Supporting Information for

Identification and Quantification of Anthropogenic Nanomaterials in Urban Rain and Runoff Using Single Particle-Inductively Coupled Plasma-Time of Flight-Mass Spectrometry

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1. Sampling

Table S1. Parameters of the sampling.

Sampling site	Date	Sample #	Sample type	Time of sampling	Approximate sample volume (mL)
Quail Ln	Oct. 19, 2019	QL1	Run-off	12:00 - 12:30 pm	800
		QL2	Run-off	12:30 – 12:35 pm	1000
		QL3	Run-off	12:45 – 12:50 pm	900
		QL4	Run-off	1:00 – 1:05 pm	800
		QL5	Run-off	1:15 – 1:20 pm	600
		QL6	Run-off	1:30 – 1:35 pm	800
		QL7	Run-off	2:00 – 2:05 pm	300
		QL8	Run-off	2:30 – 2:35 pm	900
		QL9	Run-off	3:00 – 3:05 pm	1000
		QL10	Run-off	3:30 – 3:35 pm	1000
		QL11	Run-off	4: 30 – 4:35 pm	100
		QL12	Run-off	5:30 – 5:35 pm	500
		QL13/R	Rain	10:33 – 17:45	150
Blossom Street	May 18, 2020	BSR1	Rain 1	14:05-16:15	200
		BSR2	Rain 2	17:25-18:35	<150
		BS1	Run-off	14:25-14:30	1000
		BS2	Run-off	14:40-14:45	1500
		BS3	Run-off	14:55-15:00	1200
		BS4	Run-off	15:10-15:15	800
		BS5	Run-off	15:25-15:30	900
		BS6	Run-off	15:40-15:45	1000
		BS7	Run-off	15:55- 16:00	600
		BS8	Run-off	16:10 -16:15	<100
		BS9	Run-off	17:30 -17:35	900
		BS10	Run-off	17:45-17:50	700
		BS11	Run-off	18:00-18:05	700
		BS12	Run-off	18:15-18:20	800
		BS13	Run-off	18:30-18:35	1000

2. Total digestion for elemental analysis

Samples were shaken vigorously for 30 s before any portion was transferred into acid-washed bottles. The bottles were capped and set in the fume hood for 5 min to bring the stored sample up to room temperature before preparing for digestion. All digestion procedure was performed on Teflon covered hotplates in boxes equipped with double-HEPA filtered forced air in a metal-free air clean lab. 10 mL aliquots of rainwater or runoff were transferred into 15 mL Teflon vessels (Savillex, Eden Prairie, MN, United States). Then the samples were dried at 110 °C and treated with 1 mL 30% trace metal grade H_2O_2 (Fisher Chemical, Fair Lawn, NJ, United States) at 70 °C for 2 h to remove organic matters. The liquid was then evaporated at 100 °C before the solid residue was digested with 2 mL HF and HNO_3 mixture (HF:HNO_3 = 3:1, both acids were ACS grade acids distilled in the air clean lab for mixing) at 110 °C for 48 h. HF was removed from samples by evaporating acid mixture at the end of the digestion. But due to the possibility of insoluble fluoride salts formed during digestion, 1 mL of distilled concentrated HNO_3 was added to the samples to react with fluoride salts and left to evaporate at 110 °C. The process was repeated at least 2 times for complete reaction. The samples were weight after drying and then mixed with 5 mL of 1% trace metal grade HNO3 (Fisher Chemical, Fair Lawn, NJ, United States). The mixture was bath sonicated for 10 min (Branson, 2800, 40kHz, Danbury, CT, United States) and left on hotplates at 50 °C for 2 h for full dissolution before transferring to 15 mL acid-washed polypropylene centrifuge tubes (Fisher Scientific, San Nicolás de los Garza, Nuevo León, Mexico) and storing at 4 °C.

Prior to ICP-MS analysis, the samples were set in the fume hood for 5 min to bring up to room temperature. Then the samples were centrifuged (Eppendorf, 5810 R, Hamburg, Germany) at 3100 g for 5 min to remove any undigested minerals. The centrifugal size cut-off is 500 nm, 350 nm, and 300 nm for NNMs, TiO_2 particles, and Fe_2O_3 particles, respectively.

The digestion protocol has been applied for the digestion of different types of samples including sewage spills, stormwaters, surface waters, wastewater treatment plant liquid samples [1-4]. The efficiency (recovery >98%), precision (2-3%), and accuracy (*e.g.*, better than 5% for most elements) of the digestion protocol has been validated in previous studies [1].

3. Particle extraction for SP-ICP-TOF-MS analysis

3.1. Liquid samples (rainwater and runoff)

Samples were shaken vigorously for 30 s before an aliquot was poured into acid-washed bottle. The bottle was capped and set in the fume hood for 5 min to bring up the stored sample temperature to room temperature. An aliquot of 10 mL sample was then pipetted into an acid-washed 15-mL centrifuge tube . Triplicate were prepared for each collected sample. After vortex for 10 s, all the prepared samples were bath sonicated for 2 h. The bath temperature was monitored and adjusted to maintain sonication under 40 °C. Centrifugation was applied to all samples afterwards, at 775 x g for 5 min. Top 7 mL of the 10 mL sample was collected as 1 μm particle fraction according to Stokes' Law calculation and an assumed NNMs density of 2.5 g cm^{-3}. The supernatant was transferred into another acid-washed 15-mL centrifuge tube and stored at 4 °C prior to analysis.

3.2. Solid samples (soil)

A portion of a sample stored in freezer was poured into an acid-washed 50-mL centrifuge tube. The tube was capped and left in the fume hood to reach room temperature. 20 mg of the room temperature sieved soil sample was measured into an acid-washed 50-mL centrifuge tube, and 30 mL of UPW was added to the tube. After vortex for 10 s, the mixture was placed in a tube rotator (Fisher Scientific, Shanghai, China) and stirred at 40 rpm for 20 h. Similar to liquid samples, the mixture was sonicated for 2 h, and then centrifuged to separate the 1 μm fraction for further analysis.

4. Elemental analysis by ICP-MS

Table S2. Operating conditions for inductively coupled plasma-mass spectrometer analysis (Perkin Elmer NexION 350D).

Instrument Parameter	Value
Nebulizer Gas Flow	0.85 to 1 L/min
Auxiliary Gas Flow	1.02 L/min
Plasma Gas Flow	16 L/min
ICP RF Power	1600 W
Analog Stage Voltage	-1600 V
Pulse Stage Voltage	1600 V
Discriminator Threshold	12
Deflector Voltage	-9.5 V
Dwell time	50 ms
Sample Flow Rate	0.3 mL/min

Table S3. Operating conditions for inductively coupled plasma-time of flight-mass spectrometer analysis (TOFWERK icpTOF R).

Instrument Parameter	Value
Nebulizer Gas Flow	1.10-1.14 L/min
Auxiliary Gas Flow	0.8 L/min
Plasma Gas Flow	14 L/min
ICP RF Power	1550 W
Collision Cell Gas	Helium with 4.5% Hydrogen
Collision Cell Gas Flow	5.0 mL/min
Integration Time	2 ms
Sample Flow Rate	0.4 mL/min
Transport Efficiency	5-7%
Detected mass range	14-275 amu
TOF repetition rate	33 kHz
TOF time resolution	30 μs

Table S4. Elements monitored for single particle-inductively coupled plasma-time of flight-mass spectrometer analysis and the corresponding particle mass and size detection limits.

Element	Isotope	Particle detection limit (particles per 200s analysis)	Particle number concentration detection limit (particles/mL)	Mass detection limit (g)	Size detection limit (nm, assuming pure metallic particle)	Size detection limit (nm, assuming pure metal oxide particle)	Metal oxide form
Al	^{27}Al	26	296	4.94×10^{-15}	152	165	Al_2O_3
Si	^{28}Si	64	725	3.53×10^{-14}	307	379	SiO_2
Ti	^{48}Ti	26	298	5.05×10^{-16}	60	72	TiO_2
V	^{51}V	52	590	2.34×10^{-16}	42	62	V_2O_5
Cr	^{52}Cr	45	510	2.03×10^{-16}	38	48	Cr_2O_3
Mn	^{55}Mn	32	362	1.75×10^{-16}	36	47	MnO_2
Fe	^{56}Fe	186	2120	3.57×10^{-16}	44	57	Fe_2O_3
Co	^{59}Co	26	293	1.07×10^{-16}	28	36	Co_3O_4
Ni	^{60}Ni	14	160	5.02×10^{-16}	48	57	NiO
Cu	^{65}Cu	17	193	4.22×10^{-16}	45	54	CuO
Zn	^{66}Zn	36	410	1.31×10^{-15}	71	82	ZnO
Zr	^{90}Zr	5	60	1.42×10^{-16}	35	40	ZrO_2
Nb	^{93}Nb	4	45	7.50×10^{-17}	26	35	Nb_2O_5
Sn	^{120}Sn	13	151	1.34×10^{-16}	33	36	SnO_2
Sb	^{121}Sb	5	63	1.77×10^{-16}	37	43	Sb_2O_3
Ba	^{138}Ba	13	143	6.22×10^{-17}	32	29	BaO
La	^{139}La	4	47	3.16×10^{-17}	21	22	La_2O_3
Ce	^{140}Ce	5	62	3.41×10^{-17}	21	22	CeO_2
Pr	^{141}Pr	5	57	2.52×10^{-17}	19	21	Pr_6O_{11}
Nd	^{142}Nd	3	33	6.85×10^{-17}	27	28	Nd_2O_3
Sm	^{152}Sm	3	35	7.94×10^{-17}	27	28	Sm_2O_3
Eu	^{153}Eu	3	40	3.87×10^{-17}	24	23	Eu_2O_3
Gd	^{158}Gd	4	50	8.66×10^{-17}	28	30	Gd_2O_3
Tb	^{159}Tb	4	42	2.41×10^{-17}	18	20	Tb_4O_7
Dy	^{164}Dy	3	38	6.46×10^{-17}	24	26	Dy_2O_3
Ho	^{165}Ho	1	13	1.89×10^{-17}	16	17	Ho_2O_3
Er	^{166}Er	3	29	5.63×10^{-17}	23	24	Er_2O_3
Tm	^{169}Tm	6	67	2.15×10^{-17}	16	18	Tm_2O_3
Yb	^{174}Yb	2	27	5.55×10^{-17}	25	24	Yb_2O_3
Lu	^{175}Lu	5	62	1.67×10^{-17}	15	16	Lu_2O_3
Hf	^{180}Hf	3	33	5.45×10^{-17}	20	23	HfO_2
Ta	^{181}Ta	5	57	2.55×10^{-17}	14	19	Ta_2O_5
W	^{184}W	6	64	9.14×10^{-17}	21	26	WO_2
Pb	^{208}Pb	8	91	4.35×10^{-17}	19	21	PbO
Th	^{232}Th	2	26	1.87×10^{-17}	15	16	ThO_2
U	^{238}U	2	26	1.81×10^{-17}	12	15	UO_2

Number concentration detection limit = mean + standard deviation of the number concentration in three blank replicates

Mass concentration detection limit = minimum detectable mass

Size detection limit= calculated minimum detectable particle size assuming pure phase

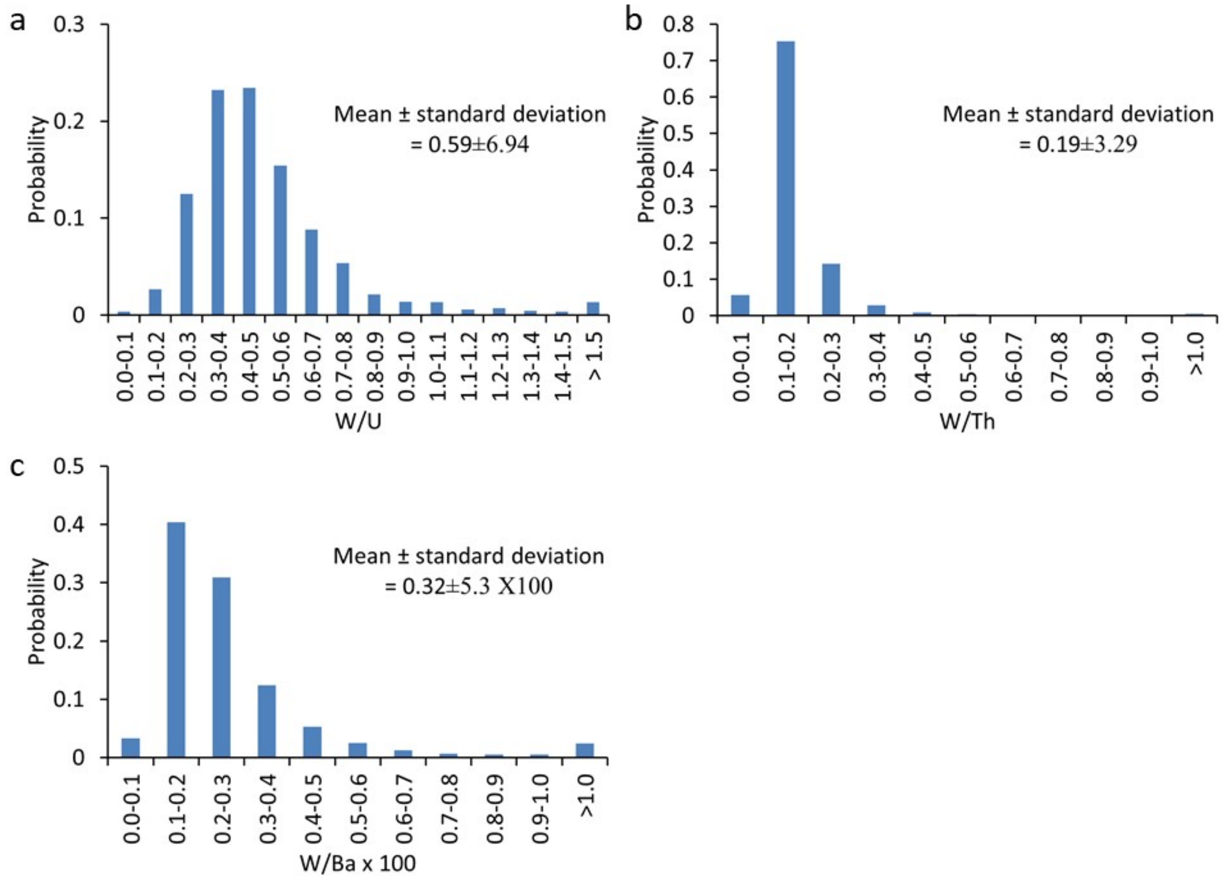


Figure S1. Elemental ratio distribution of W/U, W/Th, and W/Ba in a spatially balanced array of 4857 soil samples across the Conterminous United States. Elemental concentration data were obtained from the United State Geological Survey (USGS) publication [5].

