SUPPLEMENTARY INFORMATION

Quantification and characterization of Ti-, Ce- and Ag-nanoparticles in global surface waters and precipitation

Agil Azimzada[1,2], Ibrahim Jreije[1], Madjid Hadioui[1], Phil Shaw[3], Jeffrey M. Farner[4], Kevin J. Wilkinson[1*]

[1]Department of Chemistry, University of Montreal, Montreal, QC H3C 3J7, Canada
[2]Department of Chemical Engineering, McGill University, Montreal, QC H3A 0C5, Canada
[3]Nu Instruments, Wrexham LL13 9XS, United Kingdom
[4]Department of Civil and Environmental Engineering, University of Alberta, Edmonton, AB T6G 1H9, Canada

*** Correspondence:**
Kevin J. Wilkinson
Email: kj.wilkinson@umontreal.ca, Tel: +1 (514) 343-6741, Fax: +1 (514) 343-7586

Keywords: titania, ceria, silver, engineered nanoparticles, rain, surface waters, environmental impact

Additional information on NP data processing

Data processing was performed using NuQuant version 2.2 (or NuQuant Vitesse prototype for simultaneous multi-element analysis). This method is extensively discussed in Hadioui *et al*.[1], but can briefly be summarized as:

- Data smoothing
- Creating a peak search window that rolls over the span of the whole acquisition period
- Searching for a maximum (within a window) and establishing pre-max and post-max inflection points, where PEAK data points = in between pre-max and post-max inflection points
- Establishing local background (mean and SD) based on the remaining points in the window
- Calculating Net PEAK area (*i.e*. subtraction of equivalent background from PEAK raw data)
- Setting NP qualification criteria: I_{thld} = [local background average] + n x [local background standard deviation], where n was often set to 3 (in this case)
- PEAKs that meet the above criterion are now qualified as a "NP peak"
- Data can be viewed with respect to isotope type, intensity (counts) or full-width half-maximum (FWHM) values, which allows for flexible screening of possible artifacts

Supplementary Figures

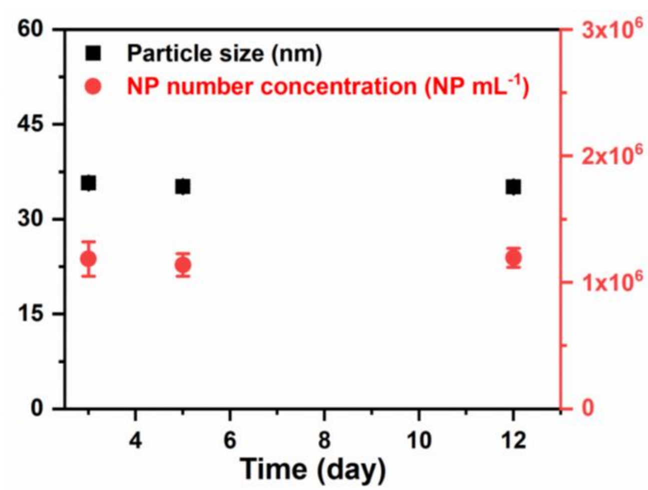

Figure S1. **Particle stability**. Time-resolved particle number concentrations and sizes as measured for TiO_2 NPs in a melted snow sample collected in Montreal, Quebec. Measurements were performed using a sector-field ICP-MS in a single particle mode, 3, 5 and 12 days following the filtration of the sample.

