

## Article

# Nickel Uptake by Cypress Pine (*Callitris glaucophylla*) in the Miandetta Area, Australia: Implications for Use in Biogeochemical Exploration

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**Table S1.** Details of analytical methods.

<b>Method:</b>	<b>BQ-INAA-1</b>
Laboratory:	Becquerel Laboratories, Canada
Sample form:	Milled vegetation (<2mm)
Sample weight:	15 g in plastic containers
Digestion:	Nil
Analysis:	Instrumental neutron activation analysis (INAA)
Analytes:	Ag, As, Au, Ba, Br, Cd, Ce, Co, Cr, Fe, Ir, La, Mo, Na, Ni, Rb, Sb, Sc, Se, Sm, Ta, Th, U, W, Zn
<b>Method:</b>	<b>BVeg/OES</b>
Laboratory:	Genalysis Laboratories
Sample form:	Milled vegetation (<2mm)
Sample weight:	15 g
Digestion:	aqua regia
Analysis:	ICP-OES
Analytes:	Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Ti, V, Zn
<b>Method:</b>	<b>ME-ICP44</b>
Laboratory:	ALS-Chemex
Sample form:	1 kg bulk sample dried at 60° C, 250 g pulverised to 85% < 75µm in low Cr steel ring mill.
Sample weight:	0.5 g
Digestion:	Aqua regia digestion
Analysis:	ICP-AES
Analytes:	Au, Sc, Ag, As, Ba, Bi, Ca, Cd, Co, Cu, Fe, Mg, Mn, Mo, Ni, P, Pb, S, Sb, Zn
<b>Method:</b>	<b>MSA-06</b>
Laboratory:	LabWest
Sample form:	Milled vegetation (<2mm)

Sample weight:	1 g
Digestion:	Microwave assisted aqua regia at 2455 Hz in sealed Teflon® containers
Analysis:	ICP-MS
Analytes:	Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr
<b>Method:</b>	<b>pXRF</b>
Laboratory:	UNSW
Sample form:	Milled vegetation (<2mm)
Sample weight:	3 g compressed into 50µm-thick polythene bags (minimum sample depth 10 mm)
Digestion:	Nil
Analysis:	pXRF - Olympus Vanta 30s count on each of three beams in 'Geochem' mode
Analytes:	Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr

### Sequential selective extractions:

#### *Exchangeable metals.*

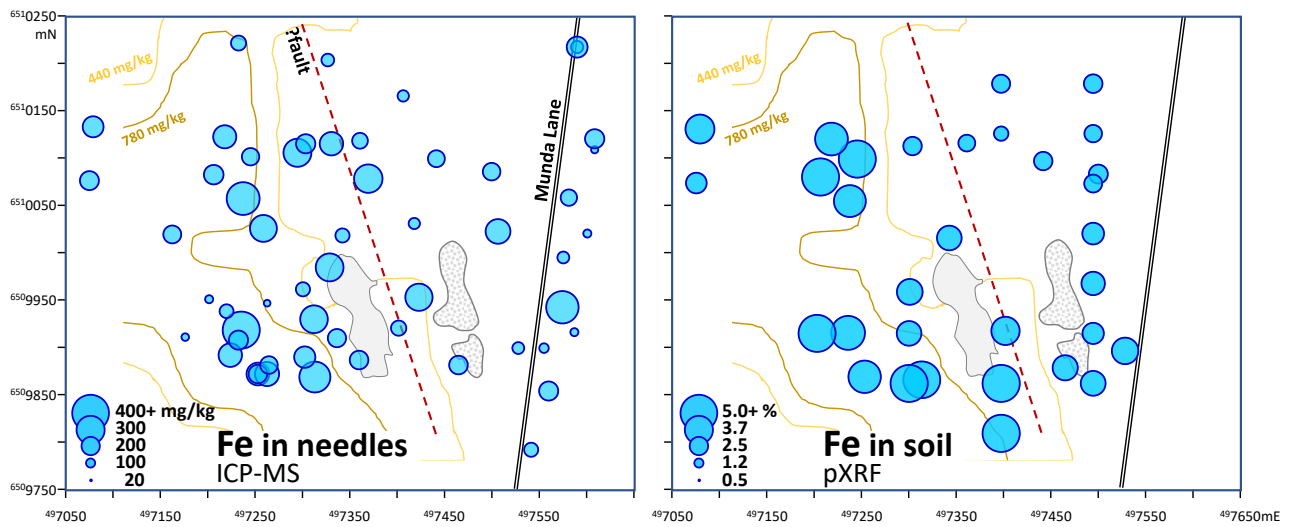
Forty mL of 0.11 mol L<sup>-1</sup> acetic acid was added to each of the 1.00 g sixteen dry soil samples in a 50 mL polypropylene centrifuge tubes. The mixtures were tumbled for 20 hours at 22±5°C (overnight). The extract was separated from the solid phase by centrifugation at 3800 rpm 20 min. The supernatant liquid was decanted and filtered through a 45 µm into a 15 ml tube. The residue was washed by adding 20 ml of double-distilled water, shaking for 15 min and then centrifuging. The second supernatant liquid was discarded without any loss of residue.

