

Release of TiO₂ nanoparticles from painted surfaces in cold climates: characterization using a high sensitivity single-particle ICP-MS

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1 **Abstract**

2 Paints and coatings represent one of the major applications of TiO₂ nanoparticles
3 (NPs). While it has been previously shown that NPs are released from painted surfaces,
4 there is still a lack of experimental data on their release rates under natural conditions and
5 on the size distributions of the NPs following release. This study quantifies TiO₂ NP release
6 from painted surfaces under natural weathering conditions and identifies the main seasonal
7 factors that contribute to increased NP release. First, an analytical methodology using a
8 highly sensitive single particle inductively coupled plasma mass spectrometer (SP-ICP-
9 MS) was developed that improved the size detection limit (SDL) of the technique down to
10 < 20 nm for TiO₂ NPs. Precipitation (rain, snow) was collected after it came into contact
11 with painted panels that were exposed to natural weathering. NPs that were released from
12 the paint, as well as those pre-existing in the precipitation were thoroughly characterized
13 with respect to their size distributions, particle number concentrations and total metal
14 content. During the 10-week winter exposure, 3×10^{11} NP/m² were released,
15 corresponding to <0.001% of the TiO₂ NP load on the panels, with most of the NPs found
16 in the 20-60 nm range. Significantly fewer NPs were released during the summer than the
17 winter, in spite of the fact that there was more precipitation in the summer. Controlled lab
18 weathering experiments revealed that NP release was significantly enhanced for wet
19 surfaces, particularly, when the samples underwent freeze-thaw cycles. The results also
20 indicated that NP release and loss (*i.e.* through agglomeration, sedimentation or sorption,
21 etc.) are dynamic processes that are a function of the physical and chemical properties of
22 the external medium. Although NP release is a primary determinant in environmental risk,
23 subsequent NP behavior leading to losses or re-suspension can be equally critical.

24 **Introduction**

25 Recent advances in nanotechnology have led to greater numbers of nano-enabled
26 products and increased production volumes of engineered nanomaterials (ENMs).¹ With
27 the growing production and applications of ENMs, their release into the environment is
28 inevitable, necessitating research into their environmental fate.²⁻⁴ TiO₂ nanoparticles (NPs)
29 are the most widely produced ENM on a mass basis.⁵⁻⁷ Among other applications, they are
30 extensively used in paints and coatings, where they can provide UV protection and self-
31 cleaning properties.⁸⁻¹⁰

32 While the use of TiO₂ NPs in paints is on the rise and their release from aged painted
33 surfaces is imminent, their reliable risk assessment remains a challenge in environmental
34 systems.^{1, 9, 10} This is largely due to limited existing knowledge on their mass and number
35 concentrations, measurements of their surface-release rates and information on their
36 particle size distributions and persistence in the environment.^{5, 11, 12} Among the limited
37 analytical data available, lab-controlled tests conducted in simple media have clearly
38 shown significant NP leaching of painted surfaces, with some of the released NPs still
39 embedded in the organic paint matrix.^{13, 14} Olabarrieta *et al.*¹⁵ and Al-Kattan *et al.*¹⁶
40 demonstrated that TiO₂ NPs were released from coatings weathered by flowing water,
41 while Zhang *et al.*¹⁷ and Zuin *et al.*¹⁸ showed that static immersion in water could induce
42 NP release.

43 Outdoor studies^{13, 19-21}, while more difficult to control, are more appropriate for
44 evaluating real-world NP release scenarios. For example, Kaegi *et al.*^{19,13} followed the
45 release of Ti and Ag from a painted exterior façade over 1 year and concluded that much
46 of the released metal was in nanoparticulate form, with the estimated primary particle sizes

47 for TiO₂ between 20 and 300 nm and Ag below 15 nm. To the best of our knowledge,
48 outdoor studies investigating NP release in cold climates – where snow, freezing and
49 freeze-thaw conditions are relevant – are not yet available.

50 Most of the above studies estimated release based on an increase in total metal
51 concentrations in the waters that were in contact with the painted surface and confirmed
52 the presence of NPs using microscopic data. In such cases, it is difficult to quantify to what
53 extent NPs or dissolved metals were released. An additional difficulty in outdoor studies
54 is the significant presence of the target elements in the incoming precipitation^{22,23}. Overall,
55 NP analysis in complex waters is a challenging task,²⁴⁻²⁶ requiring accurate NP release
56 determinations that can identify, size and quantify the NPs on a particle by particle basis.
57 To that end, single-particle ICP-MS (SP-ICP-MS) is well suited to provide information on
58 NP size distributions and number concentrations in natural waters.^{27,28} It is based on the
59 ultrafast measurement and analysis of the transient ICP-MS signal. NPs typically generate
60 high intensity signals (spikes, ca. 300-500 μs) that can be discriminated from a continuous
61 (generally low-intensity) background, representative of the dissolved metals (and small
62 NPs).²⁹ While the technique is extremely sensitive for several metallic NPs (*e.g.* Ag, Au,
63 Ce), the analysis of TiO₂ is more challenging, due primarily to high levels of background
64 interferences.^{24,25,29} For this reason, most of the reported size detection limits (SDL) for
65 TiO₂ NPs are above 50 nm,³⁰⁻³² restricting characterization of the smaller NPs, which are
66 thought to be of higher risk to both the environment and human health.³³

67 Given this context, the goal of the study was to quantify the release of TiO₂ NPs
68 from nano-enhanced surfaces under natural weathering conditions. The study was designed
69 to: (i) characterize release of TiO₂ NPs by measuring NP concentrations and size

70 distributions with time and (ii) explore the role of temperature fluctuations (*i.e.* freeze,
71 thaw) and wet/dry conditions on NP release. Experiments were designed to provide insight
72 into the release and persistence of these important NPs in the environment.