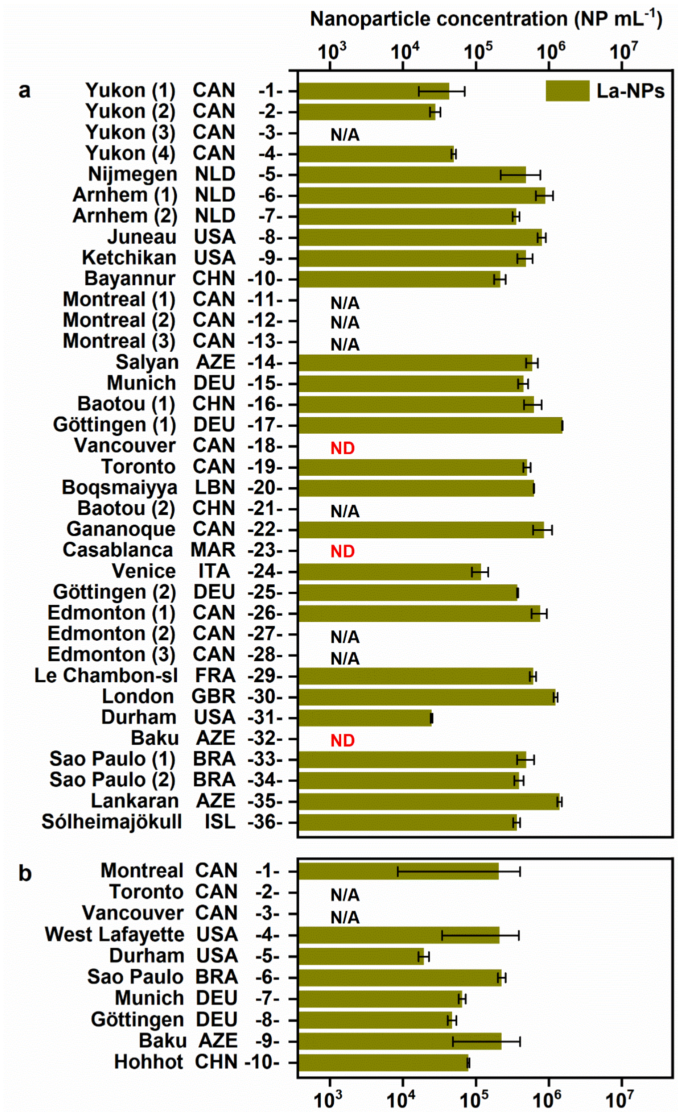

Figure S2. Concentrations of La nanoparticles in global precipitation and surface waters. a,b, Particle number concentrations for La-containing NPs as measured in surface waters (**a**) and precipitation **(b)** collected at 46 sampling sites across 13 countries. Sampling sites are indicated by city/province names and ISO country codes. Measurements were performed using a sector-field ICP-MS. ND stands for “not detected” and refers to concentrations below the detection limits of the technique. N/A refers to samples that were not analyzed.

