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


# Supplementary Information

# Release of $TiO_2$ nanoparticles from painted surfaces in cold climates: characterization using a high sensitivity single-particle ICP-MS

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**Optimization of SP-ICP-MS for $TiO_2$ NPs**. Since the lowest size that can be detected (*i.e.* SDL) is inversely related to the ratio of signal (S) to background (B) ($SDL=f(B/S)^{1/3}$), SDL will increase with increasing complexity of the matrix and is particularly high in the environmental media, where $^{48}Ca$, S, N and O (*i.e.* S-N, S-O polyatomic interferences) concentrations are important.[1, 2] Indeed, SDL of 50-100 nm are generally reported for $TiO_2$ NPs.[3-6] Therefore, several strategies were employed to improve the ratio of signal-to-noise (background) and thereby lower the SDL[7]: (i) a high sensitivity magnetic-sector ICP-MS was used rather than a quadrupole ICP-MS; (ii) interferences were minimized by analyzing an isotope, Ti-49, that had relatively few interferences in natural matrices, and (iii) very small dwell times (50 µs) were employed, which helped further reduce the background and yield well-defined NP peaks. In addition, discrimination of NP from the background signal used a powerful peak recognition algorithm that took into account the local background variations and facilitated identification of peak artifacts. Raw data showing peaks near the SDL were visually monitored to ensure that each peak consisted of at least 4 integration points (*i.e.* minimum peak width of 200 µs). Further details on the technique and data processing can be found in our previous work[7].

**Figure S1.** A photo of the outdoor weathering setup on the 4th floor roof of Wong building (McGill University, Montreal, QC). The photo was taken on the start day of winter weathering experiments, February 13, 2018.

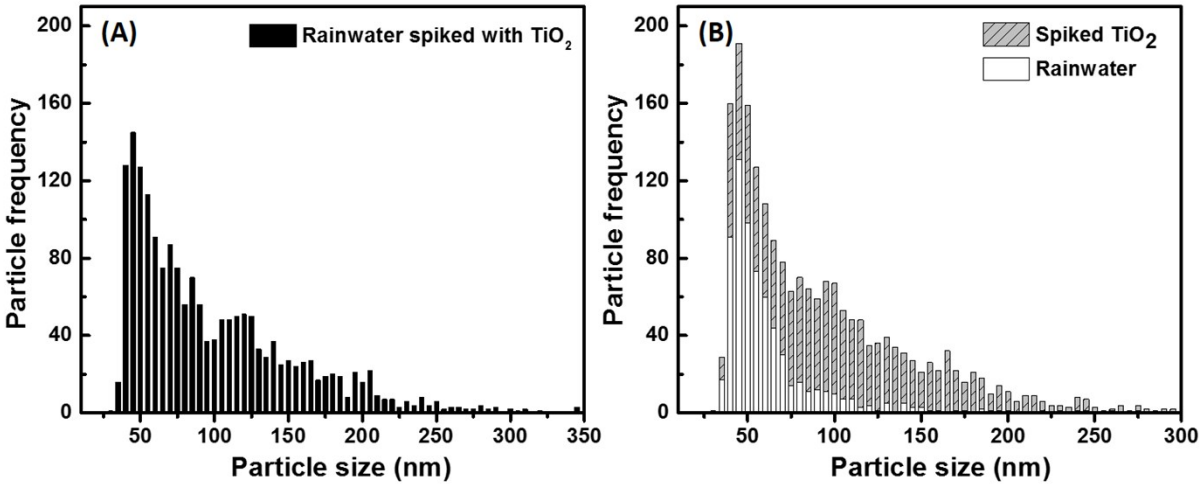


**Figure S2. (A)** Particle size distribution of $TiO_2$ NPs (148,100 NP/mL) after spiking engineered $TiO_2$ NPs (nominal size of 25 nm) into the rainwater medium, **(B)** Cumulative particle size distributions of $TiO_2$ in the rainwater (54,640 NP/mL) and for the $TiO_2$ NPs suspended in Milli-Q water (106,500 NP/mL) before mixing. Measurements were performed on a magnetic-sector ICP-MS. Particle diameter were calculated on the assumption that particles were solely $TiO_2$.

