

1 **Phosphorus Recovery and Reuse Potential from Smouldered Sewage Sludge Ash**

2 T. Fournie^{a*}, T.L. Rashwan^{a,b,1}, C. Switzer^c, J.I. Gerhard^a

3 *^a Department of Civil and Environmental Engineering, Western University, N6A 5B9 London, ON,*
4 *Canada*

5 *^b Department of Civil Engineering, Lassonde School of Engineering, York University, Toronto,*
6 *Ontario, M3J 1P3, Canada*

7 *^c Department of Civil and Environmental Engineering, University of Strathclyde, G1 1XQ*
8 *Glasgow, UK*

9 *¹Present address*

10 **Corresponding author*

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20 **Abstract**

21 Smouldering treatment of sewage sludge – and recapturing phosphorus – provides important
22 steps towards a circular economy. This study reveals that bulking sludge with sand or another
23 organic waste, e.g., woodchips, created a material that was readily converted to ash by self-
24 sustained smouldering. Simultaneous phosphorus and regulated potentially toxic element
25 releases from ash were evaluated using leaching methods from the USEPA Leaching
26 Environmental Assessment Framework (LEAF). Extraction potentials were also determined to
27 evaluate direct recovery as an alternative to land application. Compared to the parent sludge,
28 post-treatment ash from smouldering sludge with sand contained higher quantities of inorganic
29 phosphorus in sorbed and mineral phases, which can provide beneficial slow phosphorus release
30 to plants and avoid early phosphorus washout during land application. Ash also released lower
31 initial and total quantities of potentially toxic elements than virgin sludge. As an alternative to
32 land application, approximately 42% of retained phosphorus can be recovered directly using
33 acidic extraction, and an additional 30% from emissions. In contrast, co-smouldering sludge with
34 woodchips was more suited for direct recovery with 78% of phosphorus potentially recoverable
35 via emissions capture and yield increasing to 99% with acidic extraction of resulting ash. Co-
36 smouldering also produces a single post-treatment ash and can be operated continuously, which
37 aligns with current incinerator configurations at wastewater treatment plants and makes
38 adaptation highly feasible. With phosphorus reuse opportunities for land application and direct
39 recovery, smouldering sewage sludge creates an important opportunity for a phosphorus circular
40 economy as part of wastewater treatment sludge management.

41 **Keywords**

42 Phosphorus, Smouldering, Sewage sludge, Potentially Toxic Elements, Land application, Recovery

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59 **1.0 Introduction**

60 Increases in the proportion of waste components being recycled and reused compared to
61 landfilled are evidence of societal shifts towards more sustainable practices. Recent research and
62 regulations have demonstrated growing interest in circular economies, with significant focus on
63 making waste disposal processes more cyclic (Canadian Municipal Water Consortium, 2015;
64 Donatello and Cheeseman, 2013a; Fang et al., 2020; Gorazda et al., 2017; Mayer et al., 2016;
65 Mulchandani and Westerhoff, 2016). Resource recovery, in particular, for nutrients and metals,
66 not only relieves the depletion of essential elements but can also have environmental and
67 economic benefits for wastewater treatment plants (WWTPs) (Neczaj and Grosser, 2018).
68 Phosphorus is a key opportunity. Required in large quantities to produce agricultural fertilizers
69 (Mayer et al., 2016), global phosphate reserves are expected to be depleted in the upcoming
70 decades (Fang et al., 2020; Li et al., 2016). Therefore, there is significant interest in exploring
71 recovery methods to extract phosphorus and other limited resources from human waste
72 streams. Currently at WWTPs, >90% of all phosphorus ends up concentrated in sewage sludge
73 (Fang et al., 2020). For an average Canadian WWTP servicing 200,000 people, approximately 1300
74 tonnes of phosphorus is present in the sewage sludge annually (London, 2019), making it an
75 important reservoir and promising source of phosphorus recovery.

76 However, recovery and reuse of phosphorus from sludge remains a challenge for numerous
77 reasons. For example, several concerns arise when considering the direct application of sewage
78 sludge as a fertilizer. High water and organic matter content, pathogens, and numerous
79 compounds of concern in the sludge can require sludge processing prior to such use (Donatello

80 & Cheeseman, 2013; Hossain et al., 2011). Thermal processes for managing sewage sludge are
81 now common in the industry. For example, incinerating allows for volume reduction and
82 contaminant destruction (Adam et al., 2009). However, the pre-drying required to facilitate
83 sludge incineration makes the treatment process energy intensive and expensive (Khiari et al.,
84 2004; Werther and Ogada, 1999).