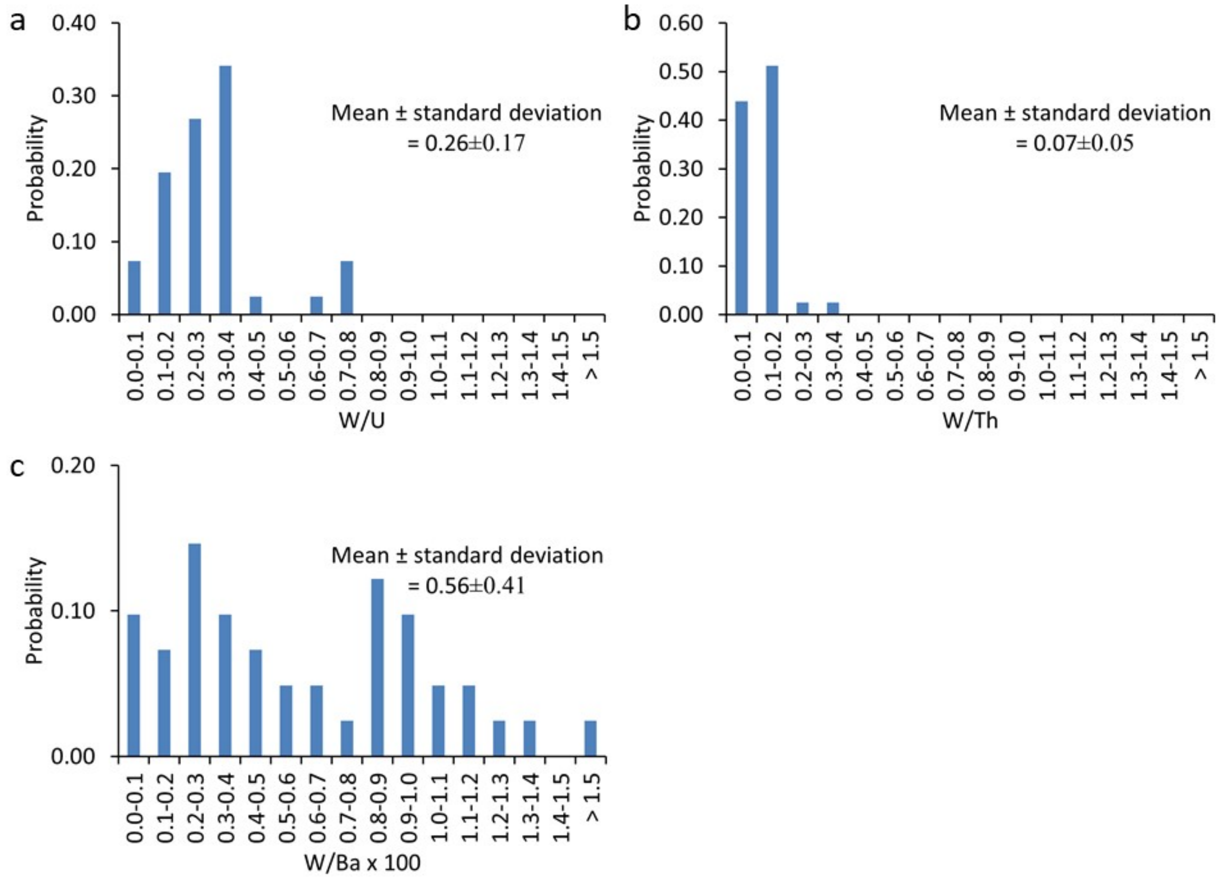


Figure S2. Elemental ratio distribution of W/U, W/Th, and W/Ba in a spatially balanced array of 41 soil samples across South Carolina, United States. Elemental concentration data were obtained from the United State Geological Survey (USGS) publication [5].

Table S5. Mean metal concentrations (µg L^{-1}) in rain and runoff in Blossom Street (heat map is provided in Figure S3a).

	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Sn	Sb	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U
R1	179.2	10.9	0.4	1.1	6.6	112.7	0.1	1.1	1.4	15.5	0.06	0.4	0.11	0.1	42.0	0.4	4.2	0.1	0.19	0.02	0.09	0.017	0.005	0.023	0.003	0.011	0.003	0.008	0.001	0.007		0.026	0.037	0.80	0.40	0.04	0.012
R2	559.5	28.4	0.7	2.1	15.1	316.4	0.2	1.5	6.8	70.6	0.16	1.2	0.14	0.1	42.0	0.6	9.1	0.3	0.69	0.08	0.29	0.053	0.012	0.073	0.008	0.032	0.007	0.020	0.003	0.018	0.003	0.057	0.029	0.41	1.04	0.10	0.031
BS1	856.3	80.3	2.0	5.1	20.0	489.8	0.7	5.7	64.1	160.5	0.61	2.2	0.18	6.5	43.7	5.1	171.9	0.7	1.30	0.21	0.67	0.185	0.070	0.175	0.023	0.096	0.022	0.065	0.011	0.062	0.012	0.113	0.051	0.70	2.27	0.21	0.180
BS2	540.0	87.7	3.4	2.1	4.9	259.1	0.3	2.9	30.2	87.6	0.23	1.1	0.10	5.6	42.9	3.4	95.7	0.4	0.67	0.10	0.31	0.090	0.037	0.081	0.010	0.039	0.009	0.026	0.005	0.024	0.005	0.074	0.029	0.55	1.15	0.11	0.087
BS3	331.0	34.3	3.2	1.6	4.2	174.3	0.2	2.6	22.0	64.8	0.16	0.8	0.07	4.4	43.2	3.0	68.0	0.3	0.47	0.07	0.22	0.064	0.027	0.058	0.007	0.028	0.006	0.019	0.003	0.017		0.047	0.024	0.46	0.68	0.07	0.071
BS4	408.5	33.7	3.1	2.0	3.9	225.2	0.2	2.3	20.8	63.0	0.16	0.9	0.08	4.1	42.8	3.2	64.5	0.3	0.50	0.08	0.23	0.064	0.026	0.060	0.007	0.028	0.006	0.019	0.004	0.017		0.050	0.023	0.47	0.79	0.08	0.070
BS5	508.1	43.5	2.9	2.1	4.9	261.5	0.2	2.5	21.9	65.0	0.18	0.9	0.09	4.3	43.7	3.7	71.7	0.4	0.60	0.09	0.27	0.073	0.029	0.070	0.008	0.032	0.007	0.021	0.004	0.019		0.049	0.021	0.52	0.95	0.09	0.071
BS6	575.2	51.8	2.9	2.1	4.3	294.4	0.3	2.4	22.1	68.8	0.19	1.1	0.10	4.6	42.4	4.1	74.5	0.4	0.65	0.10	0.29	0.077	0.030	0.074	0.009	0.034	0.008	0.022	0.004	0.020	0.004	0.057	0.019	0.49	1.09	0.10	0.073
BS7	535.3	48.6	3.1	2.0	4.2	269.7	0.3	2.4	22.0	68.0	0.19	0.9	0.10	5.1	41.8	4.6	83.4	0.4	0.61	0.09	0.28	0.079	0.032	0.071	0.009	0.033	0.008	0.022	0.004	0.020	0.004	0.046	0.017	0.50	1.04	0.09	0.072
BS8	257.9	24.6	2.9	1.5	3.5	140.3	0.2	2.5	21.2	58.0	0.14	0.5	0.06	5.3	40.3	4.7	86.4	0.2	0.37	0.07	0.19	0.064	0.030	0.049	0.007	0.024	0.006	0.017	0.003	0.015		0.054	0.016	0.52	0.69	0.05	0.071
BS9	613.0	62.0	2.9	1.9	7.4	300.8	0.3	2.4	22.0	67.2	0.22	1.0	0.11	4.1	41.6	4.5	93.9	0.4	0.69	0.10	0.32	0.088	0.036	0.082	0.010	0.039	0.009	0.025	0.004	0.023	0.005	0.060	0.019	0.35	1.07	0.10	0.095
BS10	190.2	18.5	2.3	1.3	2.2	98.1	0.2	2.0	16.9	52.1	0.11	0.4	0.04	3.7	42.9	3.5	71.5	0.2	0.28	0.05	0.14	0.053	0.025	0.038		0.020	0.005	0.014	0.003	0.013	0.004	0.027	0.011	0.27	0.44	0.04	0.063
BS11	220.1	18.4	2.5	1.7	2.2	116.4	0.2	1.8	14.7	45.4	0.11	0.5	0.04	3.3	42.6	3.0	58.4	0.2	0.30	0.05	0.15	0.048	0.021	0.038		0.019	0.004	0.013		0.012		0.031	0.010	0.33	0.47	0.04	0.060
BS12	187.3	16.1	2.1	1.9	1.7	96.2	0.1	1.8	13.6	42.2		0.4	0.04	3.1	42.7	3.0	52.9	0.2	0.24	0.04	0.12	0.042	0.019	0.032		0.016				0.010		0.025	0.010	0.33	0.40	0.03	0.049
BS13	218.2	22.1	2.3	1.9	1.9	121.4	0.2	1.7	14.5	45.4	0.10	0.5	0.04	3.2	45.9	3.2	57.8	0.2	0.28	0.05	0.14	0.047	0.021	0.037		0.018	0.004	0.013	0.002	0.012		0.025	0.009	0.27	0.48	0.04	0.051

* R1, and R2 refer to rain samples.

Table S6. Mean metal concentrations (µg L^{-1}) in rain and runoff in Quail Lane (heat map is provided in Figure S3b)

	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Sn	Sb	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U
R	32.5	2.3	0.1	0.3	1.5	13.4	0.0	0.5	1.6	8.5	0.01	0.1	0.0	0.1	21.2		1.6	0.0	0.0	0.00	0.01	0.002	0.001	0.002	0.000	0.002	0.000	0.001	0.000	0.001	0.000	0.003	0.003	0.02	0.18	0.00	0.00
QL1	2135.3	106.6	4.3	2.9	25.9	717.1	0.8	1.9	9.9	47.9	0.58	2.7	0.4	0.9	34.2		17.4	1.2	2.3	0.27	0.97	0.176	0.036	0.180	0.022	0.112	0.021	0.063	0.008	0.053	0.008	0.087	0.034	0.50	1.53	0.35	0.46
QL2	1452.7	66.8	3.3	1.8	15.4	485.6	0.5	1.3	5.8	27.4	0.31	1.3	0.2	0.6	25.3		10.3	0.7	1.3	0.16	0.56	0.103	0.022	0.104	0.013	0.067	0.013	0.038	0.005	0.030	0.004	0.044	0.019	0.38	0.90	0.21	0.21
QL3	985.4	42.0	3.0	1.3	10.3	365.9	0.3	0.9	3.9	17.6	0.24	0.9	0.1	0.4	24.4		6.6	0.4	0.8	0.10	0.35	0.066	0.015	0.067	0.009	0.045	0.009	0.026	0.003	0.022	0.003	0.035	0.013	0.28	0.48	0.13	0.14
QL4	644.3	28.3	3.0	1.0	7.7	248.6	0.3	0.8	3.4	11.5	0.16	0.6	0.1	0.4	29.0		5.3	0.3	0.6	0.06	0.23	0.044	0.012	0.046	0.006	0.032	0.006	0.017	0.002	0.015	0.002	0.020	0.012	0.27	0.34	0.09	0.10
QL5	575.5	20.8	2.8	0.9	7.4	236.5	0.2	0.8	3.5	8.5	0.11	0.3	0.0	0.3	31.8		4.5	0.2	0.4	0.04	0.15	0.030	0.007	0.030	0.004	0.020	0.004	0.011	0.002	0.010	0.002	0.012	0.006	0.24	0.22	0.05	0.08
QL6	549.4	18.7	3.2	0.9	6.6	216.3	0.2	0.7	3.6	8.4	0.11	0.4	0.0	0.3	32.9		4.0	0.2	0.3	0.04	0.15	0.027	0.006	0.028	0.004	0.019	0.004	0.011	0.002	0.009	0.002	0.013	0.006	0.24	0.23	0.04	0.09
QL7	382.1	12.8	3.0	0.9	5.2	155.4	0.2	0.7	3.8	7.2	0.08	0.3	0.0	0.4	35.8		4.1	0.1	0.2	0.03	0.10	0.019	0.005	0.020	0.003	0.014	0.003	0.008	0.001	0.007	0.001	0.010	0.006	0.27	0.28	0.03	0.08
QL8	332.2	10.6	2.5	1.1	5.7	160.4	0.2	1.0	4.3	8.4	0.09	0.2	0.0	0.5	36.0		5.6	0.1	0.2	0.03	0.10	0.020	0.005	0.020	0.003	0.014	0.003	0.008	0.001	0.007	0.001	0.008	0.003	0.32	0.21	0.03	0.10
QL9	274.9	8.7	2.8	0.6	1.9	53.8	0.1	0.4	1.7	3.8	0.05	0.2	0.0	0.3	42.2		2.6	0.1	0.1	0.02	0.09	0.016	0.005	0.017	0.005	0.011	0.004	0.008	0.003	0.006	0.004	0.009	0.020	0.22	0.10	0.02	0.04
QL10	281.4	12.1	3.2	0.6	1.8	52.7	0.1	0.5	1.9	5.8	0.05	0.2	0.0	0.2	47.2		3.0	0.1	0.1	0.02	0.07	0.012	0.003	0.013		0.008				0.005		0.008	0.016	0.18	0.09	0.02	0.05
QL11	265.4	8.0	2.4	1.2	2.8	52.7	0.3	0.7	3.6	7.3	0.07	0.2	0.0	0.5	53.7		7.2	0.1	0.1	0.02	0.07	0.014	0.005	0.014		0.009	0.002	0.006	0.001	0.005		0.008	0.012	0.21	0.12	0.01	0.19
QL12	1176.7	35.0	2.6	1.4	3.8	289.4	0.3	1.1	4.2	9.3	1.41	0.5	0.1	0.4	53.3		7.6	0.2	0.3	0.04	0.21	0.054	0.009	0.125	0.034	0.214	0.039	0.097	0.013	0.073	0.010	0.019	0.013	0.20	0.26	0.06	0.30

* R refers to rain samples.

** Sb was not measured in Quail Lane samples.

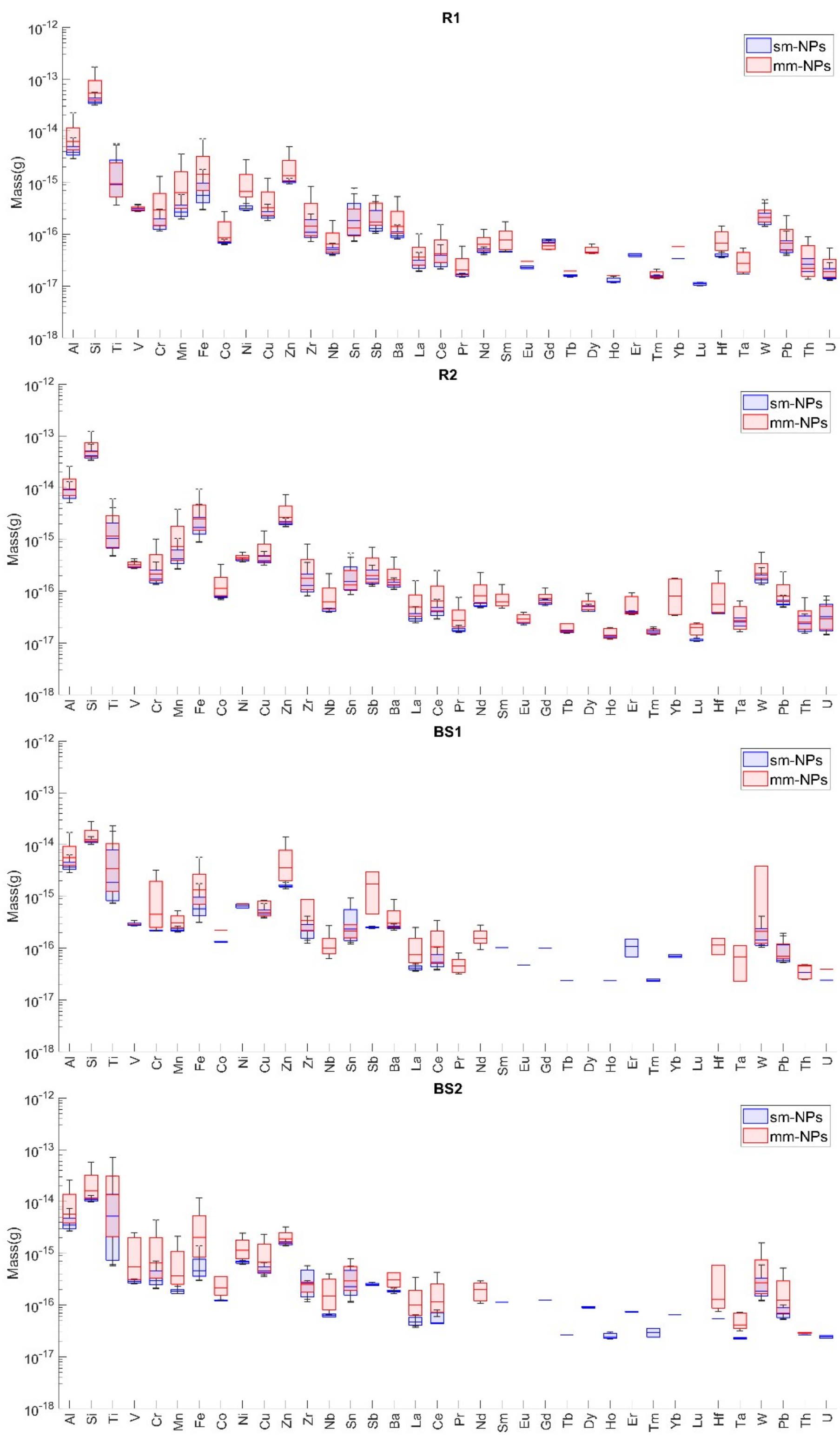


Figure S3. Mass distribution of single metal nanomaterials (smNPs) and multi metal nanomaterials (mmNMs) in representative samples of Blossom Street rain and runoff. R1 and R2 refer to rain samples number 1 and 2. BS1 and BS2 refer to Blossom Street bridge runoff samples number 1 and 2, which were collected at the beginning of the rain event.

