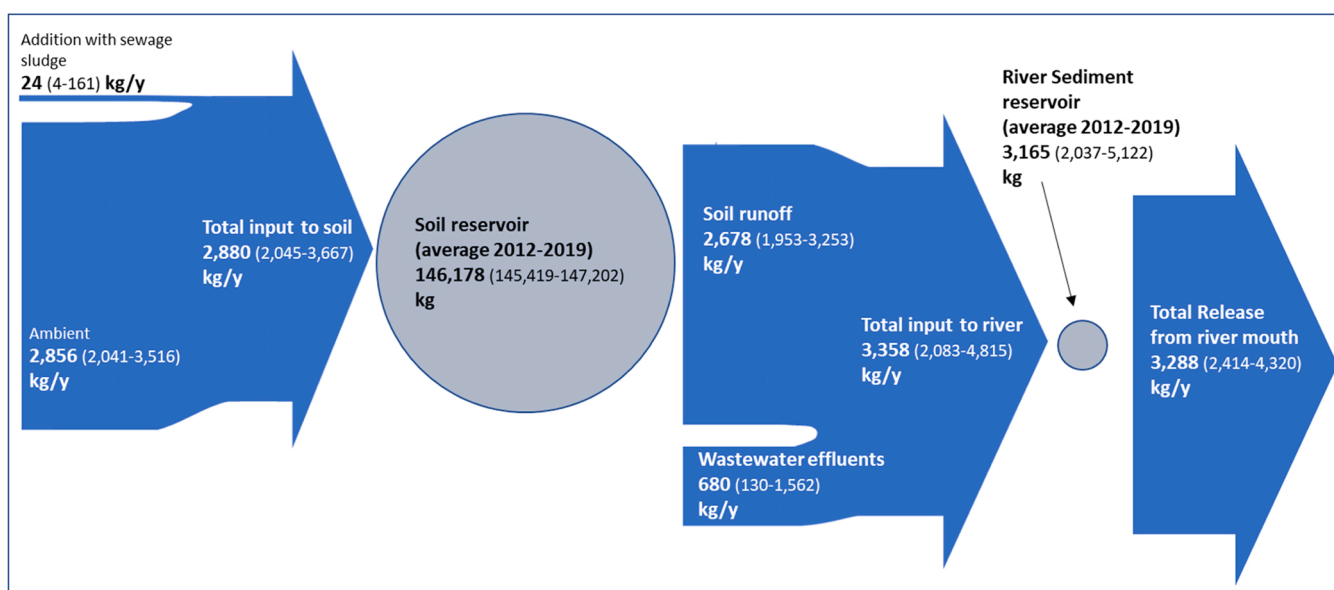


Fig. 6. : Representation of time averaged stores and time integrated fluxes of microplastic in the Henares catchment for the period of the simulation (2012–2019). The thickness of the arrows is proportional to the flux values. The area of the circles is proportional to the storage value. Bolt numbers represent median estimates, interquartiles (25th and 75th percentiles) of estimates are given in parentheses.

microplastic runoff from soils. Low data density also prevented developing calibration and predictions for subclasses of particles (e.g. divided by size or density classes), as well as the parameterization of processes such as microplastic fragmentation and etheroaggregation rates. At present, only prediction for bulk fragments and bulk fibers could be achieved successfully.

The simulation results revealed some important gap existing in the knowledge on microplastic sources to terrestrial environments. The mass budget assessment of Fig. 6 shows that measurable input of microplastics (e.g. through sewage sludge application, and wastewater effluents) only account for about a fraction (typically 25–50%) of the total input of fibers and fragments required to justify observed concentrations in stream water and river sediment.

Because of the focus on mechanisms and the geographical and meteorological drivers of microplastic transport, INCA-MP is designed to provide specific (in time and space) predictions. The outcome and conclusion provided here are therefore site-specific. While this can be seen as a limitation, this study aims at demonstrating the possibility of dynamic mechanistic predictions of microplastic fate at this scale. This is a necessary and not yet achieved milestone towards sound upscaling and more generalized future assessments.