85 Another emerging thermal option is 'STAR' (Self-Sustaining Treatment for Active Remediation).
86 First shown to treat sewage sludge in 2016 (Rashwan et al., 2016), STAR is now a fully commercial
87 technology applied regularly to remediate soil contaminated with hydrocarbons, tars, and
88 emerging contaminants such as PFAS (Duchesne et al., 2020; Scholes et al., 2015; Switzer et al.,
89 2009). STAR utilizes smouldering combustion, a flameless form of burning that occurs on the
90 surface of a fuel within a porous media, for example, glowing red charcoal in a barbecue (Rein,
91 2016). The smouldering process burns the sludge, like an incinerator, but operates at lower
92 temperatures, is more resistant to quenching, and is more energy efficient (Rashwan et al., 2016;
93 Torero et al., 2020). To initiate smouldering, a heater provides short term, localized energy input
94 to the system (Yermán, 2016). Then the injection of air (oxygen) creates a 'smouldering front'
95 that propagates forward (in the direction of air flow) through the waste bed. This front involves
96 numerous zones (drying, pyrolysis, oxidation, and cooling) (Torero et al., 2020). A positive local
97 energy balance around the front, occurring when energy generation by fuel oxidation exceeds
98 energy lost to endothermic process and lateral heat losses (Zanoni et al., 2019), allows the
99 smouldering front to propagate with a steady velocity and in a 'self-sustaining' manner (i.e.,
100 without additional, external energy input) (Switzer et al., 2009). This feature means that

101 smouldering treatment ranks highly for energy efficiency metrics and sustainability rankings
102 (Gerhard et al., 2020).

103 Smouldering can only occur within a porous fuel or fuels embedded in a porous medium. The
104 porous matrix (1) increases the surface area for reaction, (2) creates pathways for oxygen to flow
105 to the reaction, and (3) insulates the reaction thereby reducing heat losses (Ohlemiller, 1985;
106 Torero et al., 2020). Smouldering has been shown to effectively treat high moisture content and
107 low permeability fuels, including faeces (up to 75% moisture content by mass) (Yermán et al.,
108 2015) and biosolids (up to 80% moisture content by mass) (Rashwan et al., 2016). For such
109 fuels/wastes, silica sand is usually added to create the porous medium (Rashwan et al., 2016;
110 Yermán et al., 2015). This works well but has the associated post-treatment challenges of (i)
111 separating the sand from post-treatment ash (if elemental recovery is the goal), and (ii) potential
112 large volumes of typically clean and dry sand requiring management. A second option involves
113 adding granular biomass (e.g., woodchips, waste crushed carbon, nut shells) to sewage sludge
114 prior to thermal treatment to supplement low calorific values and improve treatment (Feng et
115 al., 2021; Gorazda et al., 2017; Kijo-Kleczkowska et al., 2016). The use of biomass for smouldering
116 treatment of sewage sludge is not well studied (Torero et al., 2020; Wyn et al., 2020).

117 A recent study identified that smouldered sewage sludge ash is likely safe for landfilling (Feng et
118 al., 2020). However, landfilling ignores the recovery potential of limited resources such as
119 phosphorus (Donatello and Cheeseman, 2013b; Fang et al., 2020). Moreover, recovering
120 potential toxic elements (PTEs) – such as chromium and zinc – from sewage sludge ash has a
121 twofold benefit of removing these PTEs from a pathway into the environment and providing

122 value-added recovery (Westerhoff et al., 2015), especially from compounds present in high
123 concentrations (Bosshard et al., 1996).

124 Leaching methods are often applied to extract metals from post-treatment waste ashes,
125 including bioleaching (Bosshard et al., 1996; Wu and Ting, 2006; Xu et al., 2014; Yang et al., 2009),
126 chemical leaching (Gorazda et al., 2017; Petzet et al., 2012; Stark et al., 2006; Wu and Ting, 2006),
127 and water-washing (Wang et al., 2001). Element extraction from ashes is a crucial first step
128 towards recovery since it dictates the quantity available (Fang et al., 2020). Although several
129 studies have assessed the recovery potential from incinerated sewage sludge ash (Krüger and
130 Adam, 2014; Petzet et al., 2012; Schaum et al., 2007), it is novel to evaluate the recovery
131 opportunities from smouldered sewage sludge ash.