#### *Metals bound to iron and manganese oxides.*

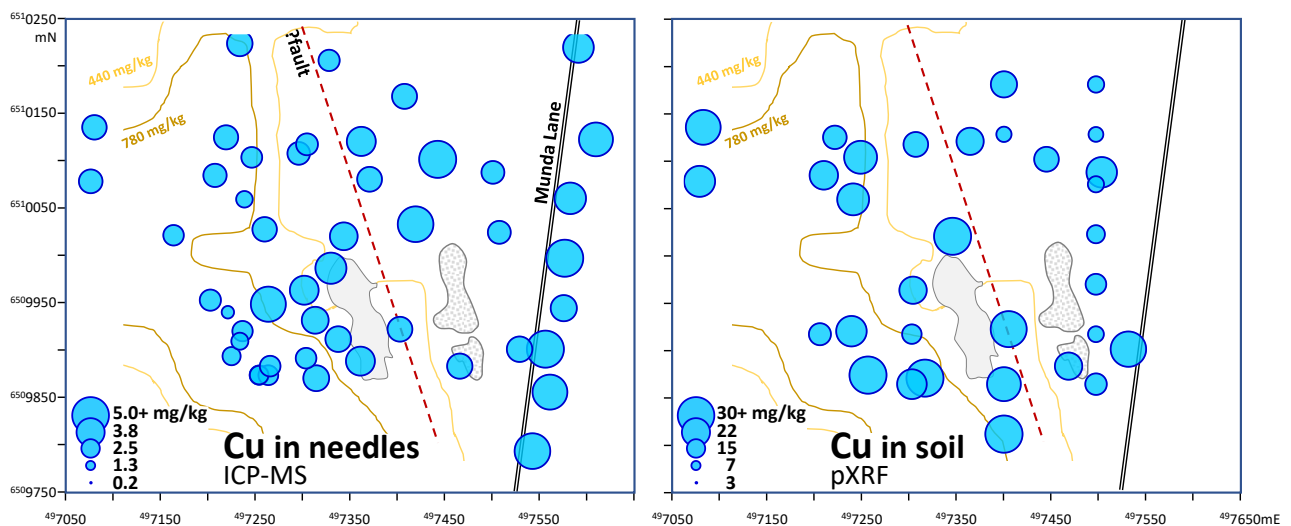
Metals bound to iron and manganese oxide were extracted by adding 40 mL of 0.1 mol L<sup>-1</sup> hydroxyl ammonium chloride (adjusted to pH 2.34 with 25 ml of 2 mol L<sup>-1</sup> nitric acid) onto the residue from the first step. After tumbling the mixture for 20 hours at 22±3°C, it was centrifuged for 15 min, and then decanted and filtered into a tube. Using 20 ml of distilled water, the residue was washed, centrifuged, and the supernatant discarded.