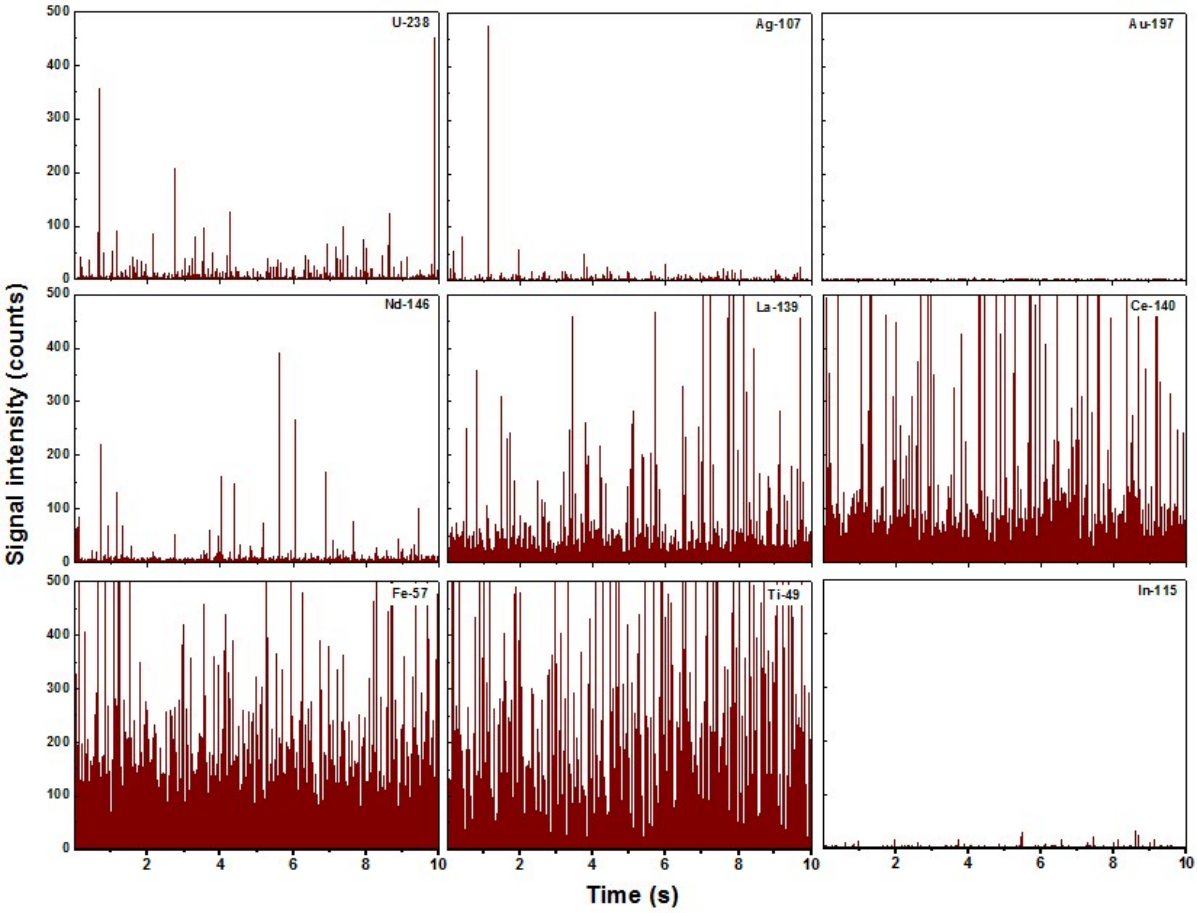


**Figure S3.** Time-resolved SP-ICP-MS signals (*i.e.* raw data) obtained for $^{238}$U, $^{107}$Ag, $^{197}$Au, $^{146}$Nd, $^{139}$La, $^{140}$Ce, $^{57}$Fe, $^{49}$Ti and $^{115}$In in a filtered (0.45 µm) rainwater sample (collected in Montreal, QC). Data were acquired for a total of 10 s using a dwell time of 50 µs on a magnetic-sector ICP-MS. Signal spikes indicate the presence of metallic particles.

