

SUPPLEMENTAL INFORMATION:

Table S1: Results of linear regression models comparing two LA-ICP-MS analysis methods with conventional acid-digestion ICP-MS analysis for all twenty-eight elements considered. Elements corresponding to table below: Nutrients: ³⁹K, ³¹P, ²⁴Mg, ⁶⁶Zn, ⁵⁷Fe ; Volatile Elements: ⁷⁵As, ¹¹¹Cd, ¹²¹Sb, ²⁰⁸Pb; Elements of Phytotoxicity Concern: ¹³⁷Ba, ⁵⁹Co, ⁵²Cr, ⁶³Cu, ⁵⁵Mn, ²⁷Al, ⁶⁰Ni, ¹⁴⁰Ce, ⁹⁵Mo; Trace Elements: ¹⁰⁷Ag, ⁷Li, ¹¹⁸Sn, V, ¹³⁹La, ⁸⁸Sr, ⁴⁷Ti.

a)

All Elements:

Independent (Predictor)	Dependent (Response)	Estimate (int,slope)	SE Estimate	of t -value	Pr(>t)	adjR ²
Acid-Dig.ICPMS ground/ashed needle	LA-ICPMS Intact needle	-0.221, 1.048	0.108, 0.063	2.04,16.5	0.05, 1.25*10 ⁻¹⁴	0.916
Acid-Dig.ICPMS ground/ashed needle	LA-ICPMS Needle pellet	0.619, 0.841	0.0776,0.046	7.98,18.49	3.31*10 ⁻⁸ , 1.05*10 ⁻¹⁵	0.932
LA-ICPMS Needle pellet	LA-ICPMS Intact needle	0.937,1.20	0.138,0.077	6.75,15.57	5.6*10 ⁻⁷ , 4.78*10 ⁻¹⁴	0.906
Acid-Dig.ICPMS ground/ashed branch	LA-ICPMS Branch pellet	0.528,0.904	0.0465,0.0270	11.36,33.51	6.61*10 ⁻¹¹ , 2.0*10 ⁻¹⁶	0.979
Acid-Dig.ICPMS ground/ashed branch	LA-ICPMS Intact branch	-0.047,1.01	0.157,0.091	0.301,11.06	0.766, 1.10*10 ⁻¹⁰	0.835
LA-ICPMS Branch pellet	LA-ICPMS Intact branch	-0.849,1.20	0.234,0.126	3.63,9.50	0.0013, 1.32*10 ⁻⁹	0.781

b)

Nutrients:

Independent (Predictor)	Dependent (Response)	Estimate (int,slope)	SE Estimate	of t-value	Pr(>t)	adjR ²
Acid-Dig.ICPMS needle	LA-ICPMS Intact needle	-0.1864,0.9852	0.6115,0.2088	-0.305,4.718	0.780, 0.018	0.842
Acid-Dig.ICPMS needle	LA-ICPMS Needle pellet	0.6543,0.8175	0.634,0.2165	1.032,3.776	0.378,0.0325	0.768
LA-ICPMS Needle pellet	LA-ICPMS Intact needle	-0.5286, 1.0552	0.8754,0.2875	-0.604,3.670	0.589,0.035	0.757
Acid-Dig.ICPMS ground branch	LA-ICPMS Branch pellet	0.06257,1.037	0.361,0.126	0.173,8.25	0.873,0.00373	0.944
Acid-Dig.ICPMS ground branch	LA-ICPMS Intact branch	-0.933,1.4025	1.47,0.511	-0.636,2.745	0.570,0.071	0.620
LA-ICPMS Branch pellet	LA-ICPMS Intact branch	-0.6492,1.2292	1.702,0.560	-0.381,2.196	0.728,0.116	0.489

c)

Volatiles:

Independent (Predictor)	Dependent (Response)	Estimate (int,slope)	SE Estimate	of t -value	Pr(>t)	adjR ²
Acid-Dig.ICPMS needle	LA-ICPMS Intact needle	0.694,0.4325	0.250,0.276	2.772,1.57	0.109,0.257	0.327
Acid-Dig.ICPMS needle	LA-ICPMS Needle pellet	0.160,0.499	0.255,0.281	0.627,1.78	0.594,0.218	0.418
LA-ICPMS Needle pellet	LA-ICPMS Intact needle	0.917,0.221	0.290,0.627	-3.16,0.352	0.087,0.758	-0.412
Acid-Dig.ICPMS branch	LA-ICPMS Branch pellet	0.286,0.747	0.2536,0.3685	1.129,2.03	0.376,0.180	0.509
Acid-Dig.ICPMS branch	LA-ICPMS Intact branch	-0.950,0.7767	1.29,1.87	-738,0.415	0.538,0.718	-0.3811
LA-ICPMS Branch pellet	LA-ICPMS Intact branch	-1.257,1.763	0.924,1.742	-1.361,1.012	0.307,0.418	0.0081

d)

Elements of Phytotoxicity Concern:

Independent (Predictor)	Dependent (Response)	Estimate (int,slope)	SE of Estimate	 t -value	Pr(>t)	adjR²
Acid-Dig.ICPMS needle	LA-ICPMS Intact needle	-0.2133,1.108	0.266,0.247	-0.801,4.48	0.450,0.00285	0.705
Acid-Dig.ICPMS needle	LA-ICPMS Needle pellet	0.676,0.859	0.151, 0.140	4.47,6.12	0.003,0.0005	0.820
LA-ICPMS Needle pellet	LA-ICPMS Intact needle	-0.976,1.19	0.370,0.259	-2.64,4.61	0.034,0.0025	0.717
Acid-Dig.ICPMS branch	LA-ICPMS Branch pellet	0.563,0.949	0.0673,0.060	8.37,15.80	6.81*10 ⁻⁵ ,9 .87*10 ⁻⁷	0.969
Acid-Dig.ICPMS branch	LA-ICPMS Intact branch	-0.0299,0.916	0.262, 0.234	-0.114,3.917	0.912,0.00578	0.642
LA-ICPMS Branch pellet	LA-ICPMS Intact branch	-0.607,0.994	0.320,0.218	-1.895,4.560	0.100,0.0026	0.712

e)

Other Elements:

Independent (Predictor)	Dependent (Response)	Estimate (int,slope)	SE of Estimate	 t -value	Pr(>t)	adjR²
Acid-Dig.ICPMS needle	LA-ICPMS Intact needle	-0.1408, 1.15	0.170,0.177	-0.829,6.487	0.445,0.0013	0.873
Acid-Dig.ICPMS needle	LA-ICPMS Needle pellet	0.633,0.724	0.165,0.173	3.84,4.30	0.0121,0.0077	0.745
LA-ICPMS Needle pellet	LA-ICPMS Intact needle	-1.05,1.32	0.215,0.273	-4.89,4.86	0.00448,0.00465	0.790
Acid-Dig.ICPMS branch	LA-ICPMS Branch pellet	0.518,0.878	0.0731,0.0765	7.09,11.48	0.000863, 8.77*10 ⁻⁵	0.956
Acid-Dig.ICPMS branch	LA-ICPMS Intact branch	-0.252,0.603	0.343,0.359	-0.734,1.679	0.496,0.154	0.233
LA-ICPMS branch pellet	LA-ICPMS Intact branch	-0.579,0.610	0.390,0.421	-1.48,1.45	0.198,0.207	0.155

Table S2: Lower detection limits of acid-digestion ICP-MS analysis technique for all twenty-eight elements considered, determined through duplicate analysis of dried, ground *P. banksiana* tissue (values determined by Activation Laboratories, Ltd.).

