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

Supplemental information for

Multi-day diurnal measurements of Ti-containing nanoparticle and organic sunscreen chemical release during recreational use of a natural surface water

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Figure S1. Image of ISCO sampler at the downstream sampling site.

Figure S2. Representative image of recreational area on Day 1, 07:30 (off-peak). Photo is taken from near the downstream sampling site, looking upstream toward recreational use.

Figure S3. Representative image of recreational area on Day 2, 16:30 (peak use). Photo is taken from near the downstream sampling site, looking upstream toward recreational use.

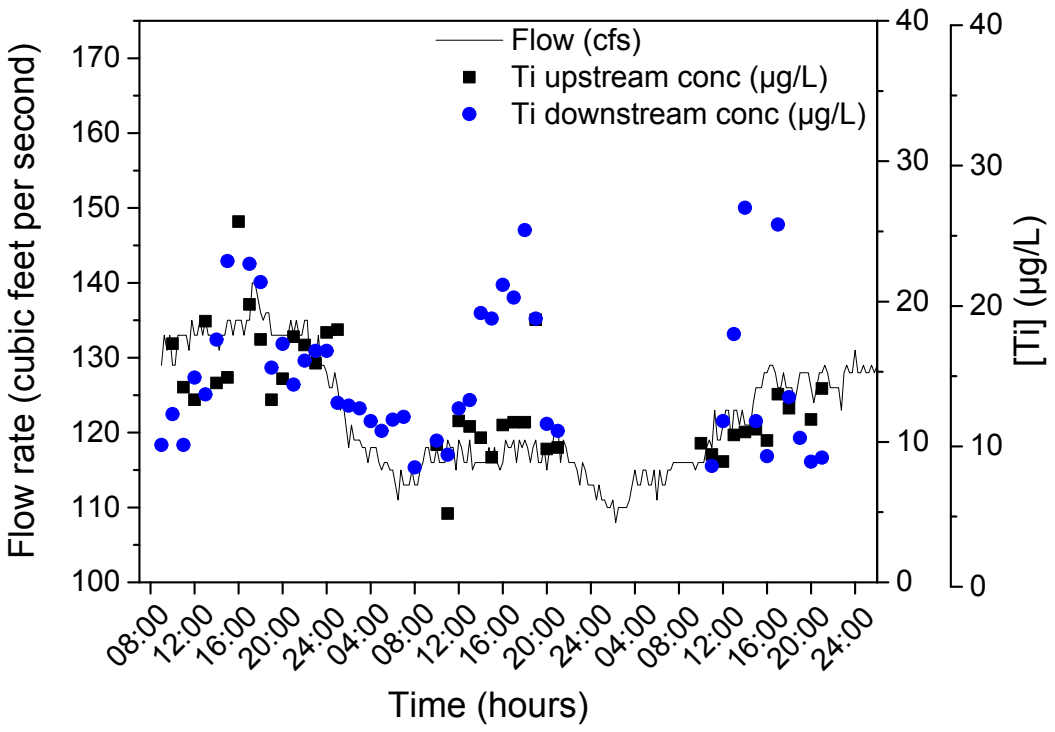

Figure S4. United States Geological Society hydrographic data for Clear Creek on the sampling weekend, plotted with Ti concentrations at upstream and downstream locations.