73 **Materials and Methods**

74 **Preparation of exposure panels.** Untreated oak slats (0.64 cm thick x 6.4 cm wide) were
75 cut to 8.4 cm long panels, which were primed and painted with a white paint advertised for
76 its Nanoguard Technology (Behr Premium Plus Ultra Exterior Satin Enamel Ultra Pure
77 White paint). A uniform coating was obtained by applying 15 mL/side to each panel and
78 removing excess paint with an applicator (Bird Film Applicator, Inc, Washington, USA)
79 in order to get a wet film thickness of 4 mm. Both sides of the panel were coated twice,
80 and the paint was allowed to dry for at least two days before the addition of the next layer.
81 The final dry paint loading on each panel was 400 ± 40 g/m² (or 4.4 g/panel).

82 **Outdoor weathering setup.** For outdoor weathering experiments, replicate samples of the
83 painted panels were placed vertically in pre-weighed, wide-mouth polypropylene
84 containers (500 mL, Fisher Scientific). Containers were randomly ordered within plastic
85 bins and placed outdoors (**Fig. S1**) on a 4th floor roof (M. H. Wong building, McGill
86 University, Montreal, Canada), where they were left uncovered. The base of the bin was
87 lined with sand bags to prevent tipping. Samples were left undisturbed during the
88 weathering period except when snowfall buried the containers. In those cases, excess snow
89 was carefully scraped off the top of the containers to prevent overflow when the snow
90 melted. Winter weathering experiments were conducted for 10 weeks beginning in mid-
91 February (2018), while 7 weeks of summer experiments were initiated in early June (2018).

92 At each experimental timepoint, four control samples (container containing no painted
93 panel) and four samples (container containing painted panels) were sacrificed.

94 **Indoor (controlled) weathering setup.** For controlled weathering experiments, panels
95 were placed in pre-weighed polypropylene containers (4 sample replicates), which were
96 either filled with 380 mL of Milli-Q water (wet) or not (dry). Samples were then aged under
97 room temperature (RT), freezing (FR), or freeze-thaw (FT) conditions. For FR and FT
98 conditions, samples were placed in a -10 °C freezer. FT conditions consisted of repeated
99 48 h cycles in which samples were first allowed to freeze overnight (for 24 h), then
100 removed from the freezer and placed in a closed box on the benchtop, where they were
101 allowed to thaw (for 24 h). The experiment was conducted for a total of 42 d (21 FT cycles).
102 At the end of the 42-d exposure, dry FR samples were soaked for 1 d in Milli-Q water,
103 while wet FR samples were allowed to thaw (1 d). For the wet samples (both RT & FT), in
104 addition to the 42 d timepoint, small samples (16-18 mL) were removed at intermediate
105 timepoints during the exposure. The sampled volume was replaced with fresh Milli-Q
106 water in order to maintain a constant exposure surface.

107 **Sample preparation for SP-ICP-MS.** For each timepoint, the outdoor and control
108 containers to be tested were capped and all snow or ice was allowed to melt. The contents
109 of the containers were then gently mixed, and the panels were carefully removed. Water
110 was weighed, mixed, and then placed in a sonicator bath for 30 minutes (Branson
111 Ultrasonic Cleaner, 5510R-DTH Model, 135 W, 42 kHz \pm 6%). Following sonication, 8-
112 10 mL of sample was filtered through a 0.45 μ m, 33 mm diameter PVDF syringe filter that
113 had been pre-rinsed with 12 mL Milli-Q water and 6 mL of sample. [Filtration on this pore-](#)

114 size was performed to avoid blockage of the microflow nebulizers, without minimizing
115 removal of the nanoparticles.

116 **SP-ICP-MS analysis and data acquisition.** All NP measurements were performed on a
117 sector field ICP-MS (AttoM ES, Nu Instruments, UK), at low resolution (300), using single
118 ion acquisition in fast-scan mode. Liquid samples were introduced through a micro-flow
119 concentric glass nebulizer (free aspiration rate of $200 \mu\text{L min}^{-1}$ for 1 L min^{-1} Ar) into a
120 quartz cyclonic spray chamber cooled at $4 \text{ }^\circ\text{C}$. The enhanced sensitivity^{27, 34} of the sector-
121 field instrument (with respect to a quadrupole-based instrument) allowed us to analyse ^{49}Ti ,
122 which has a lower natural abundance, but also fewer interferences. An optimized dwell
123 time of $50 \mu\text{s}$ was used³⁵, with an acquisition time of 50 s, which resulted in ca. 10^6
124 datapoints per replicate. Sensitivity calibrations for ^{49}Ti were based on ionic standards
125 (High Purity Standards). Transport efficiency (TE) measurements were performed using a
126 suspension of ultra-uniform 30 nm Au NPs (NanoComposix, AUXU30-1M), which were
127 prepared daily at 50 ng/L. TE measurements were validated with a second standard
128 reference material (60 nm Au NPs, NIST8013)³⁵. TE values ranged from 0.10-0.12 $\mu\text{L/s}$
129 (3.4-3.8%). Standard additions were performed on ionic Ti standards (1, 5 and 10 $\mu\text{g/L}$)
130 and spikes of engineered TiO_2 NPs (P25 Aeroxide, Evonik, Germany; nominal size 25 nm)
131 in the rain or snow melt water, in order to assess possible matrix effects. Size calculations
132 were performed using an assumed TiO_2 density of 4.23 g/cm^3 (*i.e.* rutile). Filtered samples
133 were diluted 10-50x in order to ensure that the number of particle events was significant
134 (> 500 events), while minimizing the possibility for co-incident events (less than 10,000
135 events, or 1% of the total datapoints).

