Supplementary Materials

Phosphorus Recovery and Reuse Potential from Smouldered Sewage Sludge Ash

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S1. Supplementary Information on Drum Reactor Experiments

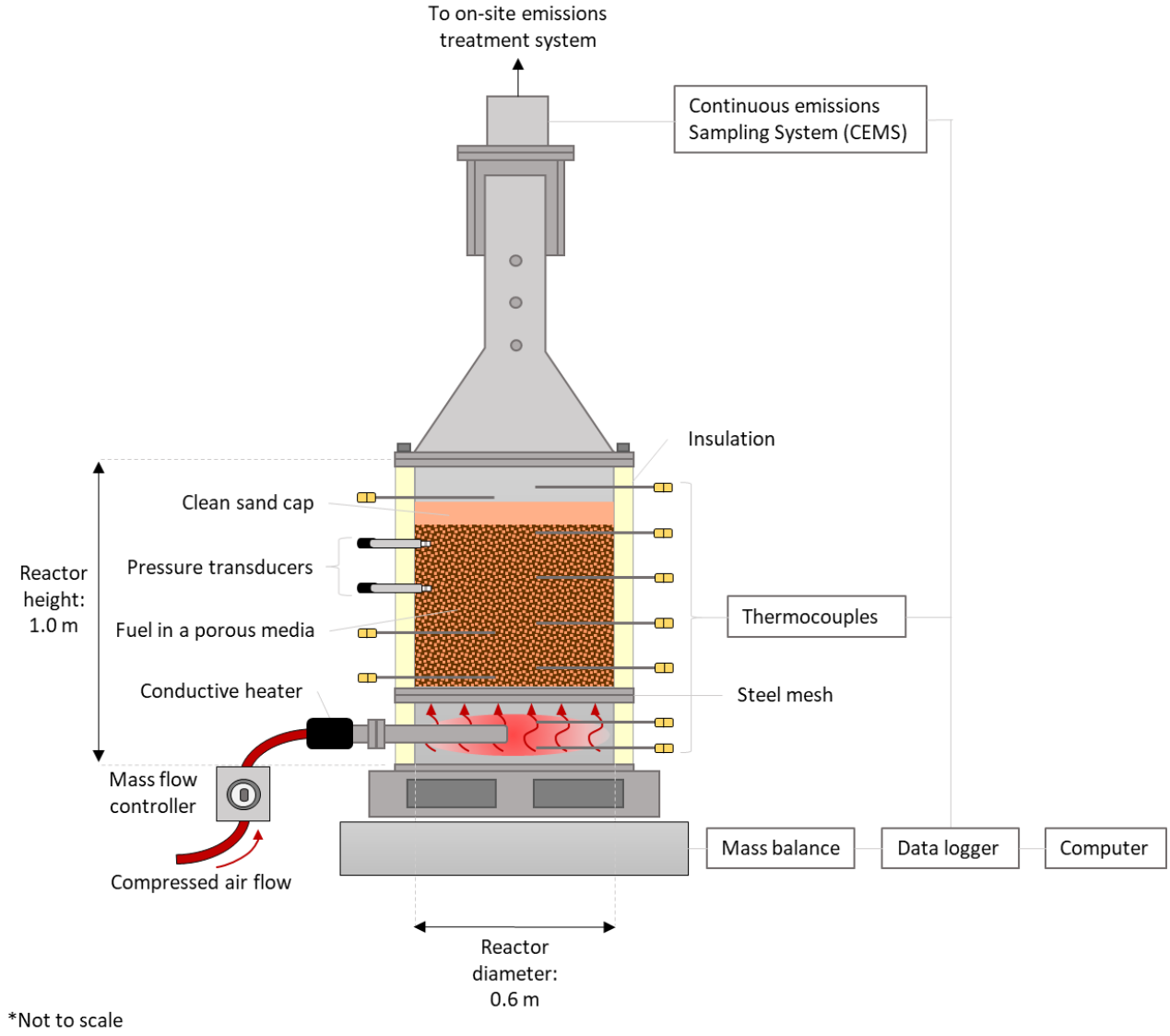

Figure S1-1: Schematic of smouldering reactor set-up.

Loading Procedure

The sludge/sand tests consisted of sludge as the fuel embedded in coarse silica sand as the porous media. The co-smouldering tests had a fuel mixture of sludge and woodchips, where the woodchips dually acted as the porous media. The experimental set-ups followed the same procedures for both tests, except for two minor differences for the co-smouldering test. An additional layer of coarse silica sand was added to the base of the reactor, 0.6-2.5 cm thick, to provide insulation between the hot smouldering mixture and the supporting screen. A subsequent layer of woodchips, 1-2 cm thick, was added above the clean sand layer to assist with ignition. Moreover, a clean sand cap was added on top of the sludge/sand pack to lower the exiting temperature for safety purposes.

The sludge mixture was loaded in small batches that were gently lowered to the base of the reactor. Furthermore, to achieve a more uniform density of mixture, while still ensuring material homogeneity, the surface was leveled instead of tamped.