#### *Metals bound to organic matter and sulphides.*

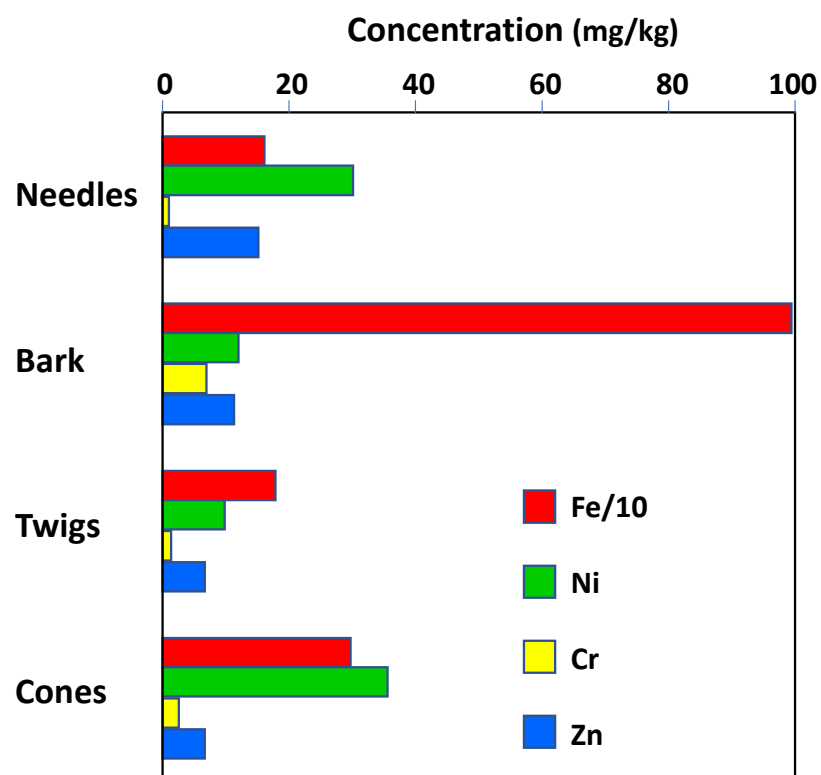
Ten mL of 8.8 mol L<sup>-1</sup> hydrogen peroxide was carefully added in small aliquots to the residue in the centrifuge tube. The tube ingredients were digested at room temperature for 1 hour with occasional manual shaking. The procedure was continued for 1 hour at 85 ±3°C in a thermostat controlled water bath. A second aliquot of 10 ml of hydrogen peroxide was added to the residue and the digestion procedure was repeated. The solution was heated to near dryness, and 50 ml of 1.0 mol L<sup>-1</sup> ammonium acetate solution (adjusted to pH 2.31 with 25ml of 2M nitric acid) was added to the moist residue. The sample solution was tumbled for 20 hours overnight and centrifuged, and the extract was separated and filtered as described above.



**Figure S1.** Spatial variation in the Fe content of *C. glaucophylla* needles (by pXRF and top 20 cm of soil (by pXRF) at Site 1, with 720 and 430 mg/kg Ni soil grid contours.



**Figure S2.** Spatial variation in the Cu content of *C. glaucophylla* needles (by pXRF and top 20 cm of soil (by pXRF) at Site 1, with 720 and 430 mg/kg Ni soil grid contours.



