

# Transport of Nano- and Microplastic through Unsaturated Porous Media from Sewage Sludge Application

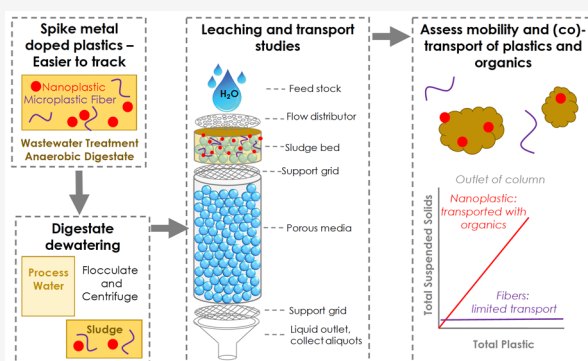
Andreas S. Keller,<sup>†</sup> Joaquin Jimenez-Martinez,<sup>†,‡</sup> and Denise M. Mitrano<sup>\*,†,‡</sup>

<sup>†</sup>Eawag—Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland

<sup>‡</sup>Department of Civil, Environmental and Geomatic Engineering, ETH Zürich, Stefano-Francini-Platz 5, 8093 Zürich, Switzerland

**S** Supporting Information

**ABSTRACT:** Wastewater treatment plants have been identified as important hubs for small particulate plastic, down to the nanometer scale, from urban areas to the environment. The reuse of sludge as fertilizer in agricultural practices can lead to accumulation of plastic in the soil. In this study, nanoplastic particles and microplastic fibers were synthesized with a passive inorganic tracer to aid in faster and more quantitative analysis using inductively coupled plasma mass spectrometry (ICP-MS). Using the anaerobic digestate of a pilot wastewater treatment plant spiked with metal-doped plastic, the excess sludge was dewatered, ensuring realistic associations between sludge and plastic. The resulting sludge cake was affixed atop an unsaturated porous-medium column of glass beads to assess: (i) the release of particulate plastic from the sludge, and (ii) the accumulation and mobility of plastic and organic matter through the column (analogous to a soil). A total of three particulate plastic treatments were assessed, in triplicate, where the plastic and mobile organic fractions were monitored for 14 pore water volumes. Due to size-limited transport, low deattachment from the sludge and reduced mobility through the column were found for microplastic fibers (>95% retention). However, cotransport between the mobile organic fraction and nanoplastic particles was observed, with 50% of both retained in the column. These results contribute to the understanding of the fate of particulate plastics and to assessing the associated environmental risks of particle mobility and percolation, particularly for nanoplastics.



## 1. INTRODUCTION

Soon after the pollution of ecosystems with plastics came more into the limelight, wastewater treatment plants (WWTPs) were identified as important hubs for particulate plastics (nanoplastic, microplastic fibers and particles) between the built and natural environments.<sup>1</sup> Particulate plastic in wastewater originates from a large variety of materials and situations, including washing of synthetic textiles, personal care products, breakdown of roadside litter, and car tire wear.<sup>2,3</sup> During wastewater treatment, particulate plastic mostly associates with activated sludge solids and is removed from the effluent by  $\geq 95\%$ .<sup>4–6</sup> Excess sludge from WWTPs is further processed and conditioned for reuse or disposal. In Europe, roughly 50% of processed sewage sludge is reused as agricultural fertilizer,<sup>7</sup> and in China 87% of the 8 million metric tons of (dry) sludge is generated each year is applied to soil and natural environments.<sup>8</sup> Therefore, the accumulation of microplastic in agricultural soils amended with sludge has been anticipated.<sup>9,10</sup> Accordingly, the WWTP excess sludge has been identified as an important release pathway of particulate plastic to the environment. Because the awareness of plastic in sewage sludge only emerged in the last several years, small particulate plastics were mostly excluded when considering benefits and risks of sludge reuse in agriculture. However, negative effects of plastic

in soils are known due to either chemical or physical processes.<sup>11–13</sup> Furthermore, as plastic size decreases (e.g., to nanoplastic), the spread of the plastic throughout the soil column may be enhanced by several mechanisms. However, little concrete information on how the presence of particulate plastic impacts soil ecosystem services has been reported to date. More research on the ingestion (and effects) in organisms, plastic in surface runoff, subsequent impacts on waterways, migration of plastic to the subsurface, and potential to reach groundwater systems is needed. To better understand these mechanisms and estimate the associated risks particulate plastic may pose, more knowledge on the release of plastic from sewage sludge and mobility through soils, especially for particulate plastic on the nanoscale, is needed.

Even though comparatively little is known about plastic-specific mobility mechanisms in porous media, the processes for solid transport have been previously studied and can be used as a reference. Particulate plastic must be detached from the sludge matrix or be dragged together with the organic

**Received:** October 28, 2019

**Revised:** December 11, 2019

**Accepted:** December 11, 2019

**Published:** December 16, 2019

solids by rainfall and/or irrigation before further infiltration in the soil. Flow in soils typically occurs under unsaturated conditions, i.e., the void space between solid grains or porosity is occupied by water and air. Preferential flow paths, high fluid flow velocity regions, and stagnation zones, as well as low fluid flow velocity regions may all develop along the soil profile.<sup>14,15</sup> In this regime, preferential flow paths promote high(er) transport rates of solids.<sup>16</sup> On the contrary, stagnant zones and interfaces (air/water and water/solid) are known to enable efficient retention of solids in the medium.<sup>17</sup> As it occurs in common filtration processes, two main mechanisms controlling mobility of particulate plastics are expected: (i) by straining, which depends on the soil texture (i.e., distribution of grain sizes) and structure (i.e., existence of macropores), and (ii) by physical and chemical forces between particles and the media.<sup>18</sup> Therefore, we hypothesized that the percolation and accumulation of organic solids and particulate plastic in porous media will be controlled by the size of the particles, the size of pore throats between solid grains, and the morphology of the transported particles. Substantial particle accumulation can lead to a decrease in porosity and permeability. For the particular case of nanoplastics, we expect suspended nanoplastics to show a more conservative behavior, i.e., less retention, as observed for other colloids.<sup>19,20</sup> However, organic compounds in soils are known to influence transport rates of other materials.<sup>21</sup> Depending on the surface charge and characteristics of dissolved substances, colloids can adsorb to organic matter in the soil or be a carrier of sorbing contaminants.<sup>22</sup> Since aggregation of nanoplastic with organic compounds is known to occur, this process is expected to lead to additional retention of plastic in soils.<sup>23</sup> Agricultural soils are also subject to bioturbation and farming practices (e.g., tillage) that can displace particulate plastic deeper into the soil.<sup>17</sup> This can alter the distribution pattern of plastic in the topsoil but does not per se affect the physical mechanisms of particle transport described above. Finally, the risk that particulate plastic reaches groundwater bodies will also be controlled by the thickness of the unsaturated zone, i.e., depth of the groundwater level. In this way, the thicker the unsaturated zone, the higher the buffering capacity to reduce particulate plastic from reaching the aquifer.

The lack of data on mechanistic processes that dominate particulate plastic mobility and ultimately the fate of plastic is linked to analytical challenges of quantitatively assessing plastics. Typically, even state-of-the-art methods include laborious sample preparation to isolate plastic from the matrix and have a lower limit of size resolution in the micrometer range.<sup>24,25</sup> Ultimately, this limits the number of replicates that can be assessed (even in laboratory studies), and consequently, the understanding of basic transport processes of particulate plastic is limited. We have circumvented these analytical limitations and challenges by synthesizing nanoplastic particles and microplastic fibers containing an inorganic tracer.<sup>26,27</sup> By measuring the metal as a proxy for the plastic, more simple and reliable measurements at trace concentrations can be performed, even for small-sized particles in complex matrices such as sludge and soil. Importantly, because the time of analysis has been expedited, a far greater number of samples can be analyzed, which allows us to collect more temporal data and better assess mass balance and recovery across the system.