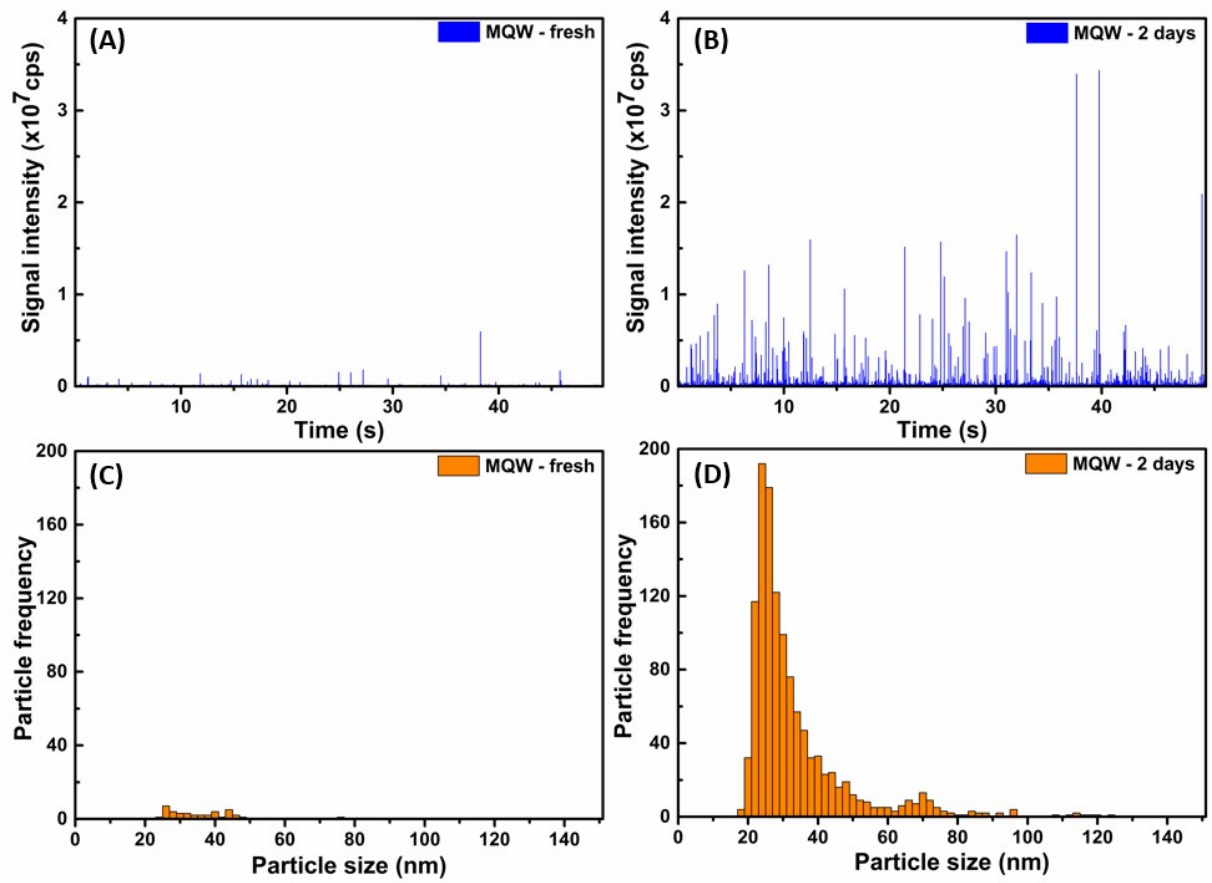


**Figure S4.** Time-resolved SP-ICP-MS signal obtained following the analysis of **(A)** fresh Milli-Q water and **(B)** Milli-Q water exposed to outdoor air for 2 days, as well as **(C, D)** their corresponding particle size distributions. Particle diameters were calculated on the assumption that particles were $TiO_2$.

