



Supporting material for

Extraction of silicon-containing nanoparticles from an agricultural soil for analysis by single particle sector field and time-of-flight inductively coupled plasma mass spectrometry

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Table S2. Physicochemical parameters of the McGill MacDonald College soil sample [1]

Physicochemical parameter	
pH ^a	7.2
Organic matter (%)	6.1
P (mg kg ⁻¹)	183
Ca (mg kg ⁻¹)	3999
Mg (mg kg ⁻¹)	325
K (mg kg ⁻¹)	349
Al (mg kg ⁻¹)	717
N (NO ₃ ⁻) (mg kg ⁻¹)	6.4
N (NH ₄ ⁺) (mg kg ⁻¹)	2.5

^a A 1:1 (w/v) solution of soil to water was shaken for 30 min, then left to rest for 1 hour.

Table S2. Results comparing the signal: noise (S/N) of the quartz and alumina torches in wet and dry mode of the instrument. Also, two types of polypropylene tubes (PP and DigiTube) were tested for contamination for Si. S/N were given for 10 ug L⁻¹ of a Si solution in 2% HNO₃. Signal intensities were determined for ²⁸Si using the medium resolution of instrument.

	S/N			Signal (x 10 ⁴ cps)		
	Quartz torch		Alumina torch	PP tube		Digi tube
Wet mode	6.7	± 2.6	4.0 ± 1.5	20.8	± 2.2	6.7 ± 0.1
Dry mode	1.1	± 0.1	1.09 ± 0.02			

Table S3. Percentage of Si-containing NPs below different size cut-offs for the different extractants.

Extractant	NPs<70nm (%)			NPs<80nm (%)			NPs<90nm (%)			NPs<100nm (%)		
Ca(NO ₃) ₂	17.5	± 0.9		32.1	± 2.6		45.0	± 4.7		54.7	± 4.4	
Mg(NO ₃) ₂	13.2	± 1.9		28.8	± 1.4		39.6	± 1.6		48.2	± 0.6	
BaCl ₂	17.1	± 2.2		36.4	± 4.8		49.0	± 4.1		59.2	± 2.9	
NaNO ₃	19.8	± 0.6		38.5	± 0.8		53.2	± 1.1		64.0	± 0.9	
MQW	21.5	± 0.9		40.9	± 1.0		55.4	± 0.9		66.6	± 0.6	
FA	20.2	± 0.9		39.5	± 0.9		54.0	± 0.9		64.8	± 0.7	
EDTA	20.8	± 1.0		40.0	± 1.3		54.5	± 1.3		65.1	± 1.4	
Na ₄ P ₂ O ₇	26.2	± 0.7		48.1	± 0.7		63.0	± 0.9		73.7	± 0.7	

Table S4. Results for DLS (dynamic light scattering) of the extracted NP. All of the extractants were adjusted to pH 6.0 before mixing with the suspension of SiO₂ nanoparticles or the soil. The SiO₂ NP suspension was diluted to 100 ppm using the extractant, while the soil was extracted for 18 h at 30 rpm and then diluted 10 times using the extractant before analysis, except for the Ca(NO₃)₂, which wasn't diluted. MQW= Milli-Q water.

	Extractant	Zeta Potential (mV)		Diameter (nm)	
		Mean	SD	Mean	SD
SiO ₂ nanoparticles (80 nm)	MQW	-32.6 ± 2.0		87.0 ± 0.7	
	Ca(NO ₃) ₂	-18.0 ± 0.4		86.9 ± 8.9	
	Na ₄ P ₂ O ₇	-27.4 ± 2.8		88.7 ± 7.6	
	Fulvic acid	-44.2 ± 4.2		84.9 ± 0.6	
SiO ₂ nanoparticles (200 nm)	MQW	-43.4 ± 3.0		203.2 ± 1.6	
	Ca(NO ₃) ₂	-23.1 ± 2.0		199.1 ± 2.2	
	Na ₄ P ₂ O ₇	-33.5 ± 1.3		199.7 ± 0.9	
	Fulvic acid	-49.1 ± 2.7		201.5 ± 2.4	
Extracted soil nanoparticles	MQW	-17.1 ± 1.0		243.4 ± 2.5	
	Ca(NO ₃) ₂	-12.6 ± 0.2		792.4 ± 46.4	
	Na ₄ P ₂ O ₇	-35.0 ± 0.7		213.3 ± 2.0	
	Fulvic acid	-23.9 ± 0.5		254.8 ± 5.0	