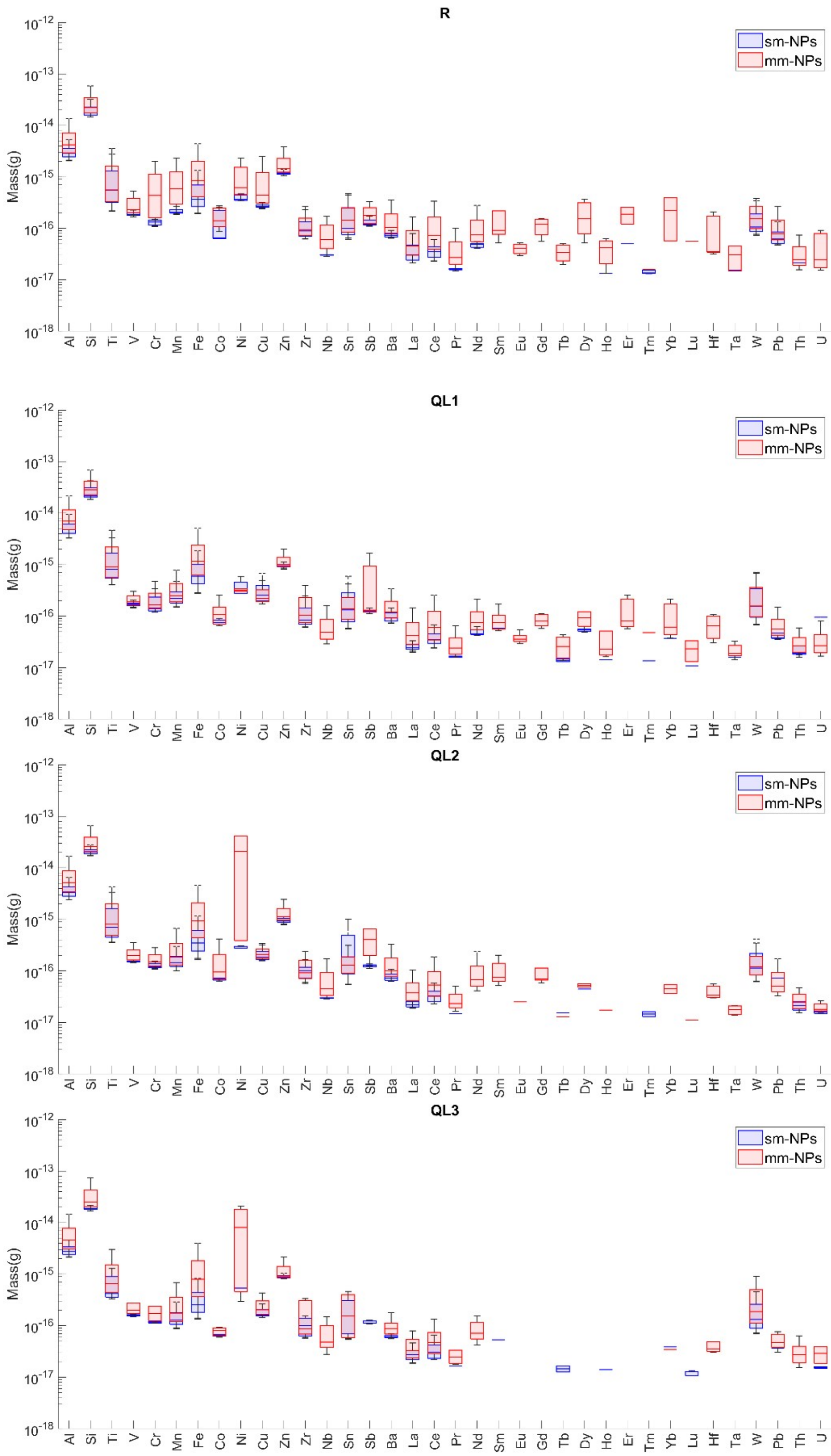


Figure S4. Mass distribution of single metal nanomaterials (smNPs) and multi metal nanomaterials (mmNMs) in representative samples of Quail Lane rain and runoff. R refer to rain sample and QL1, 2, and 3 refer to Quail Lane bridge runoff samples number 1, 2, and 3, which were collected in the first hour of storm event.

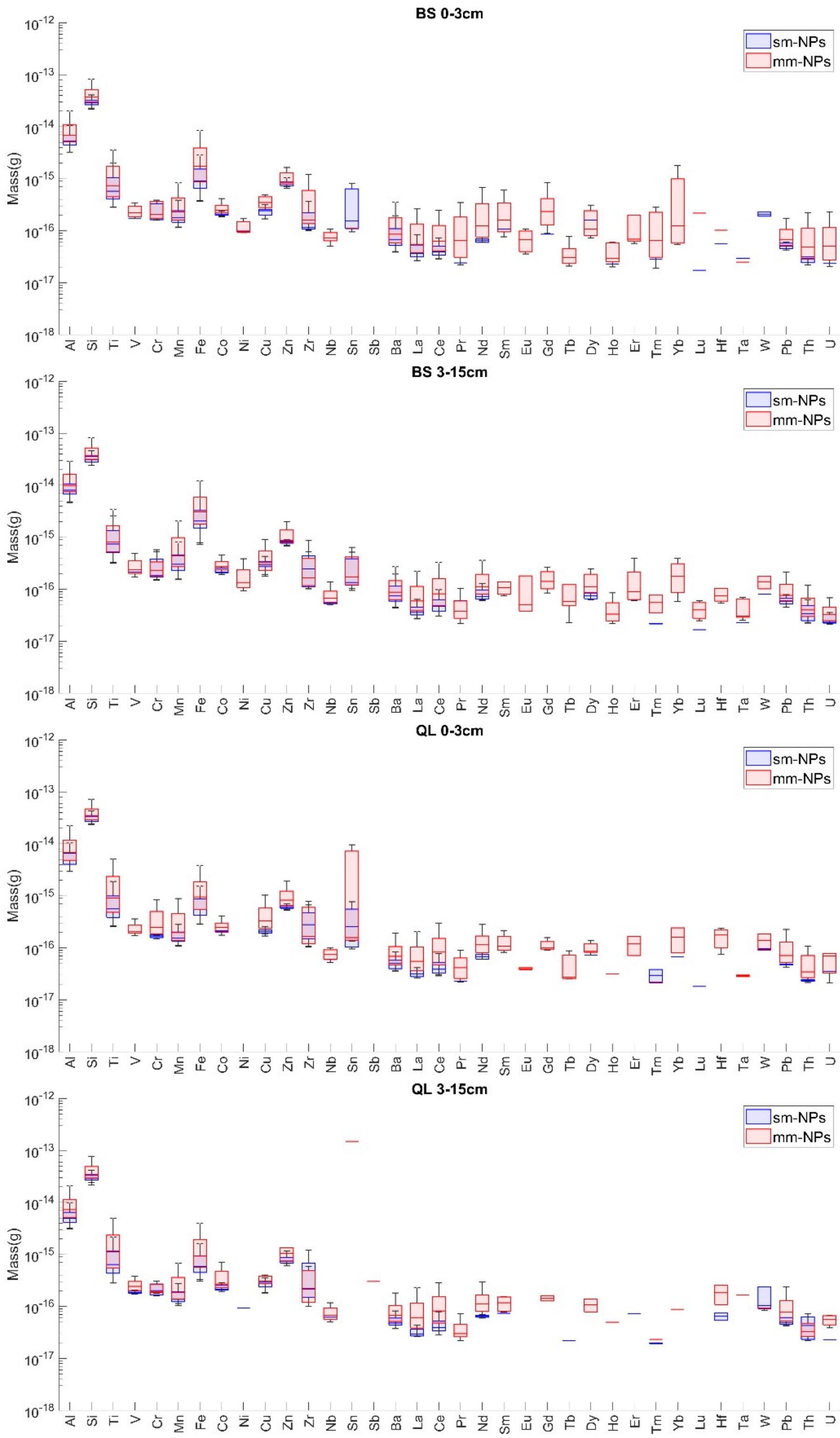


Figure S5. Mass distribution of single metal nanomaterials (smNPs) and multi metal nanomaterials (mmNMs) in soil samples collected at Blossom Street and Quail Lane. BS: Blossom Street, QL: Quail Lane, 0-3 cm and 3-15 cm refer to soil sampling depth.

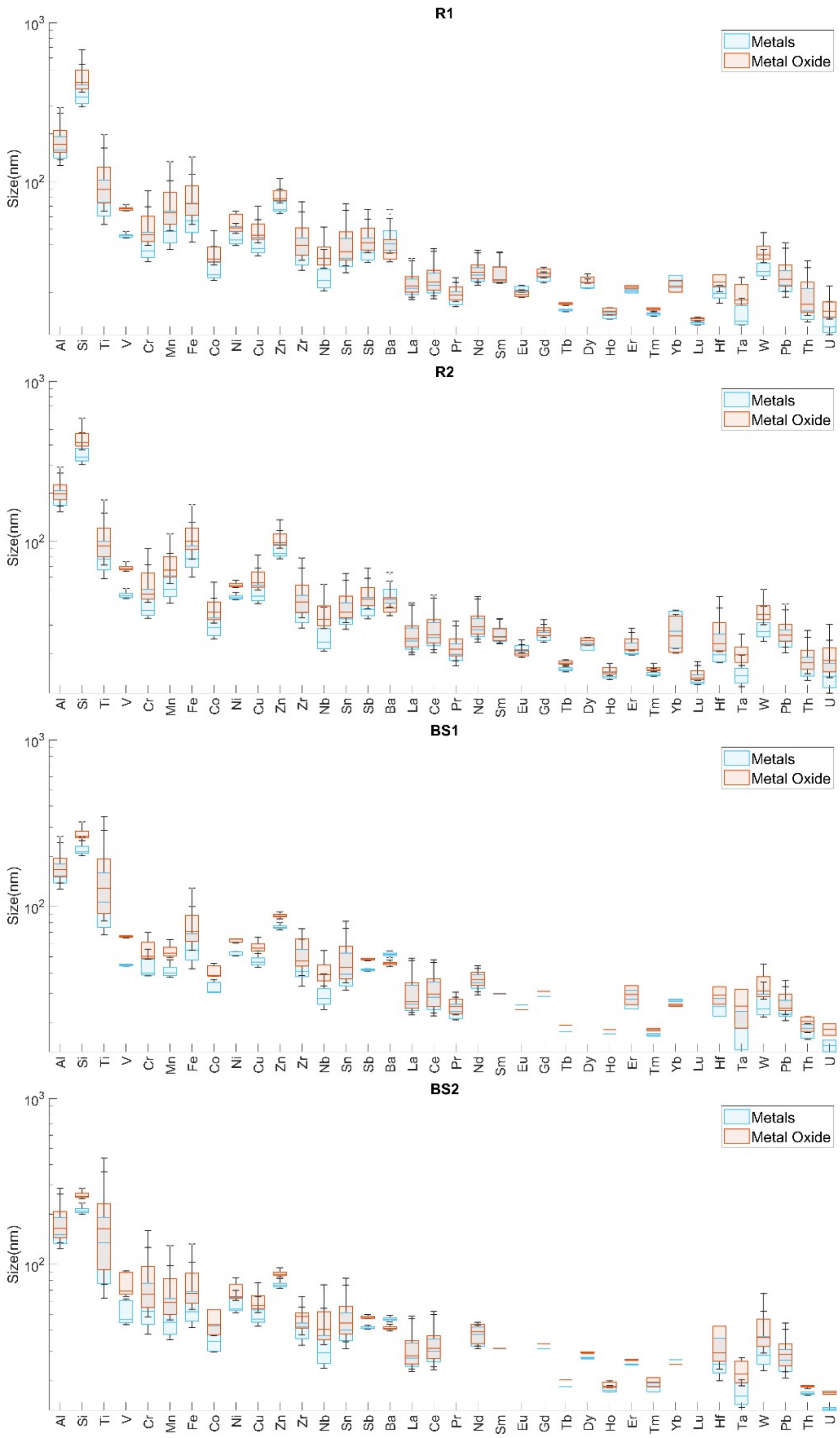


Figure S6. Particle size distribution of the detected NMs assuming pure metal and metal oxide composition (see Table S4) in representative samples of Blossom Street rain and runoff. R1 and R2 refer to rain samples number 1 and 2. BS1 and BS2 refer to Blossom Street bridge runoff samples number 1 and 2, which were collected at the beginning of the rain event.