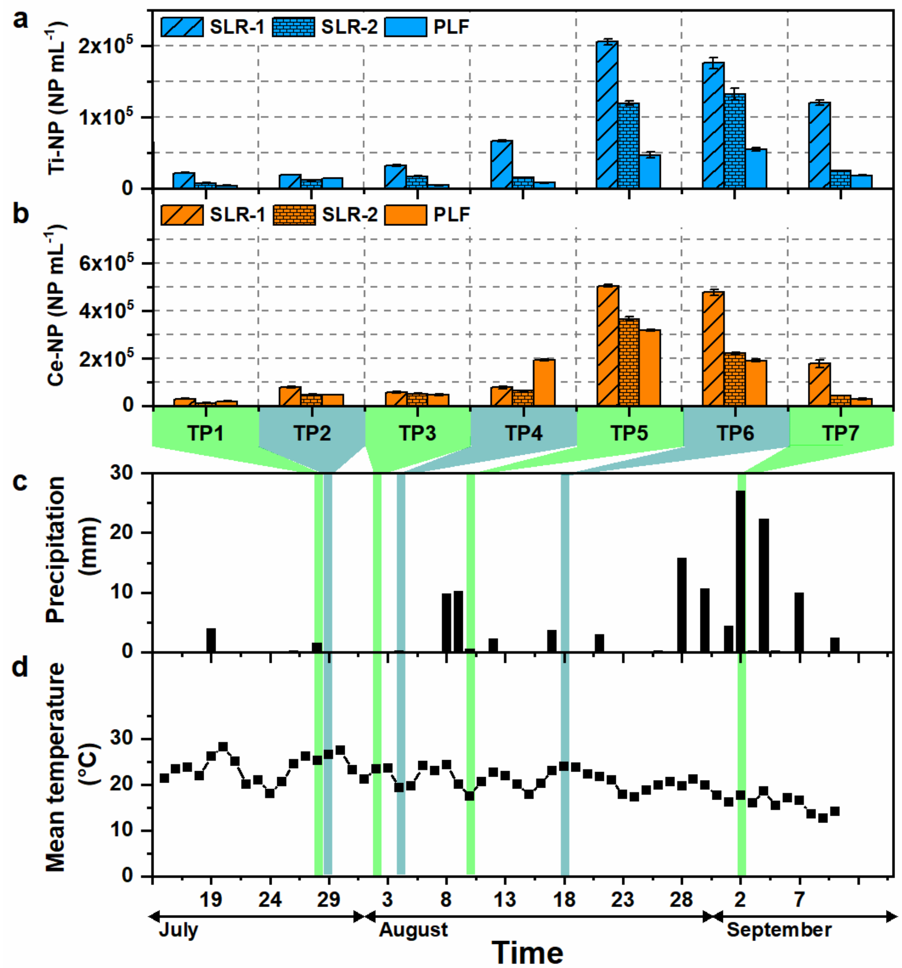

Figure S3. Time-resolved measurements of nanoparticles in surface waters. a,b, Particle number concentrations measured for Ti- (**a**) and Ce-containing (**b**) NPs in surface water samples collected from two sampling points at Saint Lawrence River (SLR) and a recreational pond in Parc La Fontaine (PLF) in Montreal (Quebec, Canada). Each timepoint (TP) refer to the date when the samplings were performed. **c,d,** Natural precipitation (**c**) and temperature (**d**) data are collected from the 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. Measurements were performed using a sector-field ICP-MS.