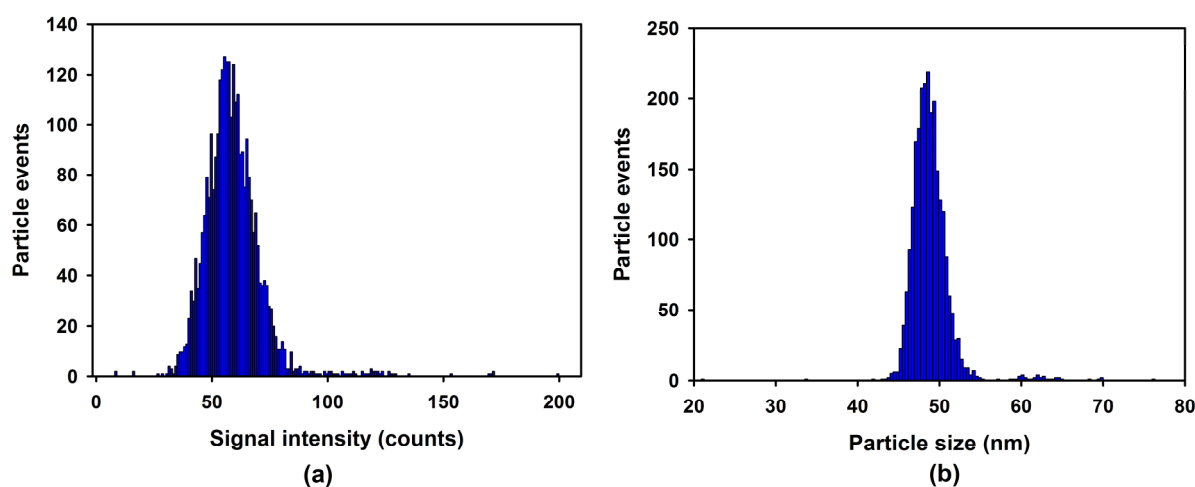


Figure S1. Measured particle distributions of the ultra-uniform gold nanoparticles for the (a) 30 nm and (b) 50 nm standard NP.

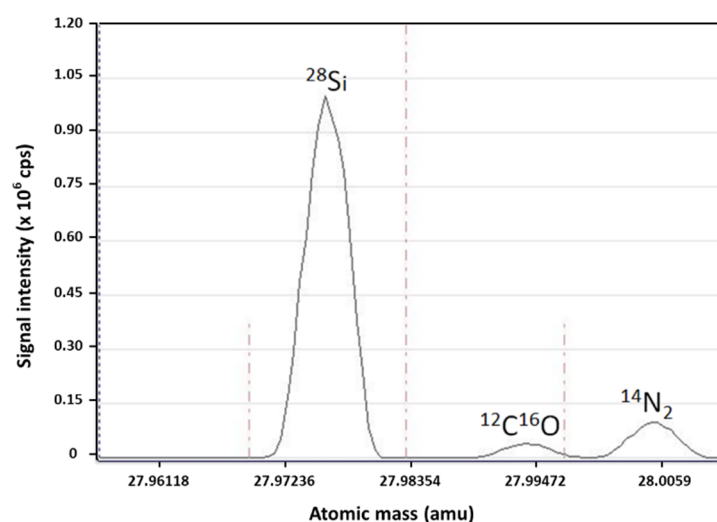


Figure S2. Magnet scan of ^{28}Si at medium resolution (2500). Si concentration was $20 \mu\text{g L}^{-1}$.

