Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Sampling Campaign

Cherry Creek originates southeast of Denver near Castlewood Canyon, CO, and is impounded in Cherry Creek Reservoir. Flow is principally a function of release from Cherry Creek Reservoir, along with notable spikes in discharge corresponding to major precipitation events, and cuts through urban tracts of Denver, CO. Eventually the creek feeds into Denver's primary water source, the South Platte River, near downtown Denver, CO. Typical flows along Cherry Creek vary from 15-30cfs across the year with peak flows due to mountain snowmelt coming in Mar-Jul.

Daily grab sampling (5/19/22-5/23/22) of Cherry Creek surface water was performed to capture a major precipitation event (5/20/22-5/22/22). The sampling site in Denver CO was roughly equidistant from the confluence with the South Platte River and Cherry Creek Reservoir (39°41'43.7"N 104°55'14.3"W). Water was collected near the center of the channel using a 2-m pole sampler (HDPE) and transferred to 1L HDPE bottles for storage. Both the bottles and pole sampler were triple rinsed with water from the stream prior to collection. Streamflow was obtained from the USGS gauges at the confluence between the South Platte River and Cherry Creek (USGS Gauge ID 06713500) and the gauge along Cherry Creek at Cherry Creek Reservoir (USGS Gauge ID 06713000) (SI Figure S2). Although streamflow increased at the confluence during the precipitation event, there was no concurrent increase at the inlet from the Reservoir indicating that localized stormwater was driving the increase in discharge rather than releases from the reservoir.

Laboratory Analyses

Scanning Electron Microscopy. Dry powder was mounted to a glass slide using carbon tape and imaged using a ESCAN MIRA3 LMH Schottky field emission-scanning electron microscope (FE-SEM) at magnifications of 200-2x with a beam voltage of 5kev.

Single Particle Inductively Coupled Plasma Mass Spectroscopy (sp-ICP-MS). All spICP-MS analyses were performed on a Nexion 300D Quadrupole ICP-MS (Perkin Elmer, Waltham, MA USA). A mass-based method for determining transport efficiency of Pace, et al 2011 was used for all single particle analyses. A 50nm Au nanoparticle (Fortis Life Sciences, citrate-stabilized, mean size of 50 ± 4nm by TEM) was used as a known mass standard in the method. Dissolved Au standards (0, 1, 10, 100 ug/L) [Inorganic Ventures, MSAU-100PPM, 100ug/mL Au in 10% v/v hydrochloric acid] were prepared through dilution with Milli-Q Water (18.2 M-ohm Barnstead International). Measured TE ranged from 5% to 8% over the course of the experiments. Ta (0, 0.2, 2, 20 ug/L) [High Purity Standards, ICP-MS-68A-B, 10mg/L in 2% nitric acid + trace hydrofluoric acid] and Al (0, 1, 2, 20ug/L) (Aristar, BDH82026-120, 100mg/L in 3% nitric acid) were prepared through dilution using nitric acid (Fisher Scientific, Trace Metal Grade, 32-35%). All standards were prepared the day of analysis. Sample containers were sonicated for 10min, subsampled and the subsample was 10 μm-filtered (nylon, Tisch Scientific) prior to sp-ICP-MS analysis. Microplastic suspensions of PVP and PMMA were prepared by resuspending dry powder immediately before analysis. All sample dilutions for sp-ICP-MS analysis used MilliQ Water.

Samples were analyzed by sp-ICP-MS for ^{197}Au, ^{181}Ta or ^{27}Al at a flow rate of 0.3mL/min, with 100 µsec dwell times, over a total data collection time of 60 sec. No settling time was used and a very short detector dead time of 35ns was utilized. Raw ICP-MS data was processed for single particle analysis using Syngistix 2.3 (Perkin Elmer, Waltham MA USA) with threshold values set to the mean plus three times the standard error (µ + 3σ). A minimum of 1 count for the threshold value was used when the Syngistix-derived threshold was <1 count. MATLAB Build R2021b (MathWorks, Natick MA USA) was used for all post-processing and fitting of sp-ICP-MS data.