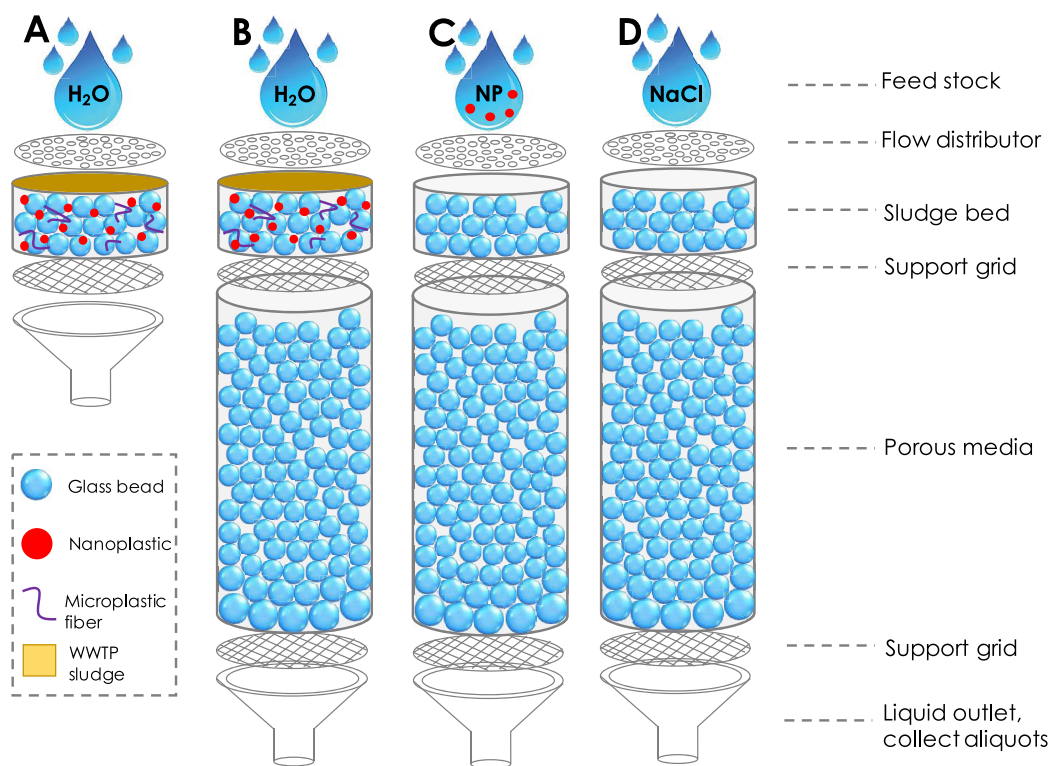
To gain insights on the path of particulate plastic from the WWTP to the field, the aim of this study was to assess (i) the association of nanoplastic particles and microplastic fibers with

sludge during the dewatering process, (ii) assess the detachment of these materials as individuals or jointly with organic solids from the sludge matrix, and (iii) simulate sludge application and rain/irrigation events to investigate factors that influence particle mobility through porous media as an analog to soils. Given our increased analytical capabilities stemming from our use of metal-doped plastics, we were able to differentiate and quantify the flux of particulate plastic and organic material throughout these stages. The experimental design developed in this work uniquely allows us to independently study the cotransport of mobile organics (from sewage sludge) with particulate plastics without the interference of organics from the soil. In the absence of the physicochemical and biological complexity of natural soils, we are better able to understand the transport processes of plastics in a different way than has been done before. Ultimately, this allows us to improve our mechanistic understanding of how particulate plastic behaves in sludge-amended soils.

## 2. MATERIALS AND METHODS

**2.1. Metal-Doped Particulate Plastic.** To overcome the analytical challenges to detect and quantify particulate plastic in complex media, metal-doped nanoplastic particles and microplastic fibers had previously been synthesized and characterized in-house and assessed in proof-of-concept studies representing the activated sludge stage of wastewater treatment.<sup>26,27</sup> Briefly, the nanoplastic particles consisted of a polyacrylonitrile (PAN) core in which palladium was incorporated as an inorganic tracer. The PAN was covered by a polystyrene (PS) shell with a rough surface morphology. The resulting nanoplastic particles resemble spheres with an average diameter of  $187 \pm 22$  nm. The Pd content of the particles was approximately 0.5% by weight, which did not significantly change the density of the particles. Microplastic fibers were produced by fiber melt spinning of granular poly(ethylene terephthalate) (PET) and the addition of indium oxide nanoparticles as an inorganic tracer. The filament from the melt spinning had a diameter of approximately  $30 \mu\text{m}$  and was cut in-house to the length of  $510 \pm 12 \mu\text{m}$ . The content of indium oxide in the fibers, evenly distributed across the length, was  $0.213 \pm 0.05\%$  by weight and did not significantly change the density, tensile strength, or chemistry of the fibers. During development, both materials were tested extensively to ensure no leaching of the tracer occurred. As the outward surface chemistry and morphology are similar to industrially relevant materials, the plastics used in this study are good proxies for particulate plastics that are found in the environment.

**2.2. Plastic Analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).** Palladium and indium oxide concentrations were measured by ICP-MS (8900 ICP-MS Triple Quad, Agilent Technologies), and rhodium was used as the internal standard. Calibration solutions ranging from 0.01 to  $10 \mu\text{g/L}$  were produced from palladium (palladium standard for ICP 10 000 mg/L, Sigma-Aldrich) and indium (indium standard for ICP 1000 mg/L, Certipur, Merck, Germany) standard solutions in 13% nitric acid (Rotipuran Supra 69%, Carl Roth, Germany). Degradation of the matrix and the particulate plastic was conducted by acid microwave digestion (Table S1) and was proven effective with spiked-addition experiments. In ten replicates ( $n = 10$ ), nanoplastic particles and microplastic fibers were spiked in deionized (DI) water and clean digestate (i.e., digestate that did not contain any



**Figure 1.** Characterization of particulate plastic leaching from sewage sludge and transport in unsaturated porous media. (A) Leaching test for assessing the release of organic solids and particulate plastic from the sewage sludge. (B) Infiltration test of the leached organic solids and particulate plastic into an unsaturated porous medium ( $\varnothing$  1 mm glass beads). (C) Transport of nanoplastic (pristine) particles suspended in DI- $\text{H}_2\text{O}$ . (D) Assessment of hydrodynamic conditions in the unsaturated porous medium with a conservative tracer ( $\text{NaCl}$ ). The openings of the support grids were  $3 \times 4.5 \text{ mm}^2$ .

measurable concentrations of indium or palladium) from ARA Neugut (Dübendorf, Switzerland) (Table S2). Accounting for dilution factors during digestion, the detection limits for nanoplastic particles and microplastic fibers were 0.003 and 0.0001 mg plastic/kg, respectively.

