

## **Supporting Information**

# **Quantification of Small (1-10µm) Microplastic Particles in Soil Matrices Using Automated Scanning Electron Microscopy: Possibilities and Limitations**

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The supporting information contains one section on the characterization of polyethylene (PE) and polyvinyl chloride (PVC) stock suspensions (S1), one section on particle losses during filtration and filter handling (S2), 12 Figures and 6 Tables.

## **S1: Characterization of PE and PVC from stock suspensions**

To obtain FT-IR spectra of the microplastic particles (MPs) from polyethylene (PE) and polyvinyl chloride (PVC) stock suspensions ~5mL of either stock suspension were filtered (Polyethersulfon filter, 0.22 $\mu$ m pore diameter, 47mm diameter, Merck, Germany), the retained MPs were transferred to a glass slide and compressed into a central pile. Attenuated total reflection Fourier Transform – Infrarot (FT-IR) spectra (Fig. S1) of these MP powders showed the characteristic absorption peaks of PE and PVC (Table S1). In addition to the suspensions, the source material of the PE suspensions was also available as pellets. Individual pellets of ~ 3mm diameter were investigated using  $\mu$ -x-ray fluorescence spectroscopy ( $\mu$ -XRF) for the presence of elements related to filler materials. Energy dispersive x-ray fluorescence spectra of individual pellets indeed showed a minor peak of calcium (Ca) (Fig. S2), which probably was related to a filler material. This issue will be further discussed based on electron microscopy data presented in the main manuscript (section 4.2).

## **S2: Quantification of (apparent) particle losses associated with filtration, filter handling and particle analysis.**

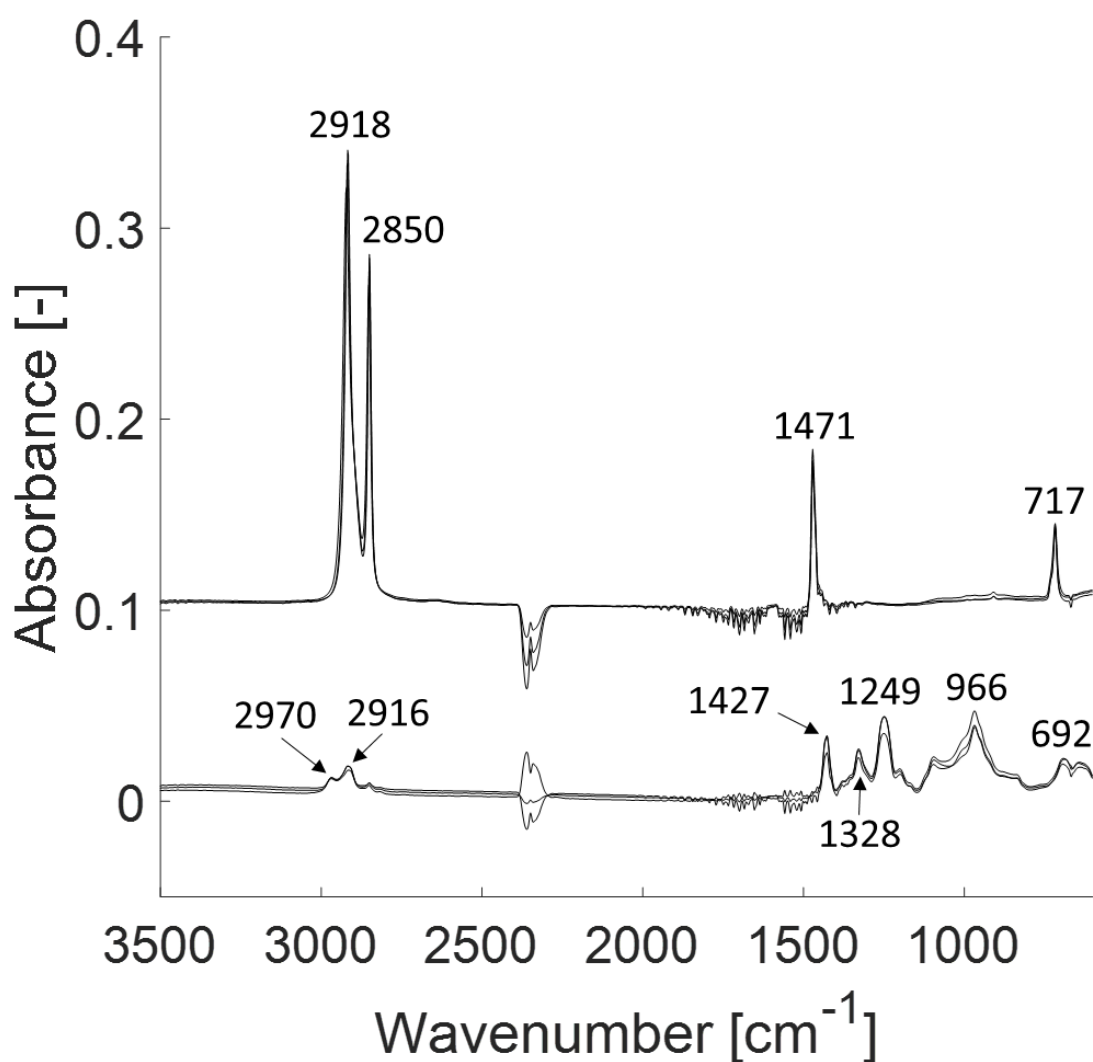
To evaluate to what extent MPs were lost during the filtration step, 4.5mL of a PS (3 $\mu$ m diameter) suspension with a certified particle number concentration (23'140#/mL  $\pm$ 10%, Count Check Beads) were filtered on gold (Au) coated PC membranes. The particle numbers were evaluated on recorded images. Results from duplicate experiments demonstrated a recovery of 87 and 88% (Table S2). Considering the uncertainties associated with the number concentration in the certified suspension of

$\pm 10\%$  and additional uncertainties related to the extrapolation of the investigated areas to the whole filter area, a correction of possible particle losses associated with the filtration, filter handling and particle detection is not justified. Therefore, reported particle number concentrations ( $c$ ) of MPs in suspensions are calculated following eq. (1).

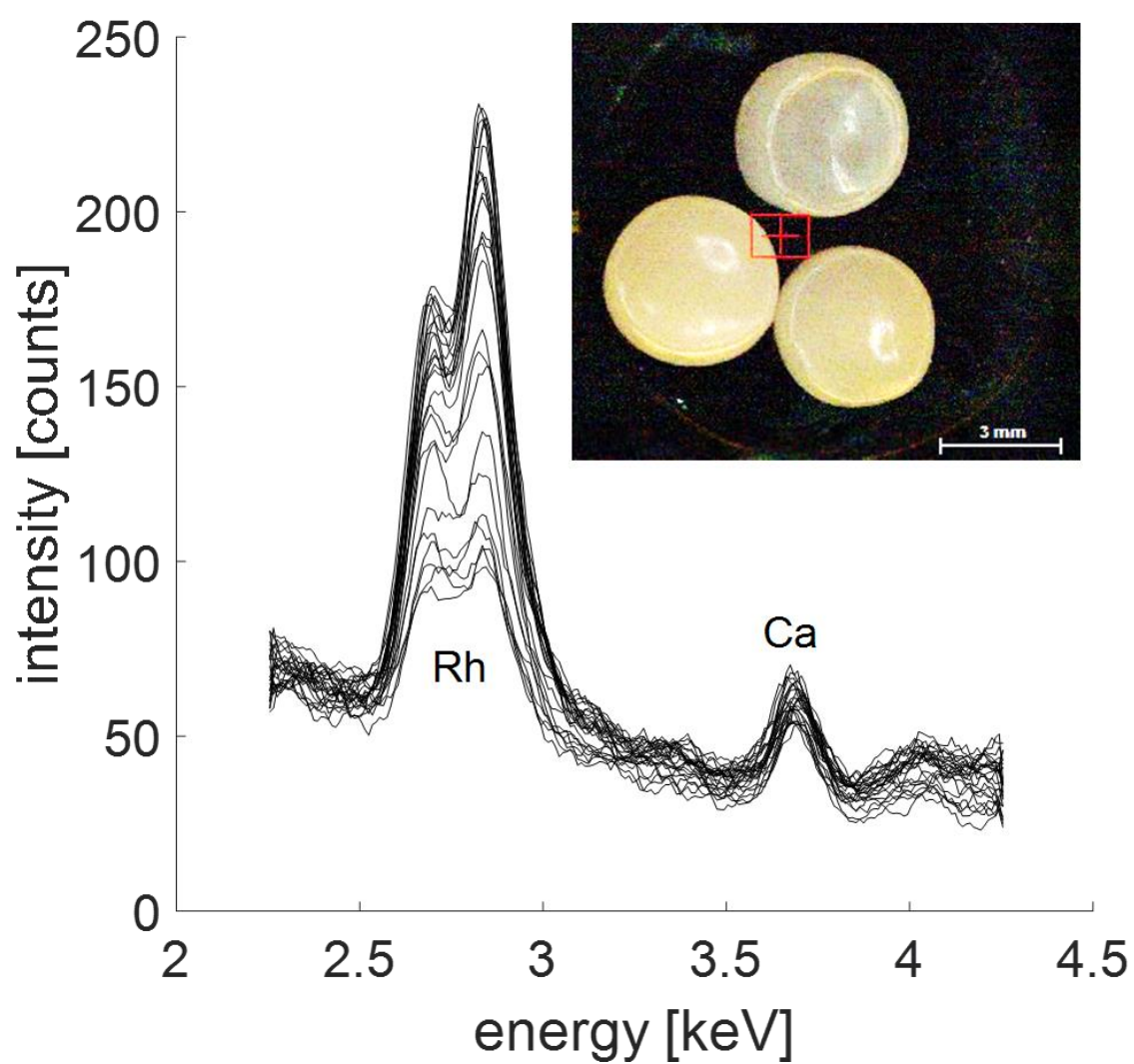
$$c \left[ \frac{\#}{mL} \right] = \frac{N_{det}[\#]}{V [mL]} \cdot \frac{A_{tot}[\mu m^2]}{A_i[\mu m^2]} \quad \text{eq. (1)}$$

Whereas  $N_{det}$ : number of MPs detected,  $A_i$ : filter area investigated,  $A_{tot}$ : total filter area, and  $V$ : filtered volume.

