

Supporting information

Figure S1: Positive ion internal standard area by injection order

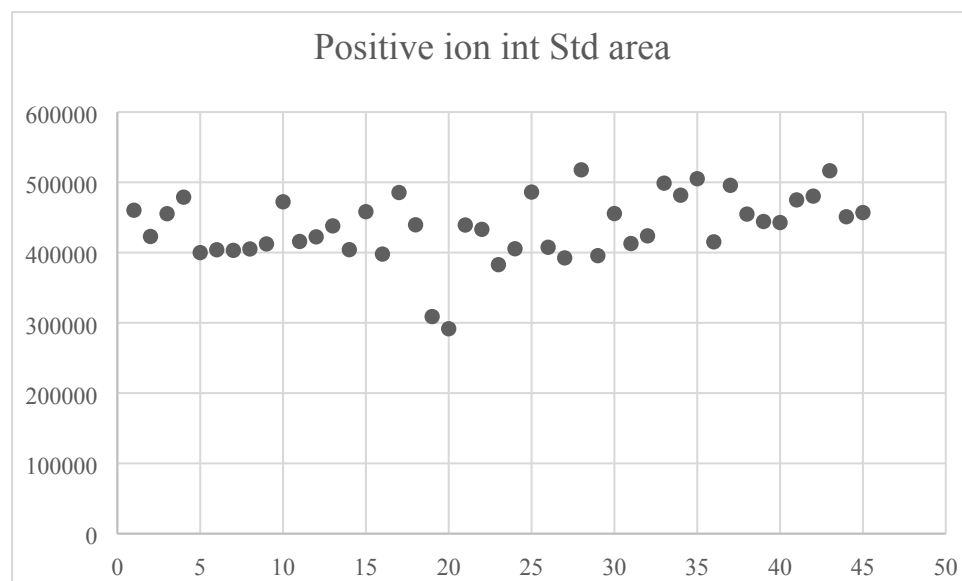


Figure S2: Leaf fresh mass of sixteen week old *N. caerulea* plants. Data represents mean \pm standard error ($n = 10$) for each Zn treatment

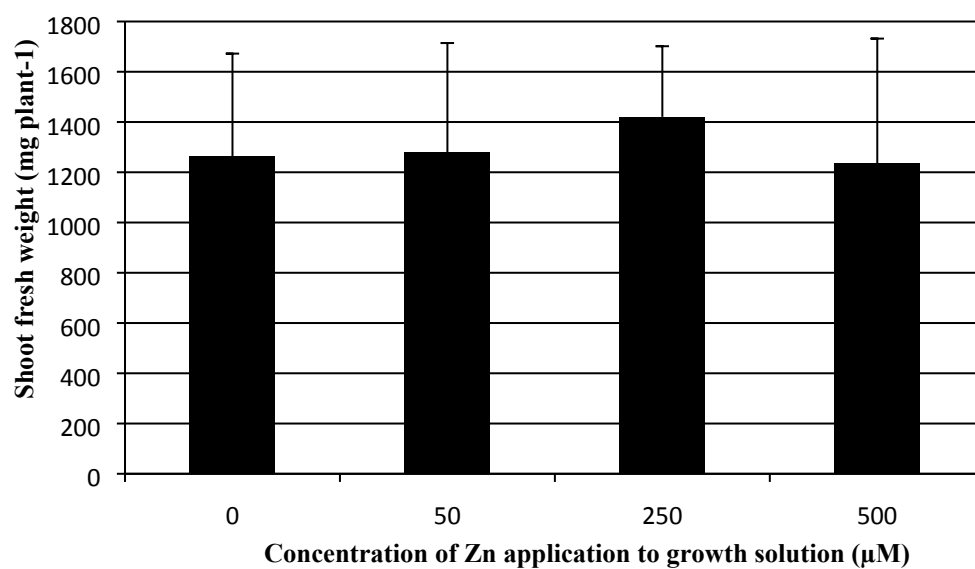


Figure S3: Principal components analysis of the negative ion dataset with 708 mass features. Zn treatment groups are: control (blue), 50 μ M (brown), 250 μ M red, 500 μ M grey (PC – principal component number).