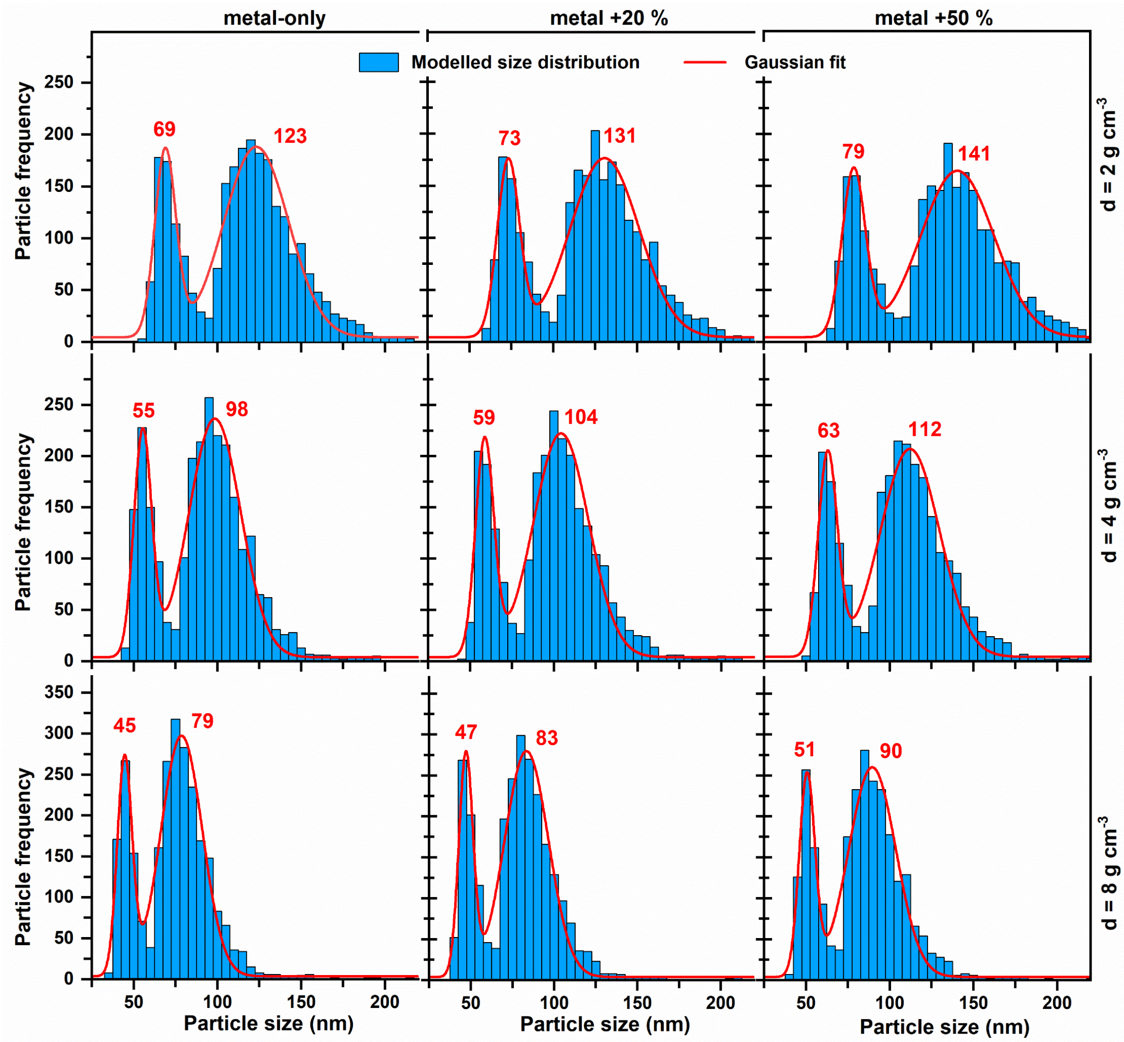

Figure S4. Modelled size distributions taking into account multi-element nature of particles. Modelled size distributions of NPs detected in snow from the Sólheimajökull glacier (ISL), assuming a range of particle densities (2-8 g cm^{-3}). Given that the experimental determinations were limited to metals and metalloids only (*i.e.* excluded oxygen, halogens, etc.), particle sizes were predicted based upon the total masses of (almost) all metals/metalloids (*i.e.* 23-238 amu) detected in single particles (*i.e.* metal only). Total masses were assigned additional mass uncertainties of 20% (column 2) or 50% (column 3), due to the presence of the undetected elements. Data is fitted with Gaussian fit (red line), and the sizes corresponding to the peak maxima of the bimodal distributions are indicated. Measurements were performed with a single-particle time-of-flight ICP-MS.