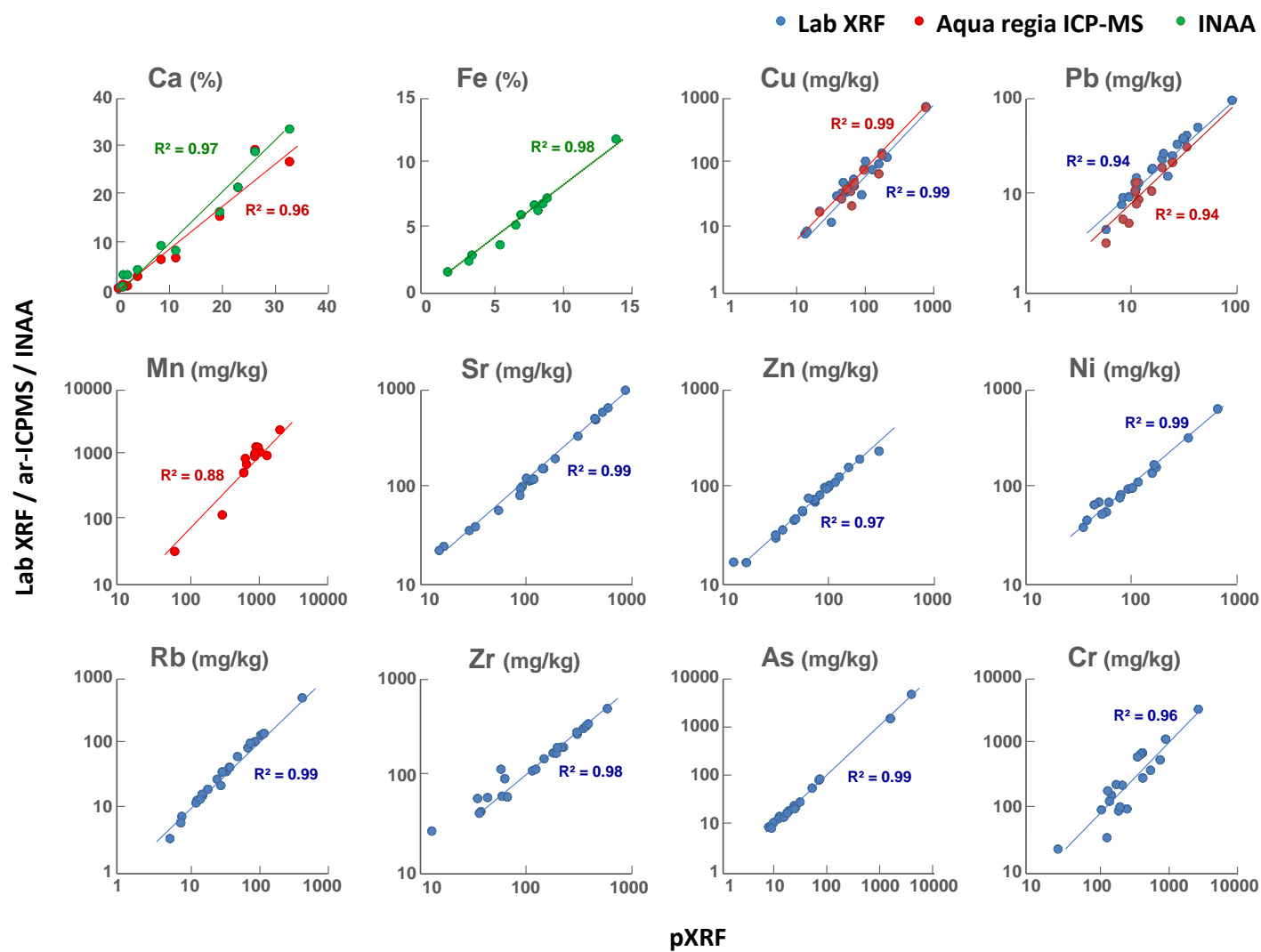
**Figure S3.** Comparison between the Fe, Ni, Cr and Zn content of the needles, cones, twigs and bark of *C. glaucophylla* tree M11.

**Table S2.** Summary statistics for element contents of *C. glaucophylla* from Sites 1 and 2 in the Miandetta area by ar ICP-MS/OES and pXRF.