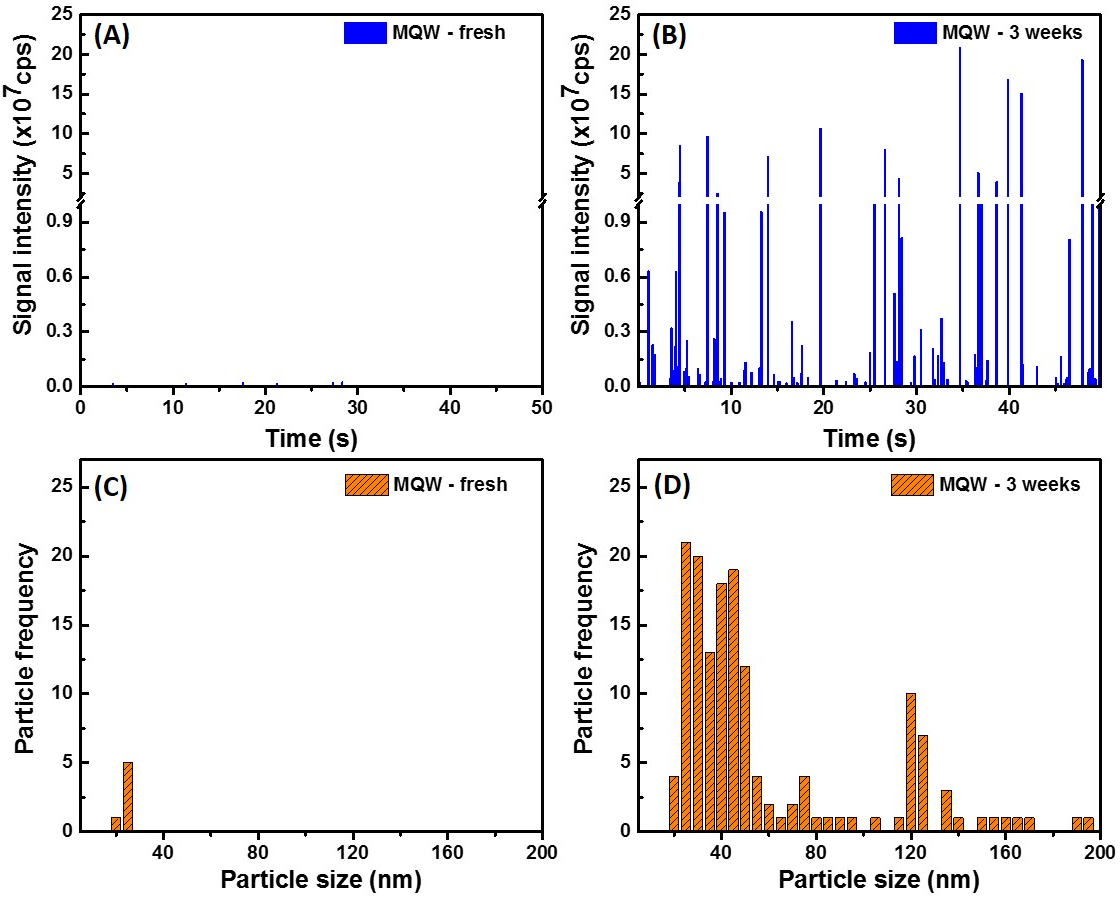


**Figure S5.** Time-resolved SP-ICP-MS signal obtained following the analysis of **(A)** fresh Milli-Q water and **(B)** Milli-Q water exposed to indoor air for 3 weeks, as well as **(C, D)** their corresponding particle size distributions. As opposed to the outdoor air, 3 weeks was required in order to get a non-negligible signal. Particle diameters were calculated on the assumption that particles were solely $TiO_2$.