MP particle sizes were calculated as a function of the detected ^{181}Ta mass in each particle which was converted to a MP particle size ($d_{polymer}$) using the equations:

$$v_{polymer} = m_{metal}\, x\, \frac{MW_{additive}}{MW_{metal}}\, x \frac{1}{\%\,(w/w)_{Additive}}\, x\, \frac{1}{\rho}{}_{polymer} \qquad \text{(Equation 1)}$$

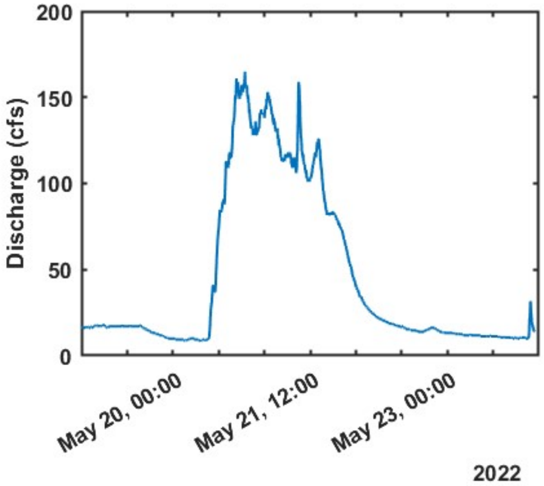
$$d_{polymer} = \sqrt[3]{\frac{6v_{polymer}}{\pi}} \qquad \text{(Equation 2)}$$

Where:

$v_{polymer}$	Volume of Polymer (cm^3)	$MW_{additive}$	Mol. Wt. of the Additive (g/mol)
m_{metal}	Mass of Metal (g)	MW_{metal}	Mol. Wt. of the Metal (g/mol)
$\rho_{polymer}$	Density of Polymer (g/cm^3)	$\%\,(w/w)_{Additive}$	(w/w) % of Additive in Polymer

The densities used fo the polymers were , 1.18 g cm^{-3} and 1.20 g cm^{-3}, for PMMA and PVP respectively. Both equations were used to convert detected ^{27}Al mass to an equivalently sized K-Feldspar Orthoclase particle (9.69% (w/w) Al, ρ = 2.56g/cm^3).

SI Figures



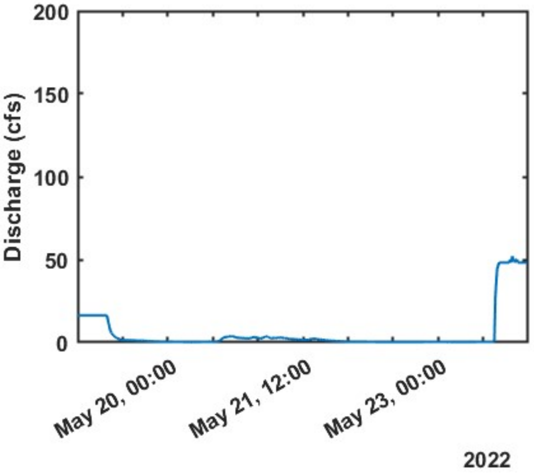


Figure S1. Hydrographs for Cherry Creek at the South Platte Confluence (Panel A, UGS GAUGE ID: 06713500) and at the mouth of Cherry Creek Reservoir along Cherry Creek (Panel B, UGS GAUGE ID: 06713000) over the course of the study time period, May 19th – May 23rd 2022. The confluence between Cherry Creek and the South Platte River is downstream of the study site whereas Cherry Creek Reservoir is upstream.