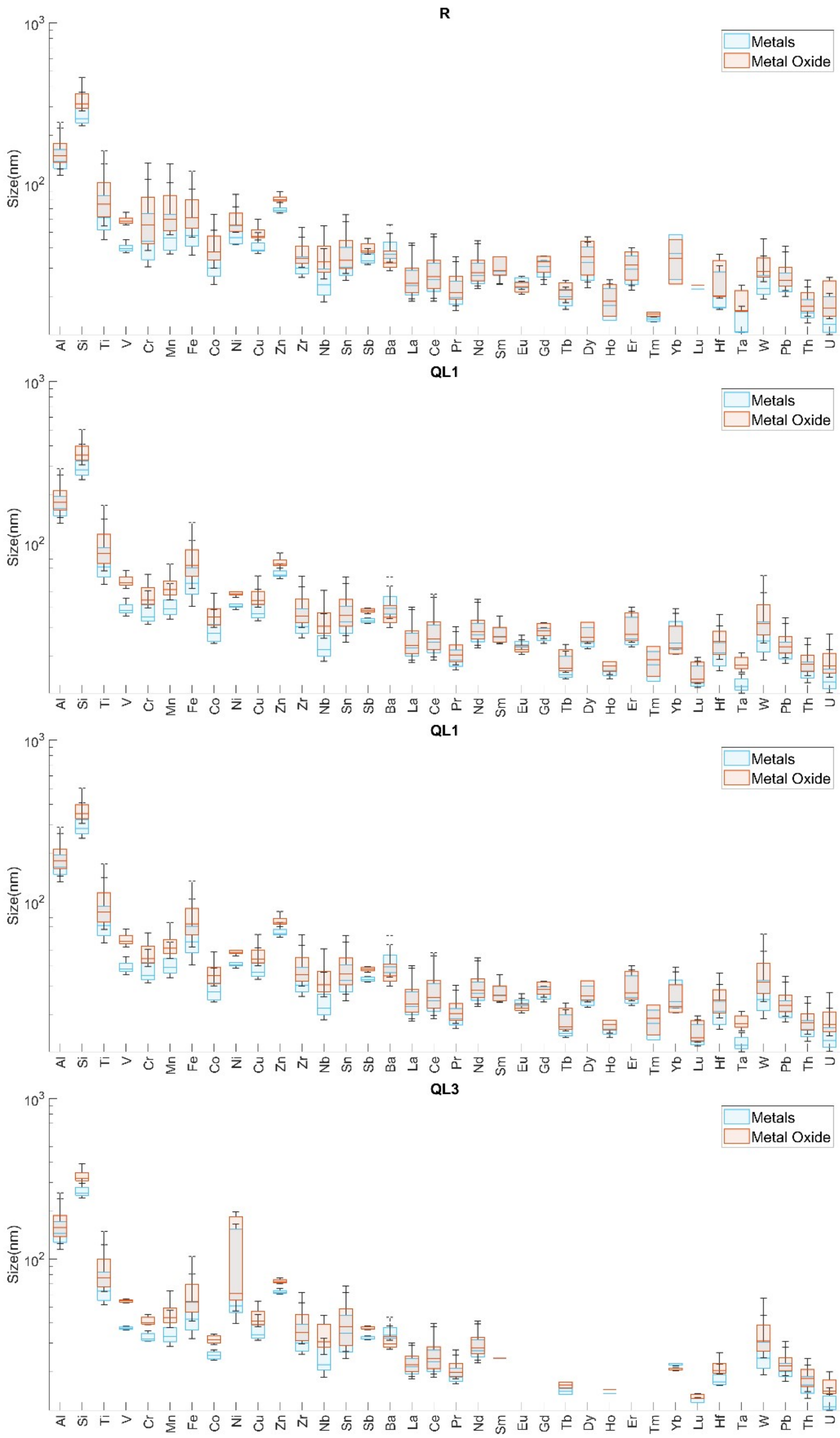


Figure S7. Particle size distribution of the detected NMs assuming pure metal and metal oxide composition (see Table S4) in representative samples of Quail Lane rain and runoff. R refer to rain sample and QL1, 2, and 3 refer to Quail Lane bridge runoff samples number 1, 2, and 3, which were collected in the first hour of storm event.

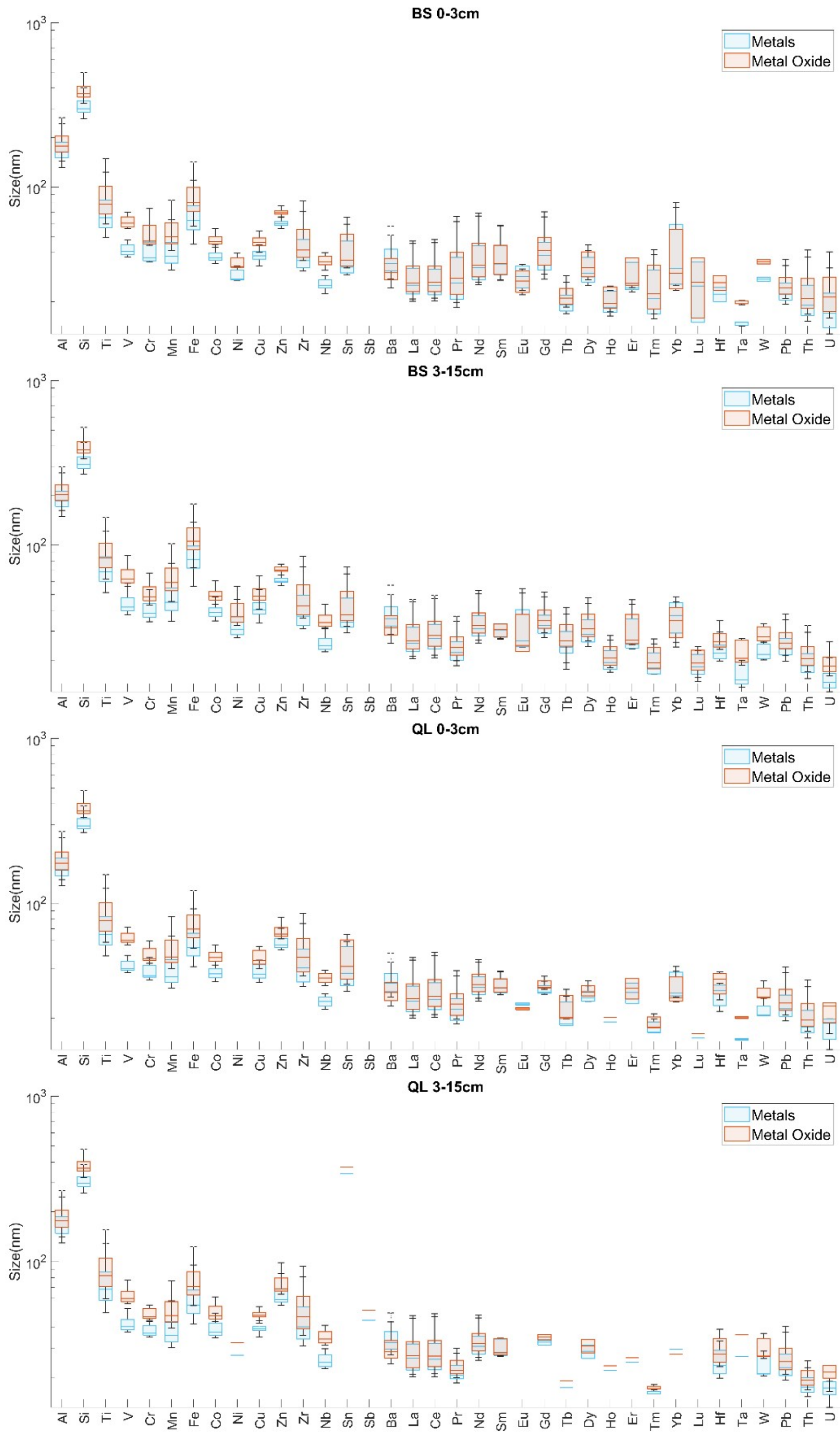


Figure S8. Particle size distribution of the detected NMs assuming pure metal and metal oxide composition (see Table S4) in soil samples collected at Blossom Street and Quail Lane. BS: Blossom Street, QL: Quail Lane, 0-3 cm and 3-15 cm refer to soil sampling depth.

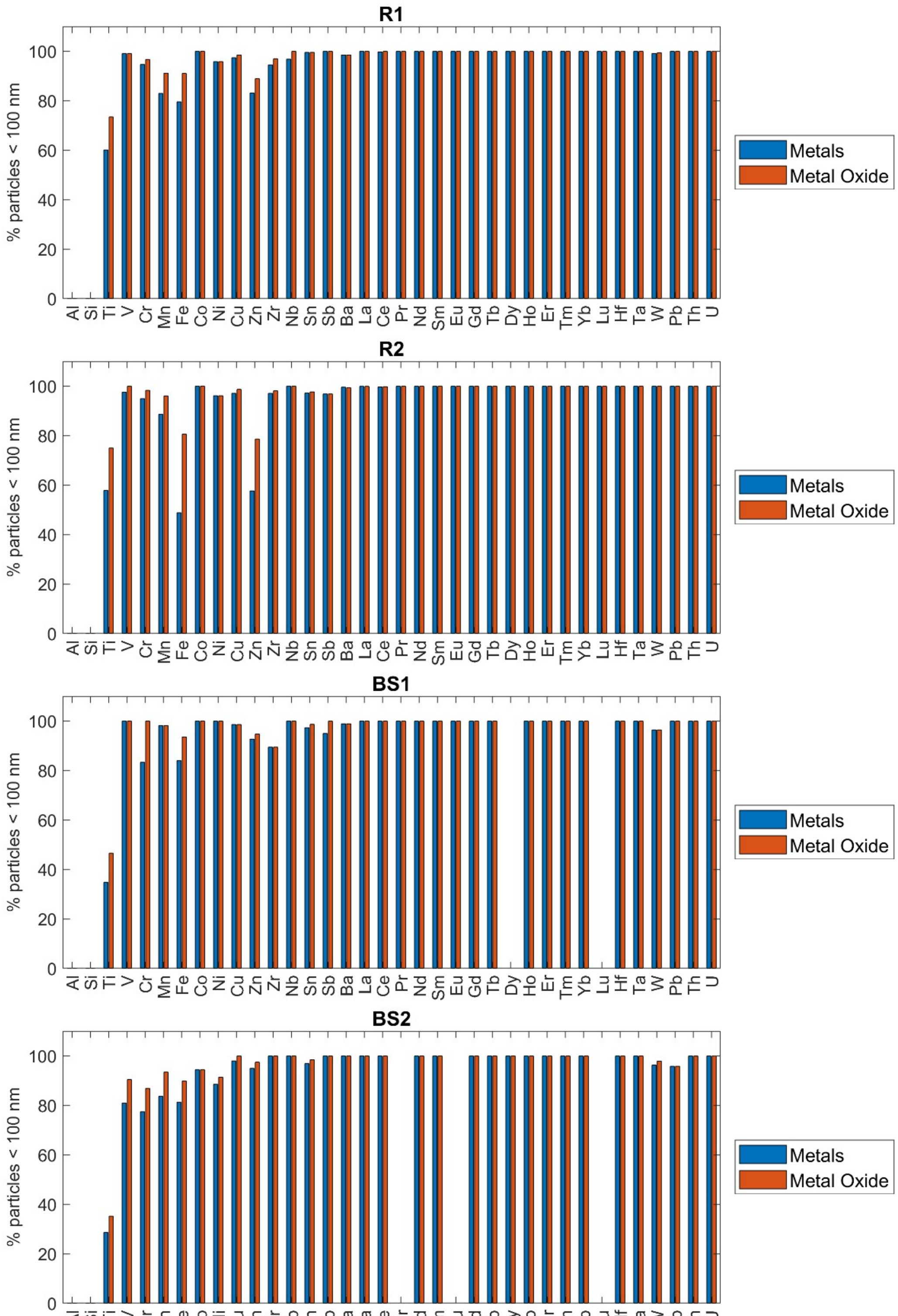


Figure S9. Percentage of particles within the nanosize range assuming pure metal and metal oxide composition (see Table S4) in representative samples of Blossom Street rain and runoff. R1 and R2 refer to rain samples number 1 and 2. BS1 and BS2 refer to Blossom Street bridge runoff samples number 1 and 2, which were collected at the beginning of the rain event.

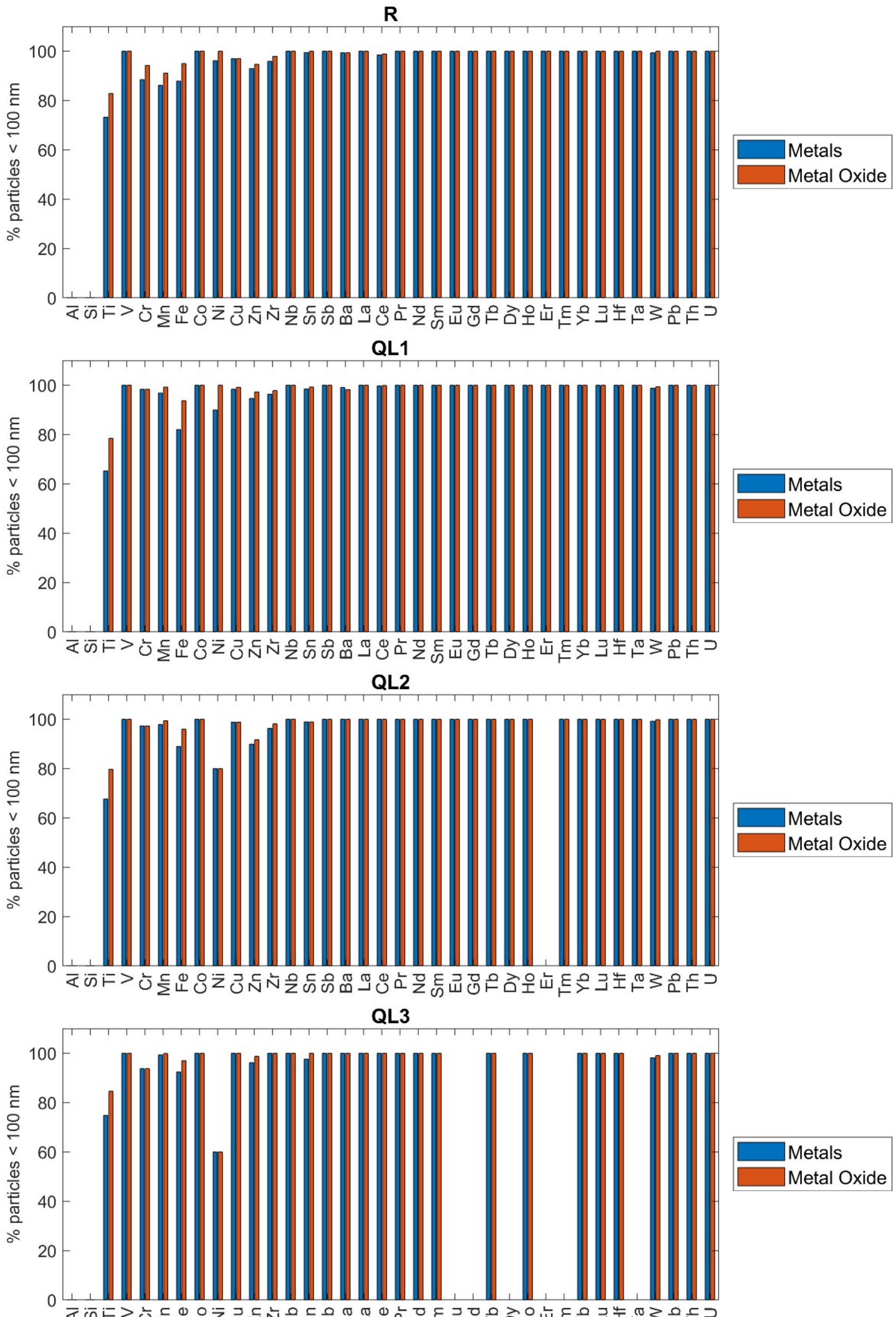


Figure S10. Percentage of particles within the nanosize range assuming pure metal and metal oxide composition (see Table S4) in representative samples of Quail Lane rain and runoff. R refer to rain sample and QL1, 2, and 3 refer to Quail Lane bridge runoff samples number 1, 2, and 3, which were collected in the first hour of storm event.