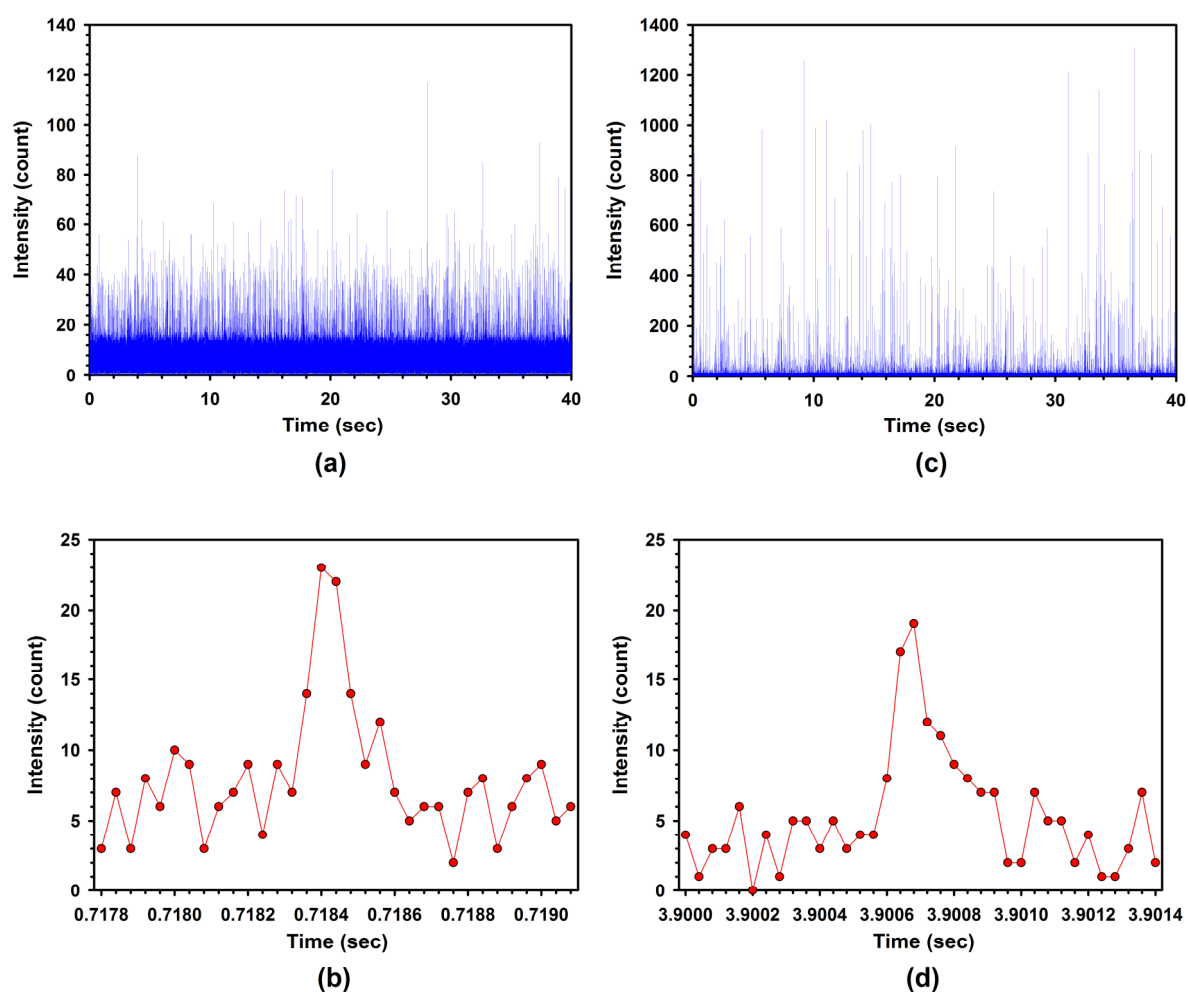


Figure S3. Time-resolved signal for (a) a suspension of engineered SiO_2 nanoparticles (80 nm nominal diameter) and (c) a soil leachate. Time-resolved signal of a small peak of SiO_2 nanoparticle for (b) the suspension of engineered SiO_2 nanoparticles (44.6 nm) and (d) the soil leachate (39.7 nm). The soil leachate was obtained using Milli-Q water as the extraction solution. The dwell time was 40 μs .

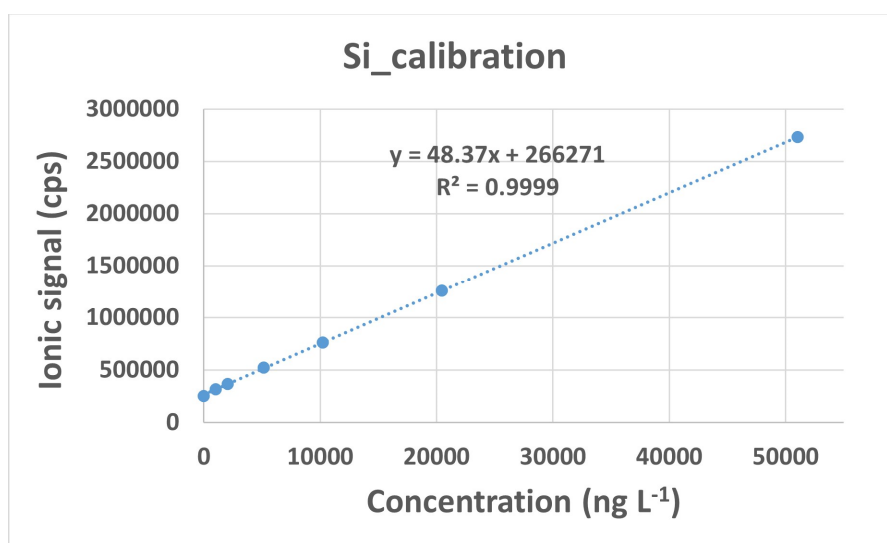
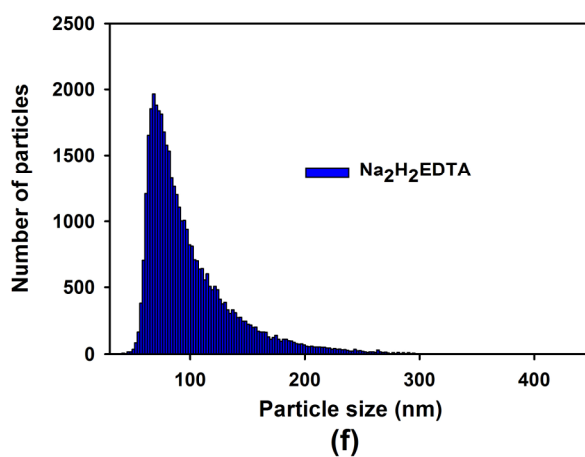
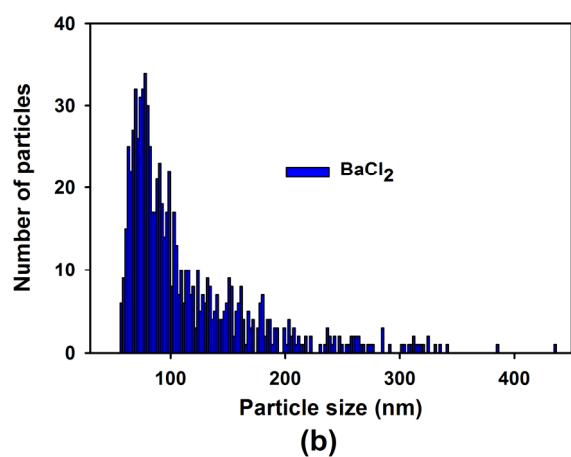
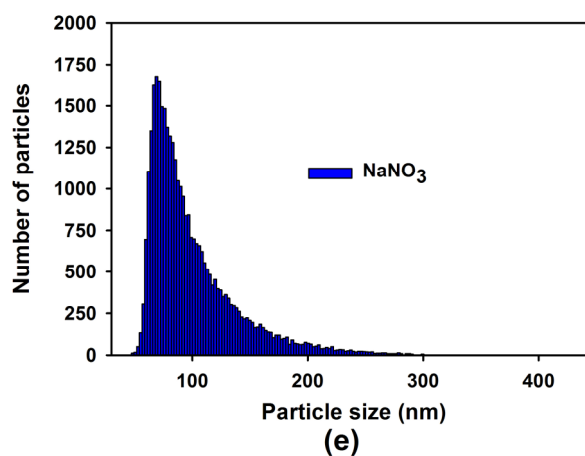
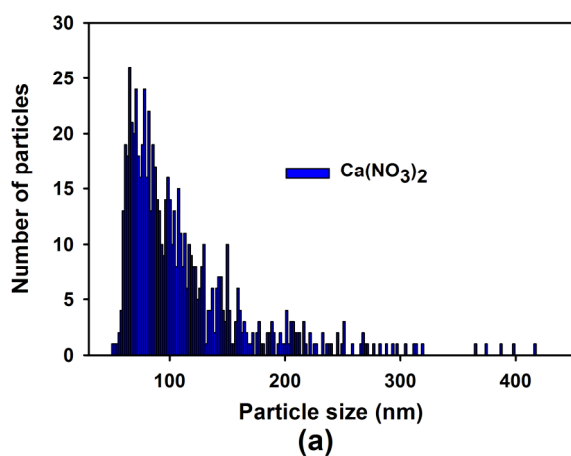