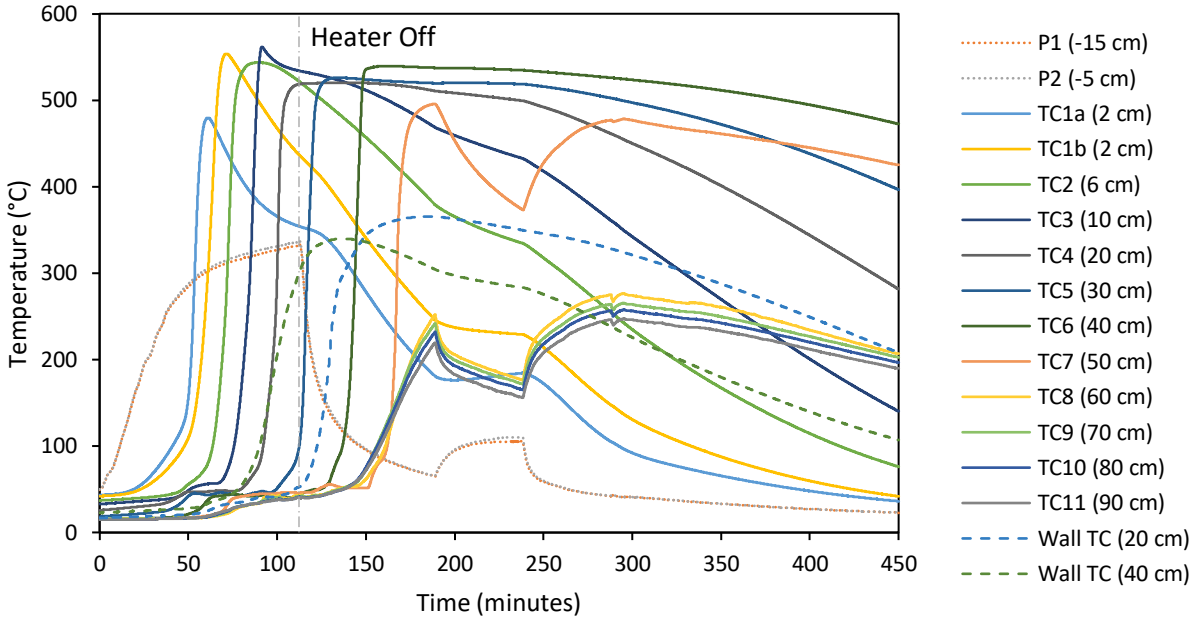

Figure S1-2: Temperature profile for the sludge-sand experiment, a self-sustaining smouldering experiment with a 3.81% moisture content sludge in a fixed bed with 25.5 g/g sand/sludge mass ratio. Plenum, centreline, and wall thermocouples are presented. Note the air flux was changed at 190, 238, 288, 290, and 296 minutes.

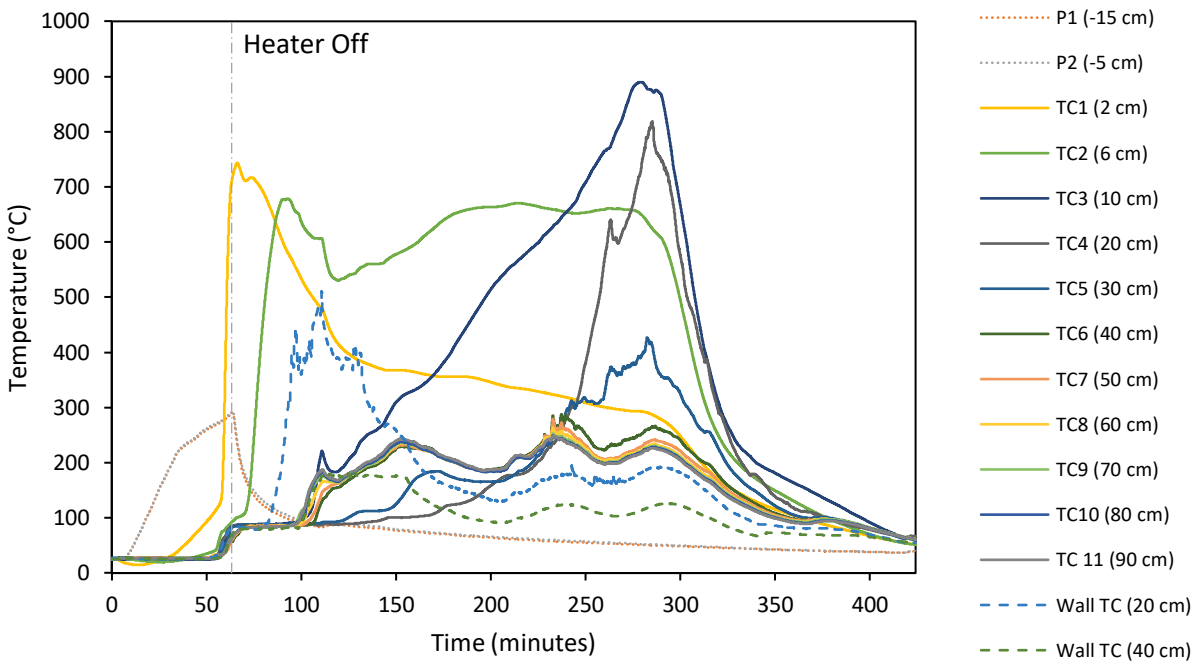

Figure S1-3: Temperature profile for the sludge-woodchips experiment, a self-sustaining smouldering experiment with a 75% moisture content sludge in a fixed bed with 0.4/0.3/1 g/g/g woodchips/extra water/sludge mass ratio. Plenum, centreline, and wall thermocouples are presented. Note the air flux was changed at 112 minutes.

S2. Supplementary Information on Material Characterization and Mass Balances

Table S2-1: Total elemental concentrations

Element	Concentration (mg/kg-dry virgin material) ± SE[a]					
	Sludge	Woodchips	Sludge Ash [b]	Sludge/Woodchip Ash [c]	Woodchip Ash [d]	Sand [e]
Al	5400 ± 300	1100 ± 400	7300 ± 1000	480 ± 90	370 ± 600	8000 ± 100
Cd	2.6 ± 0.2	0.3 ± 0.4	1.1 ± 0.8	0.2 ± 0.1	0.15 ± 0.05	1.6 ± 0.01
Co	3.8 ± 0.3	0.4 ± 0.4	3.2 ± 1	0.55 ± 0.3	0.31 ± 0.3	4 ± 0.01
Cr	120 ± 10	34 ± 2	90 ± 40	11 ± 2	10 ± 10	110 ± 0.7
Cu	480 ± 40	16 ± 4	840 ± 400	57 ± 7	8.7 ± 8	93 ± 2
Fe	53000 ± 5000	2100 ± 600	31000 ± 20000	3600 ± 1000	620 ± 800	16000 ± 200
Mg	4200 ± 400	1600 ± 300	5000 ± 1000	850 ± 90	450 ± 500	980 ± 13
Mn	260 ± 30	200 ± 40	390 ± 50	65 ± 9	76 ± 30	110 ± 1
Mo	22 ± 2	1.4 ± 0.6	15 ± 2	1.2 ± 0.3	0.57 ± 1	50 ± 0.3
Ni	47 ± 6	13 ± 2	49 ± 10	5.1 ± 1	3.1 ± 4	45 ± 0.2
P	26000 ± 3000	480 ± 90	24000 ± 6000	2600 ± 20	150 ± 20	7700 ± 50
Pb	110 ± 10	70 ± 10	62 ± 60	6.1 ± 4	10 ± 4	220 ± 0.2
Zn	630 ± 90	64 ± 30	780 ± 500	70 ± 10	23 ± 7	210 ± 3