**2.3. Incorporation of Particulate Plastic in Sewage Sludge.** In a previous work, a pilot-scale WWTP located at our research institute was operated and the fate of spiked particulate plastic was investigated. The plastic spiked sludge produced was used throughout the current work. Briefly, wastewater was obtained from a primary clarifier using real municipal wastewater and treated by an activated sludge process including denitrification, nitrification, and secondary settling. Metal-doped particulate plastics were directly fed into the denitrification tank over the course of approximately two months. To control the solid retention time in the pilot-scale WWTP system, 18 L/day of mixed liquor was drawn from the activated sludge tank before settling. All nanoplastic particles and microplastic fibers that were retained in the activated sludge were conveyed to anaerobic digestion (for operational conditions, see Table S3). The excess mixed liquor was blended 1:1 with primary sludge and treated by mesophilic anaerobic digestion.<sup>28</sup>

Treated sewage sludge was produced by dewatering the anaerobic digestate from the pilot-scale WWTP. The separation of the bulk liquid from the solids was conducted by centrifugation (Figure S1). The digestate was continuously stirred in an intermediate storage container where flocculation was conducted using 2.9 mL/L ensola floc (Ensola Wassertechnik AG, Switzerland). Then, 243 kg of digestate

was dewatered using a pilot-scale decanter centrifuge (Flottweg Dekanter 218-3/401, Flottweg GmbH, Germany) at a speed of 7000 rpm and flow rate of 1.3 L/min. The masses of dry solids and particulate plastics were assessed along the process chain (anaerobic digestate, flocculation, centrifugation, final sludge cake, and process water), which allowed for us to assess the recovery rates in each respective step (Table S4). Five replicates samples ( $n = 5$ ) were taken from each stage of the dewatering process and were measured to calculate the mean value and standard deviation of particulate plastic concentration. Sample sizes were determined gravimetrically and ranged from 3 to 500 g depending on the processing stage. To measure total suspended solids (TSSs), the sample sizes were chosen to allow a reliable measurement on the filter used while also being cognizant of preventing filter overload. Subsamples of liquids and diluted sludge were homogenized with a mechanical homogenizer (SilentCrusher M, Heidolph, Germany) at a speed of 23 rpm for 3 min. Replicates ( $n = 10$ , each matrix) were then taken from the homogenized subsample. The samples were filtered on dried and preweighed glass fiber filters ( $\varnothing$  90 mm, 1.4  $\mu\text{m}$  pore size, MN GF-4, Macherey Nagel, Germany). After use, the filters were dried for 24 h at 105  $^\circ\text{C}$ . To calculate the organic content of a sample, the dry solid mass (weight difference between the clean and loaded filters) was divided by the liquid sample mass. In assessing the relevant material that would be used for agricultural amendments, it was assumed that the process water would be recycled to the WWTP due to its high nutrient content,<sup>28</sup> and thus, only the solids from the centrifuge were retained for further experiments. The sludge was stored anaerobically at

room temperature. To assess the plastic content, a different procedure was established as filtration was necessary to concentrate the low concentration of fibers in the sample. A subsample of the digestate was homogenized, and 7.5 g was directly sampled and digested to assess plastic content by way of metal (Pd and In) inclusion. After the centrifugation process, 1.5 g of sludge was subsampled with a glass beaker, digested with anaerobic microwave digestion, and measured for both nanoplastic particles and microplastic fibers using the associated metal via ICP-MS. For the process water, 7.5 g was directly sampled to assess nanoplastic concentration in the same manner as the sludge. In contrast, 300 mL of process water was filtered to capture a higher number of fibers, and both the filter and fibers were subsequently digested and analyzed to assess the fiber content. Using the known metal contents of both nanoplastic particles and microplastic fibers with Pd and In, respectively, we could back-calculate the nanoplastic particle and fiber concentrations (in terms of either number or mass) from the metal content in samples.

**2.4. Experimental Setup and Protocol.** A suite of experiments was constructed to approximate rainfall onto freshly applied sludge to porous media (soil) (Figure 1). The mobility of particulate plastic throughout the sludge application and rain event was deconstructed into a number of different physical processes that were then addressed separately. First, a leaching experiment was used to characterize the mobility of particulate plastic and organic solids from the applied sludge and to quantify the detachment rate of particulate plastic, separately or jointly, with organic solids from the sludge matrix (Figure 1A). Second, the transport and retention of the detached components through an unsaturated porous media column were further assessed (Figure 1B). The transport of pristine nanoplastic particles (i.e., those not previously associated with sludge) through the porous medium was performed to assess the impact of the presence of organic solids on nanoplastics transport through the column (Figure 1C). Finally, a conservative tracer test was performed to characterize the hydrodynamic conditions in the porous media (Figure 1D).

**2.4.1. Leaching of Organic Solids and Particulate Plastic from Sludge.** The same leaching protocol and experimental setup were used for all experimental variants (Figure S2). DI-H<sub>2</sub>O was pumped by a peristaltic pump (Heidolph Pumpdrive 5201 Sp Quick, Heidolph, Germany) and fed into a flow distribution system (flow rate =  $2.04 \pm 0.03$  L/h). In a simulated rain event, the system evenly distributed water over the entire column surface ( $\varnothing$  98.8 mm, 76.6 cm<sup>2</sup>) as the flow was divided into 50 poly(tetrafluoroethylene) (PTFE) tubes ( $\varnothing$  1/16 in.  $\times$   $\varnothing$  0.25 mm, BGB Analytik AG, Switzerland) positioned according to a Fibonacci pattern (Table S5). In all experiments, the flow was applied from a height of 6 cm above the top of the setup. The leaching sieve consisted of a poly(vinyl chloride) (PVC) column (15 mm height) with an aluminum support grid at the bottom with openings of  $3 \times 4.5$  mm<sup>2</sup>. Mimicking a typical application rate of sludge onto agricultural soil in terms of mass of sludge per surface area covered,  $21.4 \pm 0.2$  g of sludge was used per replicate. To provide additional surface area and structure to the sludge, simulating sludge application onto topsoil, the sludge was mixed with 150 g of  $\varnothing$  4 mm glass beads (SILIBeads Type M, Sigmund Lindner, Germany) (Figure S2B). The loaded leaching sieve was placed on top of a funnel to collect the

leachate and assess (1) total organic material and (2) particulate plastic that was released from the sludge cake.

For each experimental replicate ( $n = 3$ ), the collected volume, concentration of particulate plastic, and mobile organic fraction (total suspended solids, TSSs) were measured in every bin, when applicable. Initially, sampling was done in 2 min intervals until 18 min, whereafter the leachate was collected in 4 min intervals until 30 min. The mobile organic fraction was determined gravimetrically (Ohaus Scout SXT 6201, Mettler Toledo) and ranged from 12 to 450 g. The sample sizes were chosen to be small enough to prevent filter overload with higher concentration samples (e.g., those toward the beginning of the leaching process) and larger for samples with lower expected concentrations. The samples were filtered onto dried and preweighed glass fiber filters ( $\varnothing$  47 mm, 0.45  $\mu$ m pore size, MN GF-5, Macherey Nagel, Germany). After use, the filters were dried for 24 h at 105 °C. To calculate the mobile organic fraction of a sample, the dry solids mass (weight difference between the clean and loaded filters) was divided by the liquid sample mass (XS 204 Delta Range, Mettler Toledo, Switzerland). It is worth noting that here we refer to the TSS as organics, while in fact the sludge also contains a host of other materials. As the majority of the TSS is organic material, this simplification is used throughout the text, which neglects the small fraction of inorganic materials found in typical sludge. For plastic mobility experiments, the plastic concentration was measured for every bin collected. The entire bin was shaken end-over-end for 5 s to fully mix it, and a 4 mL subsample was digested for ICP-MS analysis. The data from the sludge leaching experiment was used as an input value for the full experiments (i.e., leaching from the sludge plus transport through the glass bead column). The equivalent of four column pore volumes was passed over the sludge plug, which was approximately 1 L delivered over 30 min. Triplicate experiments with freshly prepared sludge plugs were performed, which were then averaged.