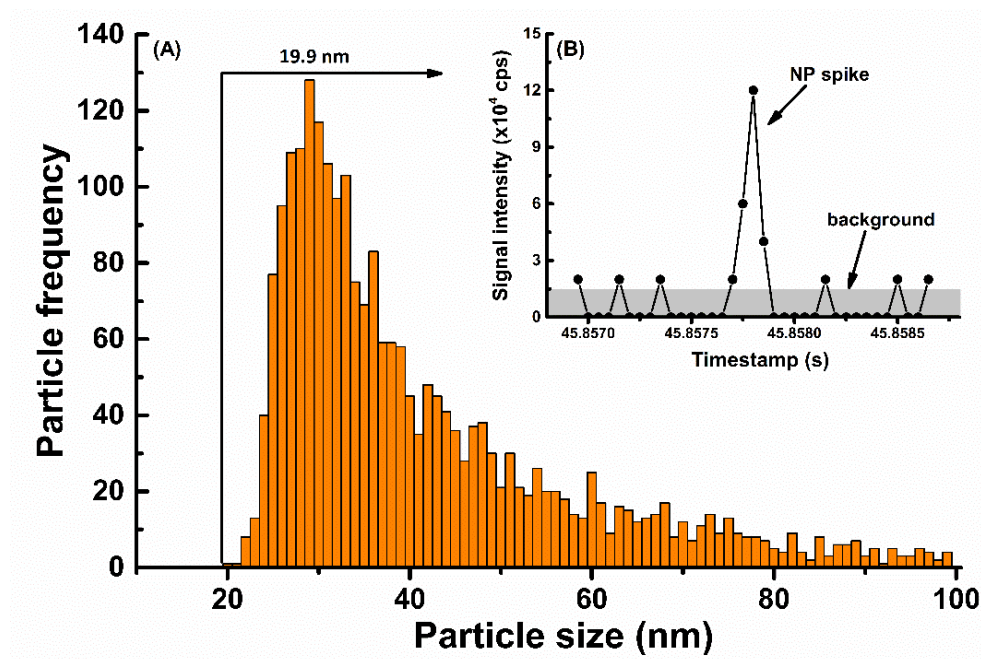
136 **SP-ICP-MS data processing.** SP-ICP-MS data was processed using NuQuant software
137 version 2.2 (Nu Instruments, UK),²⁷ based on the methodology described by Hadioui *et*
138 *al.*³⁵ and Shaw *et al.*³⁴ In summary, data processing involved the identification of NP peaks,
139 calculation of the local backgrounds and integration of the peaks. An average of the local
140 peak backgrounds was used to calculate dissolved metal content. Values of the full-width
141 at half-maximum (FWHM) were used to flag peak events that could potentially be co-
142 incident NP peaks or background artifacts (*i.e.* very slender or very wide peaks with low
143 intensity). Flagged events were visually inspected, and if necessary, the samples were
144 diluted further.

145 **Total metal analysis.** Following the filtration of samples for SP-ICP-MS, aliquots of the
146 filtered samples were added to polypropylene tubes containing 67-70 % HNO₃ (ultratrace
147 grade, BDH Aristar Ultra) in order to achieve a final acid content of 20% v/v. Tubes were
148 left for 16 h at 85 °C using a DigiPREP digestion system (SCP Science) and then diluted
149 with Milli-Q water to obtain a final HNO₃ content of 4% v/v, which was used for
150 quantitative ICP-MS analysis. Given the well documented difficulties in digesting TiO₂³⁶,
151 these measurements should be operationally defined as acid-extractable Ti.

152 **Results and Discussion**

153 **Optimization of SP-ICP-MS for TiO₂ NPs.** In comparison to other prevalent NPs such
154 as Ag, CeO₂ and Au, detection and characterization of TiO₂ NPs using SP-ICP-MS is
155 significantly more challenging.³⁰ This is primarily due to isobaric/polyatomic interferences
156 that increase the background signal for ⁴⁸Ti, which is of greatest natural abundance.³⁷ **To**
157 **overcome these challenges, SP-ICP-MS was optimized³⁵ using several strategies, including**

158 the use of ^{49}Ti , the use of a magnetic sector ICP-MS and the use of short dwell times (50
159 μs) (for further details, refer to SI). The combination of high sensitivity, low background
160 and improved NP peak resolution/recognition led to SDLs that were as low as 20 nm for
161 TiO_2 NPs in the snow and rain waters. Indeed, the particle size distribution (PSD) of TiO_2
162 NPs (**Fig. 1A**) and the raw signal intensities corresponding to the smallest detected NP
163 (**Fig. 1B**) are presented for NPs detected in a snow melt sample.



164

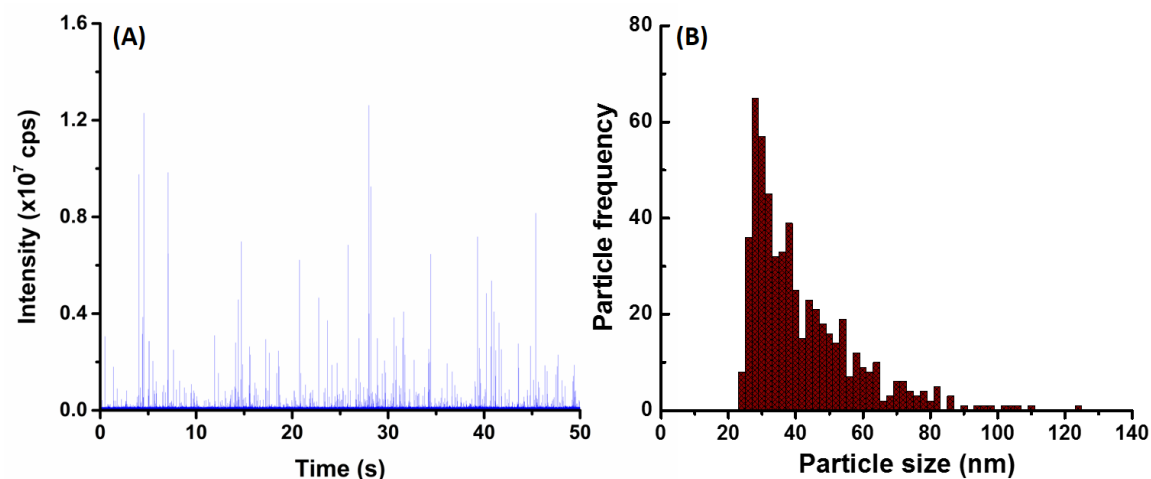
165 **Figure 1.** (A) Particle size distribution of Ti-containing NPs found in snow melt water, as measured
166 with high-sensitivity magnetic-sector ICP-MS using a dwell time of 50 μs . (B) Raw signal intensity
167 (cps) near the particle size detection limit. Particle diameters were calculated on the assumption
168 that the particles were TiO_2 .