[a] Standard error calculated as $\frac{\sigma}{\sqrt{n}}$

[b] The sludge ash is considered all materials from smouldering experiments of sand mixed with sludge finer than 0.250 mm (< #60 sieve)

[c] The post-treatment ash from smouldering experiments consisting of sludge mixed with woodchips

[d] Woodchips ash generated in the lab according to ASTM-D2866-11

[e] The sand is considered all materials from smouldering experiments of sand mixed with sludge coarser than 0.250 mm (> #60 sieve)

Table S2-2: Mass balance of sludge and sand experiment.

Element	Total Elemental Contents [a] ± SE * (mg)				Total Mass in Fraction [b] ± SE * (%)			
	Sludge	Sand [c]	Ash [d]	Sum Post-Treatment [e]	Sand [c]	Ash [d]	Sum Post-Treatment [e]	Emissions [e]
Al	45000 ± 2500	67000 ± 22000	27000 ± 2200	94000 ± 22000	150 ± 15	62 ± 6	212 ± 16	0 ± 16
Cd	21 ± 1.7	13 ± 2.2	5 ± 2.3	18 ± 3.2	62 ± 27	25 ± 11	87 ± 29	13 ± 29
Co	31 ± 2.5	34 ± 2.2	13 ± 2.3	47 ± 3.2	107 ± 21	42 ± 8	149 ± 22	0 ± 22
Cr	1000 ± 83	930 ± 150	320± 81	1300 ± 170	91 ± 24	31 ± 8	122 ± 26	0 ± 26
Cu	4000 ± 330	780 ± 450	2300 ± 600	3100 ± 750	20 ± 5	58 ± 16	77 ± 17	33 ± 17
Fe	440000 ± 42000	140000 ± 44000	130000 ± 45000	260000 ± 63000	31 ± 12	29 ± 11	60 ± 16	40 ± 16
Mg	35000 ± 3300	8100 ± 2900	18000 ± 2000	26000 ± 3500	23 ± 3	51 ± 8	74 ± 8	26 ± 8
Mn	2200 ± 250	910 ± 220	1300 ± 98	2300 ± 240	42 ± 6	62 ± 9	105 ± 10	0 ± 10
Mo	180 ± 17	41 ± 66	51 ± 3.9	92 ± 66	23 ± 3	29 ± 3	52 ± 4	48 ± 4
Ni	390 ± 50	370 ± 44	170 ± 19	540 ± 48	95 ± 16	43 ± 7	137 ± 18	0 ± 18
P	210000 ± 25000	63000 ± 11000	83000 ± 12000	150000 ± 16000	30 ± 5	39 ± 7	69 ± 9	31 ± 9
Pb	920 ± 83	1900 ± 48	240 ± 130	2100 ± 140	200 ± 109	26 ± 14	226 ± 110	0 ± 110
Zn	5200 ± 740	1700 ± 660	3100 ± 1200	4900 ± 1300	33 ± 13	60 ± 24	93 ± 27	7 ± 27

[a] Calculated as $\left(elemental\ concentration\left[\frac{mg}{kg}-dry\ matter\right]\right)\times(mass\ of\ fraction\ in\ reactor\ [kg-dry\ matter])$

[b] Calculated as $(elemental\ content[mg])\div(elemental\ content\ in\ virgin\ material\ [mg])\times 100\%$

[c] The sand is considered all materials from smouldering experiments of sand mixed with sludge coarser than 0.250 mm (> #60 sieve)

[d] The sludge ash is considered all materials from smouldering experiments of sand mixed with sludge finer than 0.250 mm (< #60 sieve)

[e] Calculated as $(elemental\ content[mg])_{sand}+(elemental\ conctent[mg])_{ash}$

* The standard error was calculated from the uncertainties from each calculation added in quadrature

Table S2-3: Mass Balance of the Sludge-Woodchips Smouldering Experiment

Element	Total Elemental Contents ± SE (mg) [a]					
	Virgin Materials		Mixed Ashes [b] *		Elemental Retention (%) [c] *	
	Sludge	Woodchips	Theoretical Maximum [d]	Actual [e]	Sludge Only [f]	Mixed Ash [g]
Al	53600 ± 3000	16300 ± 6200	70000 ± 6900	10600 ± 400	20 ± 1.3	15 ± 1.6
Cd	26 ± 2	4.0 ± 3	30 ± 5	4.4 ± 0.5	17 ± 2.2	15 ± 3.1
Co	38 ± 3	5.8 ± 5	44 ± 6	12 ± 2	32 ± 4.7	28 ± 5.1
Cr	1200 ± 100	480 ± 30	1700 ± 100	240 ± 8	19 ± 1.7	14 ± 0.9
Cu	4800 ± 400	220 ± 60	5000 ± 400	1300 ± 30	27 ± 2.3	25 ± 2.1
Fe	527000 ± 50000	30600 ± 8300	557000 ± 50000	80200 ± 4200	15 ± 1.6	14 ± 1.5
Mg	42000 ± 4000	23300 ± 4200	65000 ± 6000	18700 ± 400	45 ± 4.4	29 ± 2.6
Mn	2600 ± 300	2900 ± 500	5400 ± 600	1400 ± 40	56 ± 6.6	27 ± 3.0
Mo	220 ± 20	20 ± 20	240 ± 50	27 ± 1	12 ± 1.3	11 ± 2.7
Ni	470 ± 60	180 ± 30	650 ± 70	110 ± 3	24 ± 3.1	17 ± 1.8
P	258000 ± 30000	6900 ± 1300	265000 ± 30000	57300 ± 100	22 ± 2.6	22 ± 2.4
Pb	1100 ± 100	990 ± 140	2100 ± 200	140 ± 18	12 ± 2.0	6 ± 1.0
Zn	6300 ± 900	910 ± 340	7200 ± 1000	1600 ± 60	25 ± 3.7	22 ± 3.0