Analyte Symbol	Detection Limit Unit	Detection Limit	Recovery Rate (%)
Ag	ppb	3	
Al	ppm	4	
As	ppb	10	
Au	ppb	0.2	
Ba	ppb	100	99.1
Ca	ppm	25	101.01
Cd	ppb	6	
Ce	ppb	15	
Co	ppb	4	100.2
Cr	ppb	100	
Cu	ppb	50	
Fe	ppm	3	98.5
K	ppm	10	102.3
La	ppb	10	
Li	ppb	10	
Lu	ppb	0.5	
Mg	ppm	2	99.2
Mn	ppb	100	101.2
Mo	ppb	10	92.7
Ni	ppb	50	
P	ppm	4	101.2
Pb	ppb	50	102.7
Sb	ppb	10	
Sn	ppb	50	
Sr	ppb	40	101.7
Ti	ppb	150	
V	ppb	10	
Zn	ppb	400	100.4

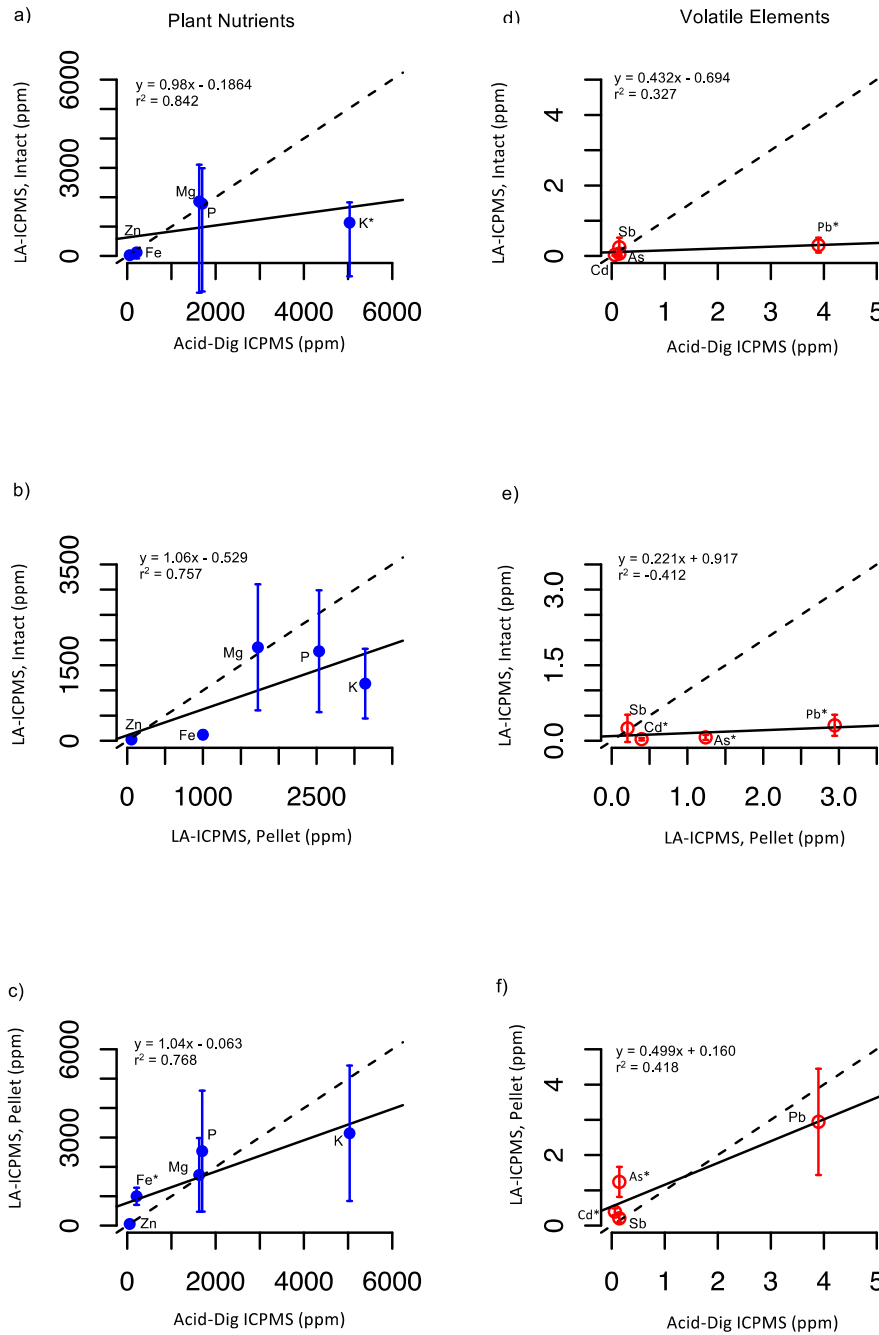


Fig. S1. Relationships for (a,b,c) major plant nutrients and (d,e,f) volatile elements between intact sample LA ICP-MS, pellet LA ICP-MS, and acid digestion ICP-MS for pine needles with values representing elemental composition. Element labels with * indicate deviation from a 1:1 relationship with significance at $p < 0.05$. Solid lines represent linear regression model fits significant at $p < 0.05$ and error bars represent $\pm$ 95% confidence interval. Dashed lines represent 1:1 relationship.