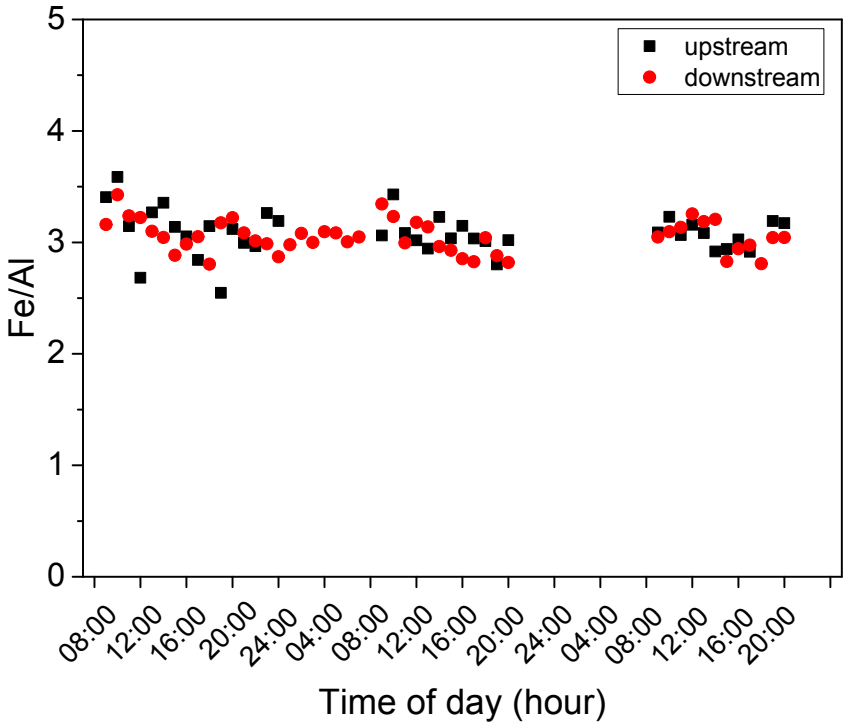

Figure S5. Fe/Al ratio in water samples collected over the sampling period.

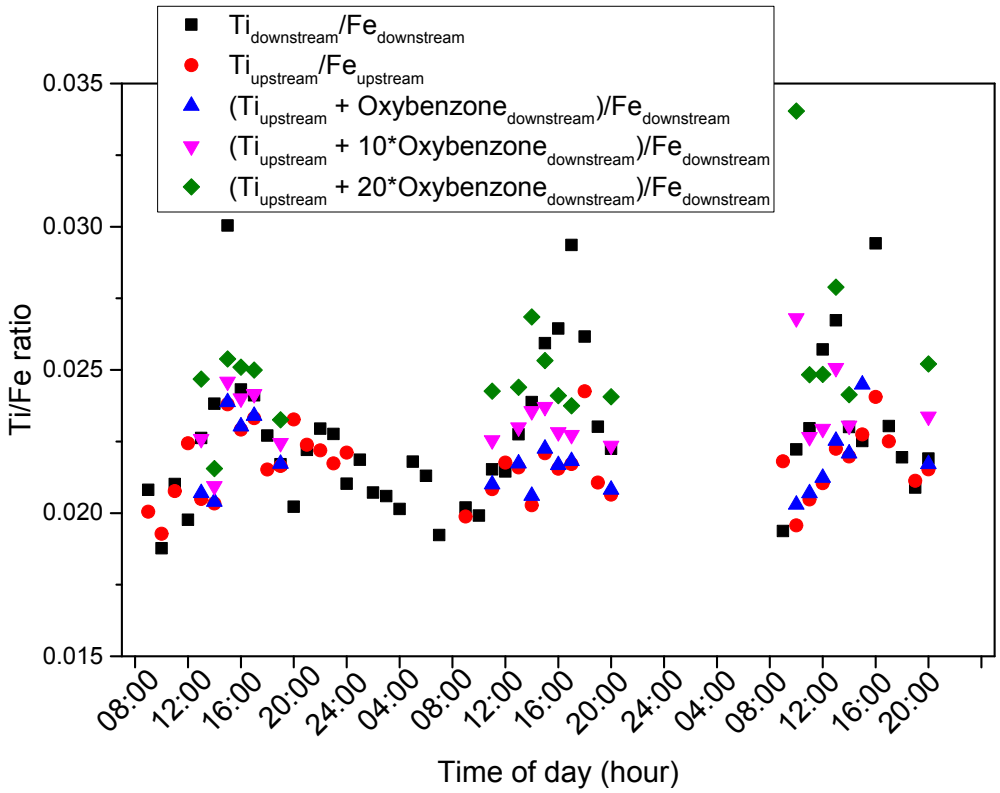

Figure S6. Sensitivity analysis for the addition of Ti and oxybenzone concentrations, and subsequent division by Fe concentrations.