**2.4.2. Transport of Particulate Plastic through Unsaturated Porous Media.** For transport experiments, the leaching sieve was placed on top of a PVC column ( $\varnothing$  98.8, 250 mm tall). At the exit of the column, an additional grid was affixed to be used as a support for the glass beads ( $\varnothing$  1 mm), which made up the porous media. To keep similar water saturation (fraction of pore volume occupied by water) with depth through the vertical column, two thin layers of  $\varnothing$  2 and 4 mm glass beads were added at the bottom to facilitate the drainage. For every experimental replicate, a new column was wet packed in DI water with clean beads.

Keeping the same input parameters as for the test of leachate from sludge (i.e., water application and duration of rain event, 30 min), the leaching sieve was placed directly on top of the porous media column to conduct the transport experiments. The water fell from approximately 6 cm from the distributor to the top of the sludge layer. After the initial 30 min, the leaching sieve was removed from the top of the column and irrigation continued for an additional 75 min with DI-H<sub>2</sub>O. Throughout the experiment, samples were collected in intervals (bins) ranging between 2 and 15 min, with higher sampling resolution at the beginning of the experiment (0–18 min) and after the initial leaching phase (34–44 min). Larger bin sizes were used at the end of the experiment (until 105 min). Three experimental replicates ( $n = 3$ ) of each column experiment were conducted and present as an average with associated standard deviation for each bin hereafter. The retention of the

compounds (organic solids and particulate plastic) in the unsaturated porous medium was calculated by comparing the recovered mass to the estimated mass input from the sludge leaching experiments. The detection limit of particles in the sludge was  $3.2 \times 10^6$  nanoparticles/kg; for fibers, the detection limit translates to 6 fibers/kg. From this, it is evident that homogenization is the most critical step to measure the fibers precisely.

#### 2.4.3. Pristine Nanoplastic Particles and Tracer Transport.

The influence of organic solids on the transport of particulate plastic through porous media was investigated by comparing plastic released from sludge with pristine nanoplastic and the conservative tracer experiments. To remain consistent with experiments that did not contain sludge (i.e., pristine nanoplastic and tracer experiments), glass beads were also placed on the leaching sieve without the presence of sludge. A nanoplastic particle suspension of  $2.1 \times 10$  particles/L was constantly stirred at 50 rpm (MR Hei Standard Stirrer, Heidolph, Germany). The nanoplastic particle concentration of the solution was measured in the reservoir after preparation and at the end of the experiment after passing through the flow distributor to ensure no nanoplastic particles were trapped or absorbed in the feeding system. After feeding the nanoplastic suspension for 30 min, the column was flushed for an additional 75 min with DI water. Sampling intervals for these experimental replicates were the same as described above.

Under steady-state unsaturated flow conditions, a conservative tracer (sodium chloride, 10 g/L) was steadily injected from the top of the column without the presence of sludge to (1) establish column hydrodynamic conditions and (2) use the breakthrough curve as a benchmark for unimpeded transport throughout the column. The same feeding protocol was followed as for pristine nanoplastic particles. The concentration of sodium chloride was measured at the exit of the column at regular intervals of 1 min by conductivity (Multi 3430 IDS, MultiLine, WTW, Germany). Electrical conductivity was subsequently converted into values of concentration. The shapes of the breakthrough curves and moments were calculated and compared to assess relative mobility of each component of interest (see [Supporting Information](#) for equations and workflow). For each experimental step described above, three replicates ( $n = 3$ ) were conducted and analyzed individually and shown as an average and standard deviation hereafter.

### 3. RESULTS AND DISCUSSION

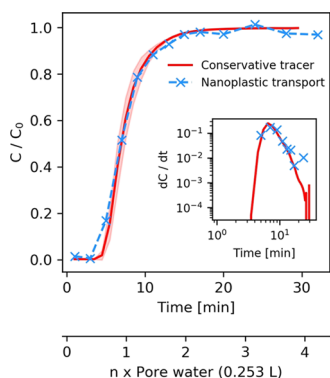
**3.1. Dewatering Anaerobic Digestate and Properties of Particulate-Plastic-Spiked Sewage Sludge.** The resulting sludge from the centrifuge procedure had typical physicochemical characteristics for processed sewage sludge even though slightly a lower solid content ( $9.5 \pm 0.6\%$ ) was achieved than in a full-scale dewatering process, likely due to changes in the flocculation routine and dewatering machinery used at the pilot scale.<sup>28</sup> In principle, the sludge has a thick and pasty structure. A high correlation of solids and plastic was found for all compartments along the sludge dewatering process chain (Figure S3 and Table S6). Throughout the dewatering process, the dominant flux of both organic solids and plastics was to the sludge (Figure S4B–D), with >90% of both in the sludge after centrifugation (Table S7). In full-scale operations, most of the bulk liquid (process water) would be recycled to the WWTP inflow via the supernatant, and thus residual plastics and organic solids from the dewatering process

would travel via this route (Figure S4A). With the use of metal tracers, the added plastic was measured without interference from other (potential) plastic, which may have been naturally in the sludge. The final sludge had a total (spiked) particulate plastic content of approximately 220 mg plastic/kg, which corresponds to  $\approx 0.2\%$  by weight of the dry solids. Based on this, we do not anticipate that the properties of the sludge were significantly changed due to the added plastic. Furthermore, a realistic incorporation of the plastic in the sludge is expected since the plastic was spiked to the activated sludge process of an operational WWTP and underwent all sludge processing steps. Loading of the number of particulate plastics in the system differed depending on the compartment and material. Microplastic fibers were in concentrations of 10 fibers/L in the supernatant and  $2.2 \times 10^5$  fibers/kg sludge, representing an average of 3 fibers sampled in a typical 300 mL supernatant sample and 340 fibers in the typical sample size of 1.5 g of sludge. Nanoplastic particles were in higher number concentrations, with  $3.4 \times 10^9$  nanoplastic particles/L in the supernatant and  $3.35 \times 10^{12}$  nanoplastic particles/kg sludge. Even though other studies have reported lower microplastic numbers in sewage sludge, a realistic comparison was elusive due to different size thresholds, measurement approaches, and high natural variability in terms of both temporal and geographic locations.<sup>6,29</sup> For nanoplastics, a detailed comparison was not possible due to the lack of reference measurements.<sup>30</sup>

Throughout the anaerobic digestate dewatering process, a strong correlation of solid concentrations versus nanoplastic particle ( $R^2 = 0.99$ ) and microplastic fiber ( $R^2 = 0.93$ ) concentrations was found (Figure S3). Through dewatering of sludge, particulate plastic remained in the solid sludge fraction, and it is unlikely that any of the other common processing steps to ready sludge for application onto fields (e.g., drying, pasteurization, composting) would alter the particulate plastic load. From these findings, it therefore can be projected that sewage sludge reuse and disposal is the most important particulate plastic flux leaving the WWTP system.