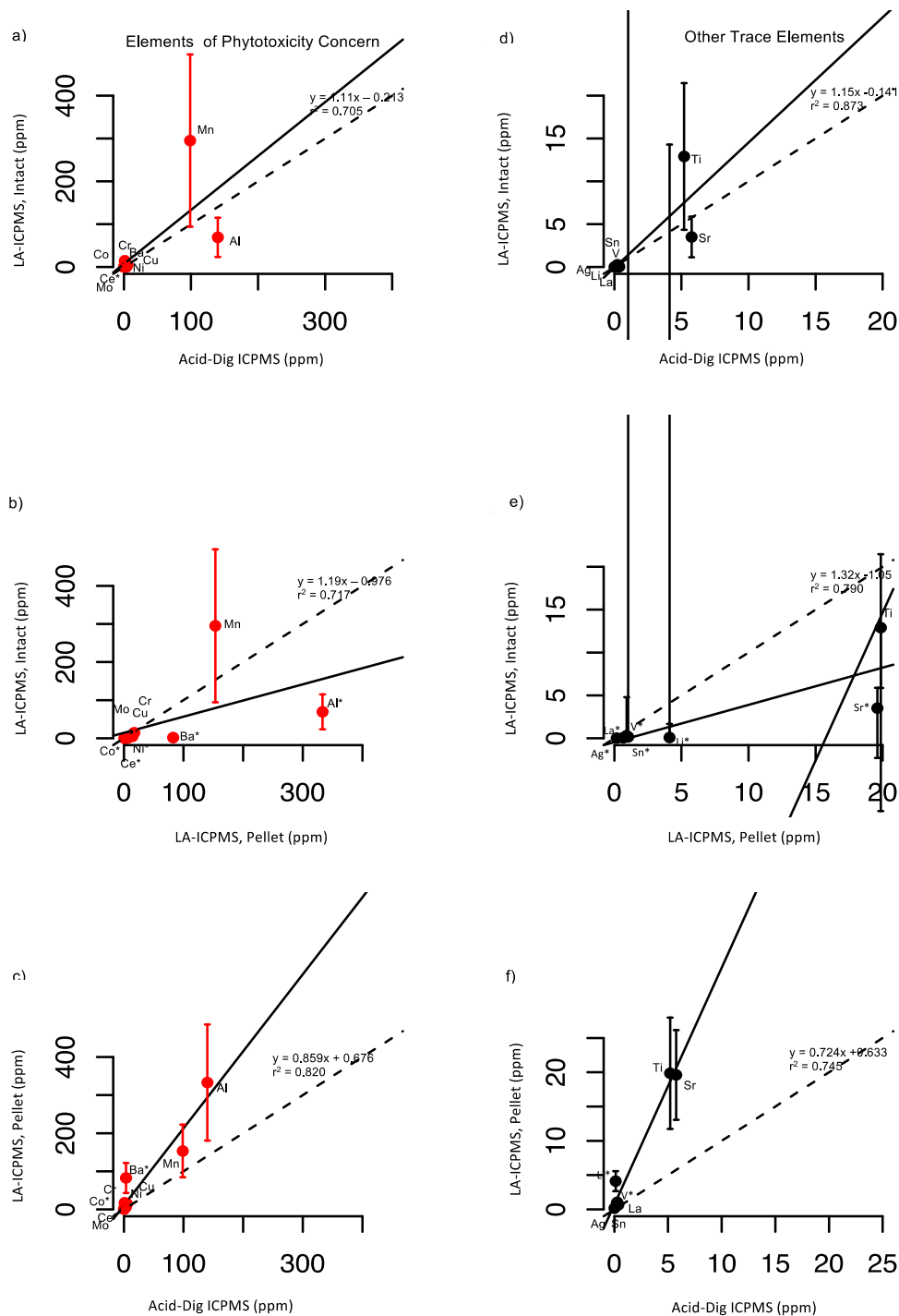


Fig. S2. Relationships for (a,b,c) elements of phytotoxicity concern and (d,e,f) other lower priority (trace) elements between intact sample LA ICP-MS, pellet LA ICP-MS, and acid digestion ICP-MS for pine needles with values representing elemental composition. Element labels with * indicate deviation from a 1:1 relationship with significance at $p < 0.05$. Solid lines represent linear regression model fits significant at $p < 0.05$ and error bars represent $\pm$ 95% confidence interval. Dashed lines represent 1:1 relationship.

Table S3:

Mean analysis values for intact needles and pellet samples, measured through LA ICP-MS and intact needles analysis through conventional acid digestion ICP-MS with associated standard error (SE; absolute values). All element values measured through LA ICP-MS, with exception of Ca⁴³ Internal Standard measure through EPMA for intact specimens and XRF for pellet samples.

Analyte	units	Intact Needle LA ICP-MS	Intact Needle SE	Pellet LA ICP-MS	Pellet SE	Acid-dig. ICP-MS	Acid-dig. ICP-MS SE
Li7	ppm	0.077	0.026	4.116	0.740	0.127	0.003
Mg24	ppm	1855.605	638.148	1725.242	640.203	1630.000	5.774