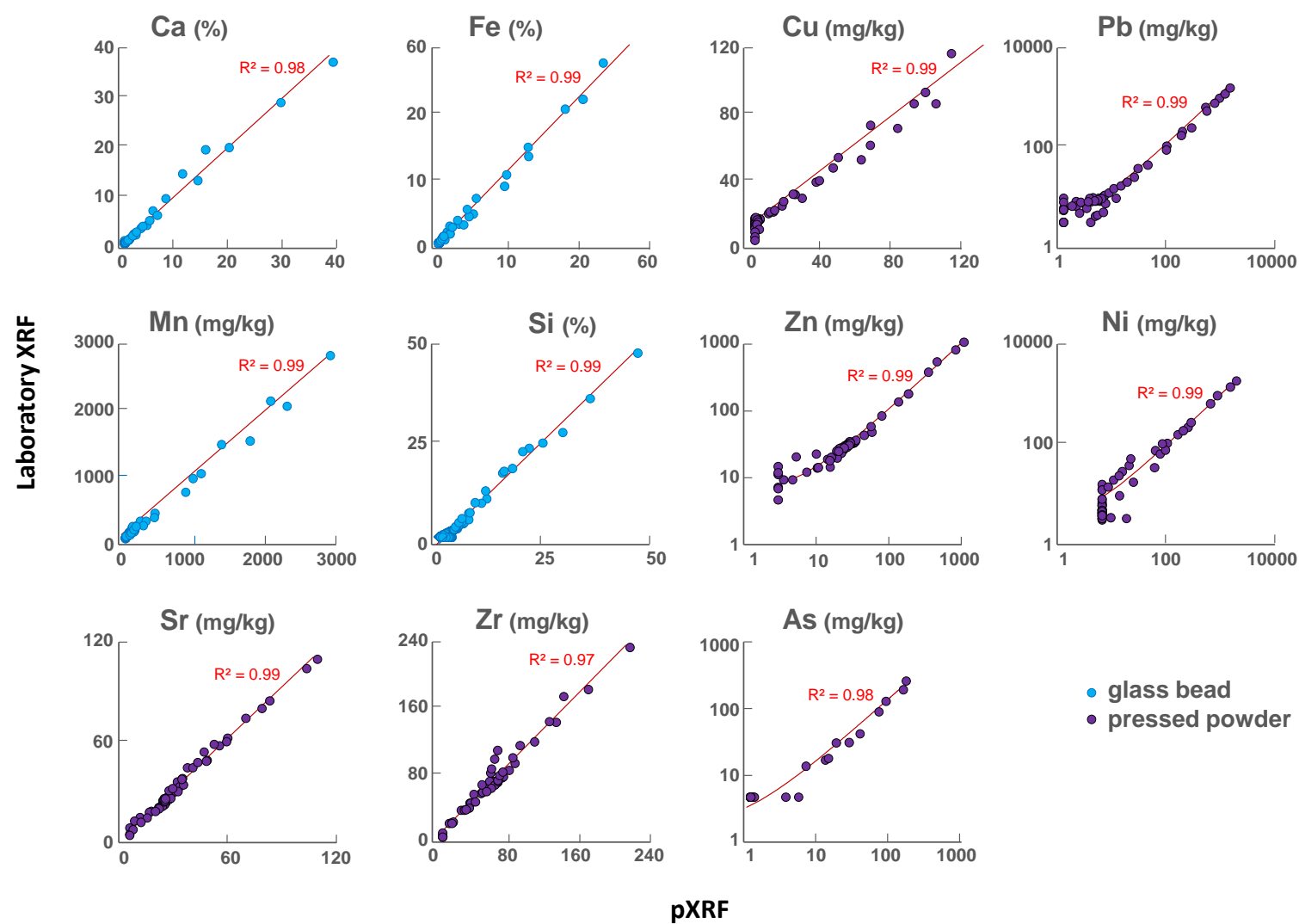
Element	Method	Units	DL	Count	Min	Q1	Median	Q2	95 <sup>th</sup> %ile	Max
Ag	ar ICP	Ppb	0.1	59	0.8	1.9	2.4	3.0	4.7	6.4
Al	ar ICP	%	0.002	79	0.006	0.020	0.029	0.039	0.057	0.086
Al	pXRF	%	0.01	59	0.12	0.14	0.15	0.16	0.17	0.18
As	ar ICP	Ppb	10	81	10	40	53	96	130	160
Au	ar ICP	ppb	0.05	59	0.05	0.08	0.20	0.41	0.74	5.47
B	ar ICP	ppb	0.5	79	9.5	21.5	27.0	32.4	43.4	63.0
Ba	ar ICP	ppm	0.05	59	2.54	7.63	13.23	26.44	45.03	47.17
Ba	pXRF	ppm	5	59	5	5	5	9	22	25
Be	ar ICP	ppb	0.5	59	2.6	11.3	16.1	24.1	40.3	52.6
Bi	ar ICP	ppb	0.5	59	0.3	1.1	1.7	2.3	5.6	9.6
Ca	ar ICP	%	0.005	79	0.397	0.744	0.860	1.031	1.380	1.599
Ca	pXRF	%	0.03	59	0.68	0.96	1.12	1.54	1.93	2.08
Cd	ar ICP	ppb	0.2	59	0.1	5.3	10.3	22.3	32.0	57.0
Ce	ar ICP	ppb	5	59	14	37	46	65	95	112
Co	ar ICP	ppb	0.01	59	0.10	0.20	0.31	0.61	1.64	2.46
Cr	ar ICP	ppb	0.1	59	0.3	0.6	0.8	1.0	1.4	1.8
Cs	ar ICP	ppb	0.5	59	10.1	20.3	25.8	33.1	49.6	62.8
Cu	ar ICP	ppm	0.003	59	0.179	0.294	0.344	0.406	0.498	0.548
Dy	ar ICP	ppb	0.5	59	5.3	19.4	27.5	36.9	51.5	56.2