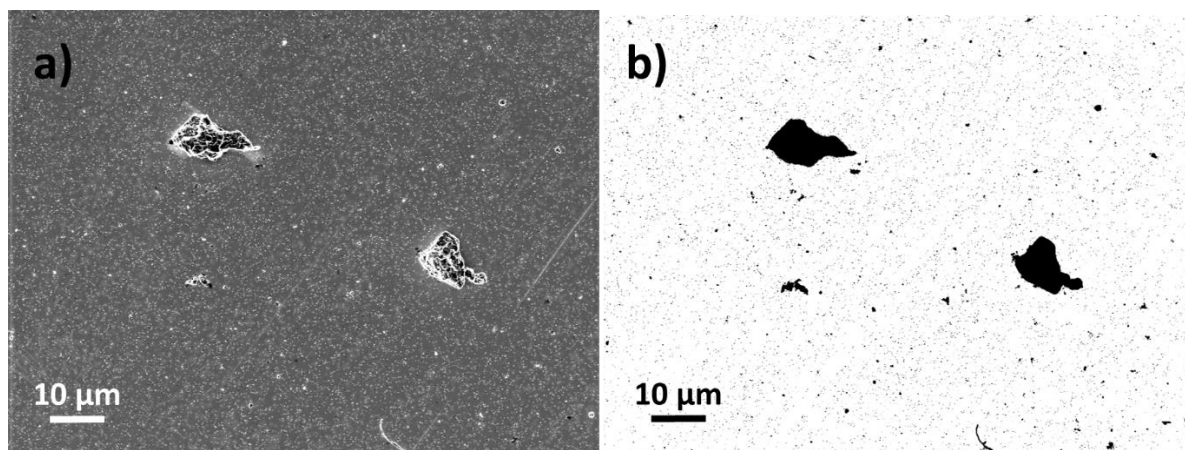
## Figures:



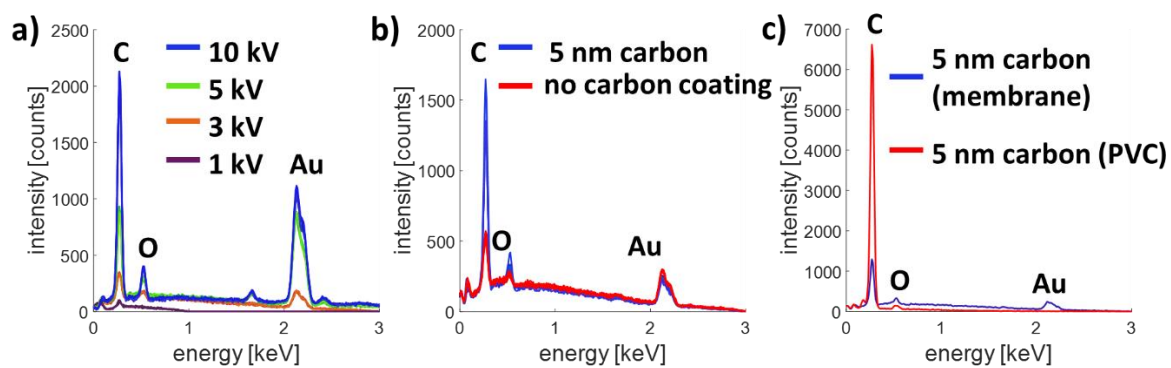
**Fig. S1** Attenuated total reflection (ATR) Fourier transform - infrared (FT-IR) absorption spectra of the polyethylene (PE) and polyvinyl chloride (PVC) particles. Stock suspensions were filtered, and microplastic particles transferred to glass slides. ATR measurements were then conducted on dried microplastic powders. Assignments of the indicated peaks are provided in Table S1. For ATR measurements, a  $\mu$ -FT-IR system (Cary 670 FTIR instrument, Cary 610 IR microscope, Agilent) was used. Measurements were performed from 4000 to 400  $\text{cm}^{-1}$  at a spectral resolution of 4  $\text{cm}^{-1}$ . Spectra from the background and from the microplastic powders were integrated 64 times.



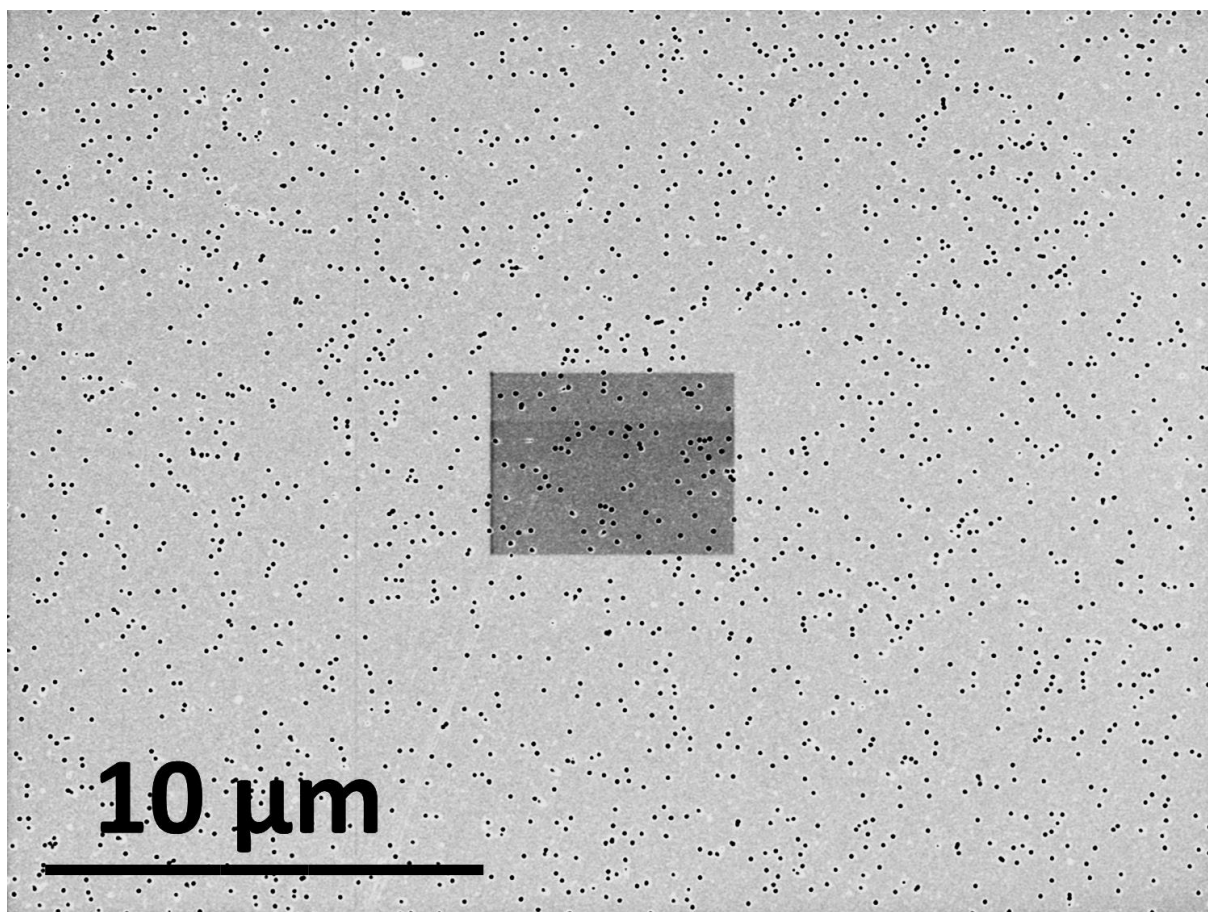
**Fig. S2** Twenty-five individual measurements from pristine polyethylene (PE) pellets which were ground by Nanofract. X-rays were generated with a Rhodium (Rh) tube (M4 Tornado, Buker), explaining the oscillations between 2.5 and 3keV. Calcium (Ca) was clearly detected in all measurements. Inset (top right) shows an optical image of the PE pellets.