169 Verification of an absence of matrix effect is difficult with TiO_2 NPs, given the
170 difficulty to obtain monodisperse TiO_2 standards. Therefore, several strategies were
171 undertaken to verify and reduce matrix effects during the measurements of TiO_2 NPs: (i)
172 tests on the matrix effect were performed using ionic Ti; (ii) TiO_2 NPs were measured
173 following their spike into a natural rainwater matrix, which had a pre-existing NP

174 background; (iii) SP-ICP-MS measurements were performed in media that were diluted at
175 least 10x. Indeed, nearly identical recoveries (*i.e.* 102 %) were obtained for a spike of ionic
176 Ti measured in Milli-Q water or rainwater (**Table S1**), suggesting that the matrix effect for
177 ⁴⁹Ti was minimal. When spiking TiO₂ NPs (nominal size of 25 nm) into the rainwater, a
178 recovery of 92% was attained, following correction for particle numbers in the unspiked
179 rainwater (**Fig. S2**). In that case, the slightly lower recoveries may have been caused by
180 TiO₂ losses following their agglomeration in the rainwater matrix.

181 **Detection of Ti NPs in natural precipitation.** Very early in the weathering study, it
182 became clear that significant NP concentrations were being detected in the precipitation,
183 prior to it coming in contact with the painted surfaces. Owing their presence to a variety of
184 natural, urban or industrial sources, nano- and micron-sized particles are ubiquitous in the
185 atmosphere, and they are especially important in urban and industrial areas subjected to
186 pollution.^{22, 23, 38, 39} Therefore, it was essential to accurately determine Ti NP concentrations
187 in the natural precipitation in order to correct for their presence during the paint-release
188 studies. Given that we have no *a priori* information on the full chemical composition of
189 the Ti containing NPs, sizes have been calculated based upon the assumption that they are
190 primarily TiO₂. It is thus important to acknowledge that, for particles that are more likely
191 to have multi-element compositions, such as natural nanominerals,^{22, 38, 40} actual particle
192 sizes would be underestimated. On the other hand, for some particles, such as Magneli
193 phase Ti (Ti_xO_{2x-1}), which are produced incidentally during coal combustion²², sizes would
194 be overestimated. Indeed, in this study, numerous metals, including Ti, Ce, Fe, La, Nd, U
195 and Ag were found in particulate forms by SP-ICP-MS time-scan (**Fig. S3**), with the results
196 strongly indicating the presence of atmospheric NPs containing Ti (**Fig. 2A**). Micron-sized

197 particles were also present in the precipitation; when comparing ICP-MS measurements on
198 acidified samples measured before and after filtration, >90% of the particulate Ti was
199 generally removed by a 0.45 μm membrane (based on total Ti mass balances). SP-ICP-MS
200 measurements performed on the filtered samples showed that the remaining NPs had
201 diameters with a mode around 30 nm and a size distribution extending from the SDL (20
202 nm) to beyond 100 nm (Fig. 2B). Snow and rain samples were analysed for both total Ti
203 by ICP-MS and Ti NPs by SP-ICP-MS, with the results showing that significant numbers
204 of Ti-containing NPs were found in the snow and rain samples. A subsequent experiment
205 where Milli-Q water was left outdoors for 2 d under dry summer conditions also showed
206 significant particle numbers (Fig. S4), suggesting that dry deposition was an important
207 source of the Ti NPs. This observation was also observed for a Milli-Q water sample
208 exposed to indoor air (Fig. S5). The ubiquitous presence of Ti NPs in the air demonstrates
209 the importance of multiple control experiments in order to avoid false positives in the paint
210 release experiments.



211

212 **Figure 2.** (A) Time-resolved SP-ICP-MS signal and the corresponding (B) particle size distribution
213 obtained for Ti-containing NPs in snow melt (10x diluted). The snow was collected during 2 weeks

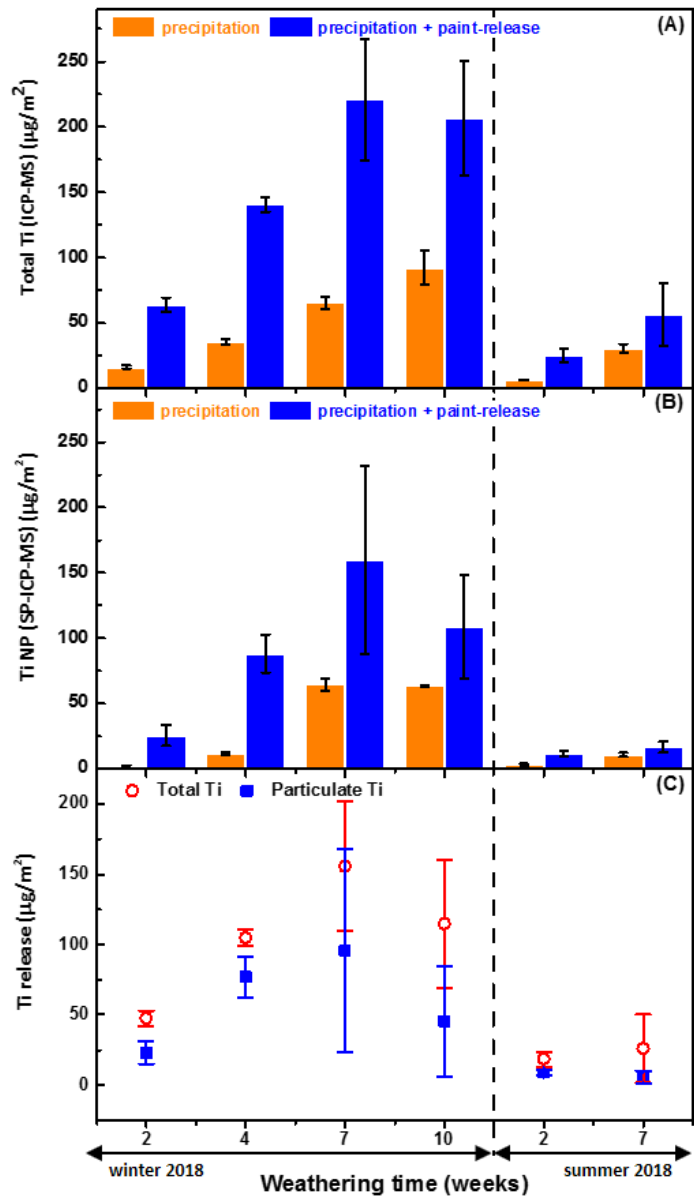
214 in February 2018, and the measurements were performed by high-sensitivity magnetic-sector ICP-
215 MS. Particle diameters were calculated on the assumption that particles were TiO₂.