Figure S4. Example of external ²⁸Si calibration curve (ionic standard) used to determine Si mass (particulate and dissolved).



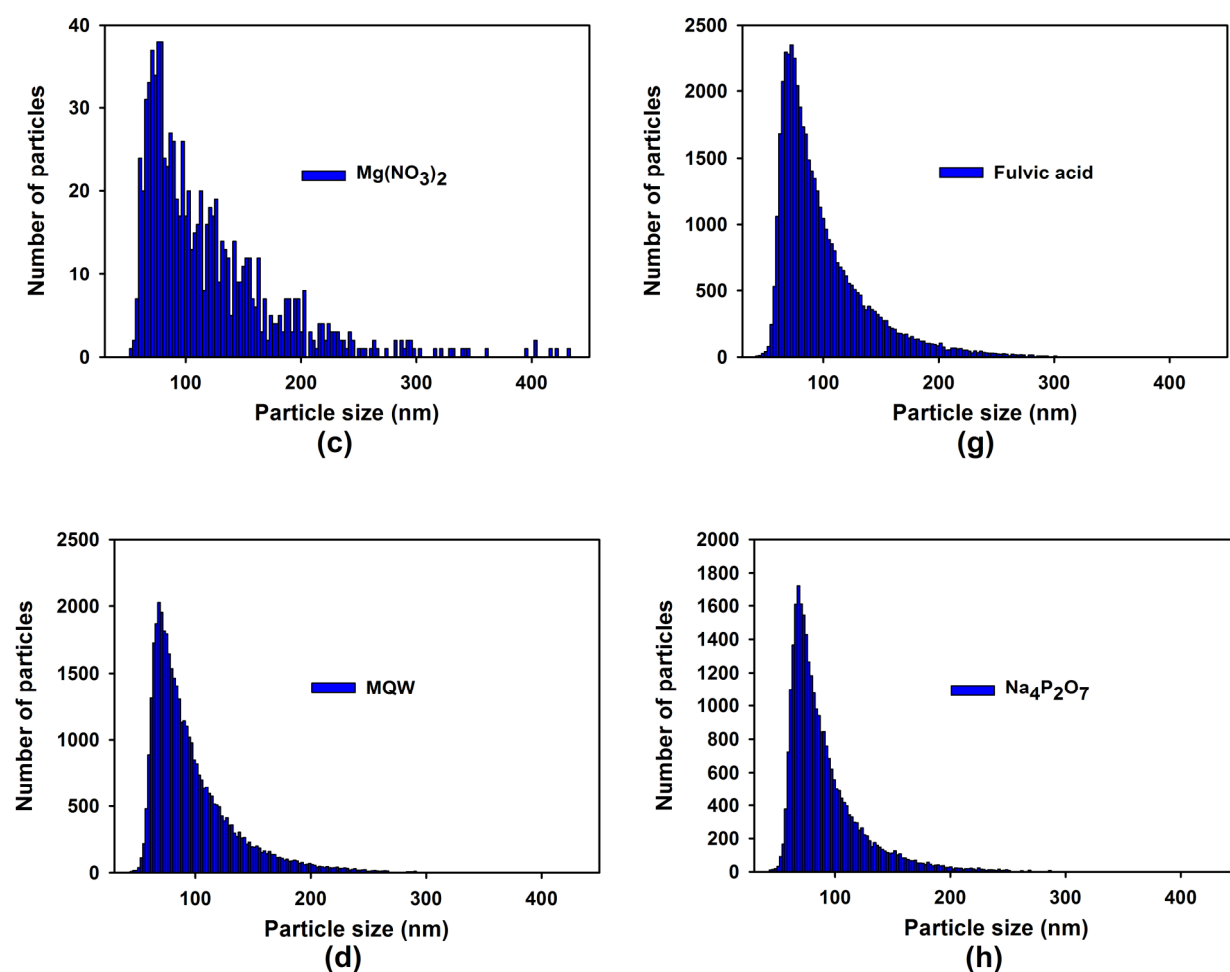


Figure S5. Particle size distribution of Si-containing NPs in the soil leachates obtained using different extractants: (a) $\text{Ca}(\text{NO}_3)_2$ (5 mmol L⁻¹), (b) BaCl_2 (5 mmol L⁻¹), (c) $\text{Mg}(\text{NO}_3)_2$ (5 mmol L⁻¹), (d) Milli-Q water, (e) NaNO_3 (5 mmol L⁻¹), (f) $\text{Na}_2\text{H}_2\text{EDTA}$ (0.1 mmol L⁻¹), (g) FA (40 mg L⁻¹) and (h) $\text{Na}_4\text{P}_2\text{O}_7$ (5 mmol L⁻¹). The pH was adjusted to 6.0 for all extraction solutions prior to contact with the soil. The leachates were diluted 40000 times prior to SP-ICP-MS analysis, except in the case of $\text{Na}_4\text{P}_2\text{O}_7$ for which a dilution factor of 250000 times was necessary. Particle sizes correspond to equivalent diameters calculated under the assumption that the NP are spherical SiO_2 .