**3.2. Hydrodynamic Conditions in the Porous Medium.** The water saturation in the porous media column under steady-state flow conditions was  $33 \pm 2\%$ . Although the water saturation degree in any porous medium depends on the texture (pore size distribution) and boundary conditions (imposed flow), in agricultural soils, a water saturation of 33% will correspond to a water content of 17%. The saturation we obtained here is slightly above the typical field capacity (i.e., water retained in the soil after gravitational drainage). Therefore, the steady-state conditions reached for running our experiments correspond to realistic conditions in agricultural soils previous to or just after a low-intensity precipitation event. Across all experimental replicates,  $99 \pm 2\%$  of the applied fluid was recovered at the outflow of the column. We have computed the breakthrough curves and their temporal derivatives ( $dC/dt$ , variation in time of the arriving concentration). The breakthrough curves of the conservative tracer indicated the existence of a heterogeneous fluid velocity field commonly observed in unsaturated flow conditions. High-velocity regions (or preferential paths) and low-velocity regions (or stagnation zones) coexisted along the porous-medium profile. The breakthrough curve of the conservative tracer showed an early tracer arrival and a very long tail (i.e., longer residence times within the porous medium), which denotes anomalous transport, also called non-Gaussian or non-

Fickian transport (Figure 2).<sup>31</sup> The breakthrough curve of pristine nanoplastic particles ( $n = 3$ ) closely followed that of

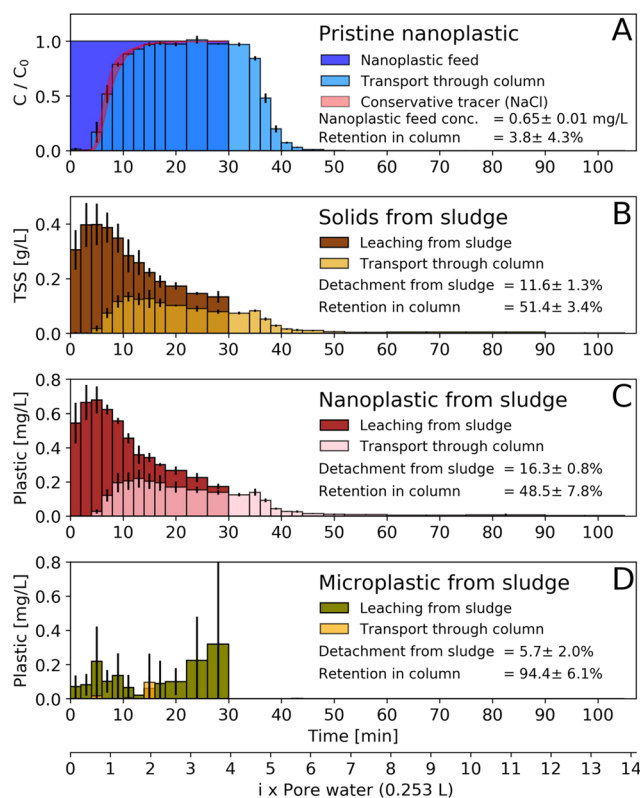


**Figure 2.** Conservative tracer vs pristine nanoplastic particles. Breakthrough curves of the conservative tracer (NaCl) and pristine nanoplastic particles in the unsaturated porous medium. The concentration in time and per pore water volume at the outlet of the column (main figure) and their temporal derivatives ( $dC/dt$ ) (inset) show that both the conservative tracer and pristine nanoplastic particles have similar behavior throughout the column. The sampling interval was 1 min for the tracer and 2–4 min for the nanoplastic particles. The red shaded area in the main figure represents the standard deviation of three experimental runs.

the conservative tracer along the duration of the experiment (Figure 2), indicating very similar transport behavior. The recovery of pristine nanoplastic particles was  $96.2 \pm 4\%$ , indicating a very small retention in the column alone (Figure 3A).

**3.3. Leaching of Plastic and Organic Solids from Sludge.** Organic solids and nanoplastic particles were mobilized from the sludge at similar proportions of  $11.6 \pm 1.3$  and  $16.3 \pm 0.8\%$ , respectively (Figure 3B,C). The leaching curve of the organic solids and nanoplastic particles had a similar shape, indicating that the nanoplastic particles were transported in association with the organic solids. The observed peak and steady decrease can be explained by high mobilization rates after an initial wetting phase and subsequent washout of the material. Microplastic fibers were released in lower proportions ( $5.7 \pm 2\%$ ) than organic solids and nanoplastic particles (Figure 3D), likely due to physical constraints.

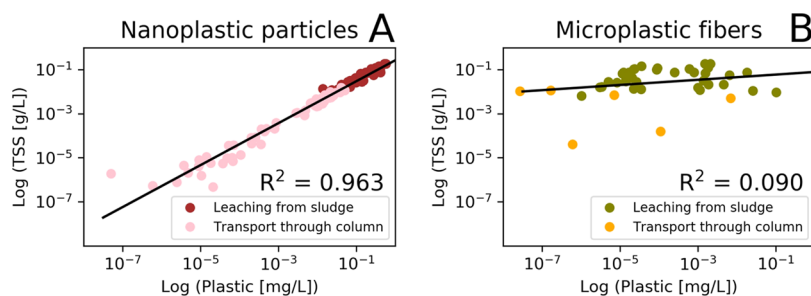
Leaching experiments suggested that nanoplastic particles were detached jointly with organic solids from the sludge matrix by the application of artificial rain, yet several simplifications in our test system should be noted as they may have implications as to the rate of plastic release from the sludge bed. The rainfall intensity applied of 262 mm/h was higher than natural rain events on a >10 year return period.<sup>32</sup> However, shear forces of single drops were much smaller compared to real rain due to the low drop falling height. Furthermore, the complex composition and structure of a soil surface were not fully represented by the sludge application on glass beads. Finally, in comparison to the control experiments in DI water with pristine nanoplastics, those replicates that contained sludge leachates had a higher ionic strength. Although ionic strength can play a role in the retention and aggregation of nanoplastic particles, where increasing retention and aggregation as ionic strength increases are expected, the high flow rate used in this study (i.e., rainfall intensity applied)



**Figure 3.** Leaching of particles from the sludge and transport through the porous medium. Pristine nanoplastic transport is shown together with the breakthrough curve of the conservative tracer (A). In (B), (C), and (D), the darker bars indicate mobility of the given substance (mobile organic solids, nanoplastic particles, microplastic fibers) from the sludge bed in leaching experiments, whereas the light bars indicate the collection of these materials at the bottom of the transport column experiments. The leaching of materials from the sludge bed can be viewed as the input in the transport column experiments. The associated proportion of detachment of materials from the sludge bed and retention in the column are indicated in each panel. Error bars indicate standard deviation of triplicate experiments.

counterbalanced this possibility.<sup>33</sup> Other differences, such as soil pH and wet/dry cycles, may also impact the absolute release of particulate plastic release from the sludge and subsequent mobility through porous media.<sup>34</sup> Despite the differences in field conditions identified, the observed patterns are generally anticipated to occur in real sludge application cases. The findings indicated similar mobilization of nanoplastic particles and organic solids but lower mobility for microplastic fibers. However, the absolute detachment rates will likely be dependent on the experimental conditions, such as the applied flow rate and/or the water content of the sludge.