216

217 **TiO₂ NPs in paint.** The water-based acrylic paint was tested for TiO₂ NPs using SP-ICP-
218 MS after dilution (2×10^7 x (w/w)) in Milli-Q water. The PSD for TiO₂ extended from 20
219 nm (SDL) to beyond 200 nm, with most of the detected NPs around 150 ± 10 nm (mode)
220 with a mean NP diameter of 131 ± 1 nm (**Fig. S6A**). There were approx. $(6.8 \pm 0.1) \times 10^{15}$
221 NPs/kg-paint (*i.e.* below 250 nm) in the liquid paint, which corresponded to about 5.0 %
222 by weight. This measured NP fraction is in agreement with other reports for paints,^{5, 8, 16, 41}
223 where experimental or predicted TiO₂ fractions are reported to be around 1-15% by weight.

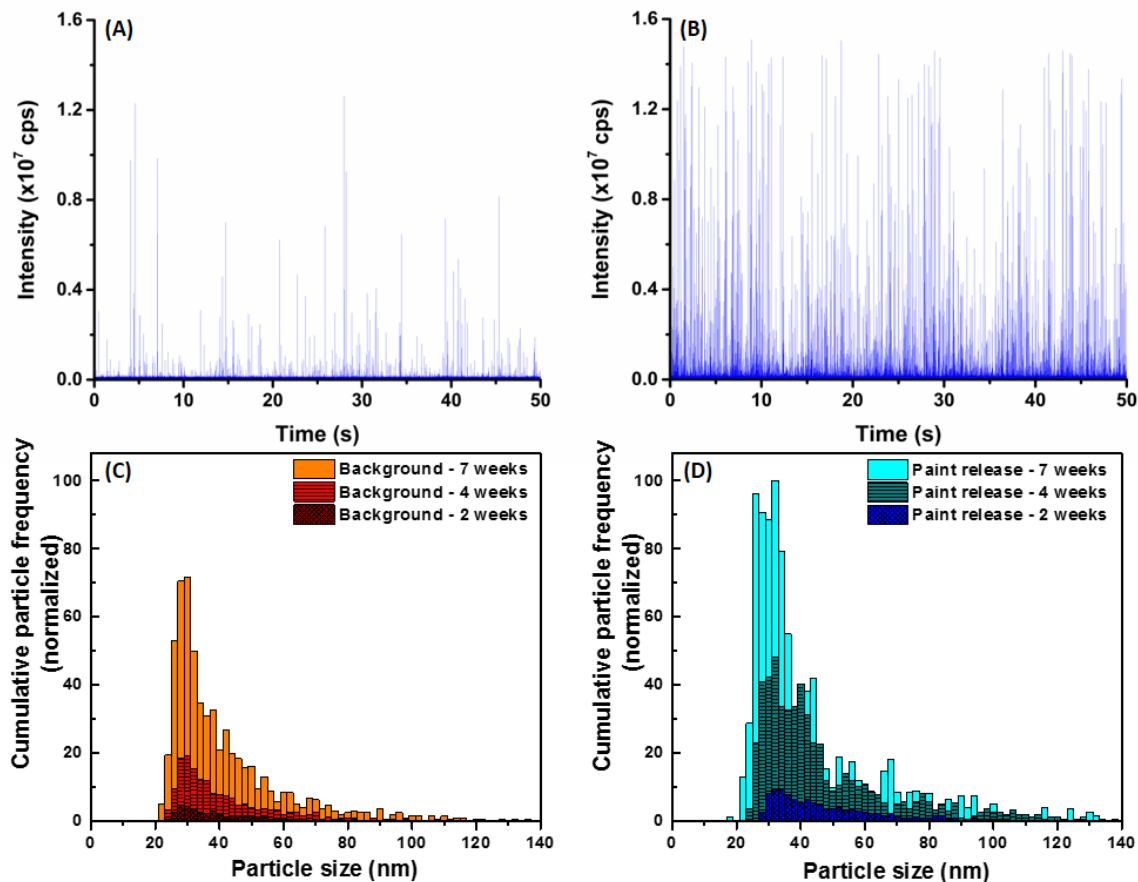
224 **TiO₂ NP release due to weathering.** Experimental containers with or without a painted
225 panel were placed outdoors. In the control samples (*i.e.* without panels), NP numbers were
226 significant and generally increased with time, in both the winter and summer sampling
227 periods. The actual measured concentrations ranged from 8.1×10^5 NP/mL after two
228 weeks to 1.2×10^7 NP/mL after 7 weeks in the winter and hovered around $2 - 4 \times 10^6$
229 NP/mL for 7 weeks during the summer. The observed increase in NP numbers is primarily
230 attributed to cumulative NP deposition (directly via rain/snow or indirectly via dry
231 deposition, see **Fig. S4**), although part of the variation can be attributed to differences in
232 the sample volumes at the time of collection (due to the timing of evaporation/precipitation
233 events). When the data were normalized by exposure surface area of the painted panels,
234 both total Ti and Ti NP (**Fig. 3A, 3B**, orange bars) consistently increased with time at an
235 approximate rate of $9.2 \mu\text{g-Ti}/\text{m}^2/\text{week}$ (this corresponds to a rate of $30.9 \mu\text{g-Ti}/\text{m}^2/\text{week}$
236 when normalized by footprint area).

237 In spite of this relatively large and increasing background signal, greater NP
238 numbers (and masses) were observed in the containers containing painted surfaces (**Fig.**
239 **3A, 3B**). Raw SP-ICP-MS data comparing the precipitation (snow meltwater) (**Fig. 4A**) to
240 snow meltwater that was in contact (2 weeks) with the painted panel (**Fig. 4B**) showed
241 significantly more spikes, which was attributed to the release of particles from the paint.
242 PSDs were strikingly similar (**Fig. 4C, 4D**), with most of the NPs uniformly observed for
243 sizes below 60 nm.