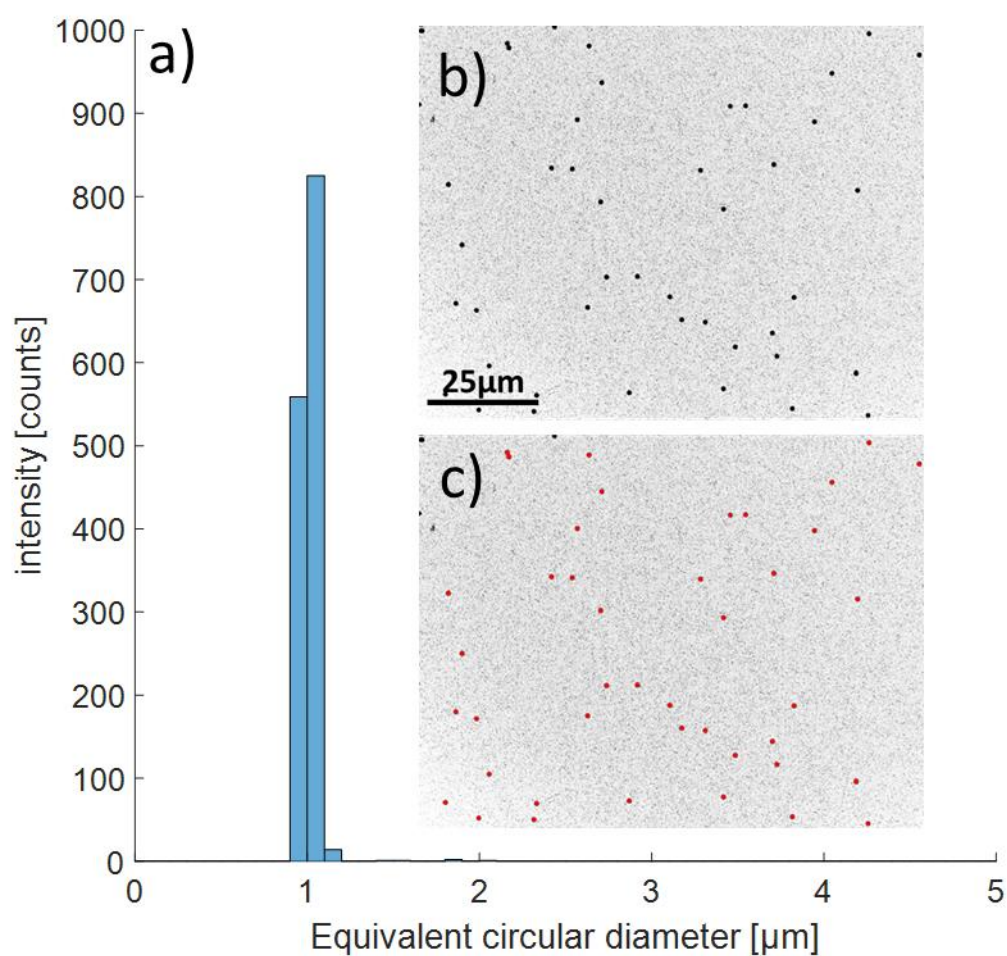
**Fig. S3** Secondary electron (SE) image (InLens detector) (a) and backscattered electron (BSE) image (InLens energy selective backscattered electron (EsB)) detector (bias set to 1500V) (b) of a polyethylene (PE) – polyvinyl chloride (PVC) – soil extract deposited on a gold (40nm) and carbon (5nm) coated polycarbonate membrane. The SE image of the particles (a), reflecting their morphology / topography and thus consisting of a suite of different greyscales - is difficult to threshold. In the BSE image (b), reflecting the average atomic weight, the particles appear in an even greyscale (dark) and well separated from the bright background of the Au-coated polycarbonate membrane. The grey dots represent the holes of the polycarbonate membrane. Acceleration voltage: 3kV.



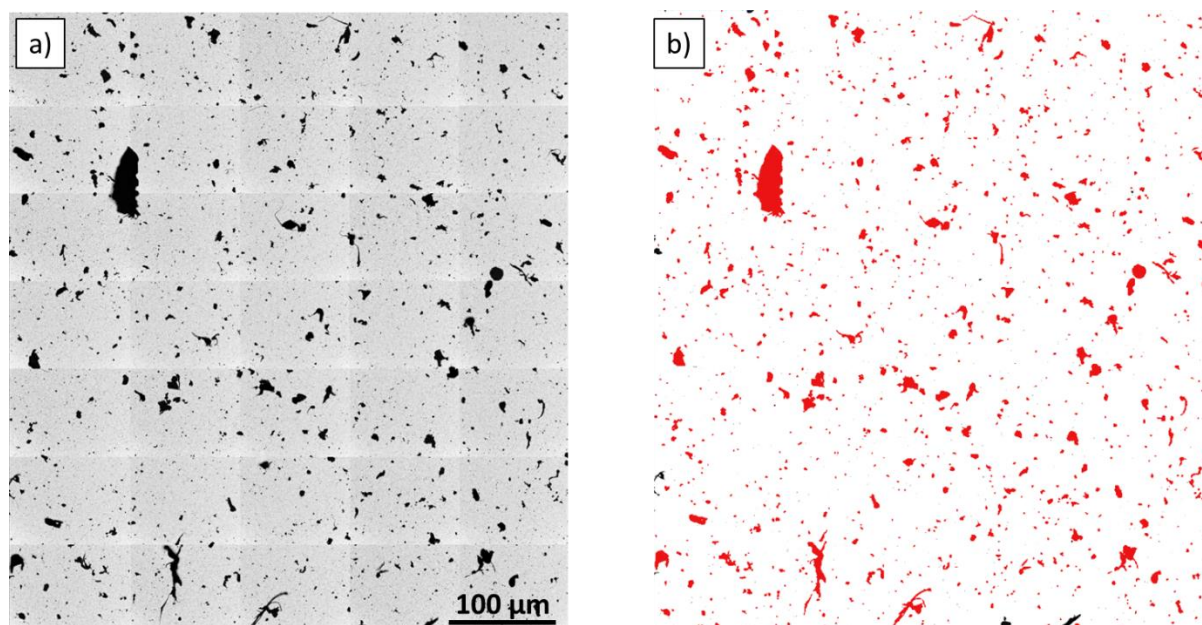
**Fig. S4** a) Impact of increasing acceleration voltage (1, 3, 5, 10 kV) on the x-ray signals of a polycarbonates (PC) membrane coated with 40 nm of gold (Au). Spectra were recorded for 1 s and using a current of 1 nA and a process time of 4. b) Impact of an additional 5 nm carbon (C) layer on top of the 40 nm Au layer. c) Spectra from the PC membrane coated with 40 nm Au and 5 nm C (blue) and from a polyvinyl chloride (PVC) particle (diameter ~4 μm) deposited on the Au coated PC membrane and coated with 5 nm C. The spectra of b) and c) were recorded at an acceleration voltage of 3 kV, a current of 800 pA and a live time of 2 s. The process time was set to '5'.



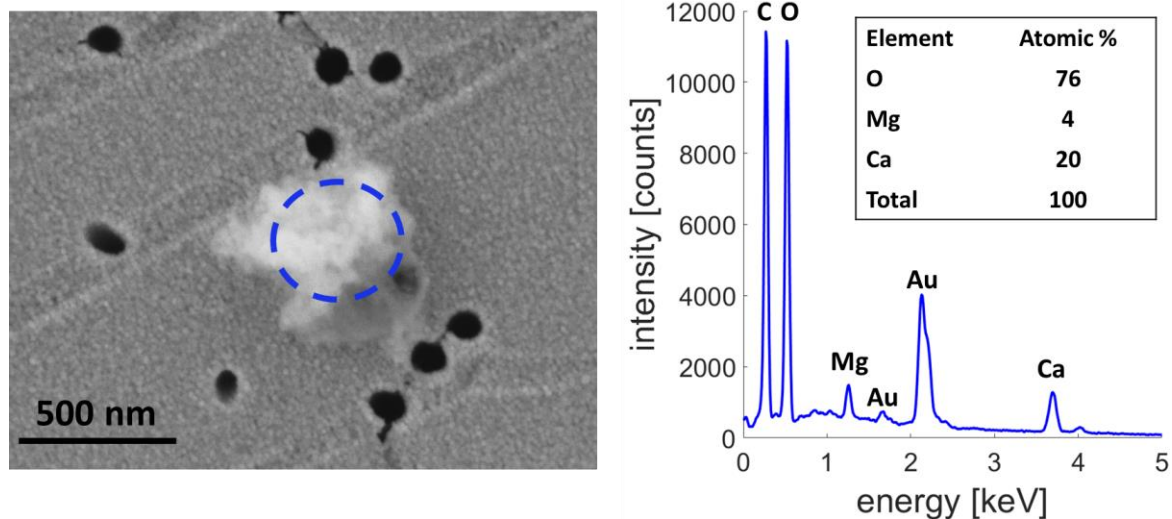
**Fig. S5** Secondary electron image (InLense detector) of a gold (40nm) coated polycarbonate membrane, recorded after exposing a smaller area (dark area in the center of the image) to the electron beam. The dark area in the center of the image represents the carbon contamination that resulted from the previous exposure of this area to the electron beam (acceleration voltage: 3kV, current: 800pA).