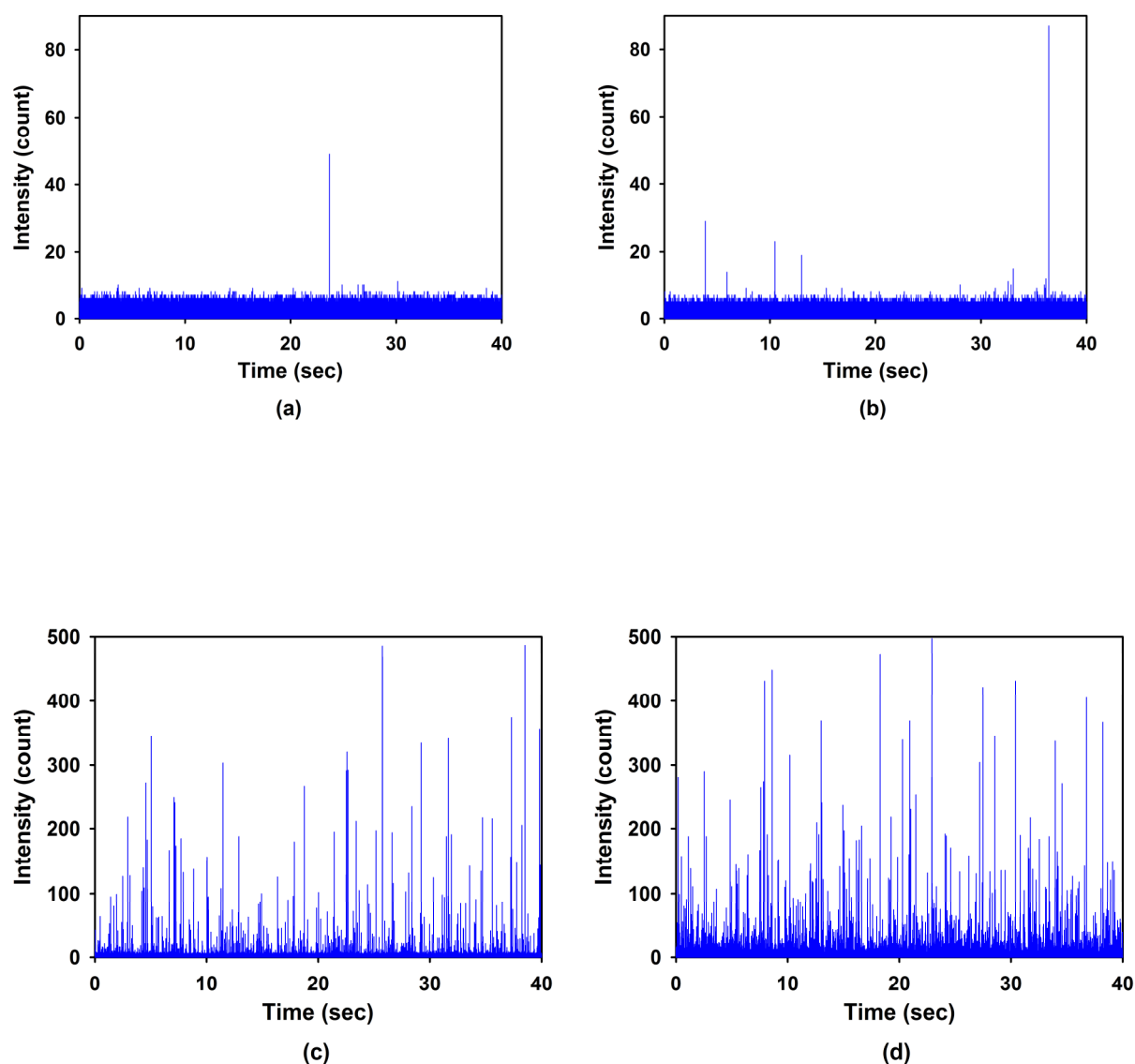


Figure S6. Raw data for SP ICP-MS analysis of ^{28}Si in a) Milli-Q water, b) solution of 40 mM $\text{Na}_4\text{P}_2\text{O}_7$ that was diluted 250000 times prior to analysis, c) diluted (250000x) soil leachate obtained using Milli-Q water, and d) diluted (250000x) soil leachate obtained with 40 mM $\text{Na}_4\text{P}_2\text{O}_7$. All dilutions were done with Milli-Q water.