244

245 **Figure 3.** Quantification of Ti in the natural precipitation as well as the precipitation following its
 246 contact with painted panels: **(A)** total Ti measured by ICP-MS, **(B)** Ti NP measured by SP ICP-
 247 MS, and **(C)** the net release of total and nanoparticulate Ti during the winter and summer seasons.
 248 The quantities are expressed in terms of Ti metal content and are normalized by the exposure area
 249 of the painted panels.



250

251 **Figure 4.** Time-resolved SP-ICP-MS signal (*i.e.* raw data) for Ti-containing NPs in (A) snow
 252 meltwater and (B) snow after 2 weeks of contact with a painted panel. Particle size distributions
 253 were obtained for (C) Ti-containing NPs in the natural precipitation background and (D) for NP
 254 released from the painted surfaces, over several weeks during the winter season. Note that paint-
 255 released NP frequencies are already corrected for background NPs occurring in the precipitation.
 256 Particle diameters were calculated on the assumption that particles were TiO₂.

257

258 Significant release of Ti (ANOVA, $p < 0.05$) was observed (**Fig. 3C**), with a large
 259 proportion (55% on average) of it being attributed to the Ti NPs. In the winter, NP release
 260 appeared to peak at $168 \pm 121 \mu\text{g}/\text{m}^2$, corresponding to $(3.4 \pm 2.5) \times 10^{11} \text{ NP}/\text{m}^2$ after
 261 7 weeks and may have decreased after 10 weeks of exposure (**Fig. 3C, Table 1**), although
 262 the data are admittedly disparate due to the dynamic nature of this long-term exposure.
 263 Since sampling was conducted in a sacrificial manner in order to take into account the

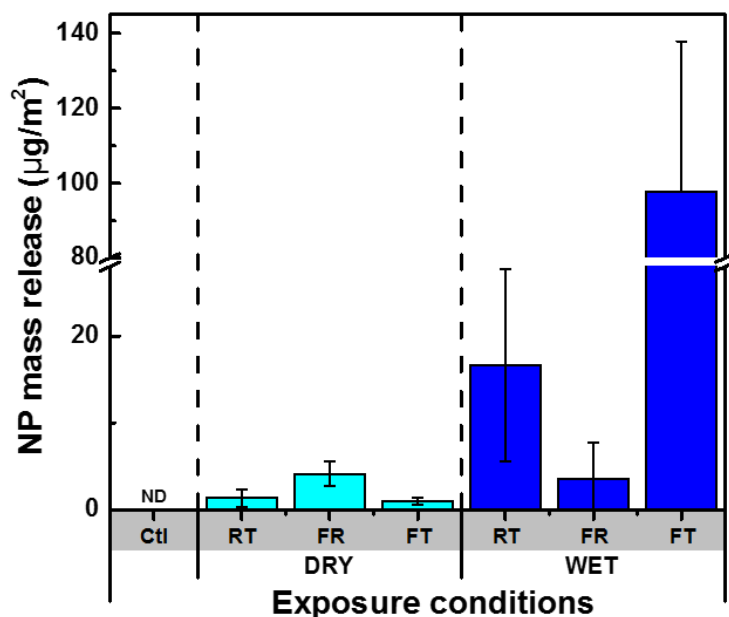
264 cumulative nature of the exposure medium, error bars increased with time, especially for
265 the longer exposures. Certainly, NP concentrations will change as the NPs undergo
266 physicochemical transformations (*e.g.* agglomeration, dissolution)^{42,43}, as the precipitation
267 undergoes modifications (*e.g.* evaporation, wind removal of snow, pH changes, new
268 precipitation renewal), or as sorptive losses occur¹¹.

269 There appeared to be greater NP release in the winter as compared to the summer.
270 While NP release during the first 2 weeks of summer weathering could be easily
271 distinguished from background levels in the precipitation, this distinction became
272 statistically insignificant (ANOVA, $p>0.05$) after 7 weeks due to lower release-to-
273 background ratios. Lower release in the summer did not appear to be correlated to the
274 quantity of precipitation since rain events during the summer averaged 3.0 mm/day over
275 the 7 weeks of exposure, whereas 2.5 mm/day (water equivalent) of snow and rain was
276 recorded during the 10 weeks of cold weather. Whereas summer precipitation was mostly
277 limited to a few abundant rainfall events, the winter precipitation was more uniformly
278 distributed (**Fig. S7**).

279 In summary, the data clearly show that weathering of the painted panels increased
280 NP concentrations in the precipitation. The outdoor data also suggest that weathering was
281 likely more important in the winter than in the summer and that the sizes of the released
282 NP were generally smaller than those in the original paint. These two points are examined
283 in more detail in the following sections.

284 **How did weathering conditions affect TiO₂ NP release?** For the experiments conducted
285 in the summer, less release was observed when compared to measurements performed in

286 the winter (*i.e.* **Fig. 3C**). The weather data (**Fig. S7**) suggested that the summer samples
287 underwent frequent wet-dry cycles with shorter liquid-surface interaction times, whereas
288 the winter samples were nearly constantly exposed to snow or ice in addition to undergoing
289 freeze-thaw cycles. Several controlled laboratory experiments were therefore designed to
290 isolate the roles of seasonal variability, including the role of temperature, the role of
291 moisture and the role of FT (freeze-thaw) cycles on the release of NPs from a painted
292 surface. For a 42-day (6 week) exposure, cold conditions, wet conditions and FT conditions
293 all contributed to increased NP release (**Fig. 5**). Among the different weathering conditions,
294 exposure to water and FT cycles stood out as being important factors to boost NP release.
295 For example, 27x more NPs were released from samples that underwent 21 FT cycles as
296 compared to samples that were simply frozen (**Fig. 5**). On the other hand, wet RT samples
297 released 12x more NPs than dry. Surprisingly, water did not appear to have an effect on
298 the samples that were kept in the freezer in the absence of FT (**Fig. 5**). The data suggest
299 that NP release is enhanced under wet conditions with high liquid-surface interaction times
300 and increased further if the surface undergoes FT cycles. These results agree well with
301 those for the natural weathering, consistent with the hypothesis that wet conditions along
302 with FT cycles could indeed explain the increased NP release that was observed during the
303 winter season.