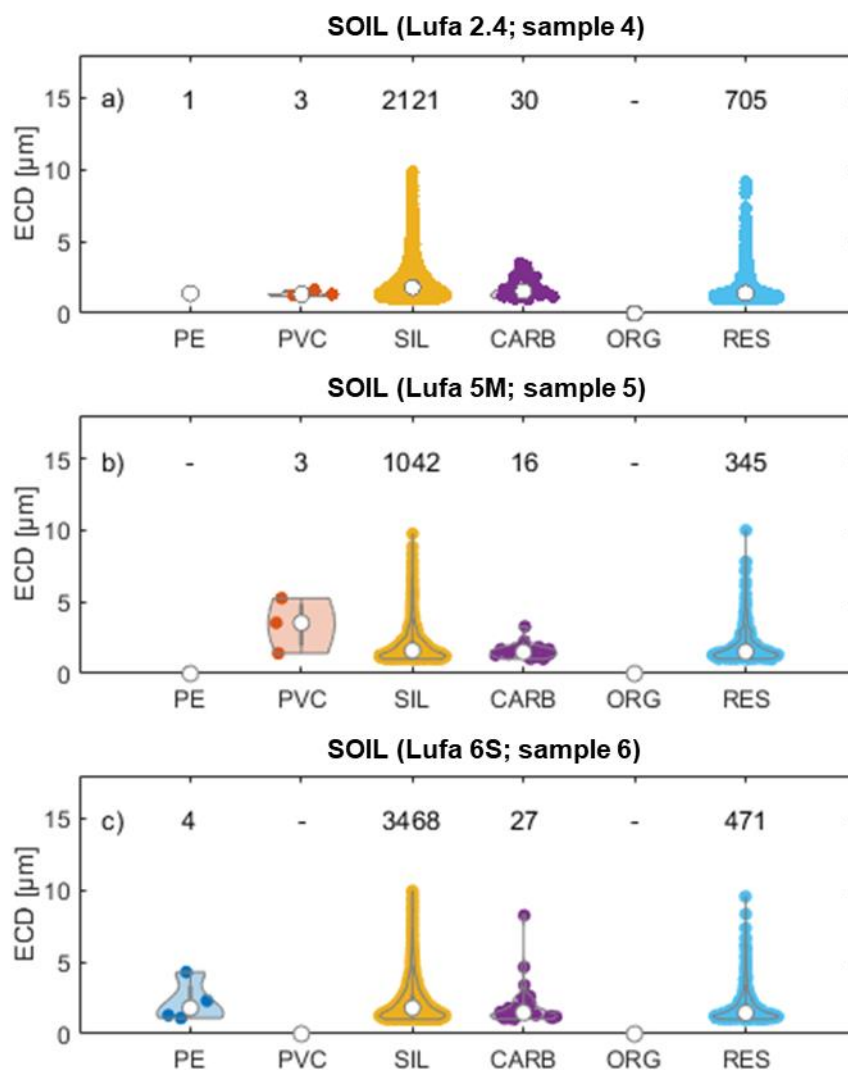
**Fig. S6** a) Particle size distribution of 1 $\mu\text{m}$  polystyrene (PS) particles (Polybead® Microspheres (No: 07310-15), Polysciences, USA) from a stock suspension filtered on 40nm gold-coated polycarbonate membranes (0.1  $\mu\text{m}$  pore diameter, 25mm diameter, Nucleopore). Total number of particles detected = 1868, mean diameter = 1.1 $\mu\text{m}$  (reported value from the manufacturer: 1.06 $\mu\text{m}$ ). b) Backscattered electron image of the PS particles using the same operational conditions as for the main experiments and c) particles automatically detected (red dots) using the software package AZtec-Feature (AZtec v6.0, Oxford Instruments, UK).



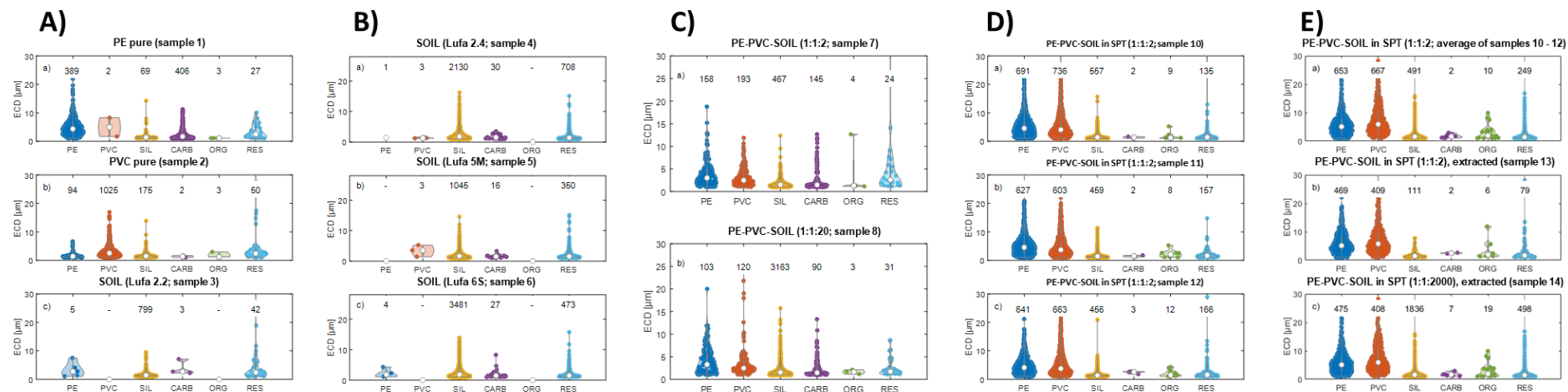
**Fig. S7** a) Mosaic image of backscattered electron (BSE) images (7×5). Shown are particles from sample 7 (PE-PVC-SOIL 1:1:2, Table 1 in the main manuscript) deposited on a gold (40nm) coated polycarbonate membrane and coated with 5nm of carbon before analysis, b) identified particles are shown in red and the background has been removed for clarity.



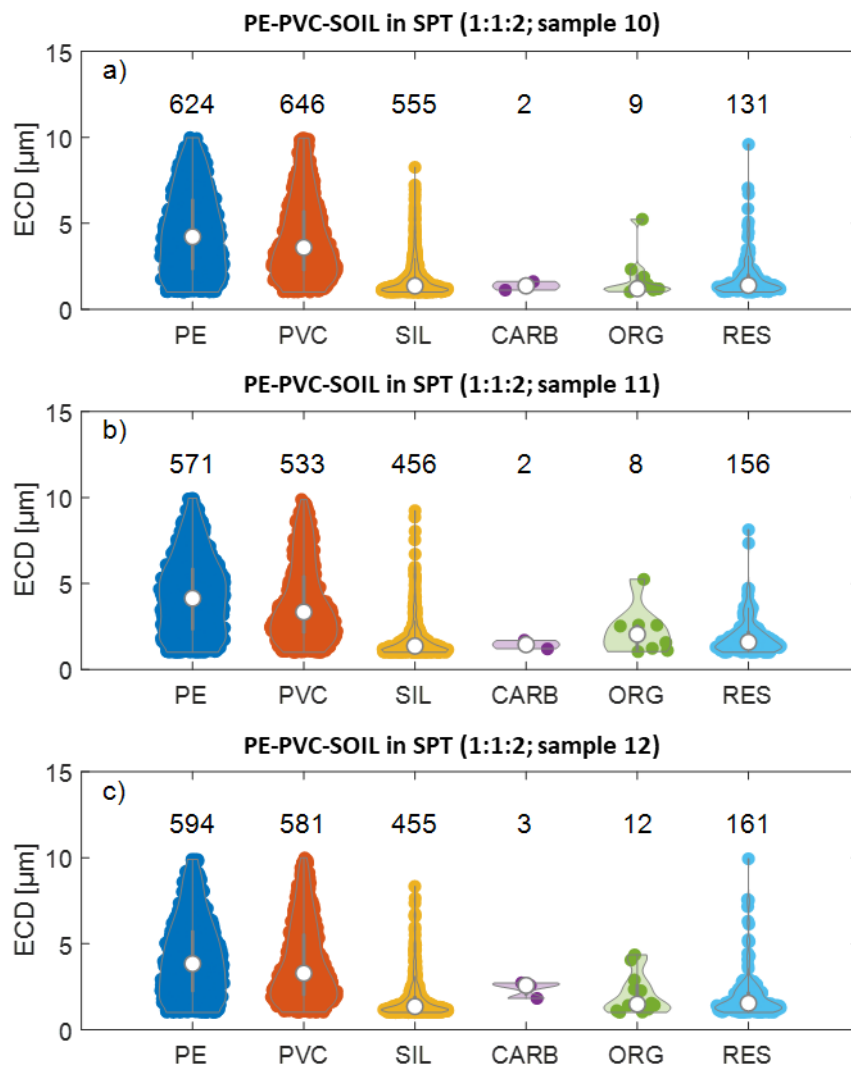
**Fig. S8** Secondary electron image of a calcium carbonate particle (left) and energy dispersive x-ray spectrum (right) of the area marked with the dashed blue circle. The inset on the right shows the elemental composition of the particle, whereas carbon (C) and gold (Au) were used for deconvolution only. The stoichiometry of  $O:(Ca+Mg) = 3:1$  fits well to the stoichiometry of (magnesium bearing)-calcite  $((Ca,Mg)CO_3)$ .