**3.4. Transport of Particulate Plastic and Organic Solids through Porous Media.** Nanoplastic particles and organic solids were both retained in the porous media at a rate of  $\approx 50\%$  (Figure 3B,C). Since pristine nanoplastic particles were found to be more mobile through the column without the presence of organic solids, the increased retention of nanoplastics that were already associated with organic solids when mobilized from the sludge bed suggests cotransport of these two materials. This cotransport behavior is further supported by the high correlation of nanoplastic particles with measured organic solid concentrations over time and concentration differences (Figure 4A). The observed correla-



**Figure 4.** Correlation of organic solids vs particulate plastic in the sludge leaching and transport experiments. A strong correlation of plastic concentrations with the mobile organic fraction was found for nanoplastic particles (A), but no trend was observed for microplastic fibers (B).

tion was robust over 6 orders of magnitude ( $R^2 = 0.96$ ), making the organic solids a good indicator of the fate of nanoplastic particles when the sludge is known to be homogeneously loaded with nanoplastics. When assuming that nanoplastic particles were already associated with organic solids in the WWTP and/or through the sludge dewatering process, their retention through the porous medium can also be explained by coretenation with sludge solids in stagnant zones of the medium.<sup>35</sup>

Microplastic fibers were retained by >90% in the porous medium (Figure 3D). In contrast to nanoplastic particles, their decreased mobility and transport were likely size limited. Microplastic fiber dimensions (30  $\mu\text{m} \times 500 \mu\text{m}$ ) are in the same range as the pore size in our system ( $\sim 300 \mu\text{m}$ ). No correlation between microplastic fiber concentrations and measured TSS values was found (Figure 4B). This indicates that microplastic fibers had a transport behavior independent of sludge solids. As microplastic fibers are long but not straight, they are unable to sustain favorable orientation over long time periods when advected.<sup>36</sup> Consequently, the nonoptimal hydrodynamic shape of microplastic fibers make them lose their orientation along the flow streamlines, which further explains the observed straining effects.

**3.5. Assessment of Particulate Plastic Transport in Soil.** Particulate plastic was found to be equally or less mobile than organic solids from sewage sludge, being vastly retained as water infiltrates. Transport experiments in unsaturated porous medium showed roughly 50% retention of nanoplastic particles and suspended solids from sludge with a high correlation ( $R^2 = 0.96$ ). In contrast to this, pristine nanoplastic particles showed a mostly conservative transport behavior. This indicates that nanoplastic particles were strongly associated with organic solids mobilized from the sludge bed and, therefore, were cotransported throughout the porous media. On the other hand, a very high retention of microplastic fibers both within the sludge bed and in the porous media, due to size and transport limitations, was observed. Other polymer types with similar sizes would therefore also likely be retained since size exclusion is a physical process. For significantly smaller particulate plastic, size exclusion may gradually become less relevant. However, coretenation with larger solids is also possible, as was shown to be the case with other engineered and natural nanomaterials.<sup>23,37</sup> Therefore, removal of particulate plastic from the soil would be only possible by surface flow, soil erosion, or degradation. The first two processes are undesired in agriculture and are therefore avoided when possible. Chemical decomposition and biodegradation are both slow for most of the commonly used polymers, especially when

not exposed to UV light and under little mechanical stress, such as when they are buried in soil.<sup>38,39</sup>

Natural soils have a broad distribution of grain sizes leading to smaller average pore sizes, pore volumes, and hydraulic conductivity than was investigated in this study.<sup>17</sup> However, anomalous solute transport is also well-known in natural soils.<sup>17,31,40</sup> From these differences, more effective retention of particulate plastic could be expected in natural soils than the glass bead column presented here. In contrast, preferential flow along macropores, bioturbation, and agricultural practices (e.g., tillage) may enhance the further dislocation and spreading of particulate plastic deeper in the soil profile in the environment in specific locations.<sup>16,41</sup> Natural soils also contain diverse organic and inorganic compounds that could influence the transport behavior of particulate plastic, especially suspended nanoplastic, which could be adsorbed to the soil matrix at significant rates. However, for nanoplastic particles that are already effectively associated with organic materials (e.g., organic solids from sludge), this may be less relevant. Due to differences in field conditions, water influx, and plastic input, the absolute transport rates in soil are likely different. Nevertheless, virtually all plastic from sewage sludge is expected to accumulate in agricultural soils since it is coretenated with solids as water infiltrates. The findings from this study can possibly be adapted for other plastic inputs to soils as plastic from composted biowaste or plastic scrap from the agroindustry.

#### 4. IMPLICATIONS AND PERSPECTIVES

The gaps in data relating to particulate plastics in soils, and more specifically in agricultural soils, is slowly being filled since it has become increasingly clear that soil may represent one of the largest environmental sinks for (particulate) plastic,<sup>42</sup> and soil quality is essential to crop agriculture. As the accumulation of (particulate) plastic in agricultural fields has been shown to alter basic soil properties,<sup>13,43</sup> there may be knock-on effects to plants and crop yields from either direct or indirect association with particulate plastic. Even though differences exist between the analog soil (glass beads) used in this study and natural soils, in terms of physicochemical properties and biological processes, the mobility and transport of particulate plastic in the latter will likely be dependent on the size and on aggregation state (e.g., with organic solids) prior to entry into the soil, as we have shown. Transport may also be shape- or possibly polymer-dependent, and to this end, particulate plastic heteroaggregation and/or attachment to organics should be investigated further. Another consideration is the high variability of conditions existing in the field, such as soil type, temperature, and water regime, which will influence

particulate plastic fate and behavior. While we found that in our system approximately 50% of the mobile organic fraction and nanoplastic particles leached from the sludge were retained by the porous media, the absolute mobility of these moieties will ultimately depend on the real field conditions at hand. Ultimately, while the cotransport of nanoplastic and organics can still be expected in natural soils, the amount (mass) of plastics passing through the column would be reduced in the case of natural soils compared to our glass bead columns.

**4.1. Sources and Accumulation of Particulate Plastic in Soils.** The accumulation of larger plastic fragments into Technosols (urban soils, which are impacted by various human activities and not only by cultivation) is not new, and it is therefore of little surprise that particulate plastic is also found in relatively high quantities in areas with a high population density or reconditioned agricultural soils.<sup>44</sup> While the direct application of sewage sludge onto fields is a significant source of particulate plastic, this figure must be put into context with other sources of (particulate) plastic accrual in farm soils, including composted biowaste, (nano)fertilizers and other direct soil amendments, and debris from agroindustrial material.<sup>45,46</sup> Organic fertilizers from biowaste fermentation and composting often contain residual particulate plastics that are not removed during typical best-practice processing. Moreover, most countries allow a certain fraction of foreign matter, including plastics, in fertilizer destined for agricultural land application. For example, Germany, which has one of the strictest fertilizer-quality regulations worldwide, allows up to 0.1 wt % of plastics (neglecting all particles smaller than 2 mm in size).<sup>47</sup> While the evaluation of relative magnitudes of sources is difficult to compare due to fragmentary data, Weithmann et al. reported 3 times higher concentrations of particulate plastic in biowaste fertilizer than in WWTP sludge, equating to between 35 billion and 2.2 trillion individual particles >1 mm in Germany per year alone.<sup>45</sup>

In contrast, some agri-nanotechnology products that contain plastic are applied purposefully to fields,<sup>48</sup> such as controlled-release (nano)fertilizers, which allow for a more targeted and controlled release of nutrients (N, P, and K), where the fertilizer slowly diffuses from a polymer shell or scaffold. While this technology has a number of benefits for agriculture (including reduced fertilizer application per unit area and managed time of application),<sup>49</sup> it is also a source of plastic pollution to the agricultural soil after the fertilizer load is exhausted. Using a One Health perspective, a systems approach to bring together disparate expertise to integrate human, animal, and environmental health may help facilitate balance the pros and cons in developing an assessment as to the suitability of (nano)plastic use in agronomy.<sup>50</sup> Additionally, plastics linked directly to agriculture such as polytunnels, plastic mulching, and silage baling constitute a direct source through degradation after UV exposure, weathering, and/or tillage.<sup>51</sup> Collectively, it is expected that a significant future (particulate) plastic accrual in agricultural soils will occur in a “business as usual” scenario, though it remains unclear how the mobility and transport may be affected given the various sources, input pathways, polymers, and size metrics of the materials in question. As it has been done in the current study, simplifications of the system will be needed to improve our mechanistic understanding of the transport processes and the fate of particulate plastics from different sources. Knowing the limitation of the latter, studies in natural conditions will also be needed.