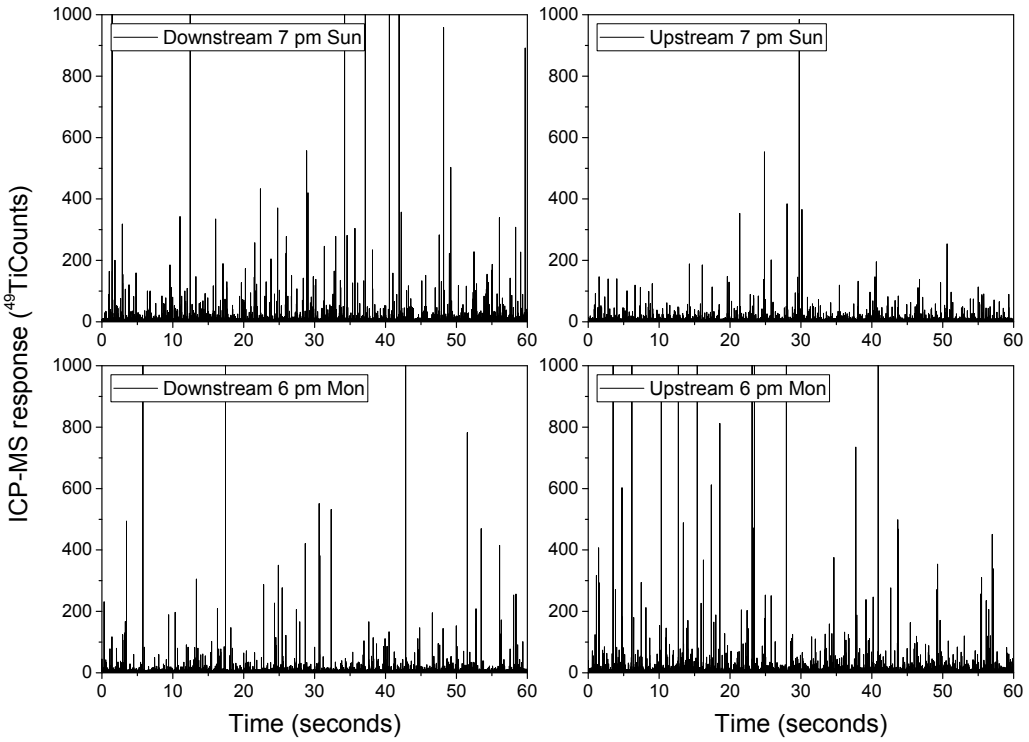

Figure S7. Time-resolved spICP-MS data for ^{49}Ti, measured upstream and downstream during recreational use of the creek.