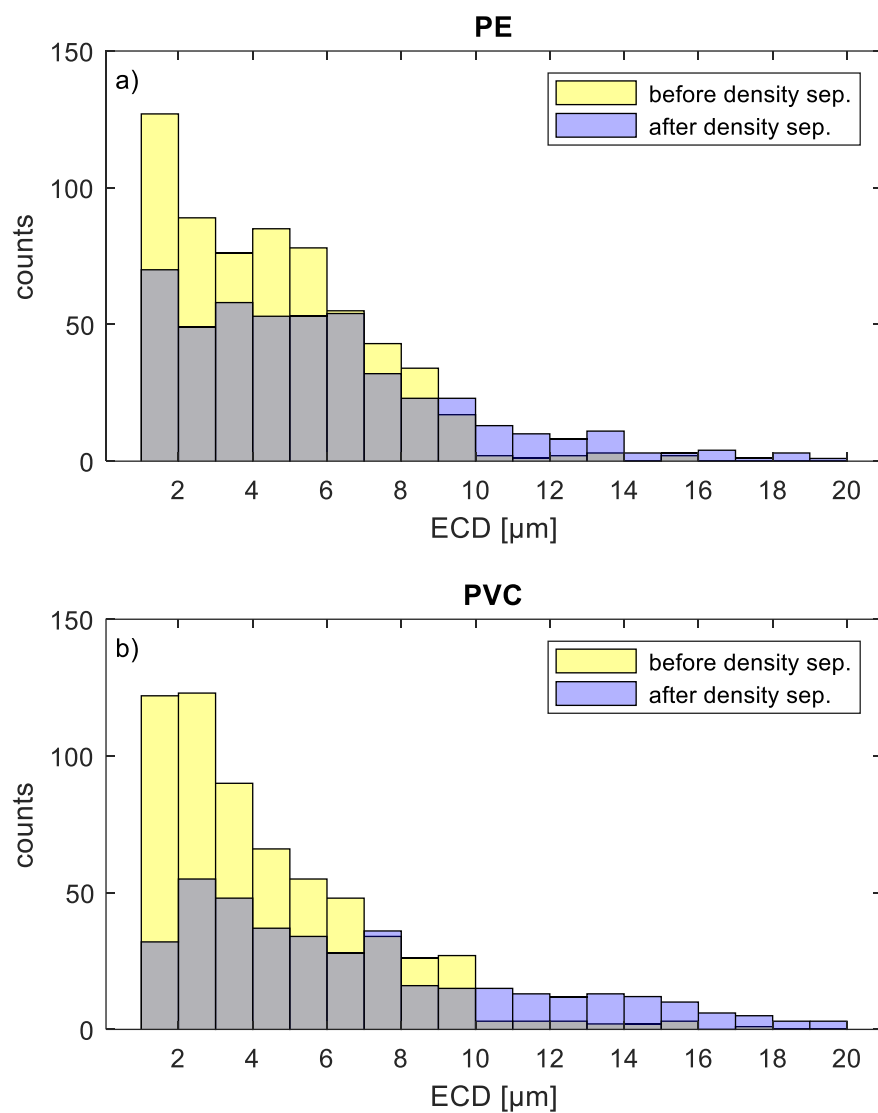
**Fig. S9** Violin plots of particles detected in additional soil extracts a) LUFA 2.4 (sample 4), b) 5M (sample 5) and c) 6S (sample 6) filtered on gold coated (40nm) polycarbonate (PC) membranes. The PC membranes with the deposited particles were coated with an additional layer of carbon (5nm) before analysis. 'SIL' refers to silicate particles (which dominated the soil particles), 'CARB' to carbonates, 'ORG' to organic material containing nitrogen and 'RES' represents the residual particle category (as assigned in Fig. 2). Numbers on top of the violin plots refer to the number of particles of the corresponding category. A lower size threshold for the equivalent circular diameter (ECD) of 1 $\mu$ m and an upper threshold of 10 $\mu$ m was set for data analysis. Data with an upper size limit extended to 100 $\mu$ m are provided in Table S3 and Fig. S10B. See Table 1 for a description of the individual samples.



**Fig. S10** Violin plots of the different particle categories including particle sizes between 1 $\mu$ m and 100 $\mu$ m. A): Stock suspensions of a) Polyethylene (PE, sample 1), b) Polyvinyl chloride (PVC, sample 2), c) Soil (LUFA 2.2, sample 3). B) Additional soils a) LUFA 2.4 (sample 4), b) LUFA 5M (sample 5) c) LUFA 6S (sample 6). C) Mixtures of PE, PVC and soil particles at ratios of a) 1 (PE) : 1 (PVC) : 2 (Soil) (sample 7) and b) 1 (PE) : 1 (PVC) : 20 (Soil) (sample 8). D) Triplicates (a-c) of a 1 (PE) : 1 (PVC) : 2 (soil) mixture in sodium polytungstate (SPT) (samples 10-12). E) a) Average of triplicate measurements (from D), b) after density separation (sample 13) and c) after 1000 $\times$  dilution in a soil suspension and following density separation (sample 14). Numbers on top of the individual violin plots refer to the number of detected particles in the respective categories. See Table 1 for a description of the individual samples. Volumes of PE and PVC stock suspension in D) and E) were always the same and thus, respective numbers directly represent the recoveries. 'SIL': silicate particles (which dominated the soil particles), 'CARB': carbonates, 'ORG': organic material containing nitrogen and 'RES': residual particle category (as assigned in Fig. 2). ECD: Equivalent circular diameter.



**Fig. S11** Violin plots of the particles detected from mixtures of polyethylene (PE), polyvinyl chloride (PVC) and soil stock suspensions (nominal ratios: 1:1:2, all in sodium polytungstate) directly filtered on gold coated polycarbonate (PC) membranes. The PC membranes with the deposited particles were coated with a 5nm carbon layer before analysis. The three panels represent triplicate samples made from the same stock suspensions (samples 10-12). 'SIL' refers to silicate particles (which dominated the soil particles), 'CARB' to carbonates, 'ORG' to organic material containing nitrogen and 'RES' represents the residual particle category (as assigned in Fig. 2). Numbers on top of the violin plots refer to the number of particles of the corresponding category. A lower size threshold for the equivalent circular diameter (ECD) of 1 $\mu$ m and an upper threshold of 10 $\mu$ m was set for data analysis. Data with an upper size limit extended to 100 $\mu$ m are provided in the supporting information (Table S3 and Fig. S10D).



**Fig. S12** Histogram of the equivalent circular diameters (ECD) of a) polyethylene (PE) and b) polyvinyl chloride (PVC) before density separation (samples 10-12, Table 1) and after the density separation (sample 13, Table 1).

## Tables:

**Table S1** Assignment of the major peaks of the polyethylene and the polyvinylchloride infrared absorption spectra, taken from [1, 2].

| Polyethylene                         |                                  |
|--------------------------------------|----------------------------------|
| Absorption peak ( $\text{cm}^{-1}$ ) | Assignment                       |
| 2918, 2850                           | $\text{CH}_2$ asymmetric stretch |
| 1471                                 | C-H bending                      |
| 717                                  | $\text{CH}_2$ rocking            |
| Polyvinylchloride                    |                                  |
| 2970                                 | stretching C-H of $\text{CHCl}$  |
| 2916                                 | stretching C-H of $\text{CH}_2$  |
| 1427                                 | deformation $\text{CH}_2$        |
| 1328, 1250                           | deformation C-H of $\text{CHCl}$ |
| 1095                                 | stretching C-C                   |
| 966                                  | rocking $\text{CH}_2$            |
| 692                                  | stretching C-Cl                  |

**Table S2:** Experimental parameters and results from recovery experiments using polystyrene beads (Count Check Beads, No: 05-4011\_R, Sysmex Partec GmbH). 'N detected' refers to the number of particles detected based on automated scanning electron microscopy analysis, 'conc. measured' refers to particle concentration calculated based on the number of particles detected and 'conc. stock' refers to the certified particle concentration of the stock suspension. The recovery was calculated relative to the stock suspension.