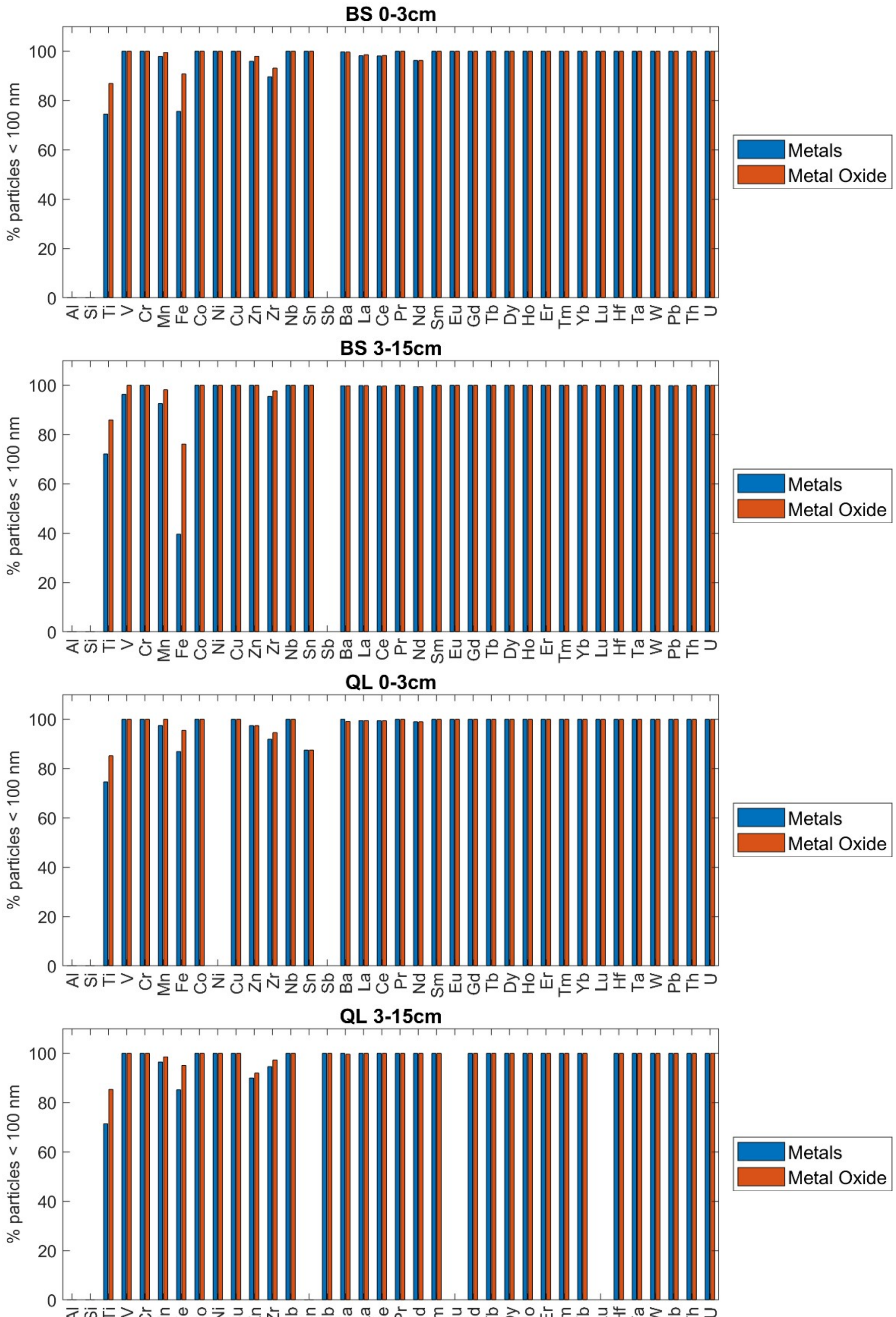


Figure S11. Percentage of particles within the nanosize range assuming pure metal and metal oxide composition (see Table S4) in soil samples collected at Blossom Street and Quail Lane. BS: Blossom Street, QL: Quail Lane, 0-3 cm and 3-15 cm refer to soil sampling depth.

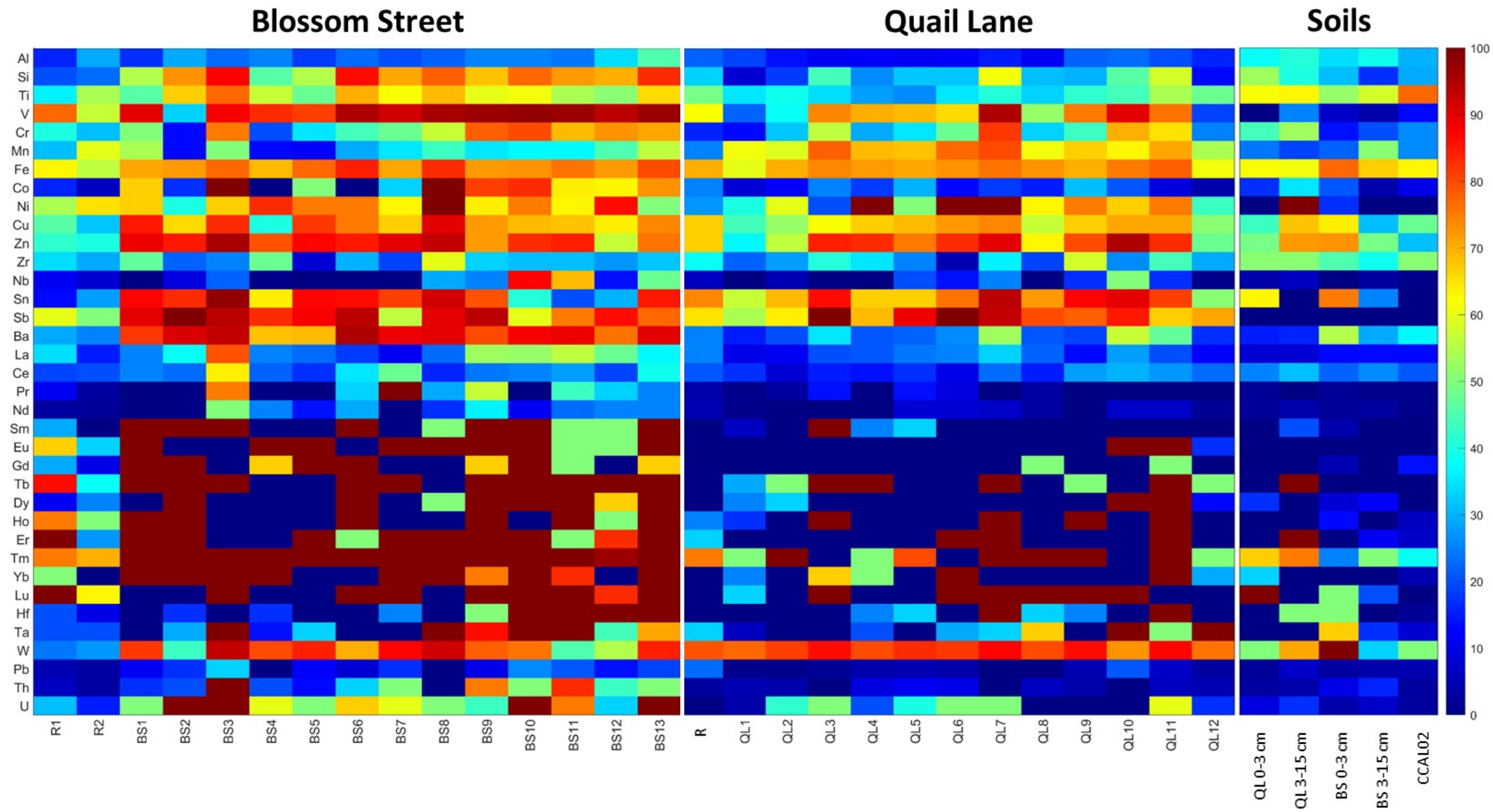


Figure S12. Heat map of the relative abundance of single metal nanomaterials (smNMs) detected in rainwater, urban runoff, and soil samples collected at the sample collection site as reference materials.

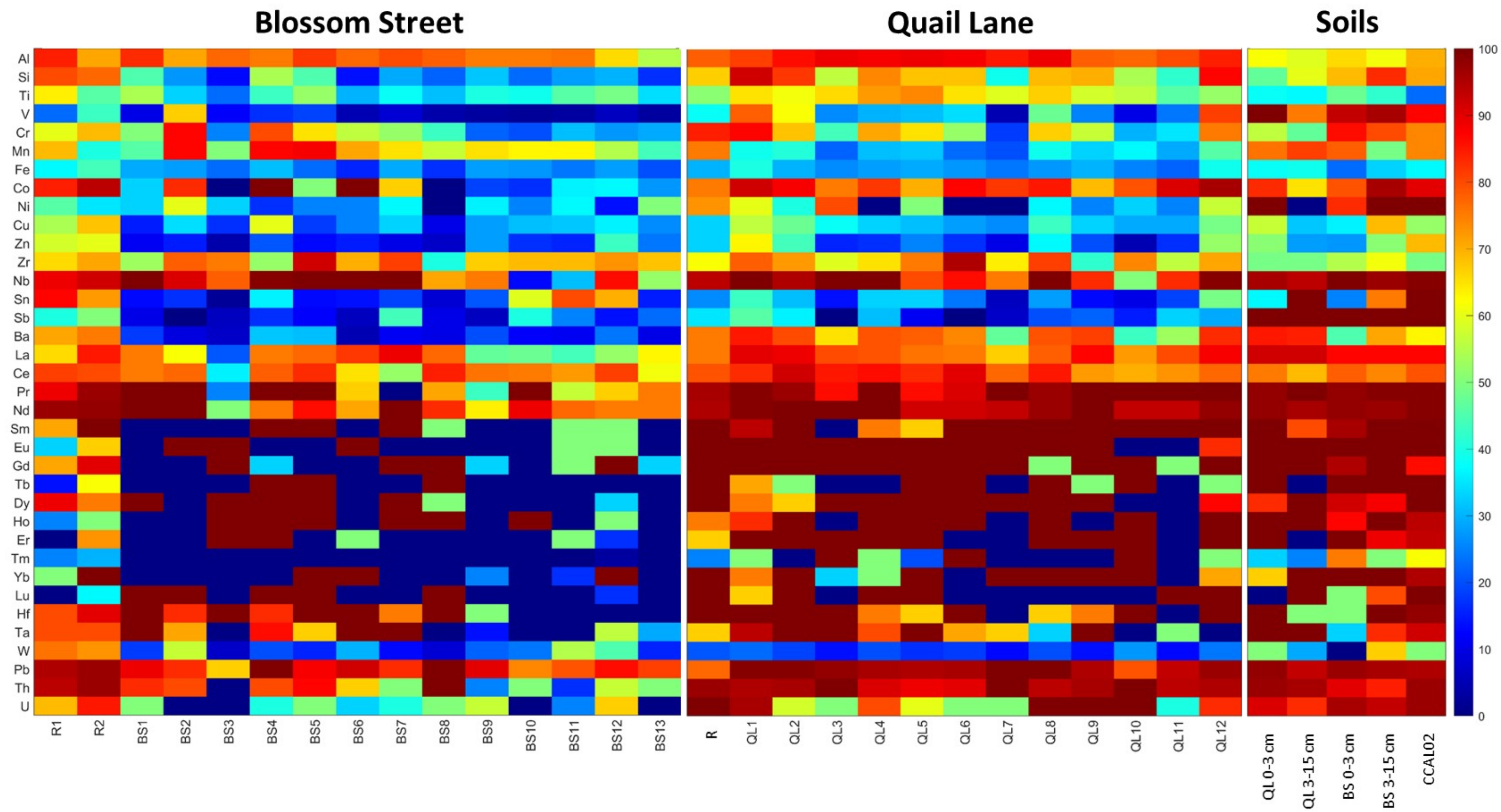
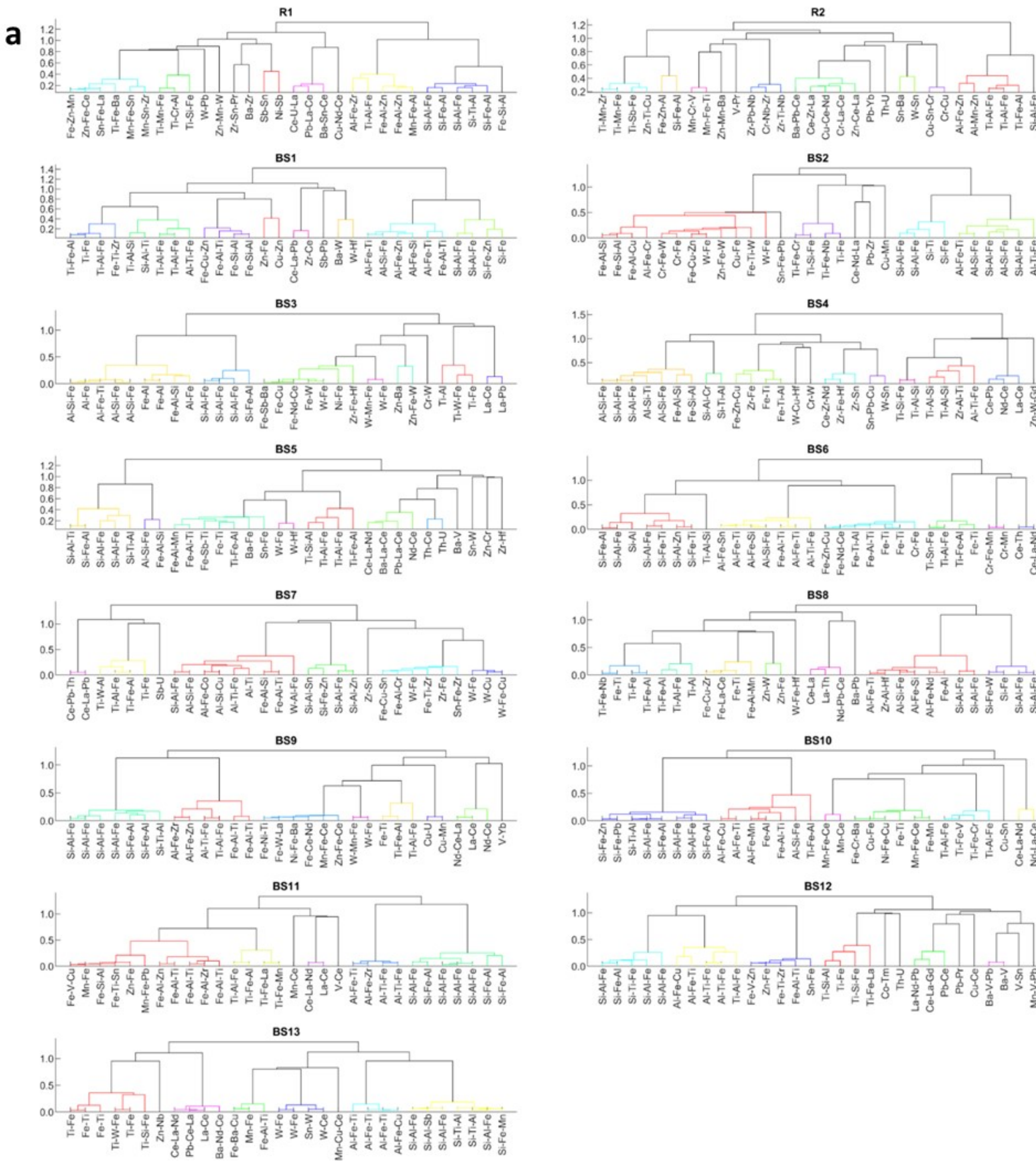


Figure S13. Heat map of the relative abundance of multi-metal NMs (mmNMs) detected in rainwater, runoff, and soil samples collected at the sample collection site as reference materials.