Er	ar ICP	ppb	0.2	59	0.1	5.4	8.0	12.1	19.6	21.6
Eu	ar ICP	ppb	0.2	59	0.1	6.0	8.5	11.8	18.1	22.6
Fe	ar ICP	%	0.001	81	0.009	0.017	0.022	0.031	0.043	0.060
Fe	pXRF	%	0.005	59	0.008	0.019	0.032	0.059	0.100	0.127
Ga	ar ICP	ppb	1	59	30	73	93	128	189	252
Gd	ar ICP	ppb	0.5	59	7.5	23.5	32.3	40.9	76.5	84.9
Ge	ar ICP	ppb	3	59	3	7	9	11	15	17
Hf	ar ICP	ppb	0.5	59	3.3	6.9	9.2	11.7	18.1	21.9
Hg	ar ICP	ppb	0.5	59	1.7	9.6	14.5	18.7	23.8	47.2
Ho	ar ICP	ppb	0.1	59	0.8	3.05	3.6	5.5	8.15	11.8
I	ar ICP	ppm	0.01	59	0.18	0.35	0.47	0.65	1.37	2.02
In	ar ICP	ppb	0.1	59	0.2	0.3	0.3	0.4	0.7	1.0
K	ar ICP	%	0.005	79	0.419	0.563	0.642	0.710	0.903	1.130
K	pXRF	%	0.01	59	0.23	0.35	0.40	0.48	0.68	1.00
La	ar ICP	ppm	0.01	59	0.08	0.19	0.24	0.33	0.50	0.56
Li	ar ICP	ppm	0.005	59	0.044	0.223	0.336	0.459	0.839	1.152
Lu	ar ICP	ppb	0.1	59	0.1	0.6	1.5	2.8	4.4	6.0
Mg	ar ICP	%	0.005	79	0.139	0.215	0.245	0.305	0.389	0.521
Mn	ar ICP	ppm	2	79	58	107	174	250	472	1403
Mn	pXRF	ppm	5	59	69	128	193	314	626	979
Mo	ar ICP	ppb	1	59	1	24	46	99	342	384
Mo	pXRF	ppm	2	59	2	4	5	5	6	7
Na	ar ICP	ppm	5	79	7	36	54	108	227	412