| Sample              | # sites<br>[-] | # images/site<br>[-] | #images<br>[-] | image width<br>[μm] | image height<br>[μm] | area<br>measured<br>[mm <sup>2</sup> ] | filter<br>diameter<br>[mm] | filter<br>area<br>[mm <sup>2</sup> ] | filtered<br>volume<br>[mL] | N<br>detected<br>[#] | conc.<br>meas<br>[#/mL] | conc.<br>stock<br>[#/mL] | recovery<br>[%] |
|---------------------|----------------|----------------------|----------------|---------------------|----------------------|----------------------------------------|----------------------------|--------------------------------------|----------------------------|----------------------|-------------------------|--------------------------|-----------------|
| CCB 01 <sup>a</sup> | 5              | 35                   | 175            | 236                 | 184                  | 7.6                                    | 16                         | 201.1                                | 4.5                        | 3431                 | 20173                   | 23140                    | 87              |
| CCB 02 <sup>a</sup> | 5              | 35                   | 175            | 236                 | 184                  | 7.6                                    | 16                         | 201.1                                | 4.5                        | 3478                 | 20449                   | 23140                    | 88              |

<sup>a</sup>: measurements of duplicate filters

**Table S3** Imaging parameters for the individual samples. In addition, the number of different particle types and the total number of particles detected are provided. N (X) refers to the number of particles detected in the respective particle class X, whereas PE: Polyethylene, PVC: Polyvinyl chloride, SIL: silicates, CARB: carbonates, ORG: organic particles, RES: residual particle category. The numbers in parentheses refer to particle numbers between 1µm and 100µm, the numbers in front of the parentheses refer to the particle number between 1µm and 10µm. Each site consists of 5×7 images, and each image was 113µm×88.5µm. Images were recorded with a 10% overlap. The corrected area/site, thus, comes to 0.29mm<sup>2</sup>. IPA: isopropanol, EtOH: ethanol, SPT: sodium polytungstate.

| sample number   | description                              | # sites<br>[-] | total area<br>[mm <sup>2</sup> ] | N (PE)<br>[#] | N (PVC)<br>[#] | N (SIL)<br>[#] | N (CARB)<br>[#] | N (ORG)<br>[#] | N (RES)<br>[#] | N (Total)<br>[#] |
|-----------------|------------------------------------------|----------------|----------------------------------|---------------|----------------|----------------|-----------------|----------------|----------------|------------------|
| 1 <sup>a</sup>  | PE pure                                  | 3              | 0.88                             | 358 (389)     | 2 (2)          | 68 (69)        | 401 (406)       | 3 (3)          | 26 (27)        | 858 (896)        |
| 2 <sup>a</sup>  | PVC pure                                 | 5              | 1.47                             | 94 (94)       | 1006 (1025)    | 174 (175)      | 2 (2)           | 3 (3)          | 43 (50)        | 1322 (1349)      |
| 3 <sup>a</sup>  | SOIL (Lufa 2.2)                          | 3              | 0.88                             | 5 (5)         | 0 (0)          | 799 (799)      | 3 (3)           | 0 (0)          | 38 (42)        | 845 (849)        |
| 4 <sup>a</sup>  | SOIL (Lufa 2.4)                          | 5              | 1.47                             | 1(1)          | 3(3)           | 2121(2130)     | 30(30)          | 0(0)           | 705(708)       | 2860(2872)       |
| 5 <sup>a</sup>  | SOIL (Lufa 5M)                           | 5              | 1.47                             | 0(0)          | 3(3)           | 1042(1045)     | 16(16)          | 0(0)           | 345(350)       | 1406(1414)       |
| 6 <sup>a</sup>  | SOIL (Lufa 6S)                           | 5              | 1.47                             | 4(4)          | 0(0)           | 3468(3481)     | 27(27)          | 0(')           | 471(473)       | 3970(3985)       |
| 7 <sup>a</sup>  | PE-PVC-SOIL (1:1:2)                      | 1              | 0.29                             | 148 (158)     | 191 (193)      | 466 (467)      | 141 (145)       | 3 (4)          | 22 (24)        | 971 (991)        |
| 8 <sup>a</sup>  | PE-PVC-SOIL (1:1:20)                     | 1              | 0.29                             | 97 (103)      | 113 (120)      | 3157 (3163)    | 88 (90)         | 3 (3)          | 31 (31)        | 3489 (3510)      |
| 9 <sup>b</sup>  | PE-PVC-SAND (2:1:3) <sup>d</sup>         | 5              | 1.47                             | 440(446)      | 541(589)       | 1801(1805)     | 3(3)            | 34(34)         | 182(182)       | 3001(3059)       |
| 10 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 5              | 1.47                             | 624 (691)     | 646 (736)      | 555 (557)      | 2 (2)           | 9 (9)          | 131 (135)      | 1967 (2130)      |
| 11 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 5              | 1.47                             | 571 (627)     | 533 (603)      | 456 (459)      | 2 (2)           | 8 (8)          | 156 (157)      | 1726 (1856)      |
| 12 <sup>c</sup> | PE-PVC-SOIL in SPT(1:1:2) <sup>e</sup>   | 5              | 1.47                             | 594 (641)     | 581 (663)      | 455 (456)      | 3 (3)           | 12 (12)        | 161 (166)      | 1806 (1941)      |
| 13 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2), extracted    | 5              | 1.47                             | 396 (469)     | 313 (409)      | 111 (111)      | 2 (2)           | 5 (6)          | 72 (79)        | 899 (1076)       |
| 14 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2000), extracted | 5              | 1.47                             | 415 (475)     | 301 (408)      | 1824 (1836)    | 7 (7)           | 19 (19)        | 479 (498)      | 3045 (3243)      |

<sup>a</sup>: Stock series 1: Individual suspensions of PE (~3,000#/µL), PVC (~9,000 #/µL) and soil particles (~60,000 #/µL), PE and soil prepared in EtOH, PVC prepared in IPA.

<sup>b</sup>: Stock series 2: Individual suspensions of PE (~500#/µL), PVC (~1,400 #/µL) and sand particles (~14 #/µL), PE and sand prepared in EtOH, PVC prepared in isopropanol IPA. Stocks made with sieved sand instead of soils and used for comparison with Raman measurements.

<sup>c</sup>: Stock series 3: Individual suspensions of PE (~800#/µL), PVC (~1,000 #/µL) and soil particles (~200,000 #/µL), all prepared in SPT solution (density 1.6g/mL).

<sup>d</sup>: Due to a shortage of PVC stock suspension, a PE:PVC ratio of 1:1 was not achievable anymore.

<sup>e</sup>: Samples made in triplicates.

**Table S4:** Measured and calculated particle number concentrations, recoveries, and particle ratios for all samples for the size range 1-10 $\mu$ m. 'PE', 'PVC' and 'SIL' refers to polyethylene, polyvinyl chloride and silicates respectively. Particle concentrations of the stock suspensions ('c (PE, PVC, SIL)') in samples 1-3) were calculated based on the number of PE, PVC and SIL particles detected by automated scanning electron microscopy analyses ('[#]') in combination with the filtered volumes ('V') and number of areas analyzed ('N (areas)') (see eq(1) in section S2). Each area consisted of 7 x 5 images (each 113 $\mu$ m x 88.5 $\mu$ m) with an overlap of 10% (total area given in Table S3). The concentrations of the stock suspensions were then used to calculate the particle number concentrations ('c (PE, PVC, SIL)'), the recoveries ('r (PE, PVC, SIL)'), the expected particle numbers per filter ('N<sub>e</sub>(PE, PVC, SIL, flt)'), and the expected ratios ('ratio<sub>e</sub>') in samples 7 and 8. The same approach was used for samples 10 – 14, whereas the average of the triplicate measurements (sample 10 – 12) was used to calculate the particle number concentrations of the stock suspension. 'N<sub>m</sub> (PE, PVC, SIL, flt)') refers to the number of the respective particles on the filter derived from the measured number of particles of the respective filters. '[–]' refers to data which were either meaningless or not accessible.