[a] Calculated as $\left(elemental\ concentration\left[\frac{mg}{kg}-dry\ matter\right]\right)\times(mass\ added\ to\ reactor\ [kg-dry\ matter])$

[b] Combined ashes from smouldering treatment of sludge mixed with woodchips

[c] Calculated as $\left((actual\ elemental\ content[mg\ element])\div(theoretical\ maximum\ elemental\ content\ [mg\ element])\right)\times 100\%$

[d] Assuming no losses, calculated as the sum of the contents in the virgin sludge and woodchips

[e] Calculated as $\left(elemental\ concentration\left[\frac{mg}{kg}-ash\right]\right)\times(mass\ of\ ash\ remaining\ in\ reactor\ [kg-ash])$

[f] Elemental retention considering only contribution of the sludge to the post-treatment ash

[g] Elemental retention considering both the contribution of the woodchips and the sludge

* The standard error was calculated from the uncertainties from each calculation added in quadrature

S3. Supplementary Information on Leaching Tests and Extraction Potentials

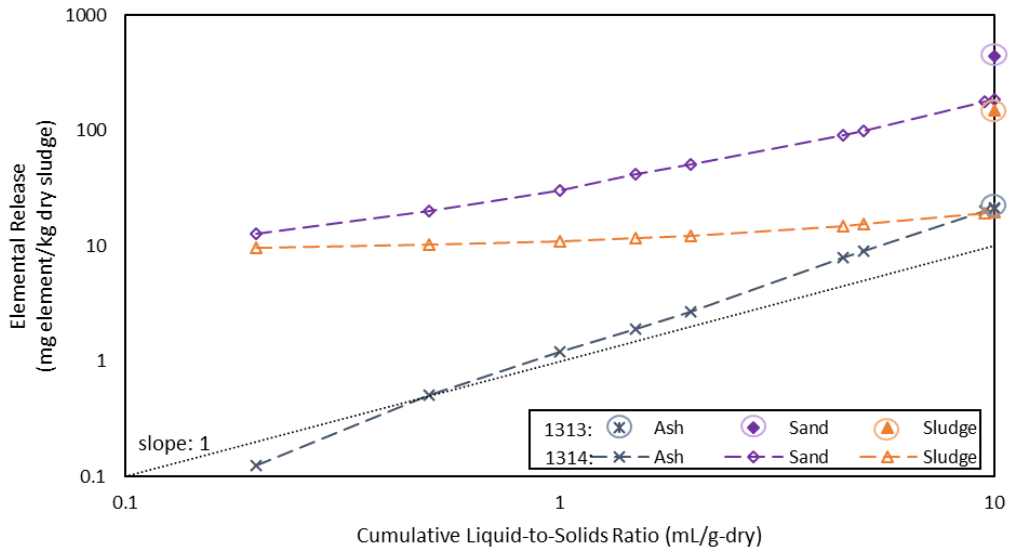

Figure S3-1: Total phosphorus release as a function of the log of the cumulative liquid-to-solids ratio with the available content of the materials from USEPA Method 1313 at native pH plotted at an L/S of 10 mL/g-dry. A dotted line with a slope of 1 has been added to each plot.

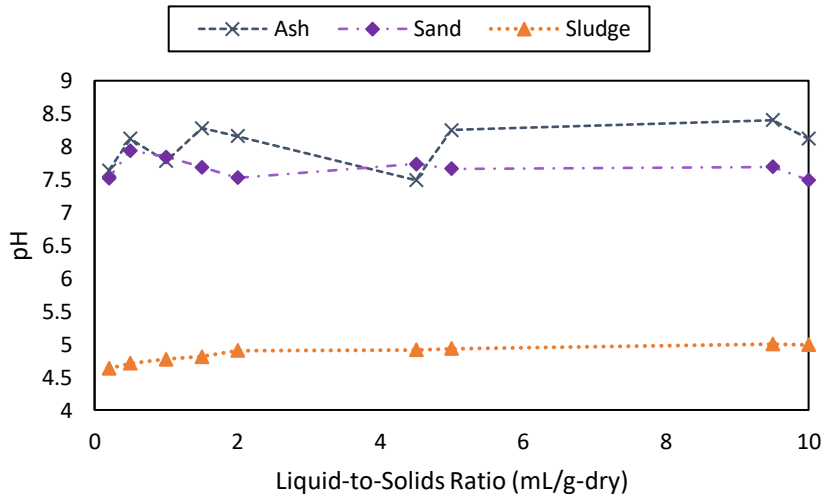

Figure S3-2: pH changes observed during the column percolation experimental (following USEPA Method 1314). The results are presented for sludge and post-treatment ash and sand as a function of the liquid-to-solids ratio.