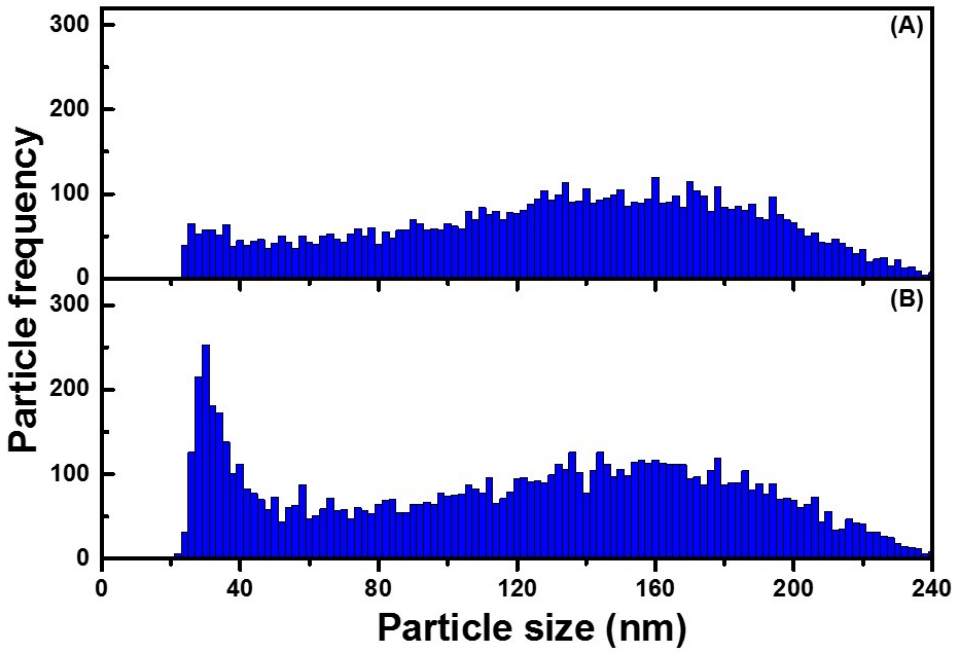


**Figure S6.** Particle size distributions obtained for $TiO_2$ NPs in a liquid paint sample diluted $2 \times 10^7$ x w/w with **(A)** Milli-Q water and **(B)** 5 mg/L of fulvic acid (Suwannee River standard fulvic acid, SRFA II) following 30 min of ultrasonication. Particle diameters were calculated on the assumption that particles were solely $TiO_2$.