| sample number   | description                              | PE<br>[#] | V(PE)<br>[ $\mu$ L] | PVC<br>[#] | V(PVC)<br>[ $\mu$ L] | SIL<br>[#] | V(SIL)<br>[ $\mu$ L] | N (areas)<br>[#] | c (PE)<br>[#/mL] | c (PVC)<br>[#/mL] | c (SIL)<br>[#/mL] | r(PE)<br>[%] | r(PVC)<br>[%] | r(SIL)<br>[%] | N <sub>m</sub> (PE,flt)<br>[#] | N <sub>e</sub> (PE,flt)<br>[#] | N <sub>m</sub> (PVC,flt)<br>[#] | N <sub>e</sub> (PVC,flt)<br>[#] | N <sub>m</sub> (SIL,flt)<br>[#] | N <sub>e</sub> (SIL,flt)<br>[#] | ratio <sub>m</sub><br>(PE/PVC) | ratio <sub>e</sub><br>(PE/PVC) | ratio <sub>m</sub><br>(PE/SIL) | ratio <sub>e</sub><br>(PE/SIL) | ratio <sub>m</sub><br>(PVC/SIL) | ratio <sub>e</sub><br>(PVC/SIL) |
|-----------------|------------------------------------------|-----------|---------------------|------------|----------------------|------------|----------------------|------------------|------------------|-------------------|-------------------|--------------|---------------|---------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|
| 1 <sup>a</sup>  | PE pure                                  | 358       | 200                 | 2          | 0                    | 68         | 0                    | 3                | 4.07E+05         | -                 | -                 | 100          | -             | -             | 8.15E+04                       | 8.15E+04                       | -                               | -                               | -                               | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 2 <sup>a</sup>  | PVC pure                                 | 94        | 0                   | 1006       | 50                   | 174        | 0                    | 5                | -                | 2.75E+06          | -                 | -            | 100           | -             | -                              | -                              | 1.37E+05                        | 1.37E+05                        | -                               | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 3 <sup>a</sup>  | SOIL (Lufa 2.2)                          | 5         | 0                   | 0          | 0                    | 799        | 10                   | 3                | -                | -                 | 1.82E+07          | -            | -             | 100           | -                              | -                              | -                               | -                               | 1.82E+05                        | 1.82E+05                        | -                              | -                              | -                              | -                              | -                               | -                               |
| 4 <sup>a</sup>  | SOIL (Lufa 2.4)                          | 1         | 0                   | 3          | 0                    | 2121       | 10                   | 5                | -                | -                 | 2.90E+07          | -            | -             | -             | -                              | -                              | -                               | -                               | 2.90E+05                        | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 5 <sup>a</sup>  | SOIL (Lufa 5M)                           | 0         | 0                   | 3          | 0                    | 1042       | 10                   | 5                | -                | -                 | 1.42E+07          | -            | -             | -             | -                              | -                              | -                               | -                               | 1.42E+05                        | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 6 <sup>a</sup>  | SOIL (Lufa 6S)                           | 4         | 0                   | 0          | 0                    | 3468       | 10                   | 5                | -                | -                 | 4.74E+07          | -            | -             | -             | -                              | -                              | -                               | -                               | 4.74E+05                        | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 7 <sup>a</sup>  | PE-PVC-SOIL (1:1:2)                      | 148       | 200                 | 191        | 50                   | 466        | 20                   | 1                | 5.05E+05         | 2.61E+06          | 1.59E+07          | 124          | 95            | 87            | 1.01E+05                       | 8.15E+04                       | 1.30E+05                        | 1.37E+05                        | 3.18E+05                        | 3.64E+05                        | 0.77                           | 0.59                           | 0.32                           | 0.22                           | 0.41                            | 0.38                            |
| 8 <sup>a</sup>  | PE-PVC-SOIL (1:1:20)                     | 97        | 200                 | 113        | 50                   | 3157       | 200                  | 1                | 3.31E+05         | 1.54E+06          | 1.08E+07          | 81           | 56            | 59            | 6.62E+04                       | 8.15E+04                       | 7.72E+04                        | 1.37E+05                        | 2.16E+06                        | 3.64E+06                        | 0.86                           | 0.59                           | 0.03                           | 0.02                           | 0.04                            | 0.04                            |
| 9 <sup>b</sup>  | PE-PVC-SAND (2:1:3) <sup>d</sup>         | 440       | 750                 | 541        | 150                  | 1801       | 20000                | 5                | 8.01E+04         | 4.93E+05          | 1.23E+04          | -            | -             | -             | 6.01E+04                       | -                              | 7.39E+04                        | -                               | 2.46E+05                        | -                               | 0.81                           | -                              | 0.24                           | -                              | 0.3                             | -                               |
| 10 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 624       | 300                 | 646        | 250                  | 555        | 2.6                  | 5                | 2.84E+05         | 3.53E+05          | 2.92E+07          | 105          | 110           | 114           | 8.52E+04                       | 8.14E+04                       | 8.82E+04                        | 8.01E+04                        | 7.58E+04                        | 6.67E+04                        | 0.97                           | 1.02                           | 1.12                           | 1.22                           | 1.16                            | 1.20                            |
| 11 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 571       | 300                 | 533        | 250                  | 456        | 2.6                  | 5                | 2.60E+05         | 2.91E+05          | 2.40E+07          | 96           | 91            | 93            | 7.80E+04                       | 8.14E+04                       | 7.28E+04                        | 8.01E+04                        | 6.23E+04                        | 6.67E+04                        | 1.07                           | 1.02                           | 1.25                           | 1.22                           | 1.17                            | 1.20                            |
| 12 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 594       | 300                 | 581        | 250                  | 455        | 2.6                  | 5                | 2.70E+05         | 3.17E+05          | 2.39E+07          | 100          | 99            | 93            | 8.11E+04                       | 8.14E+04                       | 7.94E+04                        | 8.01E+04                        | 6.21E+04                        | 6.67E+04                        | 1.02                           | 1.02                           | 1.31                           | 1.22                           | 1.28                            | 1.20                            |
| 13 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2), extracted    | 396       | 300                 | 313        | 250                  | 111        | 2.6                  | 5                | 1.80E+05         | 1.71E+05          | 5.83E+06          | 66           | 53            | 23            | 5.41E+04                       | 8.14E+04                       | 4.28E+04                        | 8.01E+04                        | 1.52E+04                        | 6.67E+04                        | 1.27                           | 1.02                           | 3.57                           | 1.22                           | 2.82                            | 1.20                            |
| 14 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2000), extracted | 415       | 300                 | 301        | 250                  | 1824       | 2600                 | 5                | 1.89E+05         | 1.64E+05          | 9.58E+04          | 70           | 51            | 0.4           | 5.67E+04                       | 8.14E+04                       | 4.11E+04                        | 8.01E+04                        | 2.49E+05                        | 6.67E+07                        | 1.38                           | 1.02                           | 0.23                           | 0.0012                         | 0.17                            | 0.0012                          |

<sup>a</sup>: Stock series 1: Individual suspensions of PE (~3,000 #/ $\mu$ L), PVC (~9,000 #/ $\mu$ L) and soil particles (~60,000 #/ $\mu$ L), PE and soil prepared in EtOH, PVC prepared in IPA.

<sup>b</sup>: Stock series 2: Individual suspensions of PE (~500 #/ $\mu$ L), PVC (~1,400 #/ $\mu$ L) and sand particles (~14 #/ $\mu$ L), PE and sand prepared in EtOH, PVC prepared in isopropanol IPA. Stocks made with sieved sand instead of soils and used for comparison with Raman measurements.

<sup>c</sup>: Stock series 3: Individual suspensions of PE (~800 #/ $\mu$ L), PVC (~1,000 #/ $\mu$ L) and soil particles (~200,000 #/ $\mu$ L), all prepared in SPT solution (density 1.6g/mL).

<sup>d</sup>: Due to a shortage of PVC stock suspension, a PE:PVC ratio of 1:1 was not achievable anymore.

<sup>e</sup>: Samples made in triplicates.

**Table S5:** Measured and calculated particle number concentrations, recoveries, and particle ratios for all samples for the size range 1-100µm. 'PE', 'PVC' and 'SIL' refers to polyethylene, polyvinyl chloride and silicates respectively. Particle concentrations of the stock suspensions ('c (PE, PVC, SIL)') in samples 1-3) were calculated based on the number of PE, PVC and SIL particles detected by automated scanning electron microscopy analyses ('[#]') in combination with the filtered volumes ('V') and number of areas analyzed ('N (areas)') (see eq(1) in section S2). Each area consisted of 7 x 5 images (each 113µm x 88.5µm) with an overlap of 10% (total area given in Table S3). The concentrations of the stock suspensions were then used to calculate the particle number concentrations ('c (PE, PVC, SIL)'), the recoveries ('r (PE, PVC, SIL)'), the expected particle numbers per filter ('N<sub>e</sub>(PE, PVC, SIL, flt)'), and the expected ratios ('ratio<sub>e</sub>') in samples 7 and 8. The same approach was used for samples 10 – 14, whereas the average of the triplicate measurements (sample 10 – 12) was used to calculate the particle number concentrations of the stock suspension. 'N<sub>m</sub> (PE, PVC, SIL, flt)') refers to the number of the respective particles on the filter derived from the measured number of particles of the respective filters. '[–]' refers to data which were either meaningless or not accessible.