a
R1
R2
BS1
BS2
BS3
BS4
BS5
BS6
BS7
BS8
BS9
BS10
BS11
BS12
BS13

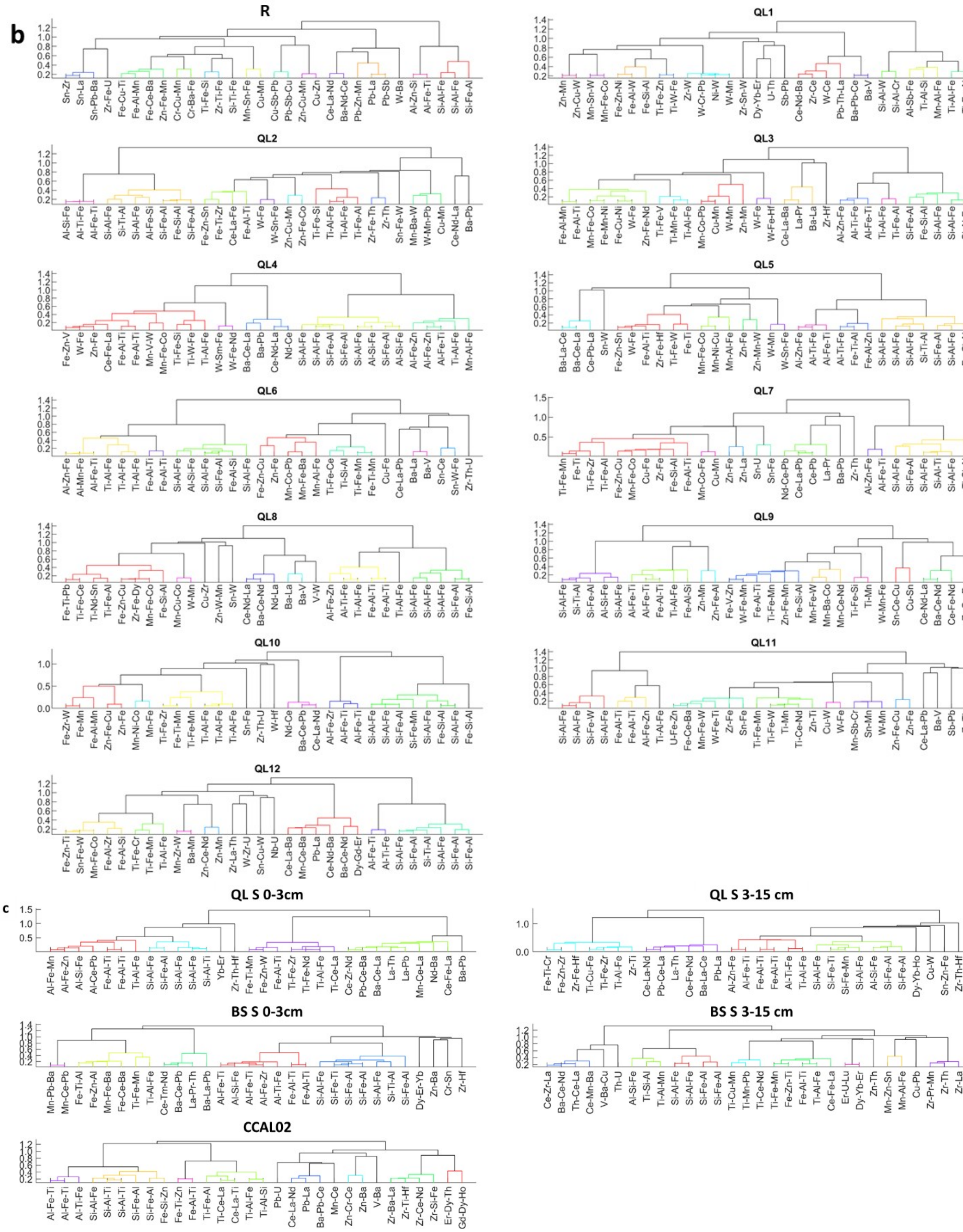
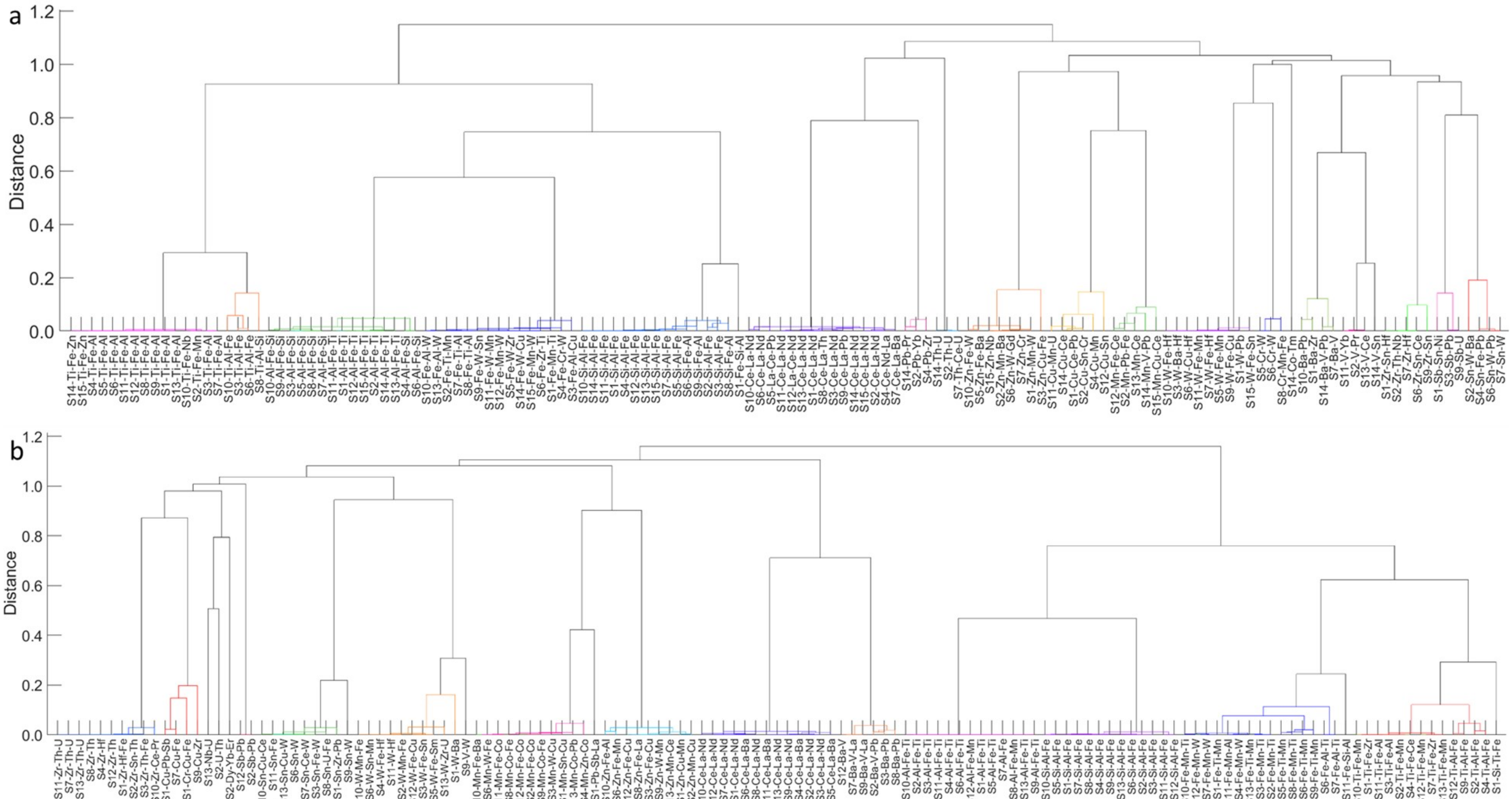


Figure S14. Dendrograms of first stage clustering of multi-metal nanomaterials (mmNMs) in (a) Blossom Street rain and runoff, (b) Quail Lane rain and runoff, and (c) soils.


a
Distance
0.0
0.2
0.4
0.6
0.8
1.0
1.2
b
Distance
0.0
0.2
0.4
0.6
0.8
1.0
1.2

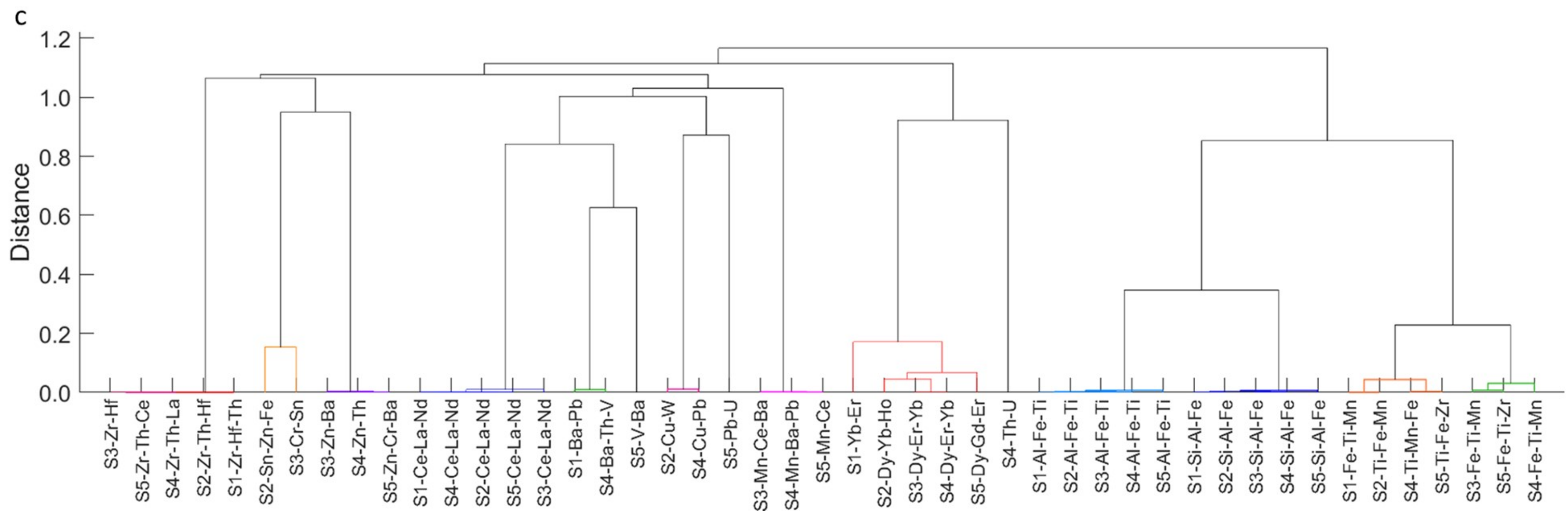
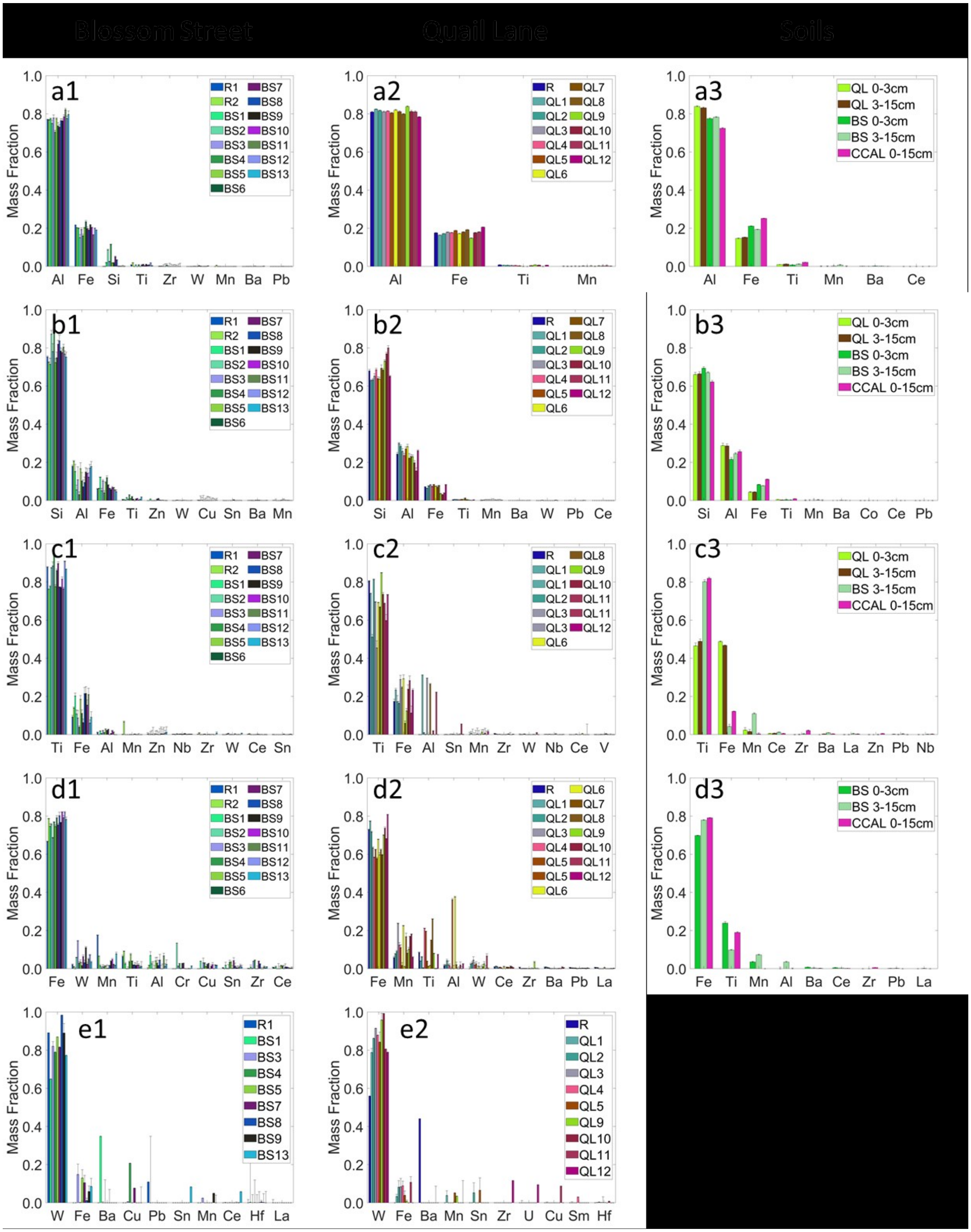
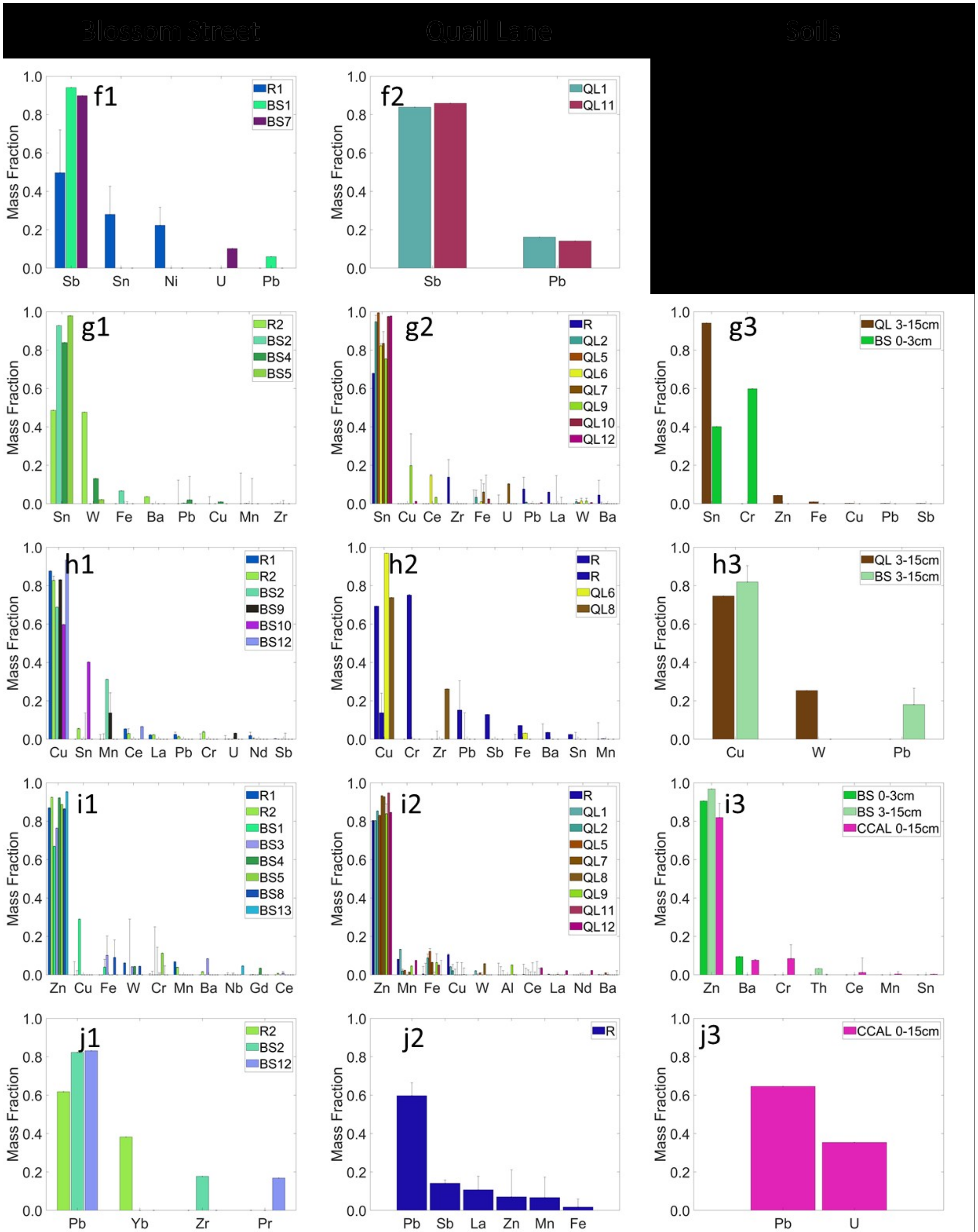