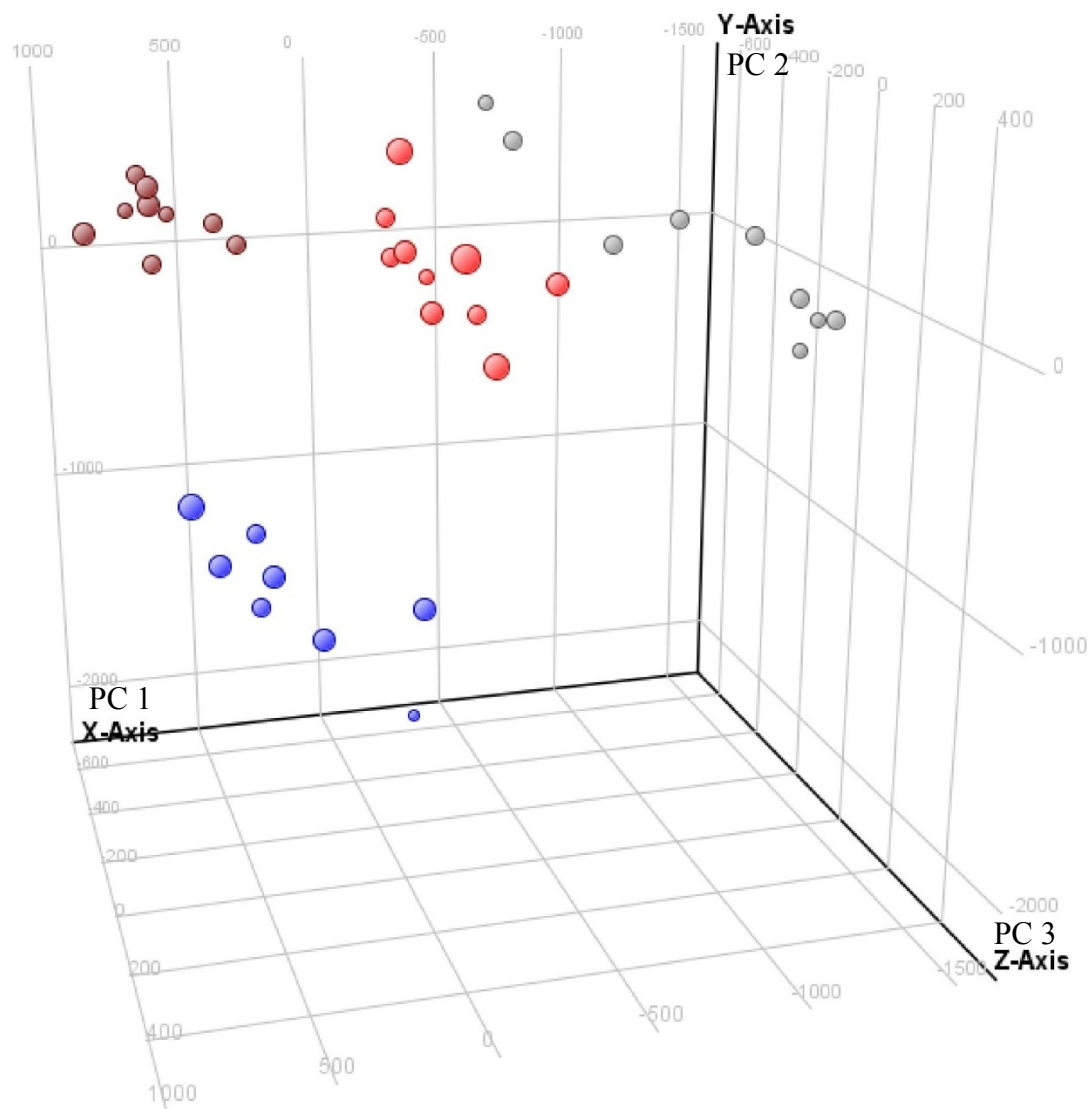


Figure S4: Principal components analyses of the GC-MS data: (top) all metabolites, (bottom) identified peaks only. Zn treatment groups are as follows: control (C), 50 μ M (L), 250 μ M (M) and 500 μ M (H). The percentage variation explained by each individual PC is shown in parentheses on each axis.