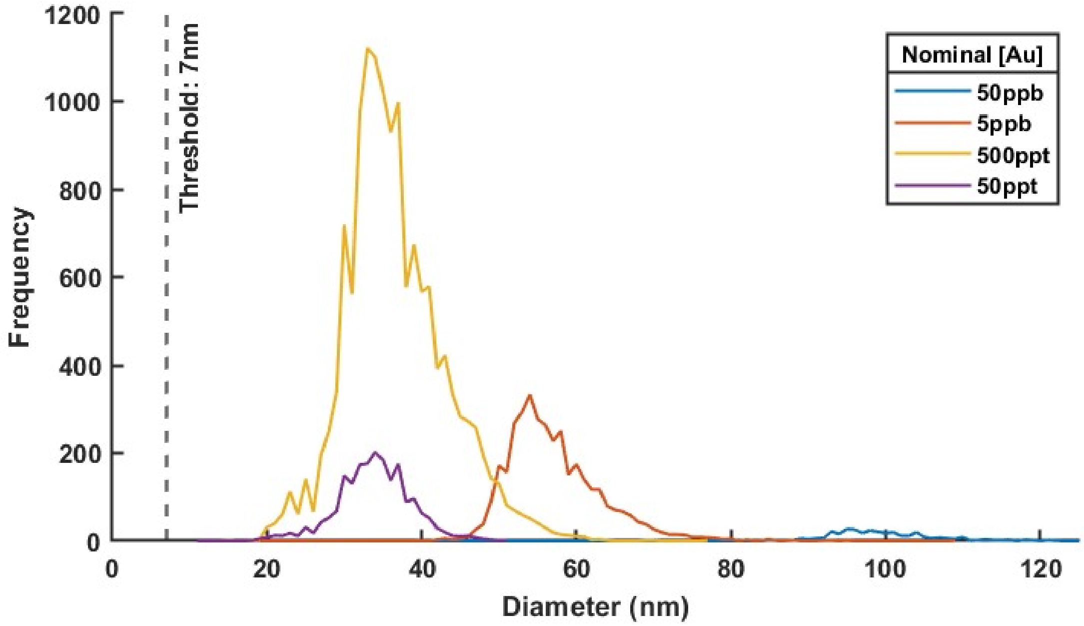


Figure S2. sp-ICP-MS analysis of dilutions of monodisperse 50nm ^{197}Au Nanoparticles (Nanocomposix, San Diego, CA) with nominal concentrations of ^{197}Au ranging from 50ppb to 50ppt. A consistent particle detection threshold was used for all dilutions that converts to a particle diameter of 7nm.

Fig S2 shows the typical effect of serial sample dilution on SD measured by sp-ICP-MS for a variety of concentrations of monodisperse ^{197}Au nanoparticles. At the highest two concentrations, coincidence and/or aggregation have caused a distortion of the SD such that particle numbers are suppressed, and the mean particle diameter is >50nm. Through serial dilution of the sample, the mean particle diameter reaches ~50nm at a [^{197}Au] of 500ppt and particle numbers scale with a further 10x dilution. Note that the threshold is well below the mean particle diameter and doesn't vary with dilution suggesting the absence of a background ^{197}Au signal.

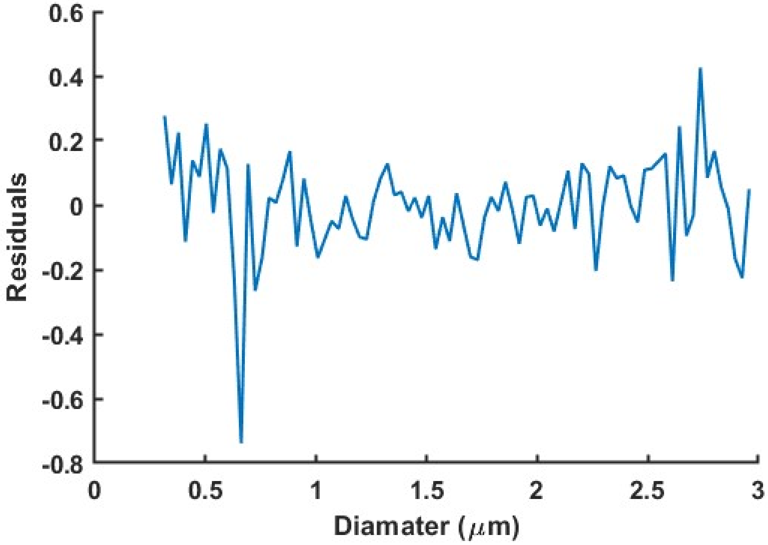


Figure S3. Residual plots for linear regression of Log N vs Log D for 0.1% (w/w) Ta-Ethoxide PVP.