| sample number   | description                              | PE<br>[#] | V(PE)<br>[µL] | PVC<br>[#] | V(PVC)<br>[µL] | SIL<br>[#] | V(SIL)<br>[µL] | N (areas)<br>[#] | c (PE)<br>[#/mL] | c (PVC)<br>[#/mL] | c (SIL)<br>[#/mL] | r(PE)<br>[%] | r(PVC)<br>[%] | r(SIL)<br>[%] | N <sub>m</sub> (PE,flt)<br>[#] | N <sub>e</sub> (PE,flt)<br>[#] | N <sub>m</sub> (PVC,flt)<br>[#] | N <sub>e</sub> (PVC,flt)<br>[#] | N <sub>m</sub> (SIL,flt)<br>[#] | N <sub>e</sub> (SIL,flt)<br>[#] | ratio <sub>m</sub><br>(PE/PVC) | ratio <sub>e</sub><br>(PE/PVC) | ratio <sub>m</sub><br>(PE/SIL) | ratio <sub>e</sub><br>(PE/SIL) | ratio <sub>m</sub><br>(PVC/SIL) | ratio <sub>e</sub><br>(PVC/SIL) |
|-----------------|------------------------------------------|-----------|---------------|------------|----------------|------------|----------------|------------------|------------------|-------------------|-------------------|--------------|---------------|---------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|
| 1 <sup>a</sup>  | PE pure                                  | 389       | 200           | 2          | 0              | 69         | 0              | 3                | 4.43E+05         | -                 | -                 | 100          | -             | -             | 8.86E+04                       | 8.86E+04                       | -                               | -                               | -                               | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 2 <sup>a</sup>  | PVC pure                                 | 94        | 0             | 1025       | 50             | 175        | 0              | 5                | -                | 2.80E+06          | -                 | -            | 100           | -             | -                              | -                              | 1.40E+05                        | 1.40E+05                        | -                               | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 3 <sup>a</sup>  | SOIL (Lufa 2.2)                          | 5         | 0             | 0          | 0              | 799        | 10             | 3                | -                | -                 | 1.82E+07          | -            | -             | 100           | -                              | -                              | -                               | -                               | 1.82E+05                        | 1.82E+05                        | -                              | -                              | -                              | -                              | -                               | -                               |
| 4 <sup>a</sup>  | SOIL (Lufa 2.4)                          | 1         | 0             | 3          | 0              | 2130       | 10             | 5                | -                | -                 | 2.91E+07          | -            | -             | 160           | -                              | -                              | -                               | -                               | 2.91E+05                        | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 5 <sup>a</sup>  | SOIL (Lufa 5M)                           | 0         | 0             | 3          | 0              | 1045       | 10             | 5                | -                | -                 | 1.43E+07          | -            | -             | 78            | -                              | -                              | -                               | -                               | 1.43E+05                        | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 6 <sup>a</sup>  | SOIL (Lufa 6S)                           | 4         | 0             | 0          | 0              | 3481       | 10             | 5                | -                | -                 | 4.75E+07          | -            | -             | 261           | -                              | -                              | -                               | -                               | 4.75E+05                        | -                               | -                              | -                              | -                              | -                              | -                               | -                               |
| 7 <sup>a</sup>  | PE-PVC-SOIL (1:1:2)                      | 158       | 200           | 193        | 50             | 467        | 20             | 1                | 5.40E+05         | 2.64E+06          | 1.59E+07          | 122          | 94            | 88            | 1.08E+05                       | 8.86E+04                       | 1.32E+05                        | 1.40E+05                        | 3.19E+05                        | 3.64E+05                        | 0.82                           | 0.63                           | 0.34                           | 0.24                           | 0.41                            | 0.38                            |
| 8 <sup>a</sup>  | PE-PVC-SOIL (1:1:20)                     | 103       | 200           | 120        | 50             | 3163       | 200            | 1                | 3.52E+05         | 1.64E+06          | 1.08E+07          | 79           | 59            | 59            | 7.03E+04                       | 8.86E+04                       | 8.20E+04                        | 1.40E+05                        | 2.16E+06                        | 3.64E+06                        | 0.86                           | 0.63                           | 0.03                           | 0.02                           | 0.04                            | 0.04                            |
| 9 <sup>b</sup>  | PE-PVC-SAND (2:1:3) <sup>d</sup>         | 446       | 750           | 589        | 150            | 1805       | 20000          | 5                | 8.12E+04         | 5.36E+05          | 1.23E+04          | -            | -             | -             | 6.09E+04                       | -                              | 8.04E+04                        | -                               | 2.47E+05                        | -                               | 0.76                           | -                              | 0.25                           | -                              | 0.33                            | -                               |
| 10 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 691       | 300           | 736        | 250            | 557        | 2.6            | 5                | 3.15E+05         | 4.02E+05          | 2.93E+07          | 106          | 110           | 114           | 9.44E+04                       | 8.92E+04                       | 1.01E+05                        | 9.11E+04                        | 7.61E+04                        | 6.70E+04                        | 0.94                           | 0.98                           | 1.24                           | 1.33                           | 1.32                            | 1.36                            |
| 11 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2) <sup>e</sup>  | 627       | 300           | 603        | 250            | 459        | 2.6            | 5                | 2.85E+05         | 3.29E+05          | 2.41E+07          | 96           | 90            | 94            | 8.56E+04                       | 8.92E+04                       | 8.24E+04                        | 9.11E+04                        | 6.27E+04                        | 6.70E+04                        | 1.04                           | 0.98                           | 1.37                           | 1.33                           | 1.31                            | 1.36                            |
| 12 <sup>c</sup> | PE-PVC-SOIL in SPT(1:1:2) <sup>e</sup>   | 641       | 300           | 663        | 250            | 456        | 2.6            | 5                | 2.92E+05         | 3.62E+05          | 2.40E+07          | 98           | 99            | 93            | 8.76E+04                       | 8.92E+04                       | 9.06E+04                        | 9.11E+04                        | 6.23E+04                        | 6.70E+04                        | 0.97                           | 0.98                           | 1.41                           | 1.33                           | 1.45                            | 1.36                            |
| 13 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2), extracted    | 469       | 300           | 409        | 250            | 111        | 2.6            | 5                | 2.14E+05         | 2.23E+05          | 5.83E+06          | 72           | 61            | 23            | 6.41E+04                       | 8.92E+04                       | 5.59E+04                        | 9.11E+04                        | 1.52E+04                        | 6.70E+04                        | 1.15                           | 0.98                           | 4.23                           | 1.33                           | 3.68                            | 1.36                            |
| 14 <sup>c</sup> | PE-PVC-SOIL in SPT (1:1:2000), extracted | 475       | 300           | 408        | 250            | 1836       | 2600           | 5                | 2.16E+05         | 2.23E+05          | 9.64E+04          | 73           | 61            | 0.4           | 6.49E+04                       | 8.92E+04                       | 5.57E+04                        | 9.11E+04                        | 2.51E+05                        | 6.70E+07                        | 1.16                           | 0.98                           | 0.26                           | 0.00                           | 0.22                            | 0.00                            |

<sup>a</sup>: Stock series 1: Individual suspensions of PE (~3,000#/µL), PVC (~9,000 #/µL) and soil particles (~60,000 #/µL), PE and soil prepared in EtOH, PVC prepared in IPA.

<sup>b</sup>: Stock series 2: Individual suspensions of PE (~500#/µL), PVC (~1,400 #/µL) and sand particles (~14 #/µL), PE and sand prepared in EtOH, PVC prepared in isopropanol IPA. Stocks made with sieved sand instead of soils and used for comparison with Raman measurements.

<sup>c</sup>: Stock series 3: Individual suspensions of PE (~800#/µL), PVC (~1,000 #/µL) and soil particles (~200,000 #/µL), all prepared in SPT solution (density 1.6g/mL).

<sup>d</sup>: Due to a shortage of PVC stock suspension, a PE:PVC ratio of 1:1 was not achievable anymore.

<sup>e</sup>: Samples made in triplicates.

**Table S6** Comparison of results obtained from automated scanning electron microscopy energy dispersive x-ray analysis (SEM-EDX) and automated Raman microspectroscopy measurements. PE: Polyethylene, PVC: Polyvinyl chloride. 'N<sub>m</sub> (PE,PVC, SAND)' refers to the number of particles detected within a certain area ('A<sub>m</sub>'). 'V (PE, PVC, SAND)' refers to the volume of respective stock suspensions that were used to prepare the samples. 'N<sub>A</sub> (PE, PVC)' refers to the number of particles per mm<sup>2</sup> and 'recovery (PE, PVC)' refers to the abundance of PE and PVC particles detected by automated Raman analysis relative to the amount detected by automated SEM-EDX analysis.

| method             | N <sub>m</sub> (PE)<br>[#] | V (PE)<br>[μL] | N <sub>m</sub> (PVC)<br>[#] | V (PVC)<br>[μL] | N <sub>m</sub> (SAND)<br>[#] | V (SAND)<br>[μL] | A <sub>m</sub><br>[mm <sup>2</sup> ] | N (PE)<br>[#/mm <sup>2</sup> ] | N (PVC)<br>[#/mm <sup>2</sup> ] | recovery (PE)<br>[%] | recovery (PVC)<br>[%] |
|--------------------|----------------------------|----------------|-----------------------------|-----------------|------------------------------|------------------|--------------------------------------|--------------------------------|---------------------------------|----------------------|-----------------------|
| SEM-EDX            | 446                        | 750            | 589                         | 150             | 1805                         | 20000            | 1.47                                 | 303                            | 400                             | -                    | -                     |
| RAMAN <sup>a</sup> | 434                        | 750            | 228                         | 150             | NA                           | NA               | 1.44                                 | 302                            | 159                             | <b>100</b>           | <b>40</b>             |
| RAMAN <sup>a</sup> | 366                        | 750            | 240                         | 150             | NA                           | NA               | 1.44                                 | 255                            | 167                             | <b>84</b>            | <b>42</b>             |
| RAMAN <sup>a</sup> | 428                        | 750            | 247                         | 150             | NA                           | NA               | 1.44                                 | 298                            | 172                             | <b>98</b>            | <b>43</b>             |

<sup>a</sup>: triplicate measurements on the same filter

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