Minimization of these various sources of particulate plastic to agricultural soils may be achieved through various routes. Regulations in both the European Union and United States already generally prohibit the use of sludge containing excess of harmful substances (including heavy metals and some organic substances).<sup>52</sup> The results from this study may indicate that the current sludge reuse policy may also be questioned for the direct inputs of particulate plastic to agricultural fields. As some (smaller-sized fraction) plastic fraction may be mobile, a meaningful threshold of how much plastic may be safe for sludge reuse is difficult to derive without understanding the corresponding mechanisms of fate, transport, and associated hazards in soils.<sup>53</sup> A legal threshold would also be difficult to enforce in practice with regard to challenging measurements of particulate plastic in natural systems, including in sludge and in soil.<sup>30,54</sup> Assessing mobility in situ, including risks associated with particulate plastic runoff from sludge-amended fields and/or percolation through natural soils, is even more challenging to grasp at this stage. Further experimental work needs to be conducted to assess how particulate plastic (and in particular, nanoplastic) may be transported through agricultural soils and how the increased interaction between the mobile organic fraction/nanoplastic aggregates will interface with static solid components. Accordingly, particulate plastic in sewage sludge and other biosolids should specifically be considered in future reuse policy.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b06483>.

Sample sizes and digestion methods, spiked recovery experiments, methods for sewage sludge production and processing, mass balance across dewatering process, photos of the experimental setup, test results for water and particles from the irrigation device, results from sewage sludge dewatering and processing (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [denise.mitrano@eawag.ch](mailto:denise.mitrano@eawag.ch).

### ORCID

Denise M. Mitrano: 0000-0001-8030-6066

### Funding

We would like to thank the Swiss National Science Foundation, Ambizione Grant number PZP002\_168105, for funds to conduct this work.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We would like to thank Alexander Gogos and Marco Kipf for assisting with processing the anaerobic digestate and operating the centrifuge.

## ■ REFERENCES

- (1) Mason, S. A.; Garneau, D.; Sutton, R.; Chu, Y.; Ehmann, K.; Barnes, J.; Fink, P.; Papazissimos, D.; Rogers, D. L. Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent. *Environ. Pollut.* **2016**, *218*, 1045–1054.
- (2) Prata, J. C. Microplastics in wastewater: State of the knowledge on sources, fate and solutions. *Mar. Pollut. Bull.* **2018**, *129*, 262–265.