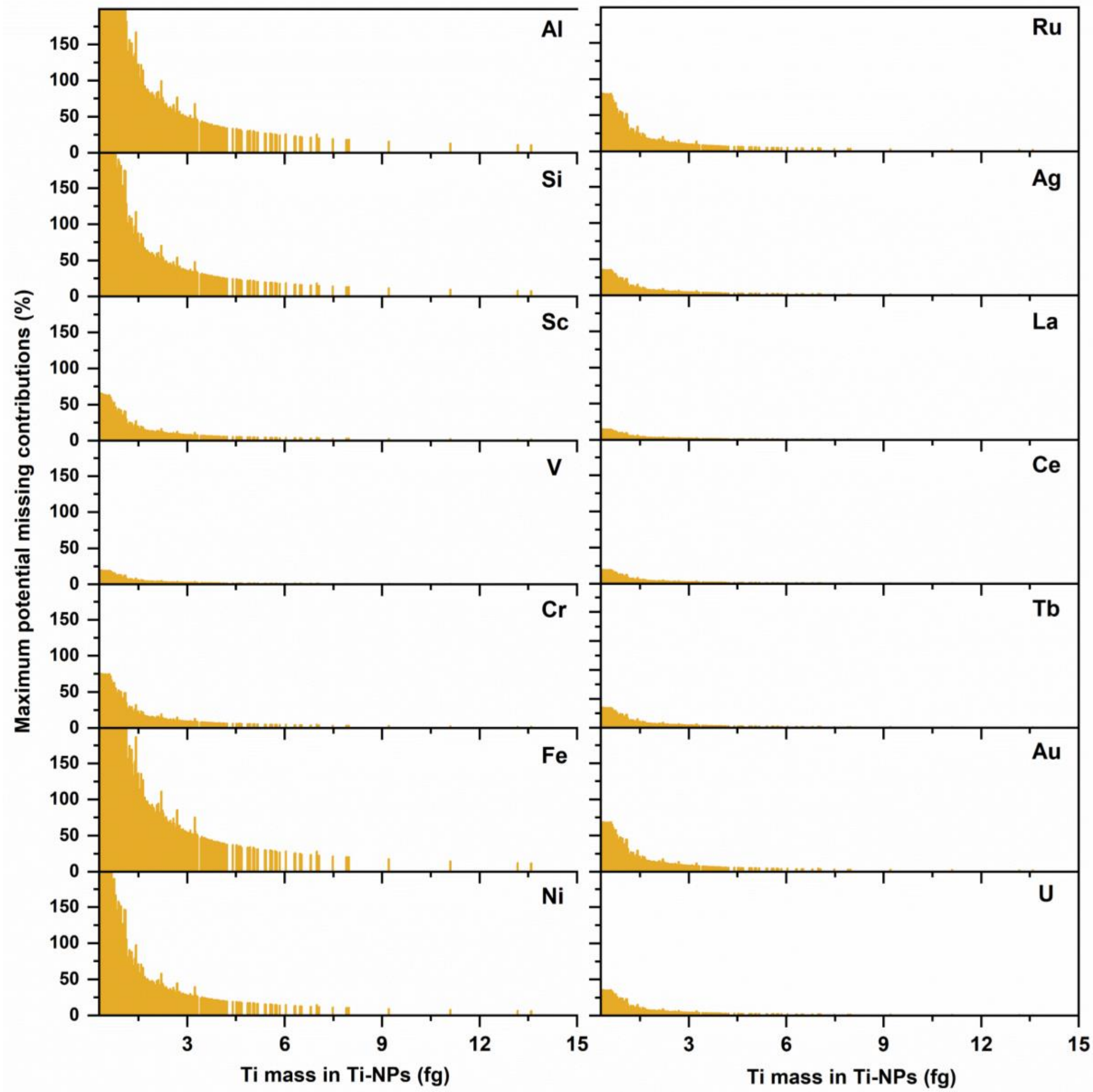

Figure S5. Detection limits of the multi-element analysis. Upper limits of the potential missing contributions of 14 metals in Ti-containing NPs, for cases in which Ti was detected as the only metallic component. % values are calculated based on the mass detection limit of each metal in relationship to the Ti content detected in individual Ti-containing NPs. Measurements were performed with single-particle time-of-flight ICP-MS, using 1953 NPs detected in a Montreal rainwater. In general, the probability of labelling a NP as pure TiO_2 when it is not, increases for the very small particles and when detecting small quantities of the secondary elements with the poorest detection limits (Al, Si, Fe, Ni).

Table S1. Sampling information for global surface water samples

	Region/territory	Country		Water body	Sampling date	Geo coordinates	
					Year 2019	*Longitude*	*Latitude*
1	**Yukon (1)**	CAN	Canada	Christmas Bay (Kluane Lake)	May 29	-138.368602	61.0626
2	**Yukon (2)**	CAN	Canada	KLRS (Kluane Lake)	May 31	-138.416049	61.027543
3	**Yukon (3)**	CAN	Canada	*- (lake)*	Jun 6	-138.372576	61.080076
4	**Yukon (4)**	CAN	Canada	*- (lake)*	Jun 6	-138.371875	61.069704
5	**Nijmegen**	NLD	Netherlands	Waal River	Jul 25	5.858128	51.853724
6	**Arnhem (1)**	NLD	Netherlands	Nederrijn River	Jul 26	5.907252	51.975722
7	**Arnhem (2)**	NLD	Netherlands	Grote Vijver Lake	Jul 26	5.896827	51.995696
8	**Juneau**	USA	United States	Gold Creek	May 10	-134.419994	58.298831
9	**Ketchikan**	USA	United States	Ketchikan Creek	May 13	-131.642421	55.341255
10	**Bayannur**	CHN	China	Ulansu Lake	Sep 8	108.836444	40.885944
11	**Montreal (1)**	CAN	Canada	Parc La Fontaine (pond)	Sep 2	-73.5679645	45.5232449
12	**Montreal (2)**	CAN	Canada	St Lawrence River (1)	Sep 2	-73.5485275	45.5090203
13	**Montreal (3)**	CAN	Canada	St Lawrence River (2)	Sep 2	-73.5467532	45.5081442
14	**Salyan**	AZE	Azerbaijan	Kür (Mtkvari) River	Jun 3	48.963551	39.630592
15	**Munich**	DEU	Germany	Isar River	Apr 30	11.581167	48.128583
16	**Baotou (1)**	CHN	China	Yellow River	Sep 10	109.987822	40.5128
17	**Göttingen (1)**	DEU	Germany	Leine River	May 1	9.919656	51.542811
18	**Vancouver**	CAN	Canada	Strait of Georgia (Pacific Ocean)	Mar 18	-123.261953	49.262093
19	**Toronto**	CAN	Canada	Lake Ontario	Mar 2	-79.380009	43.639518
20	**Boqsmaiyya**	LBN	Lebanon	El-Jaouz River	May 1	35.727279	34.271688
21	**Baotou (2)**	CHN	China	Yellow River (2)	Sep 10	109.804561	40.500669
22	**Gananoque**	CAN	Canada	St Lawrence River (3)	Feb 9	-76.158768	44.325066
23	**Casablanca**	MAR	Morocco	Altlantic Ocean	Mar 9	-7.640465	33.604793
24	**Venice**	ITA	Italy	Rio del Gozzi Canal	Aug 6	12.337964	45.44212
25	**Göttingen (2)**	DEU	Germany	Kiessee Lake	May 1	9.921195	51.51951
26	**Edmonton (1)**	CAN	Canada	Saskatchewan River (1)	May 14	-113.520076	53.5302
27	**Edmonton (2)**	CAN	Canada	Saskatchewan River (2)	May 14	-113.525406	53.532853
28	**Edmonton (3)**	CAN	Canada	Saskatchewan River (3)	May 14	-113.514956	53.531665
29	**Le Chambon-sl**	FRA	France	Lignon du Velay River	Aug 8	4.315863	45.052825
30	**London**	GBR	United Kingdom	The Long Water Lake	Mar 3	-0.173268	51.506563
31	**Durham**	USA	United States	*- (stream)*	Mar 25	-78.9526	35.9611
32	**Baku**	AZE	Azerbaijan	Caspian Sea	Jun 14	49.800351	40.304766
33	**Sao Paulo (1)**	BRA	Brazil	Rio Passo River (1)	Aug 19	-47.716875	-22.419259
34	**Sao Paulo (2)**	BRA	Brazil	Rio Passo River (2)	Aug 19	-47.720028	-22.414361
35	**Lankaran**	AZE	Azerbaijan	Xanbulan Lake	June 8	48.771991	38.66092
36	**Sólheimajökull**	ISL	Iceland	Sólheimajökull Glacier	Feb 15	-20.634801	64.066452