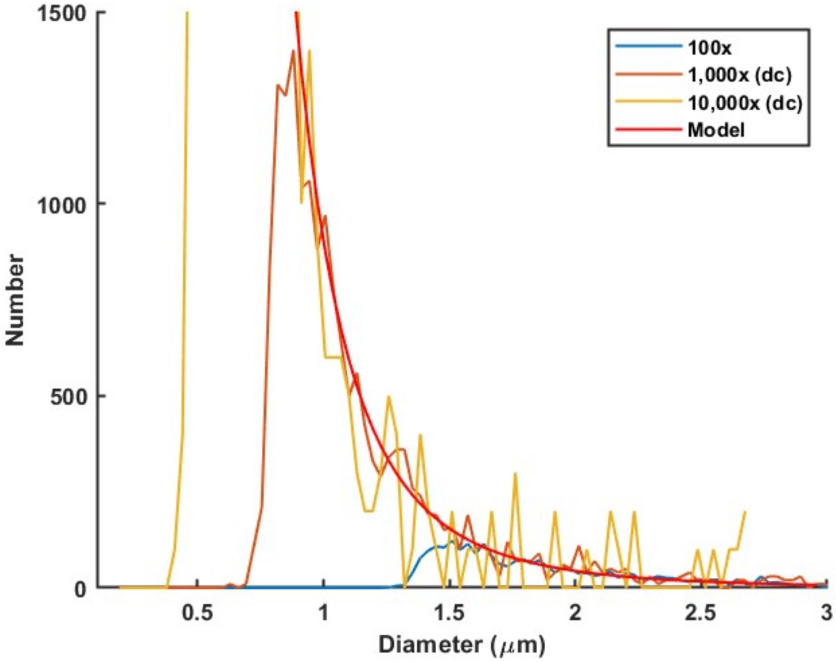


Figure S4. Comparison of the Power Law Model derived from the combined dataset to the dilution-corrected size distributions measured for the 0.1% Ta-Ethoxide (w/w) PVP suspension. The model line represents the results of linear regression of the Log-Log plot (Figure 3) and the power law model of particle number vs particle diameter generated from the linear regression. Particle numbers are normalized to the lowest dilution, denoted by (dc).

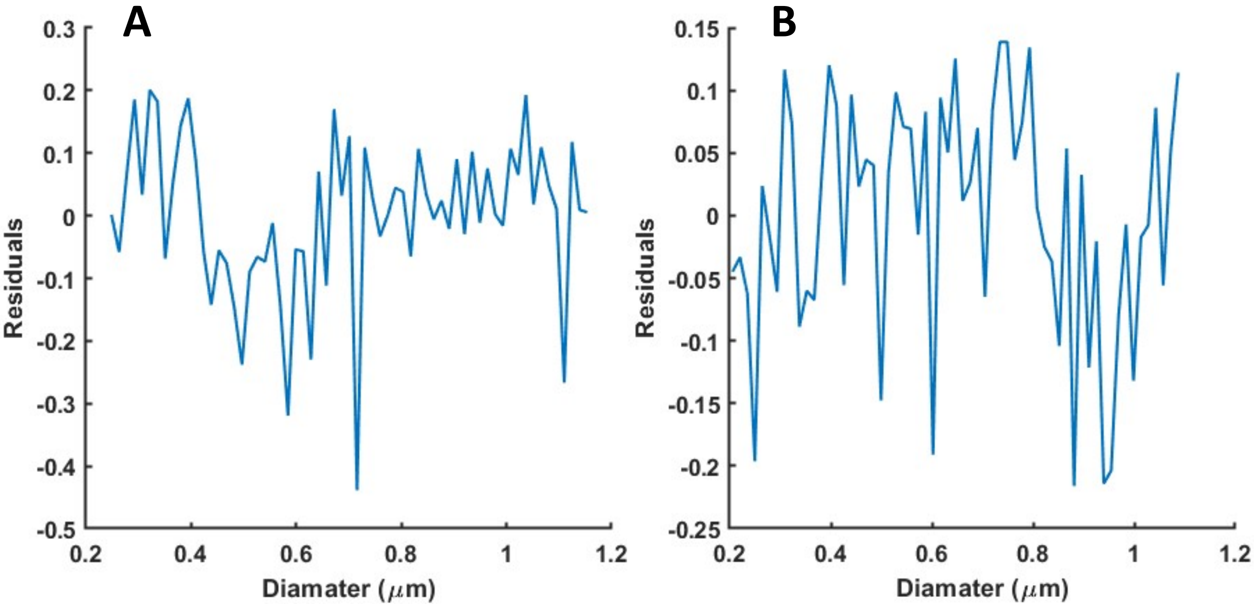


Figure S5. Residual plots for linear regression of Log N vs Log D for 1% (w/w) Ta-Ethoxide PVP (Panel A) and 0.1% (w/w) Ta-Ethoxide PMMA (Panel B).