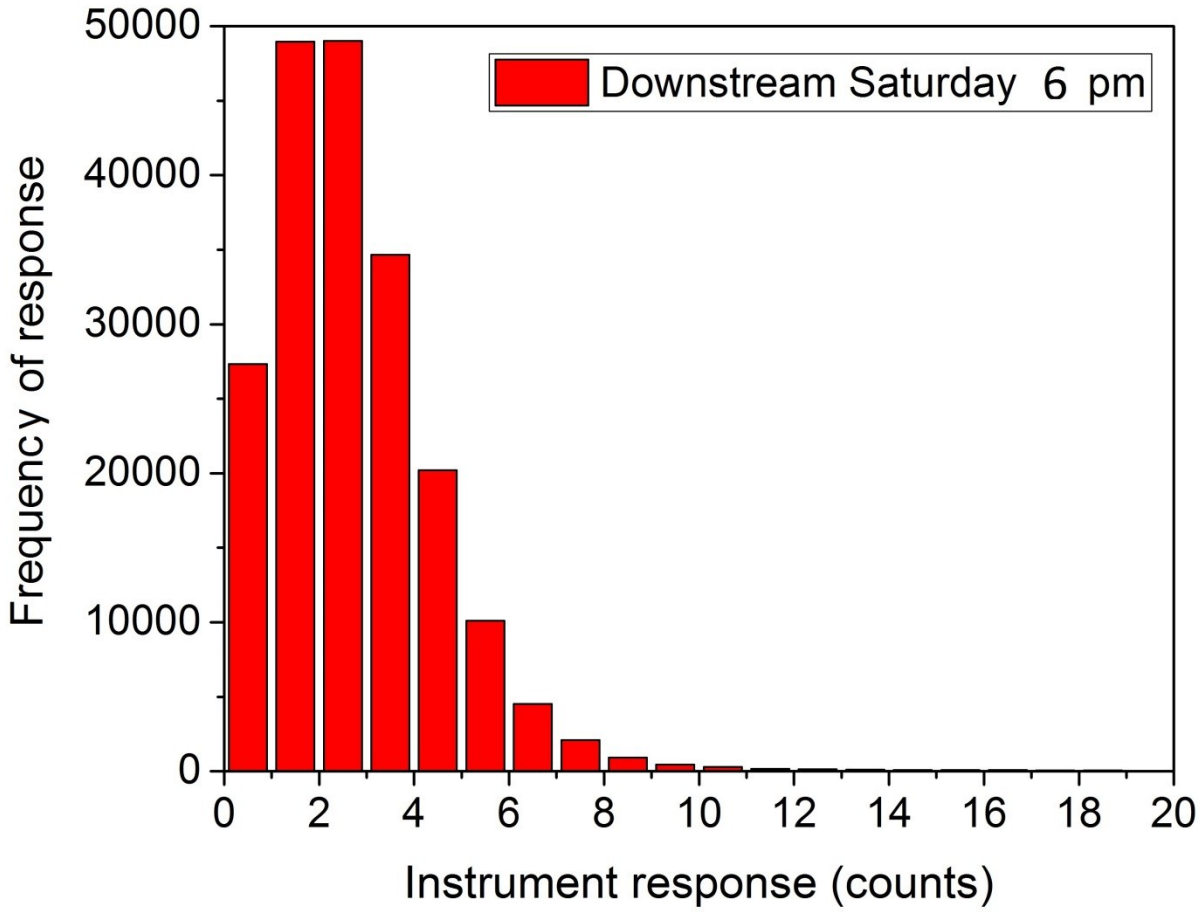

Figure S8. Data from spICP-MS analysis plotted as frequency count "bins" representing the number of times (y-axis, frequency of response) that each instrument signal (x-axis, instrument response) is observed in a single dataset. Binned data for each spICP-MS analysis was used to generate the stacked column graph in Figure S9.

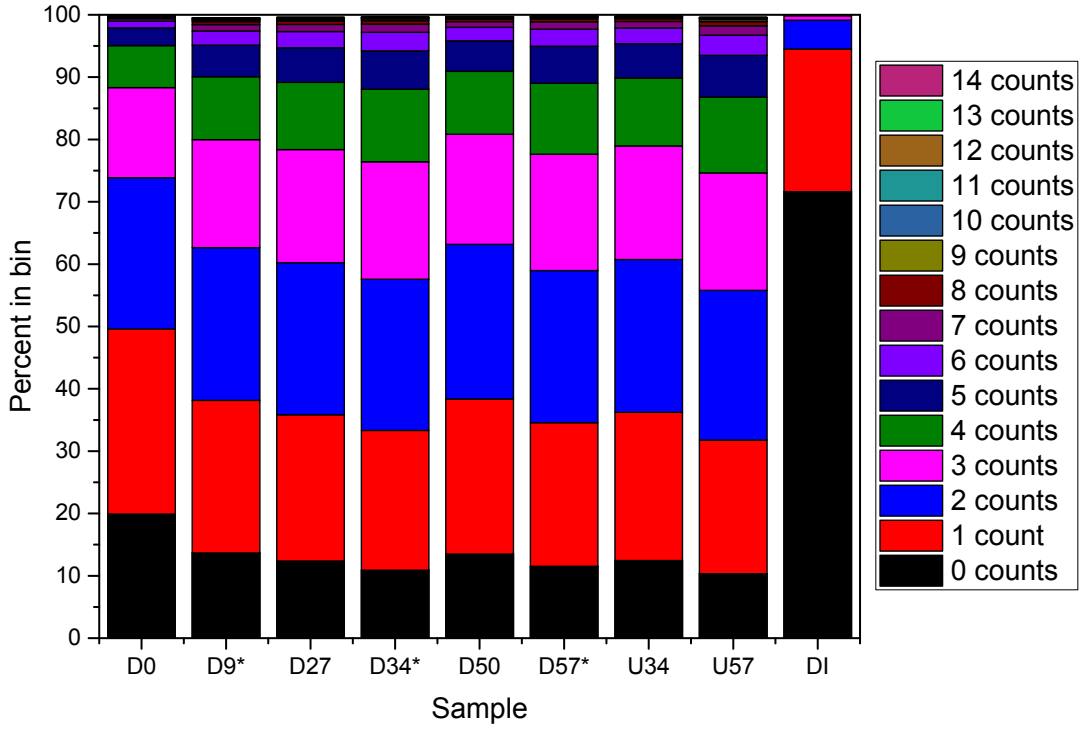

Figure S9. Selected creek samples were analyzed by spICP-MS for titanium (^{49}Ti). Downstream samples are denoted by "D", and asterisks* mark samples collected during peak recreational use of the creek. Upstream samples are marked with "U", and "DI" is a DI water blank. The time-resolved data was binned into counts (instrument response) and is presented here with the percent of binned data falling into a given count on the Y-axis. An example of binned data is shown in Figure S8.