Table S1. ctd.

Element	Method	Units	DL	Count	Min	Q1	Median	Q2	95 <sup>th</sup> % <sup>ile</sup>	Max
Nb	ar ICP	ppb	1	59	8	17	21	26	33	44
Nd	ar ICP	ppm	0.005	59	0.067	0.166	0.209	0.292	0.476	0.491
Ni	ar ICP	ppm	0.1	81	2.0	4.2	12.0	33.7	155.6	178.5
Ni	pXRF	ppm	5	59	5	5	5	29	177	250
P	ar ICP	%	0.002	79	0.061	0.074	0.090	0.104	0.127	0.153
Pb	ar ICP	ppb	1	59	76	118	140	174	248	430
Pd	ar ICP	ppb	0.1	59	0.1	0.6	0.7	1.3	2.5	3.2
Pr	ar ICP	ppb	0.5	59	15.8	42.9	54.4	76.5	117.5	127.1
Pt	ar ICP	ppb	0.1	59	0.1	0.1	0.1	0.2	0.3	0.6
Rb	ar ICP	ppm	0.01	59	0.95	1.77	2.06	2.46	3.04	3.58
Re	ar ICP	ppb	0.01	59	0.01	0.05	0.09	0.17	0.27	0.56
S	ar ICP	%	0.02	79	0.09	0.12	0.13	0.14	0.15	0.16
S	pXRF	%	0.01	59	0.01	0.03	0.04	0.04	0.06	0.08
Sb	ar ICP	ppb	0.5	59	1.1	2.9	3.8	5.4	8.2	9.3
Sc	ar ICP	ppb	1	59	18	42	55	67	88	119
Se	ar ICP	ppb	10	59	46	83	111	180	295	351
Si	pXRF	%	0.10	59	0.10	0.13	0.14	0.15	0.16	0.17
Sm	ar ICP	ppb	0.5	81	12.6	29.4	38.9	57.5	90.0	120.0
Sn	ar ICP	ppb	1	59	4	12	16	24	36	41
Sr	ar ICP	ppm	3	59	43	78	101	119	164	363
Sr	pXRF	ppm	3	59	16	49	62	75	128	221
Ta	ar ICP	ppm	0.1	59	0.05	0.9	1.4	1.8	2.31	2.8
Tb	ar ICP	ppb	0.3	59	0.3	2.9	4.3	5.7	7.7	11.8
Te	ar ICP	ppb	0.3	59	0.3	0.9	1.9	2.5	4.3	6.0
Th	ar ICP	ppm	0.5	59	17.6	45.8	53.4	75.0	112.5	122.9
Th	pXRF	ppm	5	59	15	33	39	44	55	68
Ti	ar ICP	ppm	0.1	59	4.7	7.8	9.1	10.9	15.8	24.0
Ti	pXRF	ppm	25	59	25	106	171	216	333	432
Tl	ar ICP	ppb	0.5	59	0.3	0.8	1.5	2.6	4.6	6.2
Tm	ar ICP	ppb	0.1	59	0.21	0.945	1.32	1.86	2.875	4.81
U	ar ICP	ppm	0.5	59	2.0	4.3	5.5	7.9	10.8	16.2
U	pXRF	ppm	3	59	6	10	11	13	17	19
V	ar ICP	ppm	0.05	59	0.12	0.36	0.48	0.62	0.91	1.42
W	ar ICP	ppm	0.1	59	0.1	0.2	1.1	2.0	3.3	14.2
Y	ar ICP	ppb	0.5	59	37.0	100.8	120.8	164.6	228.8	276.9
Yb	ar ICP	ppb	0.5	59	1.7	5.8	8.7	13.0	17.4	26.4
Zn	ar ICP	ppm	0.1	81	9.0	12.0	14.9	17.9	24.0	25.0
Zn	pXRF	ppm	4	59	11	16	18	23	30	38
Zr	ar ICP	ppm	0.01	59	0.07	0.17	0.21	0.28	0.49	0.62