In this geographic scenario, through the estimation of the landscape retention efficiency for microplastics (\overline{eff} , %), we calculated that the catchment tend to retain, in average and over the long-time, between 20% and 50% of the microplastics added to soils and stream water. A landscape ability of retaining microplastics delaying their transport to the oceans is an important, yet elusive parameter for regional and global microplastic distribution assessments. It is inversely related to the potential for microplastics released to land to reach the marine environment and is essential for estimating mass budgets, ecosystem exposure and future trends of both terrestrial and marine microplastic pollution. To our knowledge, this is the first time such a retention efficiency is introduced and estimated in robust quantitative terms. Empirical assessments of this parameters are rare and generally focusing on study conducted on small scales. These studies provided contrasting information. For instance, a Canadian field-scale study[11] showed that a very high fraction of yearly microplastic addition to agricultural soils could be removed by regular but intense rains. In semiarid conditions, microplastic runoff was negligible when moderate rainfall occurred during a semi-controlled plot-scale runoff experiment[42]. Finally, another controlled plot-scale runoff study[37] showed that single short (1.5 h) high intensity precipitation events can mobilize 0.8–4% of high density polyethylene particles added to a soil plot, resulting in a 2–12% loss after three such events depending on particle size and soil characteristics. Preferential erosion of microplastics (compared to natural soil particles) was also observed[37]. Our model results capture this variability associated to meteorological, hydrological factors.

Because \overline{eff} is sensible to the prevailing climatic conditions, the estimates obtained from this study can be primarily seen as relevant for a Mediterranean semiarid environment. Soil and river sediment storage and microplastic riverine export fluctuates with time due to precipitation and runoff variability, whereby eff_T is maximized in wetter conditions. Hence the distribution of \overline{eff} will expectedly have a higher negative skewness (i.e. towards lower retention) in wetter environments and in region with soils presenting lower permeability.

In conclusion, the present is the first empirical evaluation of a mechanistic, landscape-scale microplastic fate and transport model across soils, streams and river sediments. Our results provide encouraging insights about the possibility of drawing accurate estimates of microplastic flows and distribution across land and waterscapes. They show that microplastic export from land and discharge by river fluctuates considerably and in a non-linear manner with precipitation and runoff variability. This indicates the need of a sufficiently accurate dynamic description of soil and stream hydrology even when modeling microplastic fate and transport in generic scenarios (including at low

spatio-temporal resolution). Good predictive ability obtained here reinforce confidence on the possibility of elaborating local, landscape and, eventually, global level microplastic budget assessments starting from a sufficiently detailed mechanistic framework. These assessments are in fact crucial for supporting the efforts of prioritizing actions to protect the environment.

Environmental Implication

Soils are main recipients of microplastic pollution that is subsequently transferred to aquatic ecosystems. Land-based sources dominate microplastics inputs to the ocean but knowledge gaps about their accumulation in soil, run-off and in-stream transport has hindered assessments of regional/global distributions and marine ecosystem exposure. These gaps must be filled to prioritize environmental protection actions. Verified mechanistic models capable of describing this process are the main avenue to advance knowledge in the field. This paper fills this gap by presenting the first empirical validation of a mechanistic microplastic fate model operating at the river catchment scale.

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CRedit authorship contribution statement

Conceptualization. MN, LN, MNF: Methodology. MN, LN, MNF: Investigation. MN, LN, RH, TS, AR, MV, AB, JLJL: Visualization. MN, LN: Supervision. LN, MNF, MV: Writing – original draft. LN: Writing – review & editing. 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.

Data Availability

Data are included in the supplementary information. Raw data can be shared upon request. The model code and a user friendly interface are available at the links specified in the manuscript. The source code for the model is available at <https://github.com/NIVANorge/Mobius/blob/master/Modules/INCA/INCA-Microplastics.h> An executable version of the model along with a setup for the Henares catchment can be found at <ftp://mobiserver.niva.no/Impasse>. Contact the lead author if you need assistance.

Acknowledgments

This paper is dedicated to the memory of our colleague and dear friend Jill Crossman.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2023.132993](https://doi.org/10.1016/j.jhazmat.2023.132993).

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