132 This paper examines opportunities for recovering phosphorus from smouldered sewage sludge
133 ash for potential reuse. This research seeks to explore the effects of bulking with (1) sand and
134 with (2) particulate organic wastes (such as woodchips, herein referred to as ‘co-smouldering’).
135 Total elemental contents of ashes from both systems were determined and compared to
136 Canadian land application guidelines to explore the suitability of each for direct land application.
137 A combination of pH-dependent leaching tests and column percolation experiments, following
138 USEPA Leaching Environmental Assessment Framework (LEAF) Methods 1313 (USEPA, 2012a)
139 and 1314 (USEPA, 2012b), were used to explore the land application potential and extraction
140 potential of the post-treatment ashes. This work progresses smouldering towards a more
141 sustainable and cyclic process that produces beneficial by-products and helps preserve the
142 environment. In addition, the practical considerations for reuse and recovery from the post-

143 treatment materials support further scaling the smouldering treatment to commercial
144 applications.

145 **2.0 Materials and Methods**

146 *2.1. Smouldering Experiments*

147 *2.1.1. Treatment System*

148 The STAR reactor set-up and instrumentation followed established smouldering research
149 methods fully described elsewhere (Rashwan, 2020; Rashwan et al., 2021b). Briefly, smouldering
150 tests were performed in a cylindrical, stainless steel reactor, with outer dimensions of 1.0 m
151 height and 0.6 m diameter (see Supplementary Materials (SM), Figure S1-1 for the full reactor
152 set-up). The reactor was wrapped in 5.10 cm thick insulation (ASTM C518 R-Value = 9.6 at 24°C,
153 FyreWrap® Elite® Blanket, Unifrax) to best represent field (low heat loss) conditions. The reactor
154 was on a load cell (KD1500, Mettler Toledo) to measure moisture loss and the sludge destruction
155 rate in real time. Thermocouples (Type K, 0.0064 m diameter Kelvin Technologies) installed along
156 the full height of the reactor recorded process temperatures. A continuous emissions monitoring
157 system (CEMS, ABB Ltd.) measured CH₄, CO₂, CO, and unburned hydrocarbons. The CEMS and
158 mass balance data were recorded every 5 and 2 seconds, respectively. All other instruments
159 were connected to a data logger (Multifunction Switch/Measure Unit 34980A, Agilent
160 Technologies) and personal computer that logged every 3 seconds.

161 *2.1.2. Sludge Mixed with Sand ("Sludge/Sand")*

162 Sludge was collected from Greenway Wastewater Treatment Plant (Greenway), London, Canada.
163 The sludge had a volatile matter content of 61.0% (ASTM-D5832-98), ash content of 27.5%
164 (ASTM-D2866-11), and fixed carbon content of 11.4% (calculated as the difference), all on a dry-
165 mass basis. An established method of sludge processing for laboratory experiments was
166 employed (Fournie et al., 2021; Rashwan et al., 2016) and is briefly summarized below. Two
167 experimental preparation methods have been used prior to smouldering treatment, (1) batch
168 drying the sewage sludge (Rashwan et al., 2016) and (2) immediate use of unprocessed sewage
169 sludge (Rashwan, 2020). The first was used for the sludge/sand test and the second for the
170 sludge/woodchips test. Both methods result in statistically similar smouldering behaviour and
171 performance (Rashwan, 2020) and is therefore not expected to influence any results or
172 conclusions.

173 For the sludge/sand test, the sludge was batch dried in an oven at 105°C, achieving a moisture
174 content of 3.81% (ASTM-D267-17). Coarse silica sand ($1.180 \leq \text{mean grain diameter} \leq 2.000$ mm,
175 porosity = 0.37, bulk density = 1670 kg/m³, Number 12, Bell & Mackenzie) was mixed with
176 processed sludge as is typical for industrial smouldering treatments. For this experiment, 8.53 kg
177 of sludge was mechanically mixed with 218 kg of coarse silica sand to achieve a sand-to-sludge
178 ratio of 25.5:1 on a dry-mass basis. If the sludge had not been dried, the sand-to-sludge ratio
179 would have been 6.5:1 on a wet-mass basis which has been shown to result in self-sustaining
180 smouldering (Rashwan et al., 2021a) The mixture was prepared in small batches of ~22 kgs in a
181 mechanical mixer before being transferred to sealed 19 L buckets for storage prior to loading.
182 This methodology provided a homogeneous sludge sample that was stable over time.