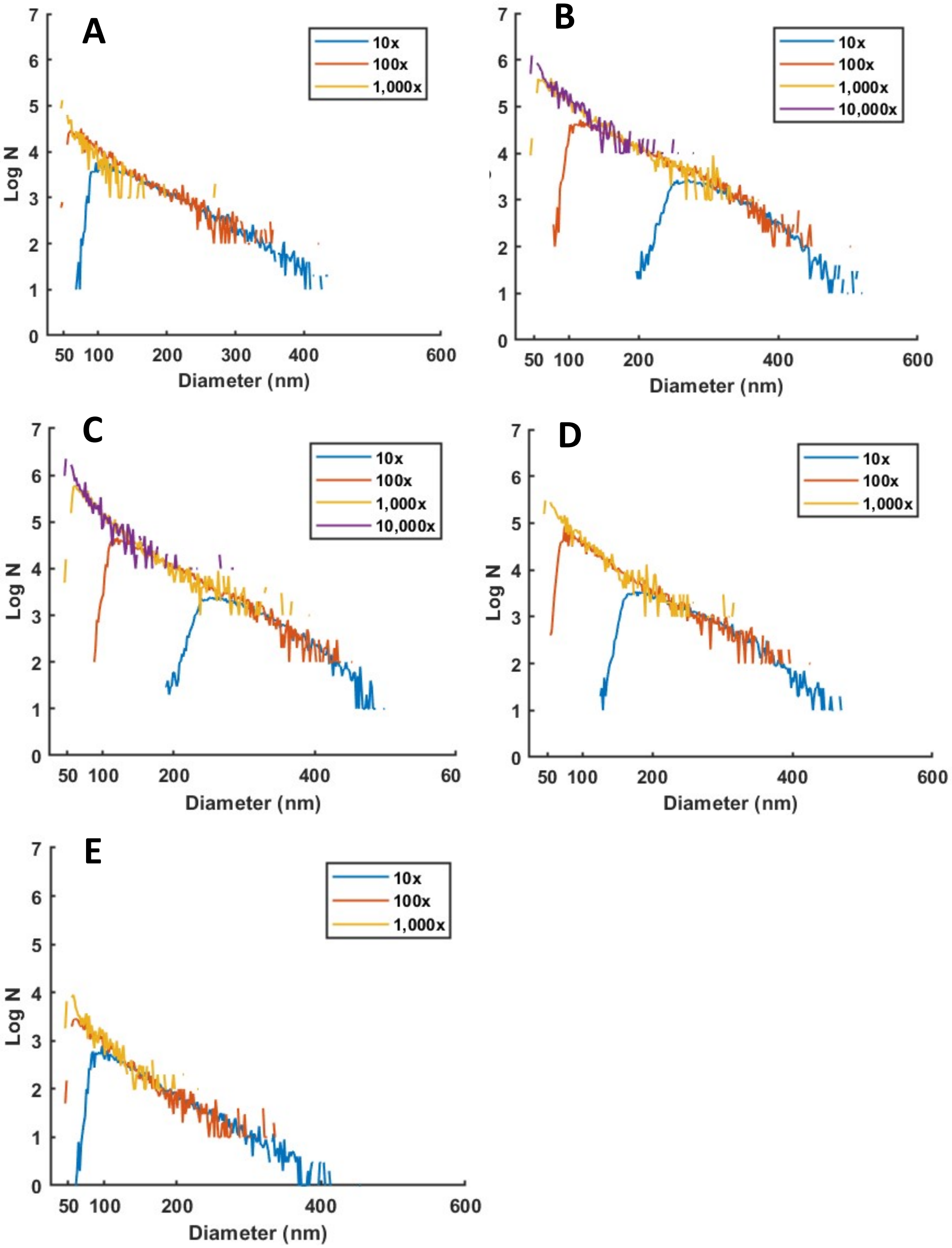


Figure S6. Log N- Log D comparisons of sp-ICP-MS PSD data measured at dilutions spanning 100x to 10,000x for Cherry Creek Samples. Panels correspond to individual samples: a. 5/19; b. 5/20; c. 5/21; d. 5/22; and e. 5/23. Particle numbers are corrected for the dilution.