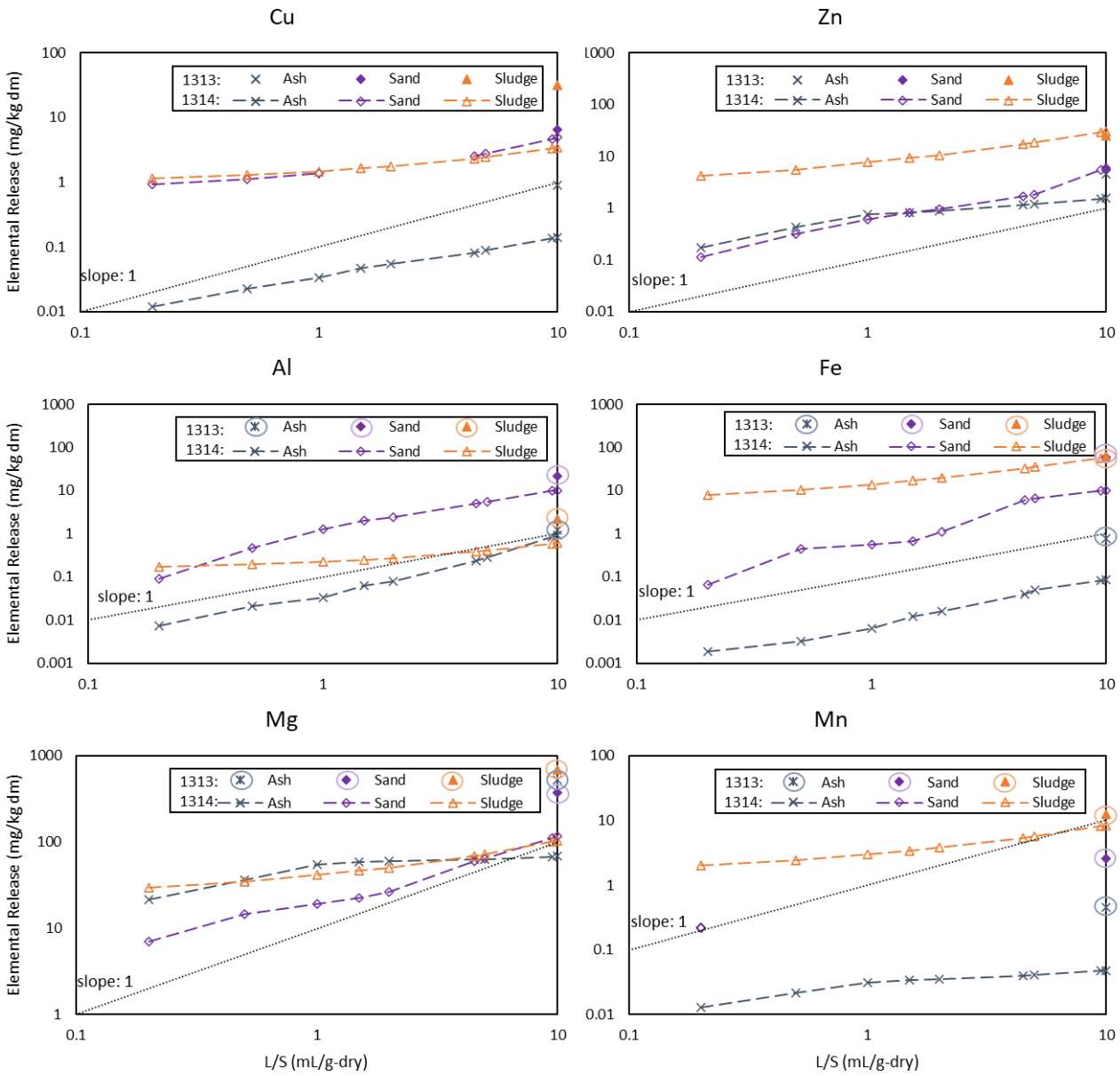

Figure S3-3: column percolation experimental results (following USEPA Method 1314) for 6 common potentially toxic elements from the virgin sludge and post-treatment ash and sand. The elemental release is shown as cumulative release as a function of the liquid-to-solid ratio. The values have been normalized to mg of element per kg of dry sludge. The available content of the materials from USEPA Method 1313 at native pH has been plotted at an L/S of 10 mL/g – dry. A dotted line with a slope of 1 has been added to each plot.