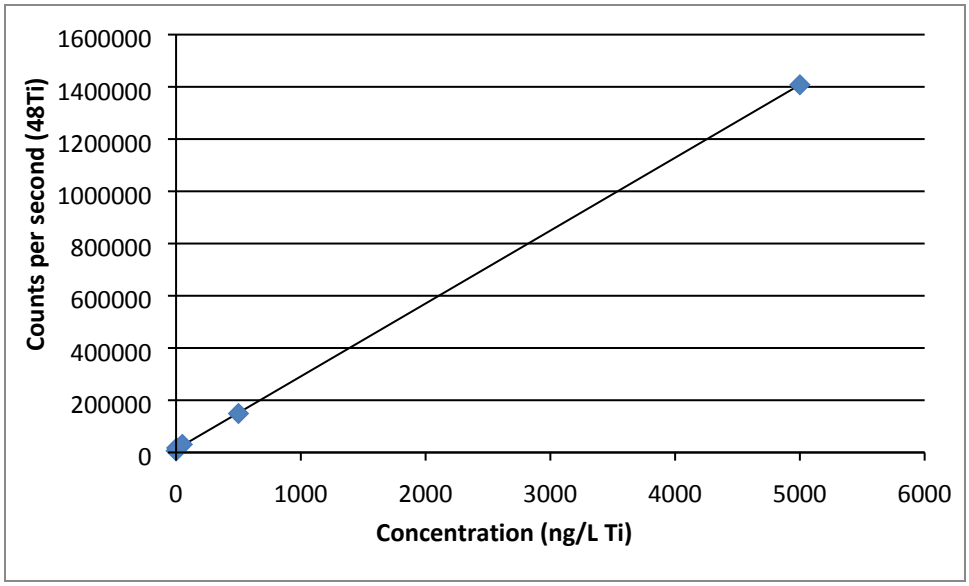

Figure S10. Calibration curve for ^{48}Ti using a high resolution ICP-MS.

Table S1. Parameters used to calculate the size detection limit by HR-spICP-MS. The ^{48}Ti calibration curve shown in Figure S10 was used to determine the equivalent mass concentration of a signal 3 standard deviations above background for a blank sample. This was converted into diameter using the parameters shown in Table S1.

Parameter	Value	Units
3s (measured as ng/L from calibration curve)	378	ng/L
flow rate	0.0002	L/min
Transport efficiency	0.07	
dwell time	0.00005	min
mass of pulse	2.64E-07	ng Ti
Ti/TiO2 ratio	0.60	
mass of TiO2	1.58E-07	ng TiO2
density of TiO2	4.23	g/cm^3
volume TiO2	37451	nm^3
diameter	41.5	nm

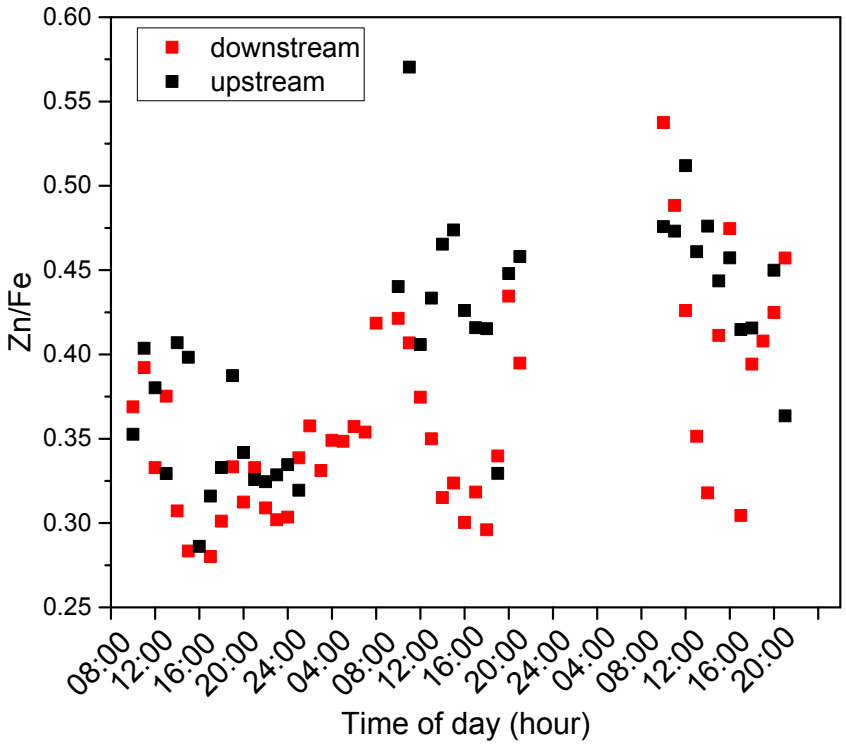

Figure S11. The ratio of Zn to Fe, both upstream and downstream of recreational creek usage. A lack of diurnal trends as observed with the Ti/Fe downstream ratios suggests that Zn is not suitable as an analyte from sunscreens in this system.