Table S2. Sampling information for global natural precipitation samples

	City/town	Country		Water type	Sampling date	Geo coordinates	
					Year 2019	*Longitude*	*Latitude*
1	**Montreal**	CAN	Canada	rain	Apr 26	-73.616052	45.502324
2	**Toronto**	CAN	Canada	rain	Mar 11	-123.241472	49.264229
3	**Vancouver**	CAN	Canada	rain	Sep 3	-79.394651	43.657773
4	**West Lafayette**	USA	United States	rain	Apr 12	-86.955001	40.438851
5	**Durham**	USA	United States	rain	Mar 3	-78.9527	35.9613
6	**Sao Paulo**	BRA	Brazil	rain	Aug 4	-47.552083	-22.398778
7	**Munich**	DEU	Germany	rain	Apr 29	11.580363	48.13405
8	**Gottingen**	DEU	Germany	rain	Apr 30	9.923772	51.531163
9	**Baku**	AZE	Azerbaijan	rain	Jun 8	49.84392	40.37331
10	**Hohhot**	CHN	China	rain	Aug 3	111.68502	40.75769

Table S3. Nanoparticle measurements on surface water samples. Measurements were performed by a high-sensitivity sector-field single-particle ICP-MS. NP mass concentrations were calculated by assuming that all Ti-, Ce- and Ag-containing NPs occurred in the forms of TiO_2, CeO_2 and Ag, respectively. ND stands for "not detected" and refers to concentrations that were below the detection limits of the technique. N/A refers to samples that were not analyzed.