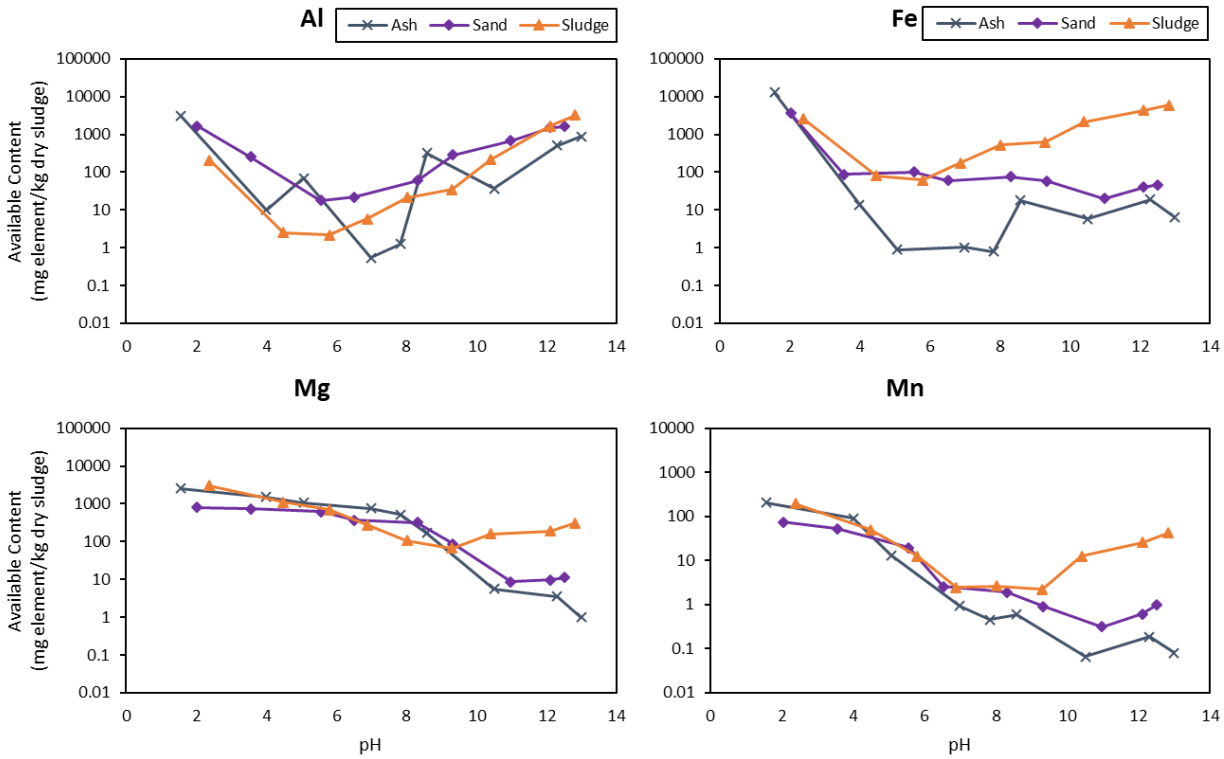

Figure S3-4: pH-dependent leaching (following USEPA Method 1313) of 4 other elements of interest from the virgin sludge compared to the post-treatment ash and sand. All values have been normalized to mg of P per kg of dry material.

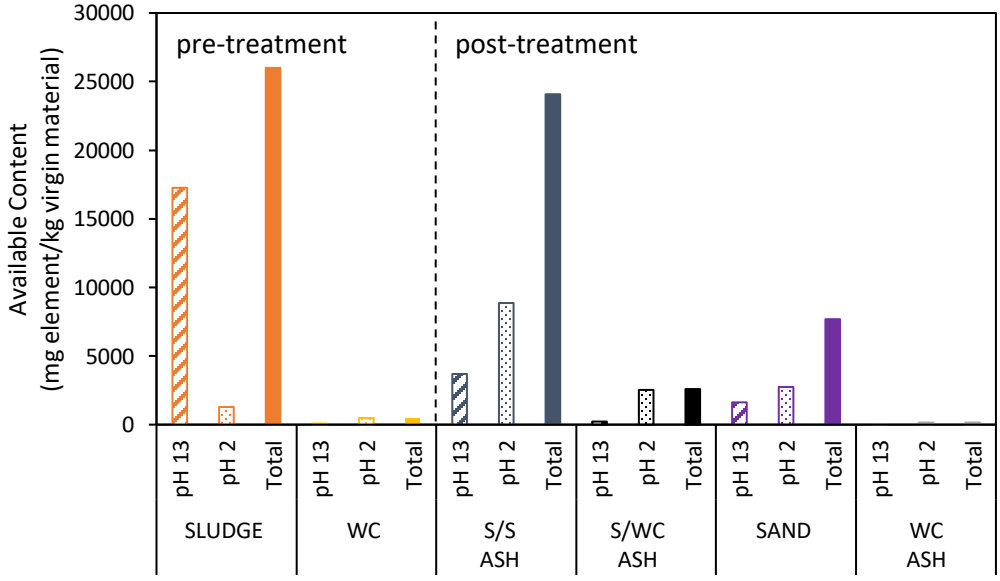

Figure S3-5: Available and total phosphorus contents within the pre- and post-treatment materials from sludge-sand and mixed sludge-woodchips smouldering experiments. Virgin woodchips are denoted as 'WC', 'S/S' is sieved ash from sludge-sand smouldering experiments, and 'S/WC' is ash from mixed sludge-woodchips smouldering.