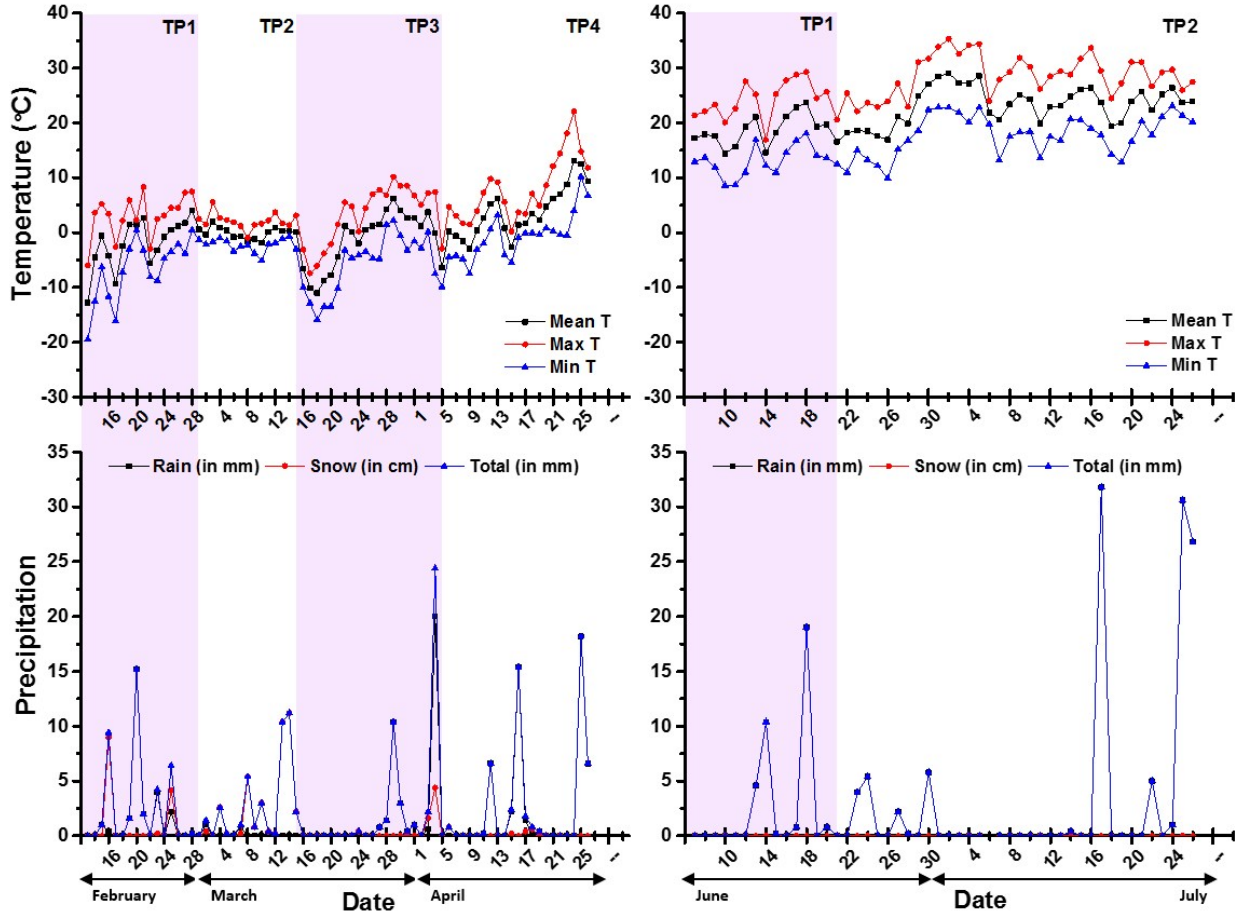


**Figure S7.** Daily temperatures (maxima, minima and mean T) as well as precipitation (rain, snow, total precipitation) in the winter and summer of 2018, as collected from Montreal International Airport weather station (45°28'14.000" N, 73°44'27.000" W) and retrieved from the Environment and Climate Change Canada database. Timepoints (TP) refer to the cumulative period in which the respective sample was taken.

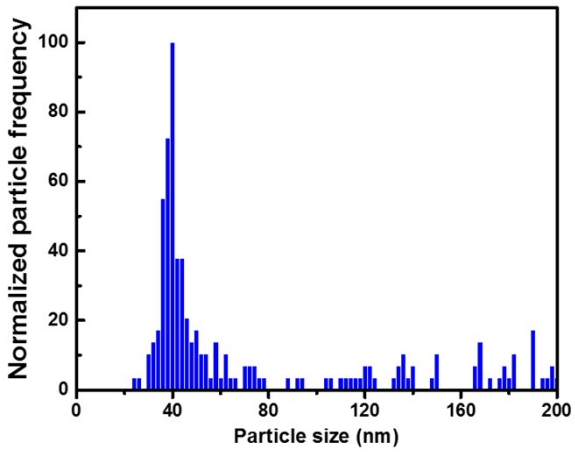


**Figure S8.** Particle size distribution of $TiO_2$ NPs released following a 4-day soaking of a painted panel in Milli-Q water (no NP background).

**Table S1.** Recoveries (%) of ionic Ti (based on Ti-49 isotope) as well as those of $TiO_2$ NPs spiked in a rainwater matrix. Given sizes are nominal particle diameters, as provided by the manufacturer.

| | **Ionic recovery (%)** | | |
|---|---|---|---|
| Ti - 1 ppb | 103.0 | ± | 1.6 |
| Ti - 5 ppb | 102.6 | ± | 0.8 |
| Ti - 10 ppb | 101.6 | ± | 1.0 |
| | **NP recovery (%)** | | |
| $TiO_2$ NPs (25 nm) | 92.2 | ± | 2.0 |

**References**


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