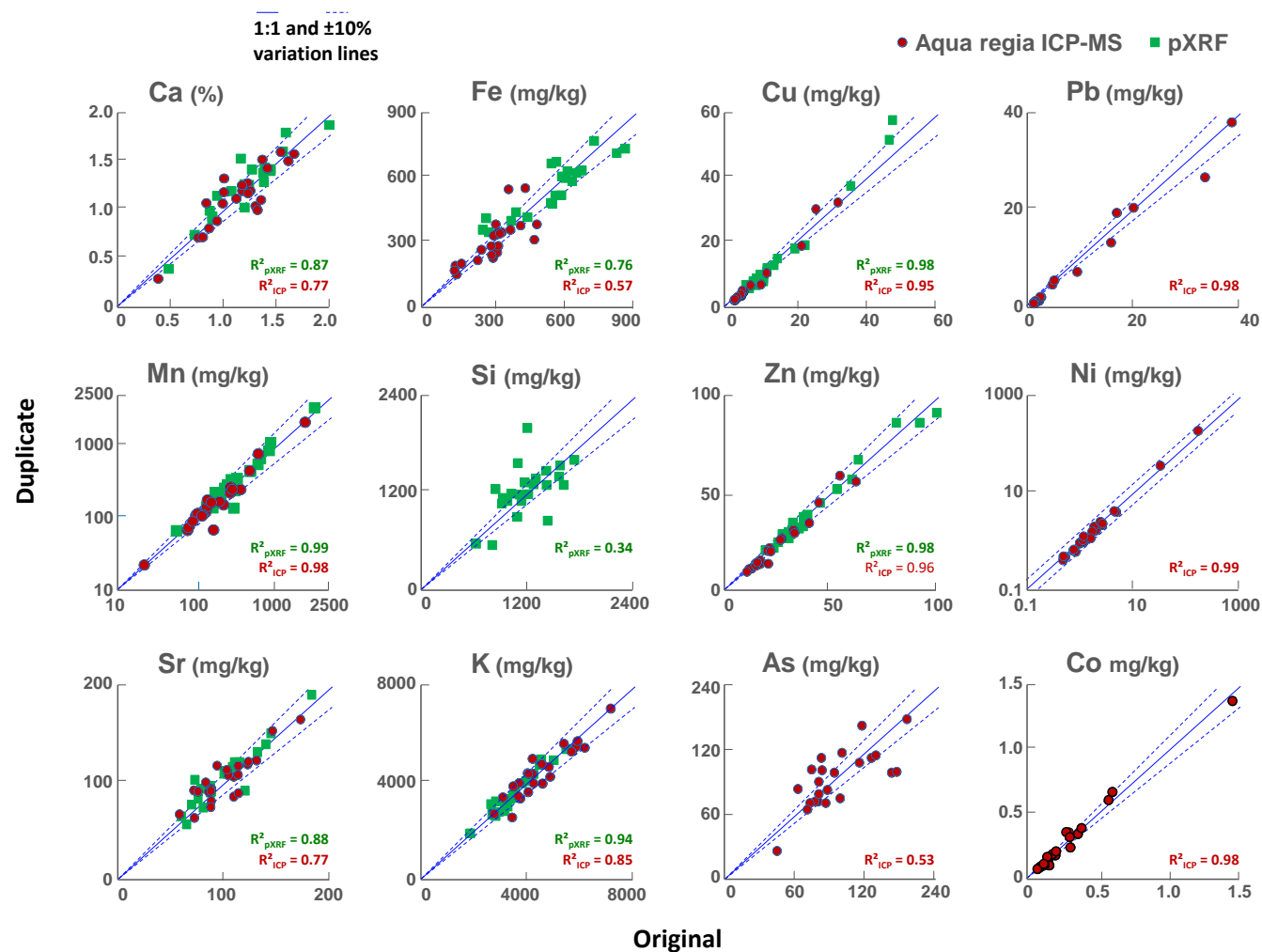


**Figure S4.** Comparison between pXRF and other analytical methods for certified and in-house soil reference materials.  $R^2$  values are significant at  $p=0.05$ .



**Figure S5.** Comparison between pXRF and laboratory XRF for series of coal-based synthetic geochemical references materials (see [21]).  $R^2$  values are significant at  $p=0.05$ .





**Figure S6.** Plots of analytical duplicates of needle samples by pXRF and ICP-MS for selected elements, with 1:1 and  $\pm 10\%$  variation lines and  $R^2$  values for correlation between duplicates. For Co, Cu, K, Mn, Ni and Zn over 90% of duplicates are within the  $\pm 10\%$  variation limits for both analytical methods. There is substantially more scatter for Ca, Fe and Sr by both methods and Si and As by ICP-MS, though the  $R^2$  values all exceed 0.5 (apart from Si) which is significant at  $p=0.05$ .