Al27	ppm	69.335	23.371	333.138	77.779	140.000	5.568
P31	ppm	1778.230	617.045	2533.239	1049.652	1696.667	3.333
K39	ppm	1134.315	352.115	3142.252	1175.408	5033.333	17.638
Ca43 *	ppm	12509.8	421.2	700.3	217	3743.333	13.333
Ti47	ppm	12.905	4.371	19.862	4.145	5.200	0.323
V51	ppm	0.153	0.052	1.026	0.196	0.273	0.007
Cr52	ppm	14.433	4.960	17.304	5.363	1.333	0.033
Mn55	ppm	295.168	102.503	153.336	35.227	98.733	0.644
Fe57	ppm	121.731	41.530	999.889	148.455	211.000	4.583
Co59	ppm	0.066	0.023	1.010	0.117	0.190	0.002
Ni60	ppm	0.348	0.118	6.368	2.184	3.470	0.150
Cu63	ppm	4.973	1.799	14.396	4.662	5.117	0.278
Zn66	ppm	25.404	9.176	55.863	23.609	54.700	0.833
As75	ppm	0.068	0.025	1.240	0.217	0.143	0.009
Sr88	ppm	3.510	1.210	19.608	3.335	5.760	0.060
Mo95	ppm	0.501	0.169	1.111	0.475	0.337	0.003
Ag107	ppm	0.006	0.002	0.177	0.055	0.013	0.001
Cd111	ppm	0.032	0.012	0.395	0.049	0.058	0.004
Sn118	ppm	0.275	0.096	0.918	0.288	0.237	0.018
Sb121	ppm	0.248	0.137	0.208	0.058	0.143	0.003
Ba137	ppm	1.715	0.711	82.634	20.093	3.533	0.067
La139	ppm	0.046	0.016	0.664	0.139	0.367	0.162
Ce140	ppm	0.066	0.024	1.753	0.184	0.671	0.300
Pb208	ppm	0.308	0.107	2.944	0.768	3.900	0.161