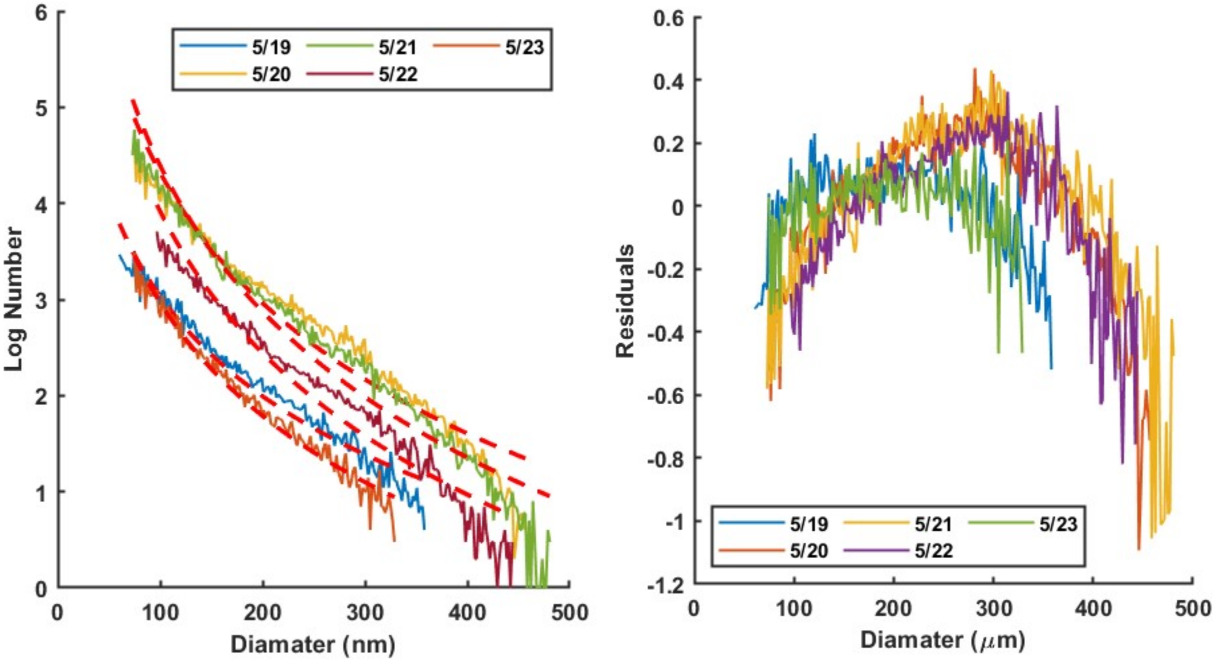


Figure S7. a. Plot of Log Number vs Diameter of the combined datasets used for power law modeling overlaid with the model line (dashed redline) for each sample. B. Residuals of power law models for each sample.

Tables

Polymer	Dilutions used for SD analysis	β	Log α	R^2
PVP	100x, 1,000x, 10,000x	-4.06 ± 0.09	3.45 ± 0.023	0.974
PMMA	10x	-1.55 ± 0.06	2.17 ± 0.02	0.916

Table S1. Results of Log-Log Linear Regression for the PVP and PMMA suspensions.

Day	**Mean Particle Diameter (nm)**	**Particle Conc (Part/mL)**	**Cherry Creek Discharge (cfs)**	**Threshold Size (nm)**
5-19	102	360,088	17	16
5-20	164	954,849	90	29
5-21	164	786,431	117	35
5-22	113	825,232	15	20
5-23	91	298,314	11	16

Table S2. Results from sp-ICP-MS analysis of a 100x dilution of samples taken from Cherry Creek, CO USA. Calculated particle size assumes that the mass of Al detected is contained in K-Feldspar ($2.7 g/cm^3$). Discharge was measured at the Cherry Creek USGS Gauge (ID: 06713500).

Day	Dilution Used	Mean Particle Diameter (nm)	Particle Conc (Part/mL)	Cherry Creek Discharge (cfs)	Threshold Size (nm)
5-19	100x	102	360,088	17	16
5-20	1,000x	97	4,389,040	90	16
5-21	1,000x	90	5,340,620	117	16
5-22	100x	113	825,232	15	20
5-23	100x	91	298,314	11	16

Table S3. Results from sp-ICP-MS analysis of a 100x/1,000x dilution of samples taken from Cherry Creek, CO USA. Sample dilutions were chosen for each date such that the threshold value for particle detection is similar. Calculated particle size assumes that the mass of Al detected is contained in K-Feldspar (2.7g/cm^3). Discharge was measured at the Cherry Creek USGS Gauge (ID: 06713500).

Day	Dilution Used	β	Log α	Cherry Creek Discharge (cfs)	Threshold Size (nm)
5-19	100x	-3.07 -± 0.08	8.19 ± 0.18	17	16
5-20	1,000x	3.38 ± 0.08	9.89 ± 0.17	90	16
5-21	1,000x	-3.97 ± 0.09	11.12 ± 0.20	117	16
5-22	100x	-3.35 ± 0.07	9.26 ± 0.15	15	20
5-23	100x	-3.77 ± 0.11	9.47 ± 0.23	11	16

Table S4. Power Law Model β and log α values obtained through linear regression of sp-ICP-MS data plotted as Log N vs Log D.