- (3) Hernandez, E.; Nowack, B.; Mitrano, D. M. Polyester Textiles as a Source of Microplastics from Households: A Mechanistic Study to Understand Microfiber Release During Washing. *Environ. Sci. Technol.* **2017**, *51*, 7036–7046.
- (4) Michielssen, M. R.; Michielssen, E. R.; Ni, J.; Duhaime, M. B. Fate of microplastics and other small anthropogenic litter (SAL) in wastewater treatment plants depends on unit processes employed. *Environ. Sci.: Water Res. Technol.* **2016**, *2*, 1064–1073.
- (5) Talvitie, J.; Heinonen, M.; Pääkkönen, J.-P.; Vahtera, E.; Mikola, A.; Setälä, O.; Vahala, R. Do wastewater treatment plants act as a potential point source of microplastics? Preliminary study in the coastal Gulf of Finland, Baltic Sea. *Water Sci. Technol.* **2015**, *72*, 1495–1504.
- (6) Talvitie, J.; Mikola, A.; Setälä, O.; Heinonen, M.; Koistinen, A. How well is microlitter purified from wastewater?—A detailed study on the stepwise removal of microlitter in a tertiary level wastewater treatment plant. *Water Res.* **2017**, *109*, 164–172.
- (7) Kelessidis, A.; Stasinakis, A. S. Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Manage.* **2012**, *32*, 1186–1195.
- (8) Li, X.; Chen, L.; Mei, Q.; Dong, B.; Dai, X.; Ding, G.; Zeng, E. Y. Microplastics in sewage sludge from the wastewater treatment plants in China. *Water Res.* **2018**, *142*, 75–85.
- (9) Zubris, K. A. V.; Richards, B. K. Synthetic fibers as an indicator of land application of sludge. *Environ. Pollut.* **2005**, *138*, 201–211.
- (10) Nizzetto, L.; Futter, M.; Langaas, S. Are agricultural soils dumps for microplastics of urban origin? *Environ. Sci. Technol.* **2016**, *50*, 10777–10779.
- (11) Teuten, E. L.; Saquing, J. M.; Knappe, D. R. U.; Barlaz, M. A.; Jonsson, S.; Björn, A.; Rowland, S. J.; Thompson, R. C.; Galloway, T. S.; Yamashita, R.; et al. Transport and release of chemicals from plastics to the environment and to wildlife. *Philos. Trans. R. Soc., B* **2009**, *364*, 2027–2045.
- (12) Huerta Lwanga, E.; Gertsen, H.; Gooren, H.; Peters, P.; Salánki, T.; van der Ploeg, M.; Besseling, E.; Koelmans, A. A.; Geissen, V. Microplastics in the terrestrial ecosystem: implications for *Lumbricus terrestris* (Oligochaeta, Lumbricidae). *Environ. Sci. Technol.* **2016**, *50*, 2685–2691.
- (13) de Souza Machado, A. A.; Lau, C. W.; Till, J.; Kloas, W.; Lehmann, A.; Becker, R.; Rillig, M. C. Impacts of microplastics on the soil biophysical environment. *Environ. Sci. Technol.* **2018**, *52*, 9656–9665.
- (14) De Gennes, P. Hydrodynamic dispersion in unsaturated porous media. *J. Fluid Mech.* **1983**, *136*, 189–200.
- (15) Jiménez-Martínez, J.; de Anna, P.; Tabuteau, H.; Turuban, R.; Le Borgne, T.; Méheust, Y. Pore-scale mechanisms for the enhancement of mixing in unsaturated porous media and implications for chemical reactions. *Geophys. Res. Lett.* **2015**, *42*, 5316–5324.
- (16) Flury, M.; Flüher, H.; Jury, W. A.; Leuenberger, J. Susceptibility of soils to preferential flow of water: A field study. *Water Resour. Res.* **1994**, *30*, 1945–1954.
- (17) Blume, H.-P.; Brümmer, G. W.; Horn, R.; Kandeler, E.; Kögel-Knabner, I.; Kretzschmar, R.; Stahr, K.; Wilke, B.-M., *Scheffer/schachtschabel: Lehrbuch der bodenkunde*. Springer-Verlag, 2016.
- (18) McDowell-Boyer, L. M.; Hunt, J. R.; Sitar, N. Particle transport through porous media. *Water Resour. Res.* **1986**, *22*, 1901–1921.
- (19) Bradford, S. A.; Torkzaban, S. Colloid transport and retention in unsaturated porous media: A review of interface-, collector-, and pore-scale processes and models. *Vadose Zone J.* **2008**, *7*, 667–681.
- (20) Mitropoulou, P. N.; Syngouna, V. I.; Chrysikopoulos, C. V. Transport of colloids in unsaturated packed columns: Role of ionic strength and sand grain size. *Chem. Eng. J.* **2013**, *232*, 237–248.
- (21) Sharma, P.; Rolle, M.; Kocar, B.; Fendorf, S.; Kappler, A. Influence of natural organic matter on As transport and retention. *Environ. Sci. Technol.* **2011**, *45*, 546–553.
- (22) Huber, N.; Baumann, T.; Niessner, R. Assessment of colloid filtration in natural porous media by filtration theory. *Environ. Sci. Technol.* **2000**, *34*, 3774–3779.
- (23) Oriekhova, O.; Stoll, S. Heteroaggregation of nanoplastic particles in the presence of inorganic colloids and natural organic matter. *Environ. Sci.: Nano* **2018**, *5*, 792–799.
- (24) Shim, W. J.; Hong, S. H.; Eo, S. E. Identification methods in microplastic analysis: a review. *Anal. Methods* **2017**, *9*, 1384–1391.
- (25) Bläsing, M.; Amelung, W. Plastics in soil: Analytical methods and possible sources. *Sci. Total Environ.* **2018**, *612*, 422–435.
- (26) Mitrano, D. M.; Beltzung, A.; Frehland, S.; Schmiedgruber, M.; Cingolani, A.; Schmidt, F. Synthesis of metal-doped nanoplastics and their utility to investigate fate and behavior in complex environmental systems. *Nat. Nanotechnol.* **2019**, *14*, 362–368.
- (27) Schmiedgruber, M.; Hufenus, R.; Mitrano, D. M. Mechanistic understanding of microplastic fiber fate and sampling strategies: Synthesis and utility of metal doped polyester fibers. *Water Res.* **2019**, *155*, 423–430.
- (28) Tchobanoglous, G.; Metcalf & Eddy. *Wastewater Engineering. Treatment, Disposal, and Reuse*; McGraw-Hill: New York, 1991.
- (29) Mahon, A. M.; O’Connell, B.; Healy, M. G.; O’Connor, I.; Officer, R.; Nash, R.; Morrison, L. Microplastics in Sewage Sludge: Effects of Treatment. *Environ. Sci. Technol.* **2017**, *51*, 810–818.
- (30) Mintenig, S. M.; Bauerlein, P.; Koelmans, A. A.; Dekker, S. C.; van Wezel, A. Closing the gap between small and smaller: Towards a framework to analyse nano-and microplastics in aqueous environmental samples. *Environ. Sci.: Nano* **2018**, *5*, 1640–1649.
- (31) Bromly, M.; Hinz, C. Non-Fickian transport in homogeneous unsaturated repacked sand. *Water Resour. Res.* **2004**, *40*, 1–12, DOI: 10.1029/2003WR002579.
- (32) Findley, D. J.; Schroeder, B.; Cunningham, C.; Brown, T. *Highway Engineering: Planning, Design, and Operations*; Butterworth-Heinemann, 2015.
- (33) Prédéus, D.; Lassabatere, L.; Louis, C.; Gehan, H.; Bricchart, T.; Winiarski, T.; Angulo-Jaramillo, R. Nanoparticle transport in water-unsaturated porous media: effects of solution ionic strength and flow rate. *J. Nanopart. Res.* **2017**, *19*, No. 104.
- (34) O’Connor, D.; Pan, S.; Shen, Z.; Song, Y.; Jin, Y.; Wu, W.-M.; Hou, D. Microplastics undergo accelerated vertical migration in sand soil due to small size and wet-dry cycles. *Environ. Pollut.* **2019**, *249*, 527–534.
- (35) Crist, J. T.; Zevi, Y.; McCarthy, J. F.; Throop, J. A.; Steenhuis, T. S. Transport and retention mechanisms of colloids in partially saturated porous media. *Vadose Zone J.* **2005**, *4*, 184–195.
- (36) Engdahl, N. B. Simulating the mobility of micro-plastics and other fiber-like objects in saturated porous media using constrained random walks. *Adv. Water Res.* **2018**, *121*, 277–284.
- (37) Alimi, O. S.; Farner Budarz, J.; Hernandez, L. M.; Tufenkji, N. Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. *Environ. Sci. Technol.* **2018**, *52*, 1704–1724.
- (38) Otake, Y.; Kobayashi, T.; Asabe, H.; Murakami, N.; Ono, K. Biodegradation of low-density polyethylene, polystyrene, polyvinyl chloride, and urea formaldehyde resin buried under soil for over 32 years. *J. Appl. Polym. Sci.* **1995**, *56*, 1789–1796.
- (39) Hamid, S. H. *Handbook of Polymer Degradation*; CRC Press, 2000.
- (40) De Smedt, F.; Wierenga, P. Solute transfer through columns of glass beads. *Water Resour. Res.* **1984**, *20*, 225–232.
- (41) Wilkinson, M. T.; Richards, P. J.; Humphreys, G. S. Breaking ground: pedological, geological, and ecological implications of soil bioturbation. *Earth-Sci. Rev.* **2009**, *97*, 257–272.
- (42) Kawecki, D.; Nowack, B. Polymer-Specific Modeling of the Environmental Emissions of Seven Commodity Plastics As Macro- and Microplastics. *Environ. Sci. Technol.* **2019**, *53*, 9664–9676.
- (43) Steinmetz, Z.; Wollmann, C.; Schaefer, M.; Buchmann, C.; David, J.; Tröger, J.; Muñoz, K.; Frör, O.; Schaumann, G. E. Plastic mulching in agriculture. Trading short-term agronomic benefits for long-term soil degradation? *Sci. Total Environ.* **2016**, *550*, 690–705.
- (44) Rillig, M. C. Microplastic in terrestrial ecosystems and the soil? *Environ. Sci. Technol.* **2012**, *46*, 6453–6454.

- (45) Weithmann, N.; Möller, J. N.; Löder, M. G.; Piehl, S.; Laforsch, C.; Freitag, R. Organic fertilizer as a vehicle for the entry of microplastic into the environment. *Sci. Adv.* **2018**, *4*, No. eaap8060.
- (46) Scalenghe, R. Resource or waste? A perspective of plastics degradation in soil with a focus on end-of-life options. *Heliyon* **2018**, *4*, No. e00941.
- (47) Kehres, B. H&K Aktuell. *Änderung der Düngemittelordnung*; BGK eV, 2015.
- (48) Kah, M.; Tufenkji, N.; White, J. C. Nano-enabled strategies to enhance crop nutrition and protection. *Nat. Nanotechnol.* **2019**, *14*, 532.
- (49) Lowry, G. V.; Avellan, A.; Gilbertson, L. M. Opportunities and challenges for nanotechnology in the agri-tech revolution. *Nat. Nanotechnol.* **2019**, *14*, 517.
- (50) Lombi, E.; Donner, E.; Dusinska, M.; Wickson, F. A One Health approach to managing the applications and implications of nanotechnologies in agriculture. *Nat. Nanotechnol.* **2019**, *14*, 523.
- (51) Briassoulis, D.; Babou, E.; Hiskakis, M.; Kyrikou, I. Analysis of long-term degradation behaviour of polyethylene mulching films with pro-oxidants under real cultivation and soil burial conditions. *Environ. Sci. Pollut. Res.* **2015**, *22*, 2584–2598.
- (52) Verlicchi, P.; Zambello, E. Pharmaceuticals and personal care products in untreated and treated sewage sludge: occurrence and environmental risk in the case of application on soil—a critical review. *Sci. Total Environ.* **2015**, *538*, 750–767.
- (53) Horton, A. A.; Walton, A.; Spurgeon, D. J.; Lahive, E.; Svendsen, C. Microplastics in freshwater and terrestrial environments: evaluating the current understanding to identify the knowledge gaps and future research priorities. *Sci. Total Environ.* **2017**, *586*, 127–141.
- (54) Dümichen, E.; Eisentraut, P.; Bannick, C. G.; Barthel, A.-K.; Senz, R.; Braun, U. Fast identification of microplastics in complex environmental samples by a thermal degradation method. *Chemosphere* **2017**, *174*, 572–584.