	Region/territory	NP number concentrations (NP mL^{-1})			NP mass concentration (ng L^{-1})		
		Ti-NPs	*Ce-NPs*	*Ag-NPs*	*TiO_2*	*CeO_2*	*Ag*
1	**Yukon (1)**	$(5.4±1.0)×10^3$	$(7.5±1.8)×10^3$	$(3.6±1.8)×10^3$	2.1 ± 0.7	0.13 ± 0.06	0.025 ± 0.010
2	**Yukon (2)**	$(1.2±0.2)×10^4$	$(1.5±0.5)×10^4$	ND	1.9 ± 0.2	0.27 ± 0.15	ND
3	**Yukon (3)**	$(7.9±0.4)×10^4$	$(2.9±1.0)×10^4$	$(3.7±0.7)×10^3$	8.8 ± 1.0	0.52 ± 0.17	0.016 ± 0.006
4	**Yukon (4)**	$(6.0±0.2)×10^4$	$(1.2±0.1)×10^5$	$(3.7±0.8)×10^3$	7.8 ± 1.7	2.03 ± 0.16	0.010 ± 0.002
5	**Nijmegen**	$(5.2±3.1)×10^3$	$(6.3±4.5)×10^4$	ND	1.5 ± 0.7	0.57 ± 0.39	ND
6	**Arnhem (1)**	$(1.7±1.2)×10^4$	$(1.8±1.1)×10^4$	ND	5.8 ± 5.6	0.14 ± 0.10	ND
7	**Arnhem (2)**	$(3.0±3.3)×10^3$	$(2.5±0.0)×10^4$	ND	0.6 ± 0.7	0.25 ± 0.12	ND
8	**Juneau**	$(3.9±1.5)×10^4$	$(5.9±1.0)×10^4$	ND	8.4 ± 4.6	0.15 ± 0.02	ND
9	**Ketchikan**	$(1.1±0.0)×10^4$	$(2.2±0.6)×10^4$	ND	1.1 ± 0.0	0.07 ± 0.02	ND
10	**Bayannur**	$(2.0±1.0)×10^4$	$(1.9±0.3)×10^5$	$(2.3±3.7)×10^3$	6.4 ± 4.8	1.66 ± 0.26	0.024 ± 0.038
11	**Montreal (1)**	$(1.9±0.1)x10^4$	$(2.8±0.3)x10^4$	ND	5.4 ± 0.6	0.12 ± 0.01	ND
12	**Montreal (2)**	$(1.2±0.0)x10^5$	$(1.8±0.1)x10^5$	ND	49.2 ± 0.8	1.04 ± 0.26	ND
13	**Montreal (3)**	$(2.5±0.0)x10^4$	$(4.2±0.0)x10^4$	ND	13.3 ± 1.1	0.49 ± 0.35	ND
14	**Salyan**	$(1.5±0.7)×10^5$	$(7.1±2.0)×10^5$	$(2.7±0.2)×10^3$	33.8 ± 12.8	4.67 ± 1.06	0.028 ± 0.005
15	**Munich**	$(1.5±0.2)×10^5$	$(4.0±0.5)×10^5$	$(1.7±0.4)×10^3$	75.1 ± 11.5	2.74 ± 0.49	0.025 ± 0.007
16	**Baotou (1)**	$(1.6±0.4)×10^5$	$(7.3±2.1)×10^5$	ND	32.7 ± 5.0	10.07 ± 3.55	ND
17	**Göttingen (1)**	$(1.9±0.1)×10^5$	$(8.5±0.1)×10^5$	$(3.7±1.0)×10^3$	101.5 ± 20.6	3.44 ± 0.17	0.105 ± 0.028
18	**Vancouver***	$(2.3±0)×10^5$	$(7.5±0)×10^3$	ND	15.5	0.04	ND
19	**Toronto**	$(2.2±0.9)×10^5$	$(9.4±2.1)×10^4$	$(1.3±0.6)×10^5$	31.6 ± 9.5	0.51 ± 0.09	0.501 ± 0.253
20	**Boqsmaiyya**	$(3.6±0.2)×10^5$	$(9.1±0.2)×10^5$	$(6.5±1.0)×10^4$	98.1 ± 8.5	8.44 ± 0.46	0.150 ± 0.038
21	**Baotou (2)**	$(4.0±2.0)×10^5$	N/A	ND	114.4 ± 60.3	N/A	ND
22	**Gananoque**	$(4.6±1.8)×10^5$	$(3.1±0.3)×10^5$	$(1.5±1.1)×10^5$	92.0 ± 26.0	1.97 ± 0.28	0.367 ± 0.275
23	**Casablanca***	$(5.2±0)×10^5$	$(1.5±0)×10^4$	ND	48.9	0.06	ND
24	**Venice**	$(8.0±1.8)×10^5$	$(1.1±0.3)×10^4$	ND	143.4 ± 113.5	0.14 ±0.10	ND
25	**Göttingen (2)**	$(1.0±0.0)×10^6$	$(4.1±0.1)×10^5$	$(2.9±0.2)×10^5$	190.3 ± 10.0	2.83 ± 0.08	1.290 ± 0.105
26	**Edmonton (1)**	$(2.0±0.7)×10^6$	$(1.1±0.3)×10^6$	$(1.7±0.5)×10^4$	954.1 ± 439.5	20.39 ± 4.46	0.188 ± 0.016
27	**Edmonton (2)**	$(1.2±0.3)×10^6$	N/A	$(2.7±2.0)×10^4$	494.1 ± 86.1	N/A	0.148 ± 0.060
28	**Edmonton (3)**	$(1.3±0.4)×10^6$	N/A	$(2.9±1.6)×10^4$	527.5 ± 125.7	N/A	0.678 ± 0.401
29	**Le Chambon-sl**	$(1.9±0.3)×10^6$	$(2.6±0.9)×10^5$	$(5.1±2.2)×10^3$	332.0 ± 56.9	4.75 ± 1.66	0.021 ± 0.008
30	**London**	$(1.9±1.2)×10^6$	$(1.9±1.0)×10^5$	$(2.1±0.2)×10^4$	134.9 ± 45.9	1.3 ± 0.65	0.066 ± 0.003
31	**Durham**	$(2.9±1.2)×10^6$	$(1.5±0.2)×10^4$	$(1.8±0.8)×10^4$	524.0 ± 255.1	0.18 ± 0.09	0.170 ± 0.150
32	**Baku***	$(3.8±0)×10^6$	ND	ND	347.1 ± 0	ND	ND
33	**Sao Paulo (1)**	$(7.0±0.6)×10^6$	$(4.7±1.1)×10^5$	N/A	2324.2 ± 131.6	7.86 ± 1.98	N/A
34	**Sao Paulo (2)**	$(6.8±1.2)×10^6$	$(4.3±0.8)×10^5$	N/A	2262.2 ± 422.5	7.53 ± 1.60	N/A
35	**Lankaran**	$(1.2±0.2)×10^7$	$(1.5±0.1)×10^6$	$(9.3±1.4)×10^3$	2961.0 ± 318.0	78.10 ± 4.0	0.092 ± 0.039
36	**Sólheimajökull**	$(1.5±0.0)×10^7$	$(2.3±0.0)×10^6$	ND	3140.7 ± 68.0	19.45± 1.50	ND