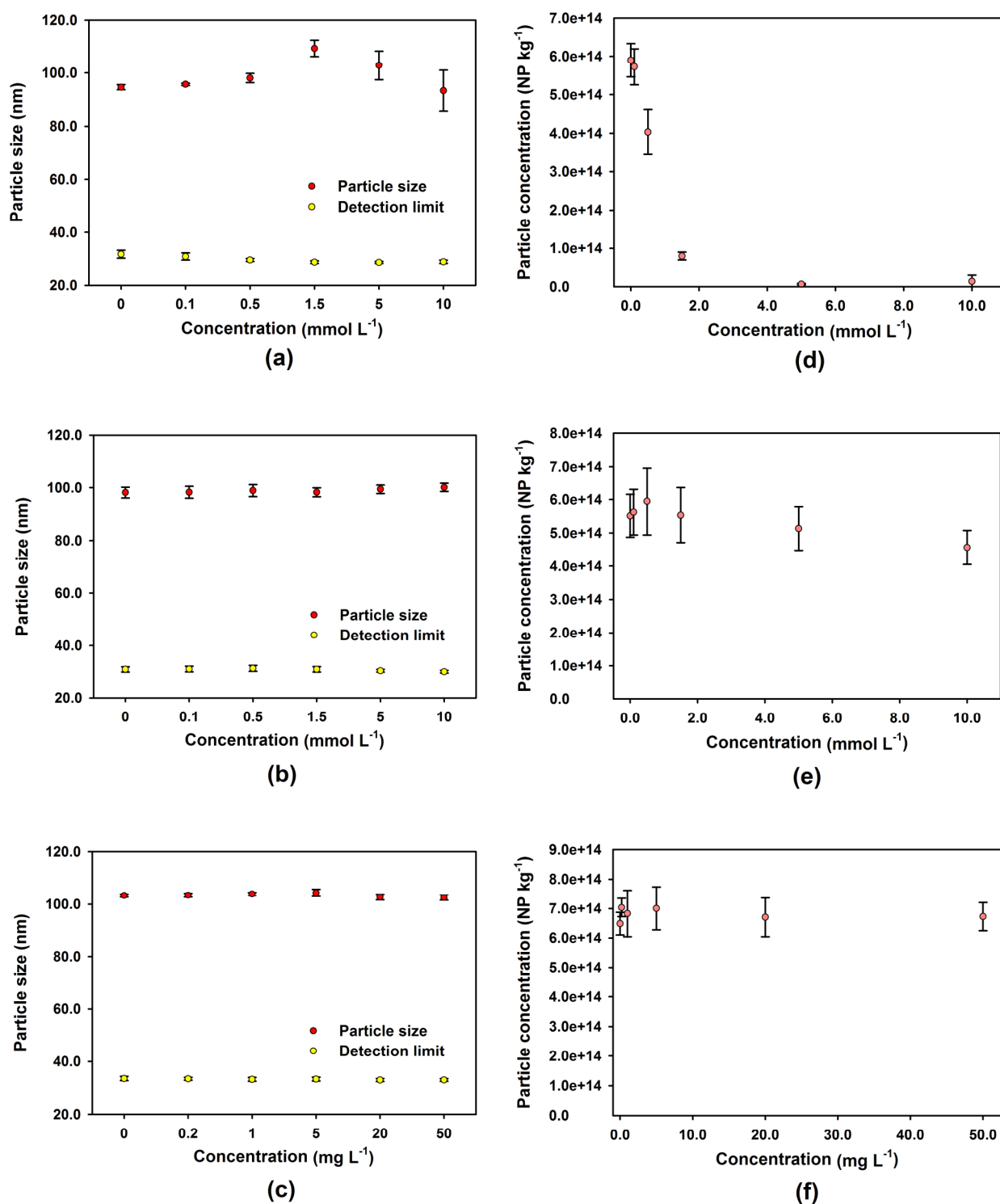


Figure S7. (a, b, c) size and (d, e, f) concentration of Si-containing NPs in the extraction solutions of a soil in contact (18 hours) with different extractants as a function of the concentration of (a, d) $\text{Ca}(\text{NO}_3)_2$, (b, e) NaNO_3 , and (c, f) FA. The concentration of 0 represents the initial extraction using Milli-Q water. Particle sizes correspond to equivalent diameters calculated under the assumption that the NP are spherical SiO_2 .