Figure S15. Dendrograms of second stage clustering multi-metal nanomaterials (mmNMs) in (a) Blossom Street rain and runoff, (b) Quail Lane rain and runoff, and (c) soils.


a1
Mass Fraction
R1 R2 BS1 BS2 BS3 BS4 BS5 BS6 BS7 BS8 BS9 BS10 BS11 BS12 BS13
Al Fe Si Ti Zr W Mn Ba Pb
a2
R QL1 QL2 QL3 QL4 QL5 QL6 QL7 QL8 QL9 QL10 QL11 QL12
Al Fe Ti Mn
a3
QL 0-3cm
QL 3-15cm
BS 0-3cm
BS 3-15cm
CCAL 0-15cm
Al Fe Ti Mn Ba Ce
b1
Si Al Fe Ti Zn W Cu Sn Ba Mn
b2
Si Al Fe Ti Mn Ba W Pb Ce
b3
Si Al Fe Ti Mn Ba Co Ce Pb
c1
Ti Fe Al Mn Zn Nb Zr W Ce Sn
c2
R QL1 QL1 QL2 QL3 QL3 QL6 QL8 QL9 QL10 QL11 QL11 QL12
Ti Fe Al Sn Mn Zr W Nb Ce V
c3
QL 0-3cm
QL 3-15cm
BS 3-15cm
CCAL 0-15cm
Ti Fe Mn Ce Zr Ba La Zn Pb Nb
d1
Fe W Mn Ti Al Cr Cu Sn Zr Ce
d2
R QL1 QL2 QL3 QL4 QL5 QL5 QL6 QL6 QL7 QL8 QL9 QL10 QL11 QL12
Fe Mn Ti Al W Ce Zr Ba Pb La
d3
BS 0-3cm
BS 3-15cm
CCAL 0-15cm
Fe Ti Mn Al Ba Ce Zr Pb La
e1
R1 BS1 BS3 BS4 BS5 BS7 BS8 BS9 BS13
W Fe Ba Cu Pb Sn Mn Ce Hf La
e2
R QL1 QL2 QL3 QL4 QL5 QL9 QL10 QL11 QL12
W Fe Ba Mn Sn Zr U Cu Sm Hf


Blossom Street
Quail Lane
Soils
Mass Fraction
f1
R1
BS1
BS7
Sb Sn Ni U Pb
f2
QL1
QL11
Sb Pb
g1
R2
BS2
BS4
BS5
Sn W Fe Ba Pb Cu Mn Zr
g2
R
QL2
QL5
QL6
QL7
QL9
QL10
QL12
Sn Cu Ce Zr Fe U Pb La W Ba
g3
QL 3-15cm
BS 0-3cm
Sn Cr Zn Fe Cu Pb Sb
h1
R1
R2
BS2
BS9
BS10
BS12
Cu Sn Mn Ce La Pb Cr U Nd Sb
h2
R
R
QL6
QL8
Cu Cr Zr Pb Sb Fe Ba Sn Mn
h3
QL 3-15cm
BS 3-15cm
Cu W Pb
i1
R1
R2
BS1
BS3
BS4
BS5
BS8
BS13
Zn Cu Fe W Cr Mn Ba Nb Gd Ce
i2
R
QL1
QL2
QL5
QL7
QL8
QL9
QL11
QL12
Zn Mn Fe Cu W Al Ce La Nd Ba
i3
BS 0-3cm
BS 3-15cm
CCAL 0-15cm
Zn Ba Cr Th Ce Mn Sn
j1
R2
BS2
BS12
Pb Yb Zr Pr
j2
R
Pb Sb La Zn Mn Fe
j3
CCAL 0-15cm
Pb U

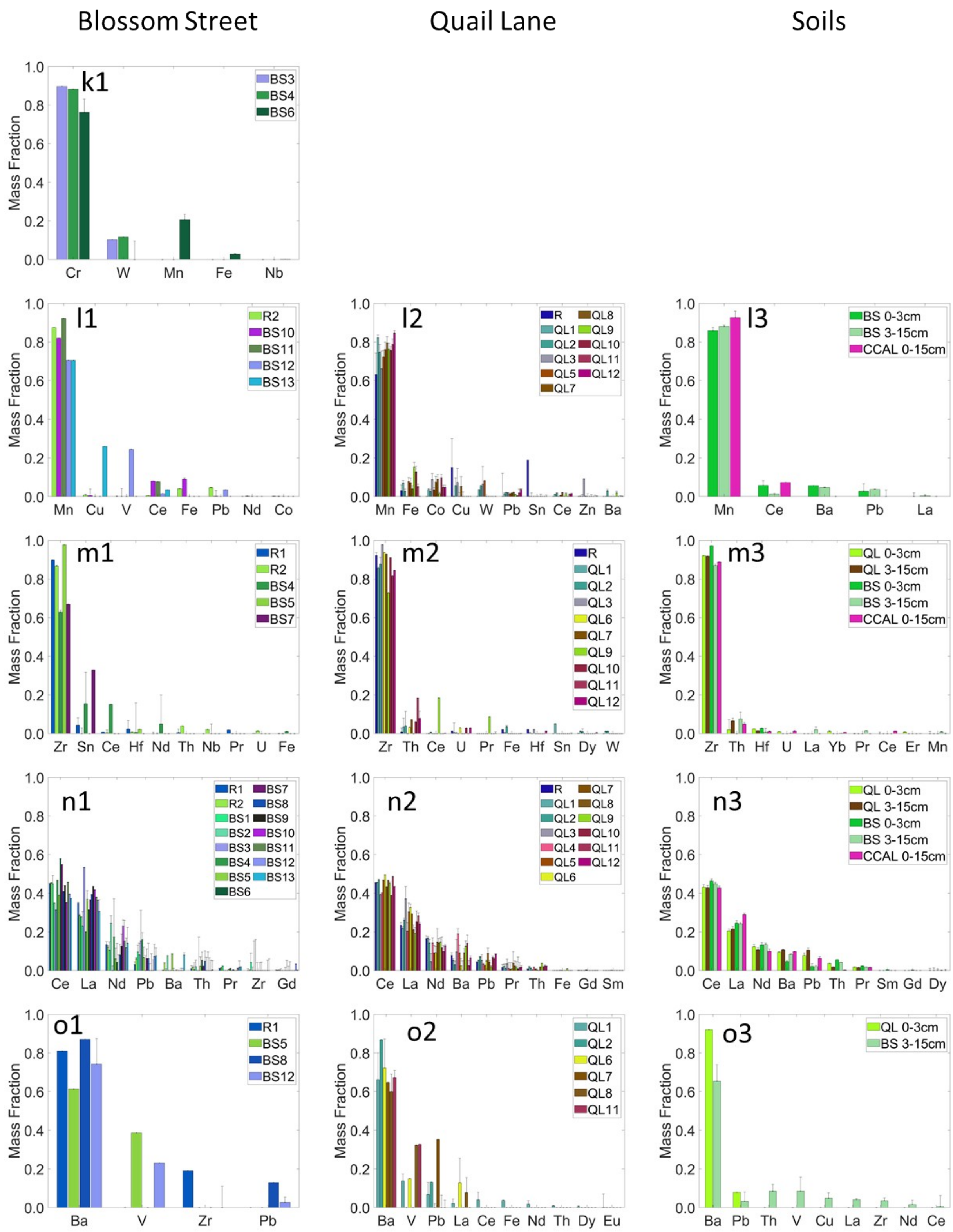
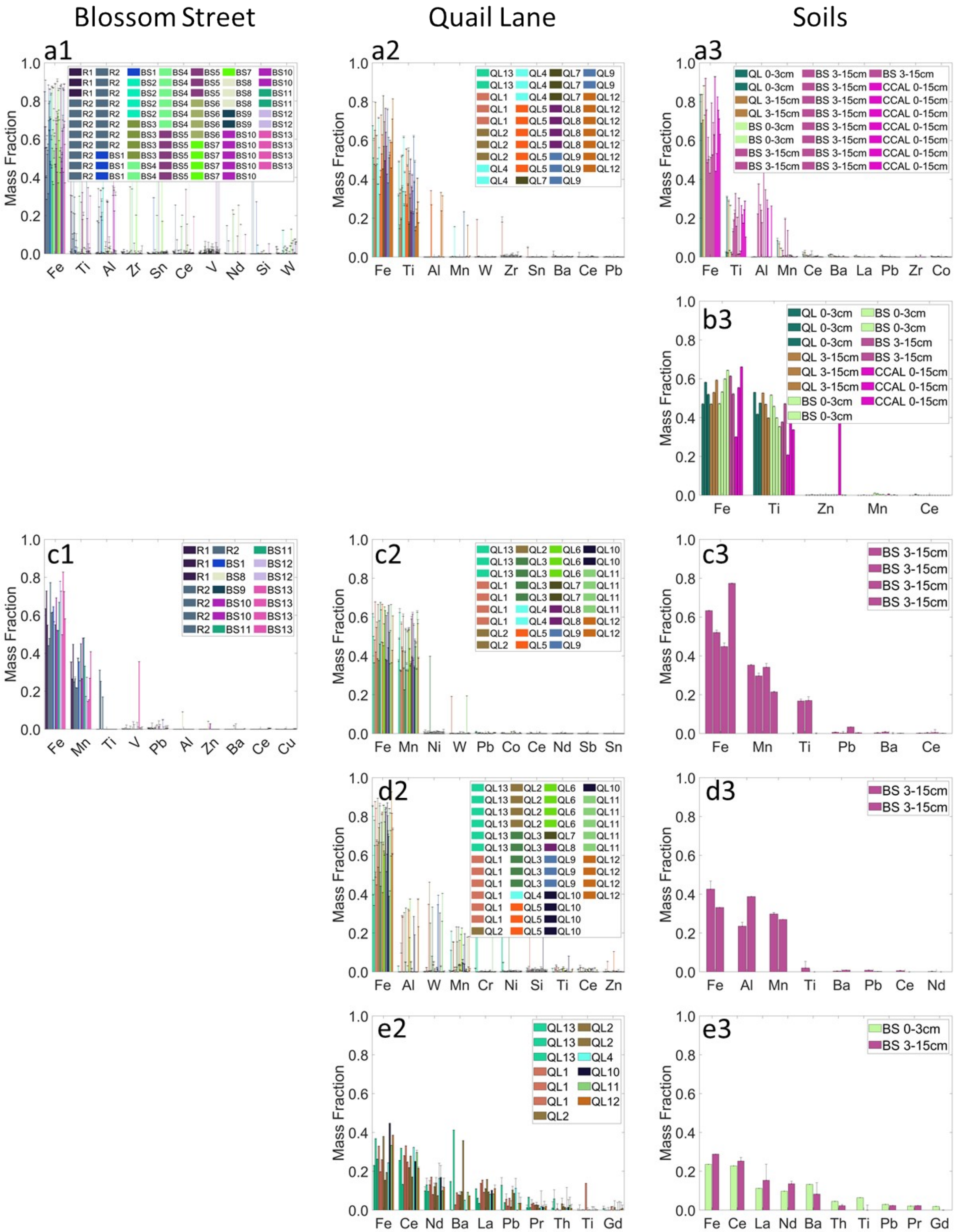
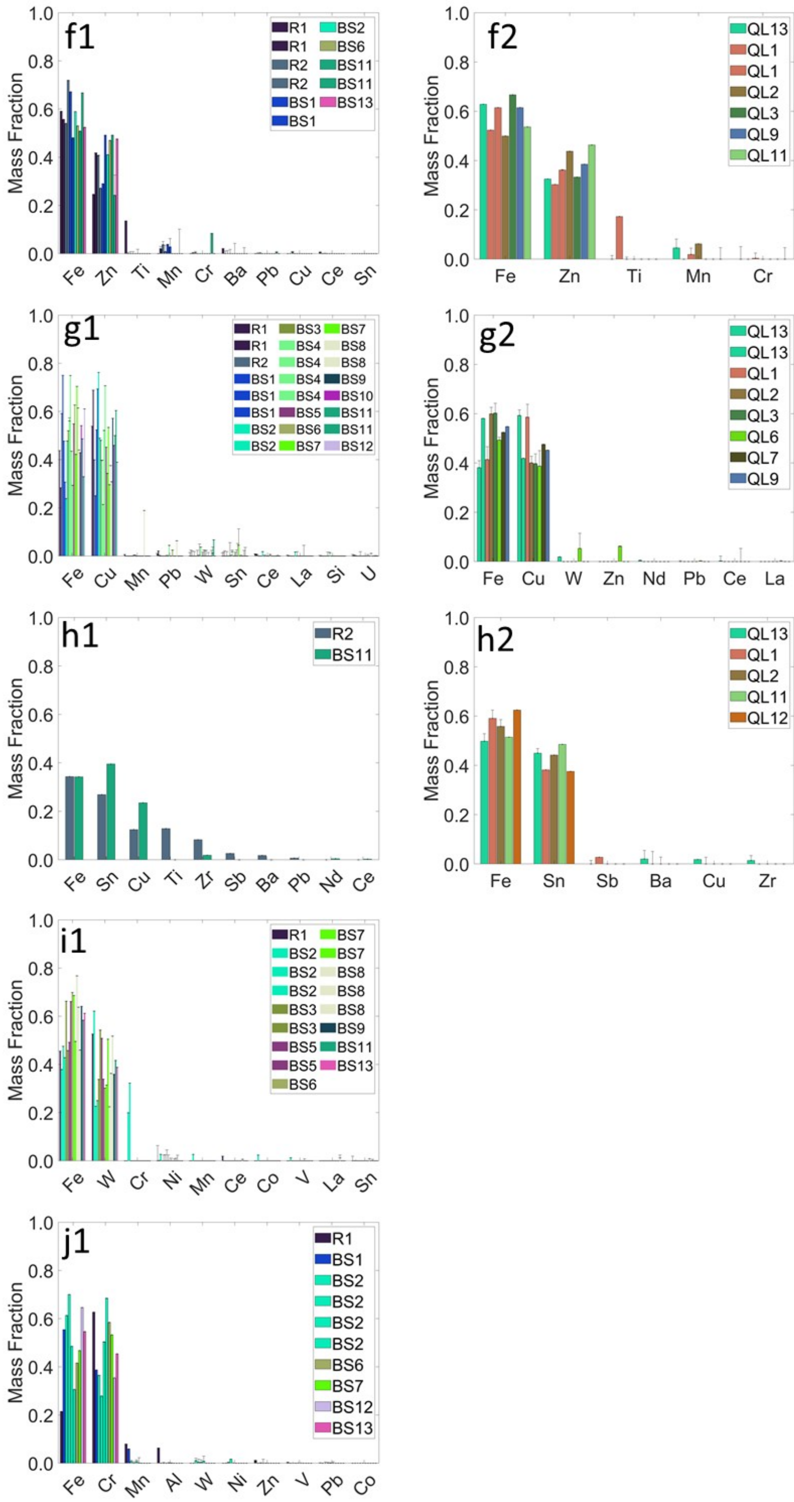