Table S4. Nanoparticle measurements on natural precipitation samples. Measurements were performed by a high-sensitivity sector-field single-particle ICP-MS. NP mass concentrations were calculated by assuming that all Ti-, Ce- and Ag-containing NPs occurred in the forms of TiO_2, CeO_2 and Ag, respectively. N/A refers to samples that were not analyzed.

	City/town	NP number concentrations (NP mL^{-1})			NP mass concentration (ng L^{-1})		
		Ti-NPs	*Ce-NPs*	*Ag-NPs*	*TiO_2*	*CeO_2*	*Ag*
1	**Montreal**	$(2.3\pm1.6)\times10^6$	$(3.5\pm2.3)\times10^5$	$(2.6\pm0.2)\times10^4$	89.7 ± 3.3	2.3 ± 1.5	0.040 ± 0.010
2	**Toronto**	$(7.0\pm0.1)\times10^4$	N/A	$(2.4\pm0.1)\times10^3$	1.7 ± 0.1	N/A	0.026 ± 0.010
3	**Vancouver**	$(1.2\pm0.0)\times10^4$	ND	$(9.9\pm1.3)\times10^2$	26.1 ± 2.8	ND	0.026 ± 0.010
4	**West Lafayette**	$(1.9\pm1.3)\times10^5$	$(9.3\pm7.5)\times10^4$	$(2.6\pm2.3)\times10^3$	42.8 ± 29.4	0.5 ± 0.4	0.014 ± 0.008
5	**Durham**	$(9.4\pm0.2)\times10^4$	$(2.4\pm0.0)\times10^4$	$(1.0\pm0.1)\times10^3$	24.0 ± 0.3	0.1 ± 0.0	0.006 ± 0.001
6	**Sao Paulo**	$(2.0\pm0.0)\times10^6$	$(2.8\pm1.2)\times10^5$	$(1.0\pm0.1)\times10^3$	846.8 ± 8.4	3.8 ± 1.6	0.005 ± 0.001
7	**Munich**	$(9.8\pm0.3)\times10^4$	$(1.0\pm0.1)\times10^5$	$(8.0\pm4.4)\times10^3$	31.0 ± 3.0	1.0 ± 0.2	0.044 ± 0.005
8	**Göttingen**	$(9.5\pm0.2)\times10^4$	$(8.1\pm1.0)\times10^4$	$(3.1\pm0.1)\times10^4$	40.6 ± 2.2	0.4 ± 0.1	0.094 ± 0.010
9	**Baku**	$(2.7\pm0.4)\times10^5$	$(3.1\pm2.2)\times10^5$	$(5.0\pm2.2)\times10^3$	86.8 ± 24.9	2.5 ± 1.2	0.035 ± 0.018
10	**Hohhot**	$(2.7\pm0.0)\times10^5$	$(1.1\pm0.0)\times10^5$	$(1.0\pm0.1)\times10^5$	119.0 ± 4.2	2.3 ± 0.4	0.281 ± 0.017

REFERENCES

1. Hadioui, M.; Knapp, G. v.; Azimzada, A.; Jreije, I.; Frechette-Viens, L.; Wilkinson, K. J. Lowering the size detection limits of Ag and TiO2 nanoparticles by Single Particle ICP-MS. Anal. Chem. **2019,** *91* (20), 13275-13284.