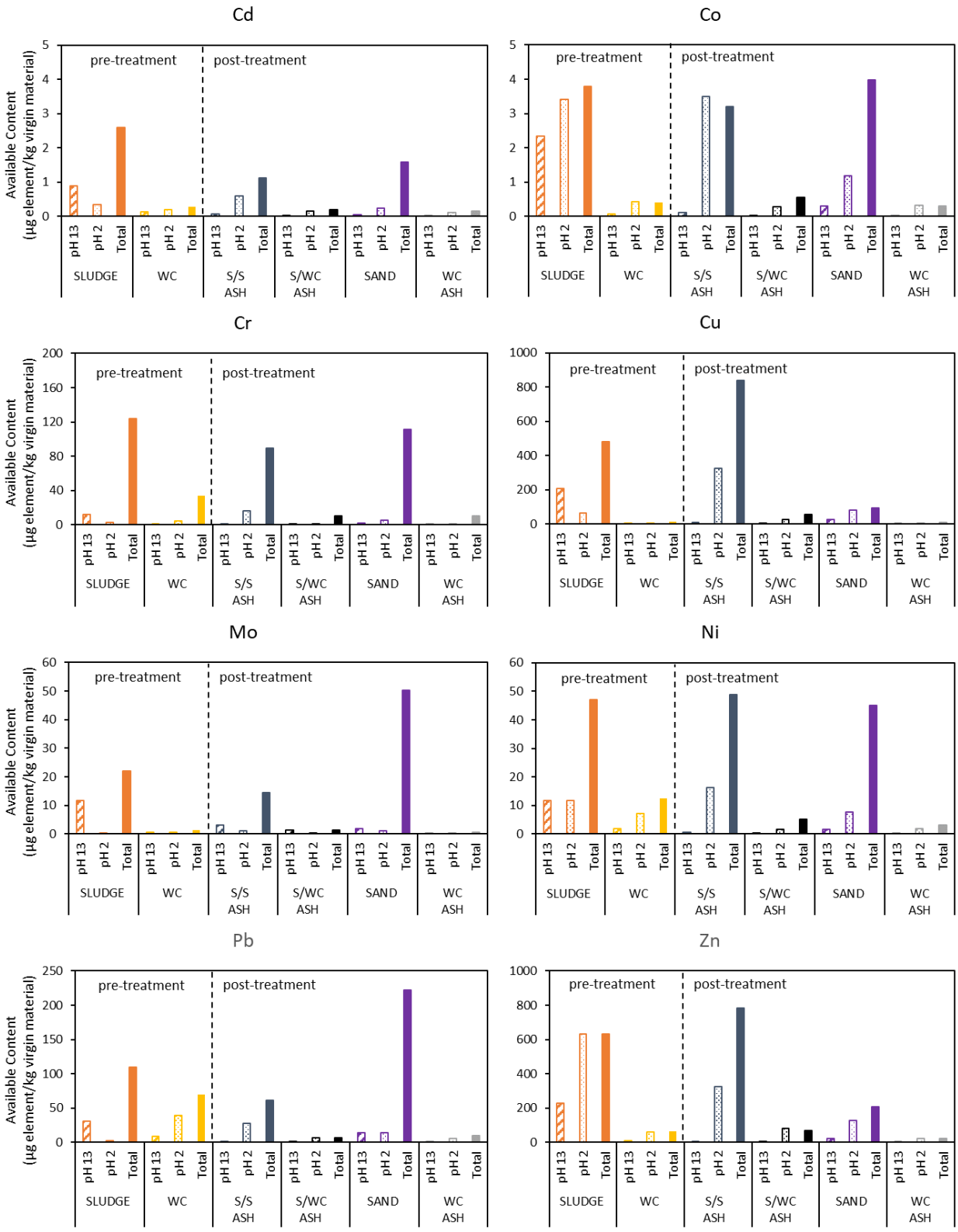

Figure S3-6: Available and total contents of 8 potentially toxic elements within the pre- and post-treatment materials from sludge-sand and mixed sludge-woodchips smouldering experiments. Virgin woodchips are denoted as 'WC', 'S/S' is sieved ash from sludge-sand smouldering experiments, and 'S/WC' is ash from mixed sludge-woodchips smouldering.

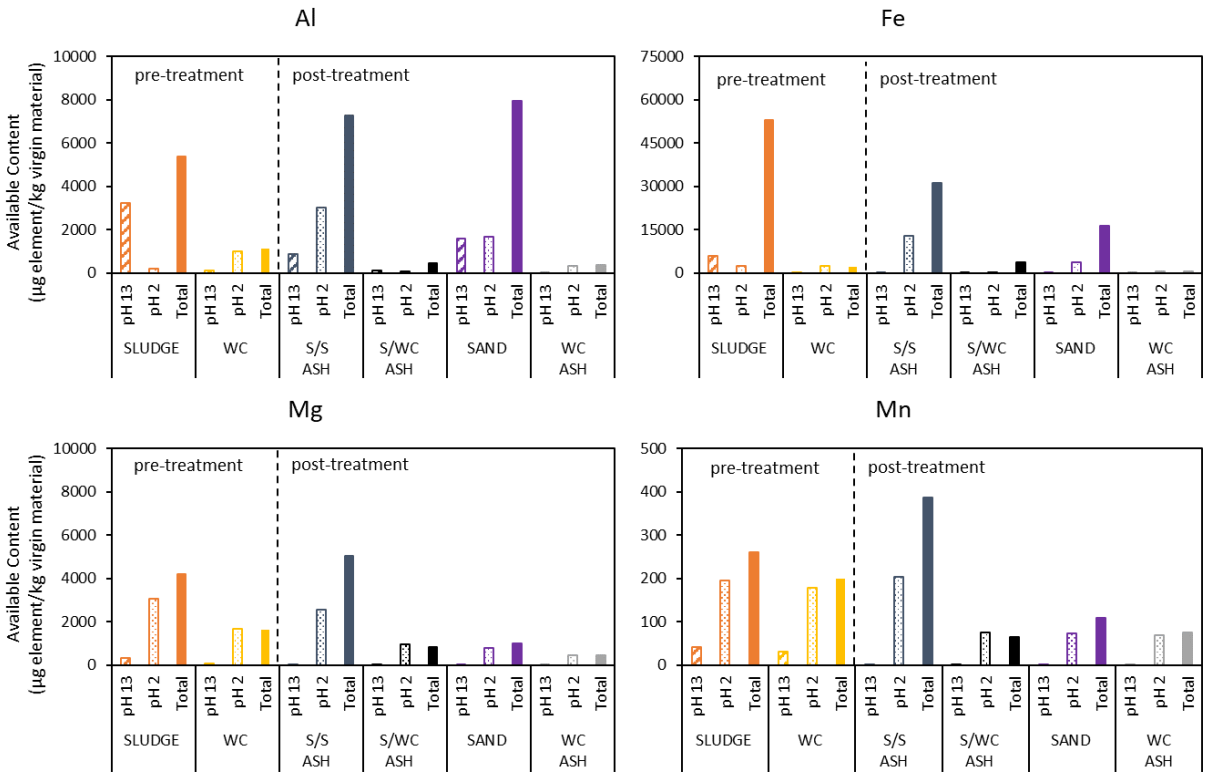

Figure S3-7: Available and total contents of aluminum, iron, magnesium, and manganese within the pre- and post-treatment materials from sludge-sand and mixed sludge-woodchips smouldering experiments. Virgin woodchips are denoted as 'WC', 'S/S' is sieved ash from sludge-sand smouldering experiments, and 'S/WC' is ash from mixed sludge-woodchips smouldering.