Figure S16. Elemental composition (mass fraction) of clusters identified in the rainwater, urban runoff, and soil samples: (a) Al, (b) Si, (c) Ti, (d) Fe, (e) W, (f) Sb, (g) Sn, (h) Cu, (i) Zn, (j) Pb, (k) Cr, (l) Mn, (m) Zr, (n) Ce, and (o) Ba. Distance cutoff for the first and second stage clustering were 0.5 and 0.2, respectively.


Blossom Street
Quail Lane
Soils
a1
a2
a3
b3
c1
c2
c3
d2
d3
e2
e3
Mass Fraction
Fe Ti Al Zr Sn Ce V Nd Si W
Fe Ti Al Mn W Zr Sn Ba Ce Pb
Fe Ti Al Mn Ce Ba La Pb Zr Co
Fe Ti Zn Mn Ce
Fe Mn Ti V Pb Al Zn Ba Ce Cu
Fe Mn Ni W Pb Co Ce Nd Sb Sn
Fe Mn Ti Pb Ba Ce
Fe Al W Mn Cr Ni Si Ti Ce Zn
Fe Al Mn Ti Ba Pb Ce Nd
Fe Ce Nd Ba La Pb Pr Th Ti Gd
Fe Ce La Nd Ba Th Ti Pb Pr Gd

Blossom Street Quail Lane Soils



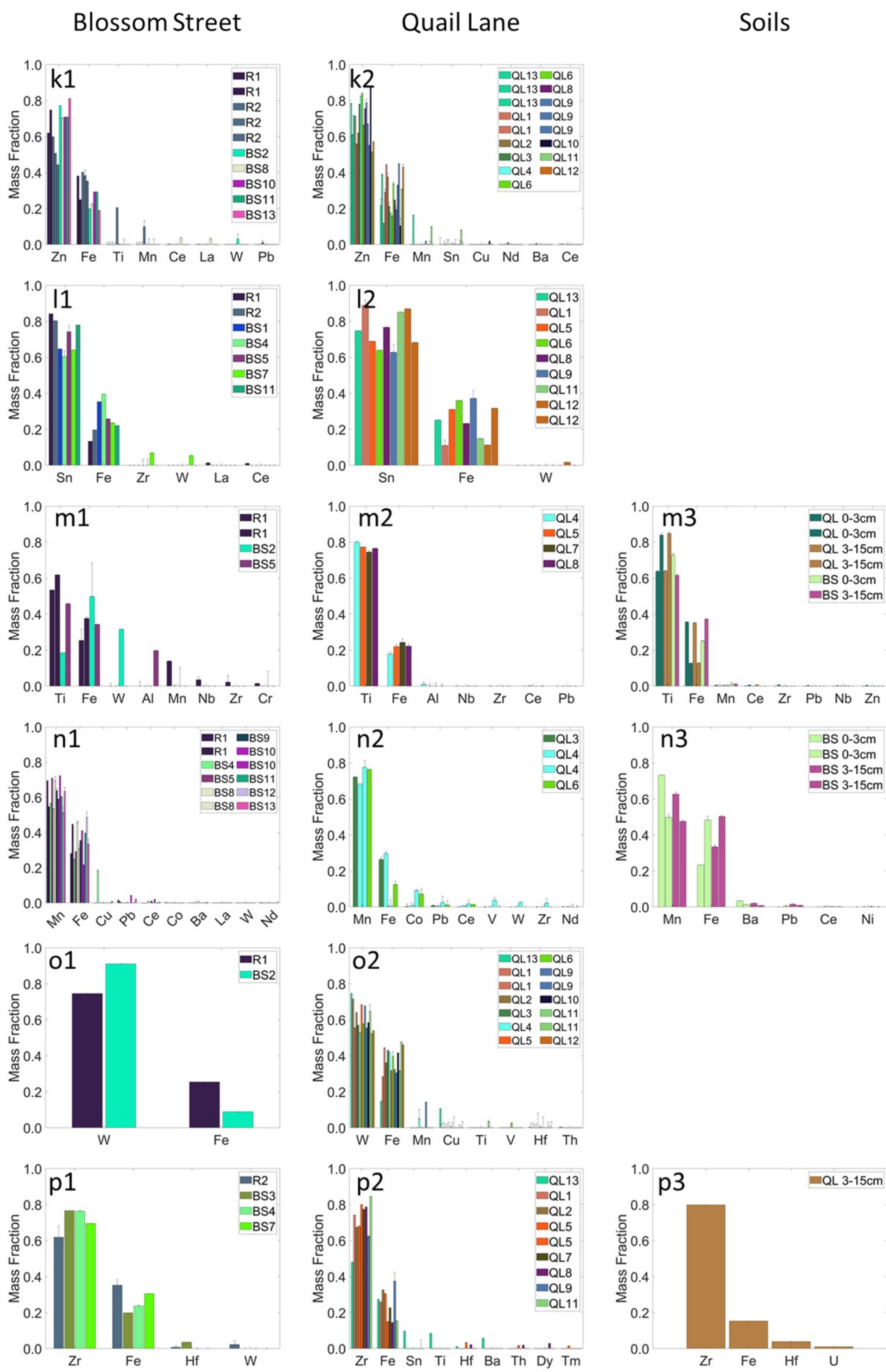


Figure S17. Elemental composition (mass fraction) of the identified sub-clusters in the Fe-cluster in rainwater, urban runoff, and soil samples. Distance cutoff for the first and second stage clustering were 0.05 and 0.2, respectively.

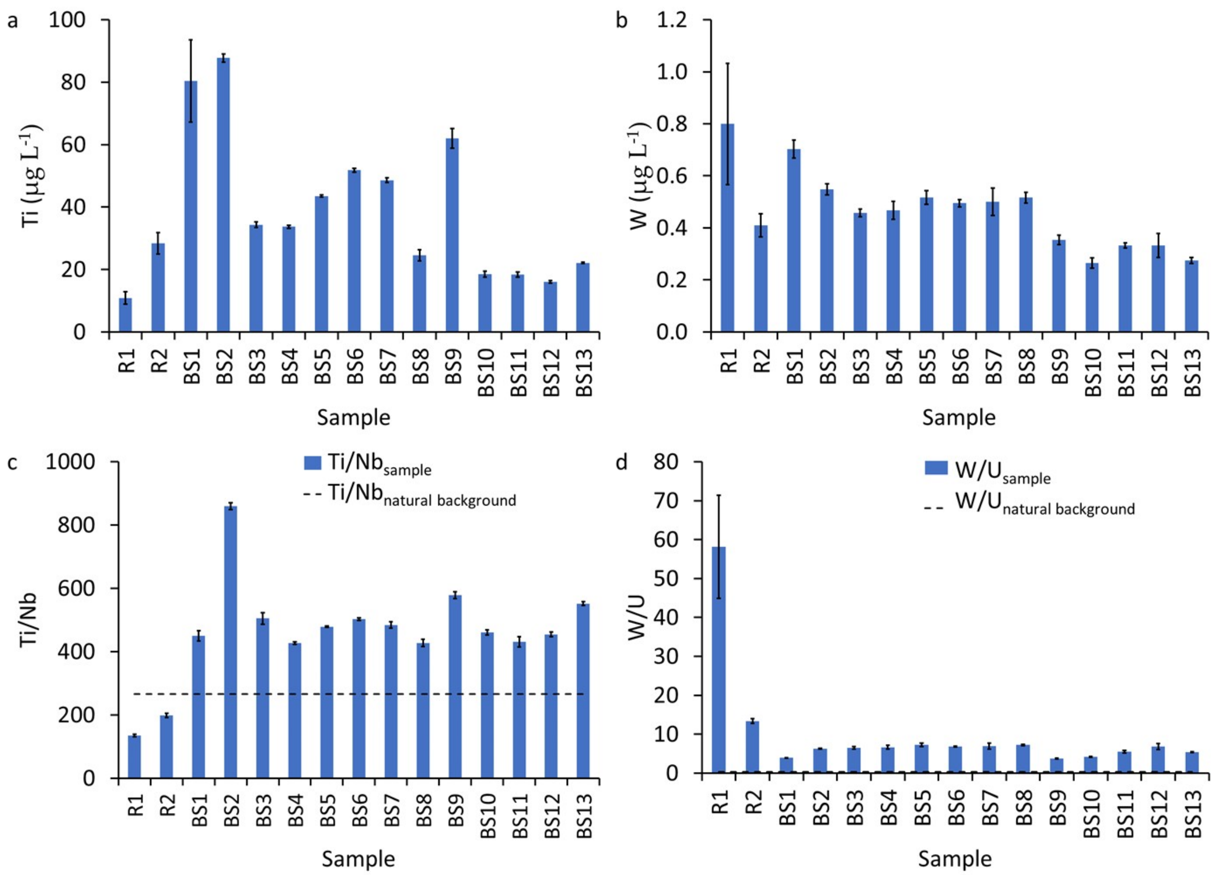


Figure S18. Total elemental concentrations of (a) Ti, and (b) W and elemental ratios of (c) Ti/Nb and (d) W/U in Blossom Street rainwater and bridge runoff as a function of sampling time after the start of the storm event. The background Ti/Nb and W/U were 266 ± 9 and 0.26 ± 0.17, respectively. Data for Quail Lane is presented in Figure S15.

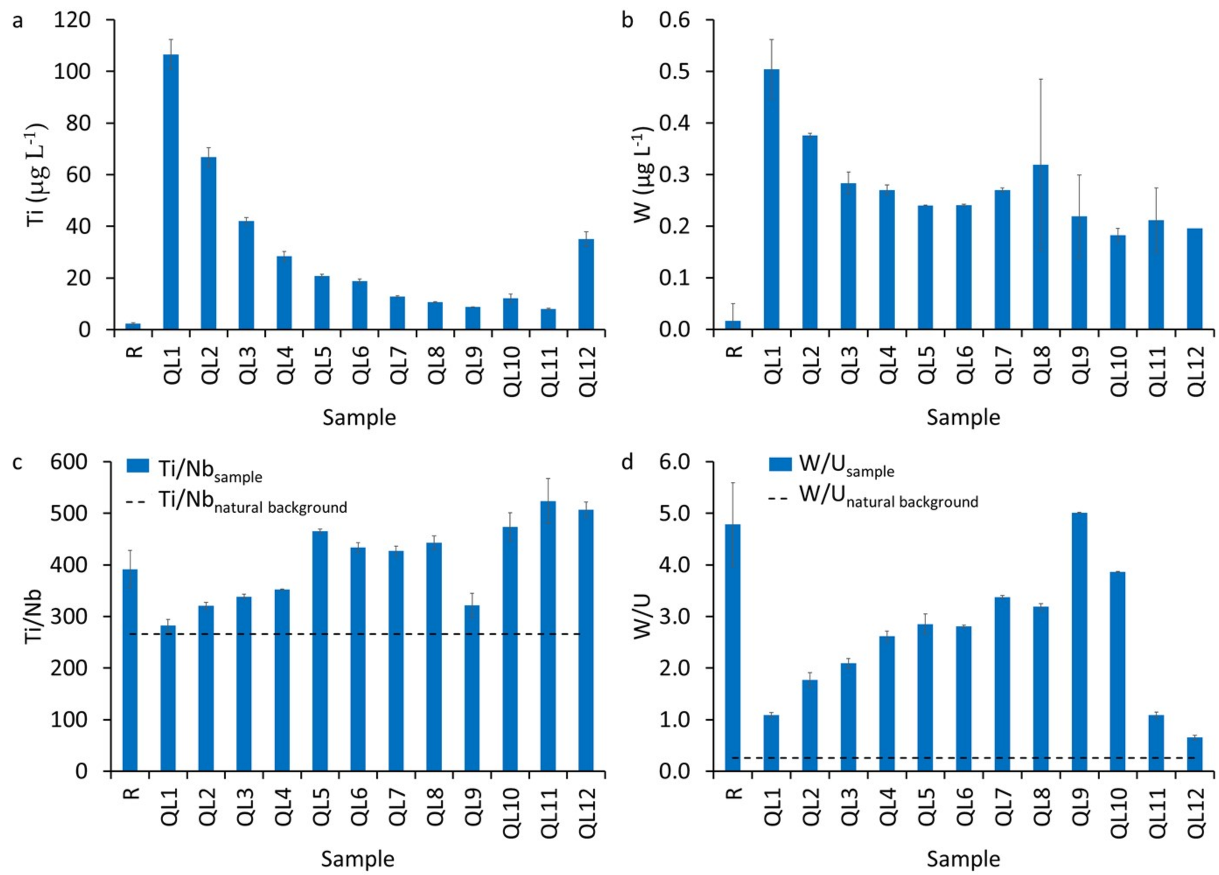


Figure S19. Total elemental concentrations of (a) Ti, and (b) W and elemental ratios of (c) Ti/Nb and (d) W/Al in Quail Bridge Lane rainwater and runoff as a function of sampling time after the start of the storm event.

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3. Nabi, M. M.; Wang, J.; Meyer, M.; Croteau, M.-N.; Ismail, N.; Baalousha, M., Concentrations and size distribution of TiO2 and Ag engineered particles in five wastewater treatment plants in the United States. *Science of The Total Environment* **2021,** *753*, 142017.
4. Nabi, M. M.; Wang, J.; Baalousha, M., Episodic surges in titanium dioxide engineered particle concentrations in surface waters following rainfall events. *Chemosphere* **2021,** *263*, 128261.
5. Smith, D. B. C.; Woodruff, W. F.; Solano, L. G.; Ellefsen, F.; Karl, J., Geochemical and mineralogical maps for soils of the conterminous United States. **2014**.