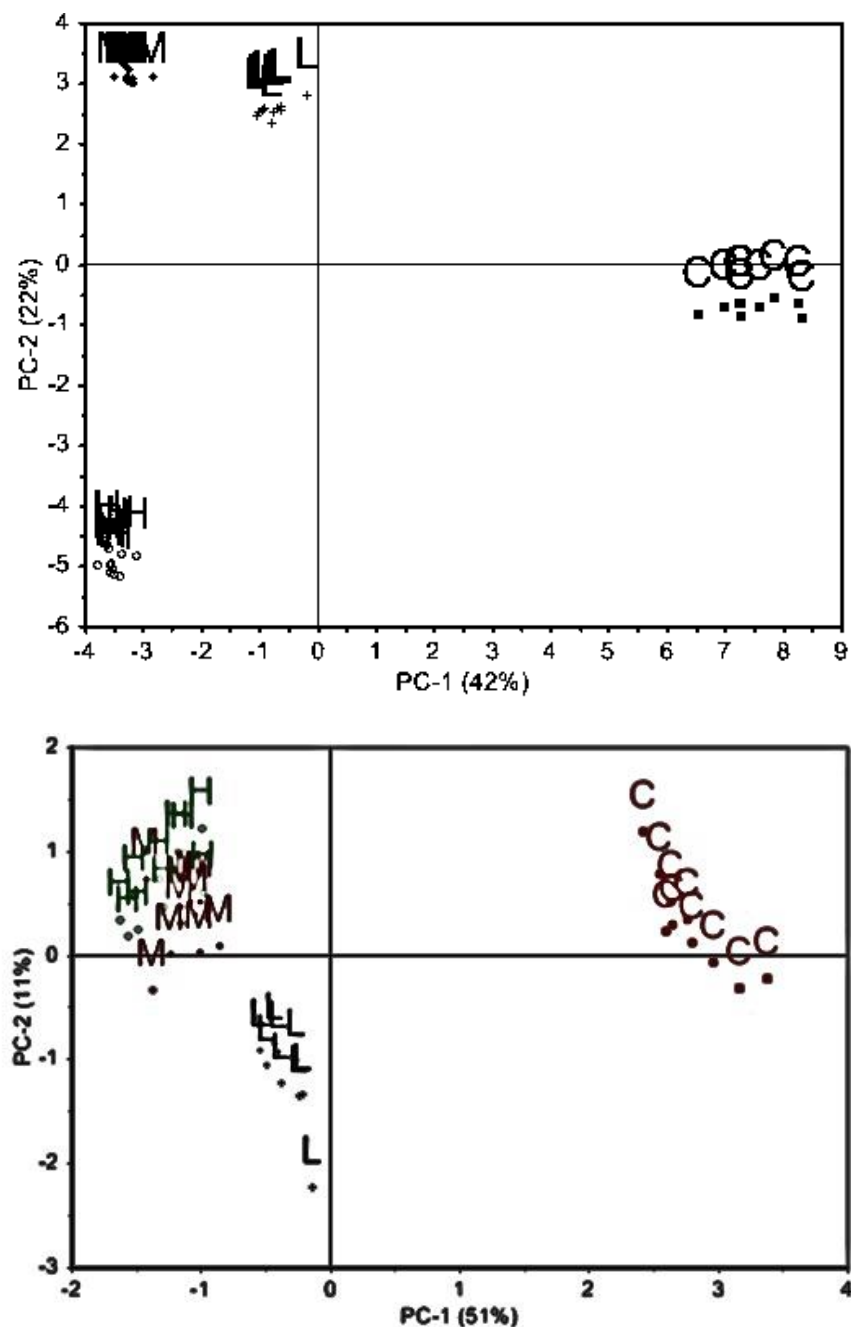


Table S1: Concentrations of hydroponic nutrients of the modified 1/5 strength Hoagland's solution, pH 6.0.