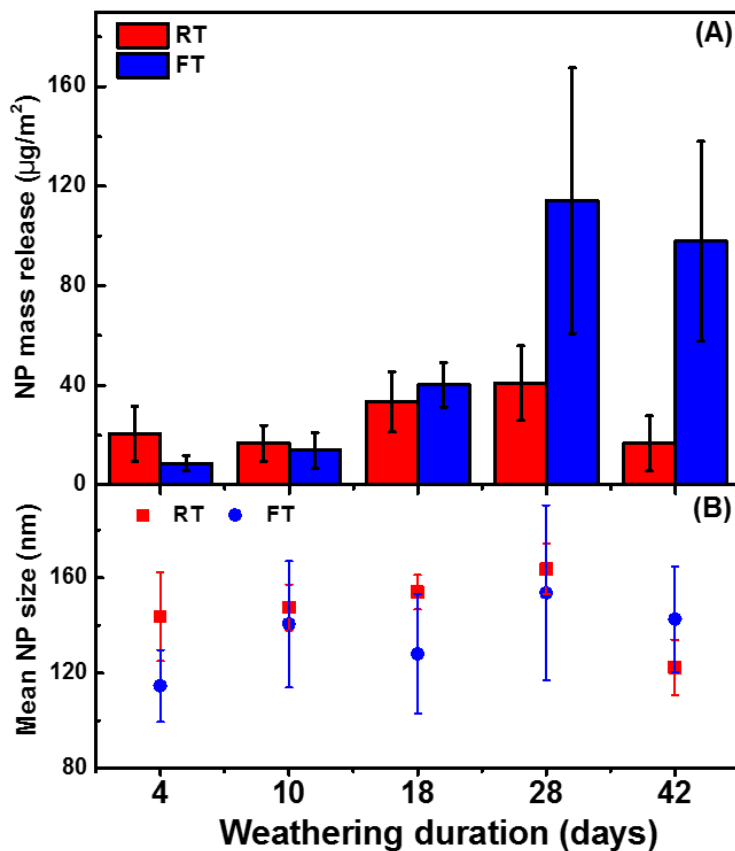


304

305 **Figure 5.** NP mass release under different exposure conditions, quantified by SP-ICP-MS and
 306 normalized by the exposure area of painted panels. Ctl refers to a control condition, where no panel
 307 was used. The exposure conditions consisted of dry and wet conditions, with RT, FR and FT
 308 denoting the sub-conditions of room temperature, only-freezing, and freeze-thaw, respectively. The
 309 exposure duration was 42 days or 21 cycles (in the case of FT). ND denotes “not detected”
 310 (ANOVA, $p > 0.05$).

311 In addition, time-resolved monitoring of the NP release was performed for the wet
 312 RT or FT (**Fig. 6**). During the first 18 days of weathering, no significant difference in the
 313 release quantities were observed; however, during the following 4 weeks of weathering (14
 314 FT cycles), the mass of NPs released under FT conditions greatly surpassed those under
 315 RT conditions (**Fig. 6A**). Furthermore, while NP mass (and numbers) appeared to increase
 316 in the later stages of the FT experiments, they stabilized or decreased for the samples held
 317 at room temperature (**Fig. 6A**). As above, we hypothesize that NP loss is primarily driven
 318 by agglomeration⁴³ leading to sedimentation⁴⁴ of the NPs, as well as sorptive processes¹¹.
 319 This is consistent with the observation that the proportion of NP >100 nm consistently

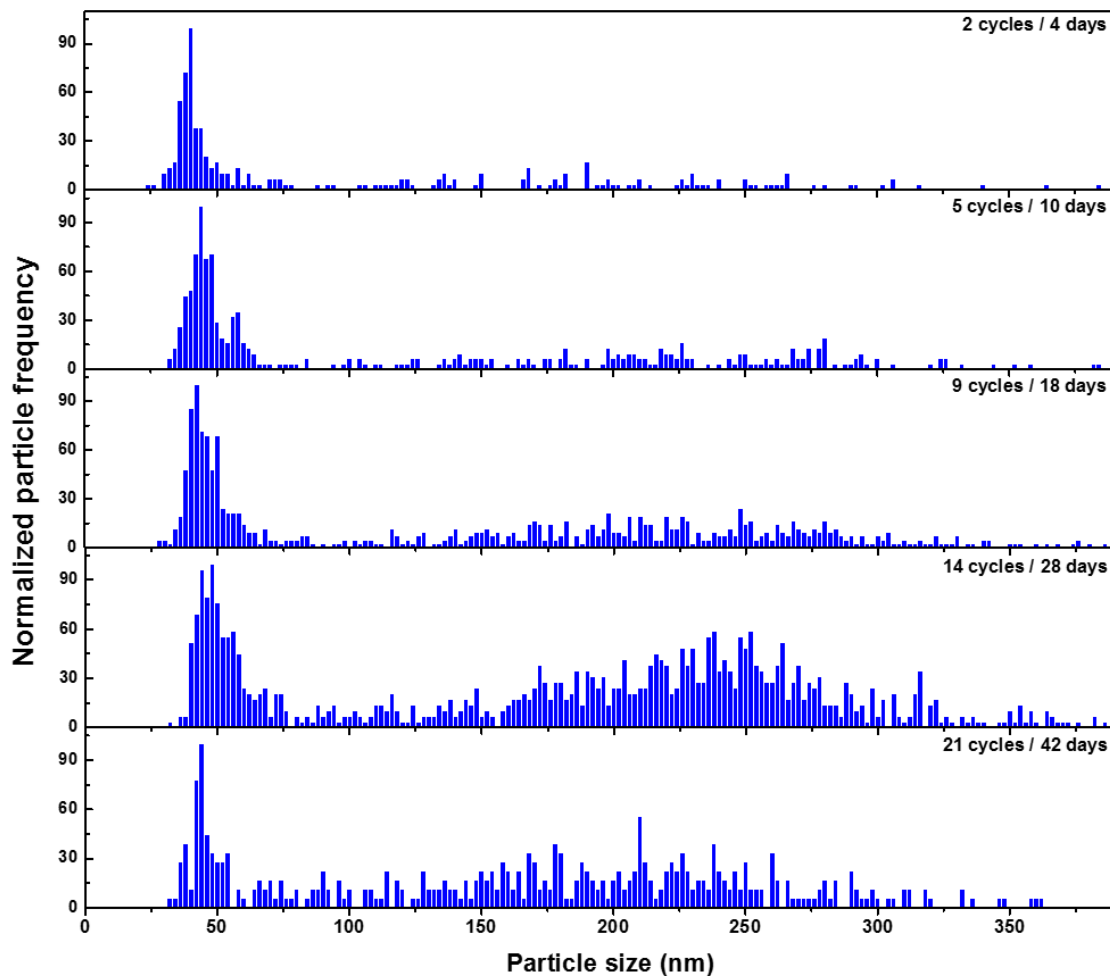
320 increased during the 4 weeks of weathering, prior to declining slightly around 6 weeks
321 (Fig. 7).