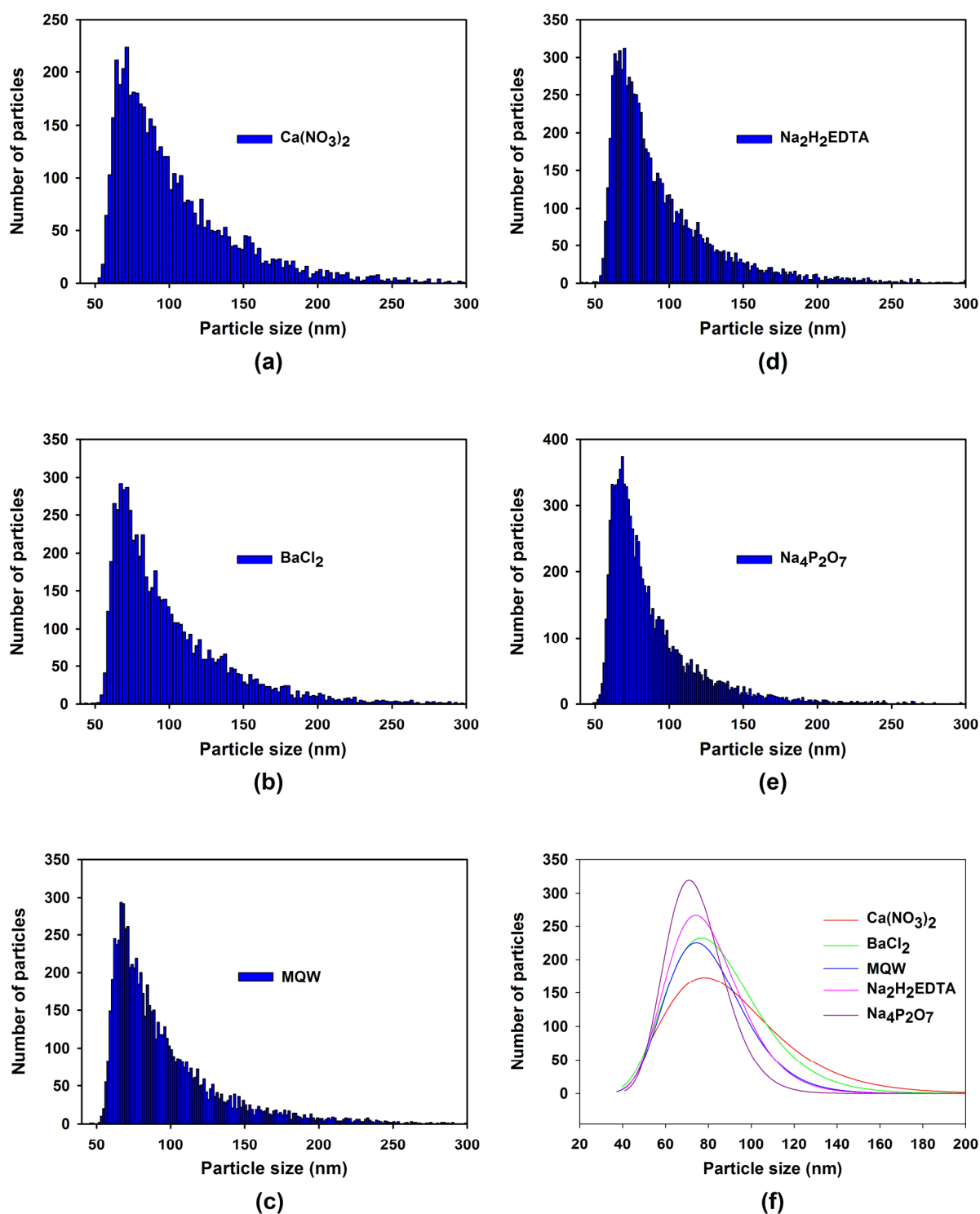


Figure S8. Particle size distribution of Si-containing NPs extracted from the soil using Milli-Q water, which were then suspended in different media: (a) $\text{Ca}(\text{NO}_3)_2$ (5 mmol L^{-1}), (b) BaCl_2 (5 mmol L^{-1}), (c) Milli-Q water, (d) $\text{Na}_2\text{H}_2\text{EDTA}$ (0.1 mmol L^{-1}) or (e) $\text{Na}_4\text{P}_2\text{O}_7$ (5 mmol L^{-1}). (f) Polynomial fitting the particle size histograms. The leachates were diluted 100000 times prior to SP-ICP-MS analysis. Particle sizes correspond to equivalent diameters calculated under the assumption that the NP are spherical SiO_2 .

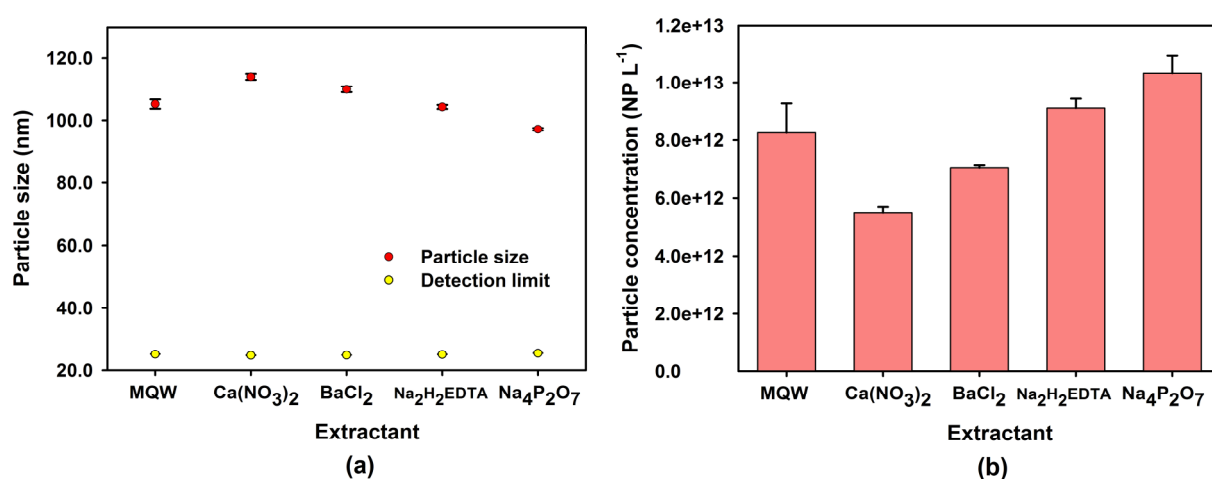


Figure S9. (a) Average size and (b) concentration of Si-containing NPs extracted from the soil using Milli-Q water, which were then suspended in different media: Ca(NO₃)₂ (5 mmol L⁻¹), BaCl₂ (5 mmol L⁻¹), Na₄P₂O₇ (5 mmol L⁻¹) or Na₂H₂EDTA (0.1 mmol L⁻¹). Particle sizes correspond to equivalent diameters calculated under the assumption that the NP are spherical SiO₂.

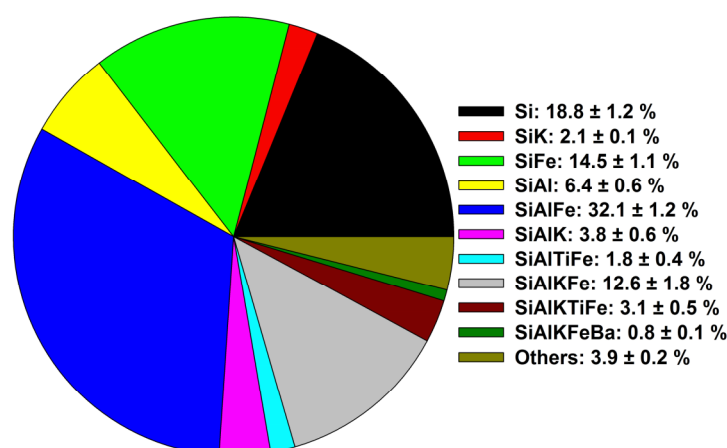


Figure S10. Proportion of each Si particle type detected in the soil leachate using pure water as the extractant and SP TOF-ICP-MS for detection. Leachates were diluted 100000 times prior to analysis. 854 particles were detected during an acquisition time of 92 sec. A dwell time of 76.8 μsec was employed.

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