Salt	Final conc. mmol/L
Ca(NO ₃) ₂ ·4H ₂ O	1.5
NH ₄ NO ₃	0.5
KNO ₃	1
MgSO ₄ ·7H ₂ O	0.5
MES	1
NaOH	0.5
KH ₂ PO ₄	0.02
H ₃ BO ₄	1.0E-03
(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	1.0E-5
Fe-EDTA	0.1
MnSO ₄ ·H ₂ O	7.0E-04
ZnSO ₄ ·7H ₂ O	5.0E-03
CuSO ₄ ·5H ₂ O	1.0E-04

Table S2: The full LC-MS and GC-MS data datasets.

Submitted as electronic file.

Table S3 Metabolites from GC-MS data set which had significantly different changes between treatment groups and control, calculated using the Student's *t*-tests (normalized values for the controls are not shown). Data obtained from TMS analysis of Zn treated *N. caerulea* leaf tissue were normalised to the mean response calculated for the control plants. Values are presented as the mean \pm SE of 10 independent biological replicates. Those that are significantly different ($P < 0.05$) to the controls are set in bold type, blue colouring are significant according to student's *t*-Test and green colouring are significant by Bonferroni-corrected *t*-Test.

Metabolites	50	\pm	SE	250	\pm	SE	500	\pm	SE
Amino acids									
Arginine	0.429	\pm	0.119	0.284	\pm	0.141	0.284	\pm	0.135
Asparagine	1.000	\pm	0.065	0.841	\pm	0.061	0.792	\pm	0.030
GABA	1.218	\pm	0.074	1.595	\pm	0.122	1.996	\pm	0.101
Glutamate	0.870	\pm	0.078	0.776	\pm	0.041	0.721	\pm	0.027
Glycine	0.792	\pm	0.075	0.613	\pm	0.075	0.625	\pm	0.069
Lysine	0.964	\pm	0.086	0.734	\pm	0.066	0.797	\pm	0.051
Ornithine	0.787	\pm	0.125	0.573	\pm	0.091	0.568	\pm	0.029
Pyroglutamate	0.829	\pm	0.087	0.812	\pm	0.061	0.756	\pm	0.026
Serine	0.933	\pm	0.077	0.732	\pm	0.071	0.750	\pm	0.045
Tyrosine	1.679	\pm	0.119	1.217	\pm	0.094	1.228	\pm	0.065
Valine	0.859	\pm	0.079	0.780	\pm	0.068	0.820	\pm	0.037
Putrescine	1.348	\pm	0.061	1.102	\pm	0.078	1.451	\pm	0.105
Organic acids									
Aconitate	1.396	\pm	0.029	1.704	\pm	0.072	1.689	\pm	0.059
Citrate	1.248	\pm	0.028	1.529	\pm	0.070	1.603	\pm	0.030
Isocitrate	1.350	\pm	0.029	1.032	\pm	0.214	0.509	\pm	0.121
Threonate	1.118	\pm	0.073	1.292	\pm	0.057	1.296	\pm	0.033
Sinapinate	1.466	\pm	0.063	1.426	\pm	0.032	1.446	\pm	0.078
Sugars									
Fructose	1.259	\pm	0.063	1.322	\pm	0.066	1.265	\pm	0.058
Galactinol	5.998	\pm	0.113	4.487	\pm	0.072	0.486	\pm	0.067
Gluconate	4.569	\pm	0.214	10.404	\pm	0.514	33.846	\pm	0.378
Raffinose	0.949	\pm	0.113	1.034	\pm	0.059	0.626	\pm	0.065
Sucrose	0.934	\pm	0.069	1.003	\pm	0.095	0.808	\pm	0.069
Disaccharide1	0.382	\pm	0.133	0.732	\pm	0.075	0.956	\pm	0.167