322

323 **Figure 6.** NP mass release normalized by the exposure area of painted panels, for samples that
324 were exposed to Milli-Q water (no NP background) under (wet) conditions of room temperature
325 (RT) and freeze-thaw (FT) and (B) the corresponding mean NP sizes. The weathering duration of
326 4, 10, 18, 28 and 42 d correspond to 2, 5, 9, 14, and 21 FT cycles, respectively.

327



328

329 **Figure 7.** Particle size distributions for TiO₂ NPs following their release from painted surfaces that
 330 were exposed to several weeks of FT cycles in Milli-Q water (no NP background). Each cycle
 331 consisted of 1 day of freezing and 1 day of thawing. Particle diameters were calculated on the
 332 assumption that particles were TiO₂.

333

334 **Are the sizes of weathered TiO₂ NPs similar to those that were originally in the paint?**

335 The particle size distributions of the weathered NPs (**Fig. 4D**) appeared to be smaller than
 336 sizes that were obtained in the original paint sample (**Fig. S6A**). Two experiments were
 337 conducted to validate this observation: (i) first, a painted board was soaked in Milli-Q water
 338 in a closed container for 4 d at room temperature (20 °C), in order to more easily detect NP
 339 release by reducing the background signal; (ii) second, under the assumption that the NPs

340 were originally agglomerated in the paint, the paint was diluted (2×10^7 x), sonicated (30
341 min.) and then stabilized through the addition of 5 mg/L of a fulvic acid.⁴⁵

342 In Milli-Q water, a significant number of NPs were leached into solution and these
343 NPs had a size distribution (**Fig. S8**) that was very similar to what was observed under
344 natural conditions, *i.e.* most of the NPs were smaller than 60 nm with a wide size
345 distribution extending beyond 200 nm. Significantly more NPs were detected at the lower
346 end of the size distribution ($(8.4 \pm 0.1) \times 10^{15}$ NPs/kg-paint or 5.5 ± 0.1 % by weight)
347 as compared to the diluted (unsonicated) paint sample ($(6.8 \pm 0.1) \times 10^{15}$ NPs/kg-paint
348 or 5.0 ± 0.1 % by weight). This observation suggests that the NPs in the paint were at least
349 partially dispersed by the sonication and stabilization (**Fig. S6B**), resulting in the detection
350 of more primary particles in the smaller size ranges.

351 **Environmental considerations and implications.** The natural and lab weathering data
352 present firm evidence that TiO₂ NPs were leached out of painted surfaces, with the
353 strongest release observed under wet and cold conditions – particularly, under conditions
354 where freeze-thaw occurred. Although release escalated during the winter, the absolute
355 quantity of release, even at its peak, was rather small, corresponding to <0.001 % of total
356 TiO₂ NP load on the boards. While the weathering was fairly harsh, the study was
357 conducted for 10 weeks only, and thus, given several years of life expectancy for painted
358 façades (before renewal), increasingly more release could be expected, during long-term
359 weathering and degradation of the surfaces. The results showed that environmental factors
360 (*e.g.* temperature, moisture) will affect the quantity of NPs released in addition to
361 influencing their fate through processes such as agglomeration, sedimentation and

362 sorption.^{31, 46-49} These processes will certainly have an impact on the mobility and bio-
363 accessibility of these released NPs and will thus alter their environmental risk.

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369

370 **Table 1.** Quantification of the release of particulate TiO₂ NPs (<450 nm) from painted panel surfaces, following their natural weathering for several
 371 weeks in Winter 2018 and Summer 2018. Quantities are reported in terms of TiO₂ NP mass and number released per painted surface area or mass
 372 of dry paint load on the panel. The measurements were performed by high-resolution SP-ICP-MS.

Released TiO₂ NPs from the painted surfaces (<450 nm fraction) after natural weathering					
Season	Weathering time	NP mass per surface area	NP mass per g-dry-paint	NP number per surface area	NP number per g-dry-paint
	<i>weeks</i>	<i>μg/m²</i>	<i>ng/g-dry-paint</i>	<i>NPs/m²</i>	<i>NPs/g-dry-paint</i>
Winter 2018	2	38.40 ± 13.62	118.67 ± 48.19	6.6 x 10 ¹⁰ ± 1.8 x 10 ¹⁰	2.0 x 10 ⁸ ± 6.5 x 10 ⁷
	4	128.41 ± 24.56	313.83 ± 39.75	2.3 x 10 ¹¹ ± 6.3 x 10 ¹⁰	5.4 x 10 ⁸ ± 1.4 x 10 ⁸
	7	168.34 ± 120.55	369.81 ± 162.99	3.4 x 10 ¹¹ ± 2.5 x 10 ¹¹	8.1 x 10 ⁸ ± 3.1 x 10 ⁸
	10	75.45 ± 65.84	166.37 ± 152.84	1.2 x 10 ¹¹ ± 1.7 x 10 ¹¹	2.3 x 10 ⁸ ± 3.9 x 10 ⁸
Summer 2018	2	14.70 ± 3.76	25.68 ± 7.4	3.2 x 10 ¹⁰ ± 5.6 x 10 ⁹	5.3 x 10 ⁷ ± 9.3 x 10 ⁶

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