Table S3-1: Extraction Potential Normalized to Sludge Content

Element	Maximum Recoverable Content (mg of element/kg of dry sludge) ± SE[a]					
	Water [b]		pH 2 [c]		pH 13 [c]	
	Sludge	Sand + Ash [d]	Sludge	Sand + Ash [d]	Sludge	Sand + Ash [d]
Al	3 ± 0.3	16 ± 7	320 ± 32	2600 ± 810	4900 ± 490	1600 ± 550
Cd	0.03 ± 0.004	0.1 ± 0.04	0.3 ± 0.04	0.4 ± 0.1	0.7 ± 0.1	0.05 ± 0.01
Co	0.6 ± 0.08	0.04 ± 0.03	2 ± 0.3	1.2 ± 0.3	1.5 ± 0.2	0.06 ± 0.05
Cr	0.3 ± 0.04	2 ± 0.6	1.6 ± 0.2	14 ± 5	7.5 ± 1	2.9 ± 0.8
Cu	10 ± 1	12 ± 9	21 ± 2	270 ± 120	67 ± 8	50 ± 35
Fe	21 ± 3	66 ± 28	900 ± 130	12000 ± 3500	2000 ± 290	57 ± 22
Mg	210 ± 30	870 ± 290	920 ± 130	2800 ± 1100	92 ± 13	16 ± 6
Mn	5 ± 1	2.6 ± 0.8	71 ± 10	180 ± 77	15 ± 2	0.9 ± 0.3
Mo	0.2 ± 0.04	1.4 ± 0.8	0.09 ± 0.02	0.9 ± 0.4	2.4 ± 0.5	3.8 ± 2
Ni	4 ± 1	0.5 ± 0.1	6 ± 1	7.5 ± 4	6 ± 1	1.5 ± 0.5
P	160 ± 25	500 ± 97	1400 ± 210	12000 ± 2800	19000 ± 2900	5500 ± 1100
Pb	0.2 ± 0.07	0.8 ± 0.4	0.8 ± 0.2	19 ± 9	9.4 ± 3	0.5 ± 0.1
Zn	13 ± 3	2.7 ± 0.7	330 ± 63	150 ± 50	120 ± 23	5 ± 1

[a] Standard error calculated as $\frac{\sigma}{\sqrt{n}}$

[b] Recovery at native pH where samples were mixed with only deionized water (pH 6 for sludge, 7 for sand, and 8 for post-treatment ash)

[c] The actual sample pH values are within ± 0.5 pH units of the specified value

[d] Combined post-treatment materials (i.e., coarse-grained quartz sand and smouldered ash)

Table S3-2: Extraction Potential from Sand Mixed with Post-Treatment Ash

Element	Percentage of total content in dry material ± SE[a]		
	Water [b]	pH 2 [c]	pH 13 [c]
Al	0.2 ± 0.1%	29 ± 11%	18 ± 7%
Cd	6.9 ± 2.1%	18 ± 5%	2.7 ± 0.7%
Co	1.1 ± 0.9%	34 ± 9%	1.7 ± 1.3%
Cr	1.8 ± 0.6%	13 ± 4%	2.6 ± 0.8%
Cu	2.4 ± 1.8%	54 ± 25%	10 ± 7%
Fe	0.2 ± 0.1%	35 ± 11%	0.2 ± 0.1%
Mg	22 ± 8%	71 ± 28%	0.4 ± 0.2%
Mn	1.1 ± 0.4%	72 ± 33%	0.4 ± 0.1%
Mo	13 ± 7%	7.9 ± 4%	34 ± 21%
Ni	1.3 ± 0.3%	27 ± 11%	3.5 ± 1.4%
P	0.1 ± 0.01%	55 ± 14%	25 ± 6%
Pb	1.3 ± 0.5%	35 ± 16%	4.1 ± 0.5%
Zn	0.4 ± 0.1%	20 ± 7%	0.6 ± 0.2%

[a] Standard error calculated as $\frac{\sigma}{\sqrt{n}}$

[b] Recovery at native pH where samples were mixed with only deionized water (pH 6 for sludge, 7 for sand, and 8 for post-treatment ash)

[c] The actual sample pH values are within ± 0.5 pH units of the specified value

Table S3-3: Recovery Potential from Mixed Sludge-Woodchips Ash

Element	Elemental Retention [a] ± SE * (%)		Maximum Recoverable Content [b] ± SE * (mg/kg – dry starting material)		Recovery Potential [c] ± SE * (%)	
	Mixed Ash [d]	Emissions [e]	pH 2	pH 13	pH 2	pH 13
Al	15 ± 1.6	85 ± 1.6	82 ± 7.4	110 ± 8.5	2.5 ± 2.3	3.3 ± 0.4
Cd	15 ± 3.1	85 ± 3.1	0.2 ± 0.04	0.01 ± 0.0	12 ± 3.0	0.9 ±0.1
Co	28 ± 5.1	72 ± 5.1	0.3 ± 0.02	0.03 ± 0.0	14 ± 2.2	1.6 ±0.2
Cr	14 ± 0.9	86 ± 0.9	1.1 ± 0.82	0.19 ± 0.0	1.3 ± 1.0	0.2 ± 0.0
Cu	25 ± 2.1	75 ± 2.1	28 ± 9.8	0.09 ± 0.06	12± 4.2	0.0 ± 0.0
Fe	14 ± 1.5	86 ± 1.5	220 ± 220	0.32 ± 0.04	0.8 ± 0.8	0.0 ± 0.0
Mg	29 ± 2.6	71 ± 2.6	980 ± 170	0.02 ± 0.00	32 ± 6.2	0.0 ± 0.0
Mn	27 ± 3.0	73 ± 3.0	79 ± 19	0.01 ± 0.00	31 ± 8.1	0.0 ± 0.0
Mo	11 ± 2.7	89 ± 2.7	0.4 ± 0.34	1.40 ± 0.14	3.9 ± 3.1	12 ± 2.2
Ni	17 ± 1.8	83 ± 1.8	1.7 ± 0.36	0.04 ± 0.01	5.5 ± 1.3	0.1 ± 0.0
P	22 ± 2.4	78 ± 2.4	2700 ± 1800	240 ± 15	21 ± 14.3	1.9 ± 0.2
Pb	6 ± 1.0	94 ± 1.0	6.6 ± 1.1	0.2 ± 0.06	6.6 ± 1.2	0.2 ± 0.1
Zn	22 ± 3.0	78 ± 3.0	83 ± 34	1.4 ± 0.30	24 ± 10.5	0.4 ± 0.1

[a] Elemental retention of the mixed sludge and woodchips ash determined in Table S2-3

[b] Available elemental content determined from USEPA Method 1313

[c] Calculated as $\left((elemental\ content[mg\ element]) \div (total\ elemental\ content\ in\ starting\ material\ [mg\ element])\right) \times 100\%$

[d] Combined ashes from smouldering treatment of sludge mixed with woodchips

[e] Calculated as $100\% - (elemental\ retention\ in\ mixed\ ash[\%])$

* The standard error was calculated from the uncertainties from each calculation added in quadrature