183 On the experiment day, the sludge mixture was carefully added into the reactor in a way that
184 ensure homogeneity and limited material compaction (SM, Section S1). The emptied buckets
185 were reweighed to account for any material retained during packing. A clean sand cap (3 – 6 cm
186 thick) was added on top of the sludge pack as done in commercial applications. Air was injected
187 into the reactor base at a Darcy flux of 5.0 cm/s throughout the test via a mass flux controller
188 (8290B045PDB67 ASCO Numatics). An inline air heater (F074736 36 kW SureHeat® MAX, Osram
189 Sylvania), operated at 300 – 400°C from the beginning of the test, provided convective ignition
190 of smouldering as is done in the field (Solinger et al., 2020). The experiment required ~61 min for
191 ignition (~34 min to increase the heater temperature and an additional ~27 min preheat).
192 Smouldering of the sludge was confirmed when the first thermocouple within the contaminant
193 pack peaked at 480°C (see SM, Figure S1-2). Following ignition, the heater was turned off and
194 ambient air was injected into the reactor, supporting a self-sustaining smouldering reaction
195 propagating up the reactor. The reaction velocity was $0.38 \text{ cm/s} \pm 10\%$ and the average
196 centreline peak temperature was $525^\circ\text{C} \pm 4\%$, which are representative of laboratory and field
197 applications (Torero et al., 2020; Wyn et al., 2020). The experiment was complete and self-
198 terminated once the smouldering front reached the end of the contaminant pack (after 180
199 minutes). The emissions data aligned with what is typically observed during smouldering (Wyn et
200 al., 2020) and showed that smouldering was robust, and the fuel was fully oxidized. These results
201 were confirmed upon excavation.

202 The post-treatment bed consisted of coarse silica sand (conserved during treatment) and sewage
203 sludge ash. Dry sieving separated them, with sand grains quantified as $>0.250 \text{ mm}$ (#60 ASTM

204 sieve) and ash quantified as the finer inert mass. The sand summed to 26.5 kg while ash
205 comprised 0.56 kg (97.9% and 2.1% of post-treatment materials, respectively).

206 *2.1.3. Sludge Mixed with Woodchips (“Co-Smouldering”)*

207 The woodchips utilized in the co-smouldering tests were obtained from construction waste
208 material (BRQ Fibre et Broyure Inc., Trois Rivieres, QC) (Cuthbertson, 2018; Rashwan et al.,
209 2021b). Proximate analysis determined that woodchips had a moisture content of 10.9% (ASTM-
210 D267-17), volatile matter content of 77.6% (ASTM-D5832-98), ash content of 10.7% (ASTM-
211 D2866-11), and fixed carbon content of 11.8% (calculated as the difference), all on a dry-mass
212 basis.

213 The moisture content of the virgin sewage sludge was 74.8%. For the smouldering test, 40.8 kg
214 of sewage sludge was mechanically mixed with 16.0 kg of woodchips and 12.1 kg of water to
215 achieve a ratio of woodchips: extra water: sludge of 0.4: 0.3: 1. The addition of water partially
216 reconstituted the sludge to better understand the limits of the fuel moisture content that would
217 still promote self-sustaining smouldering. The ability to smoulder higher moisture content fuels
218 is important since it reduces the energy cost associated with dewatering. Mixing procedures
219 were performed in batches of 6 kg. Loading the reactor followed the same process as other tests
220 (SM, Section S1).

221 Ignition by convection was completed in 58 min (~39 min to increase the heater temperature and
222 an additional ~19 min preheat). The heating period caused moisture loss via evaporation and
223 boiling, only in the bottom ~2 cm of the 45 cm tall bed. As expected, – and in contrast to the
224 sludge/sand test – the front did not migrate up the column. Instead, the self-sustained reaction

225 slowly consumed the base of the pack – since it was nearly entirely smoulderable – and the pack
226 steadily shrunk downwards. The experiment was complete after 280 minutes, when the fuels
227 were completely consumed (SM, Figure S1-3). The average centreline temperature was $812^{\circ}\text{C} \pm$
228 4%. The post-treatment ash was 20% of the initial mass of the mixture (i.e., 13.5 kg), and was
229 estimated to comprise 87% sludge ash and 13% woodchip ash. Since a single post-treatment ash
230 was produced, no sieving was required prior to analysis. The top sand cap was not used in this
231 experiment.

232 *2.2. Analytical Materials and Methods*

233 The chemical composition of the solids and elemental concentrations in all extracts were
234 determined using an Agilent 720 Inductive Coupled Plasma Optical Emission Spectrometer (ICP-
235 OES) (Agilent Technologies). Analyses were conducted in accordance with standard procedures,
236 including quality control/quality assurance, outlined by USEPA Method 6010D (Element Symbol
237 CAS Number, 2007). Solids were analyzed after acid extraction with a 3:1 ratio of concentrated
238 nitric acid (HNO_3) and hydrochloric acid (HCl), assisted by microwave digestion (170°C for 10 min
239 in a CEM MARS 6[®] Microwave Accelerated Reactor System, MFR) according to USEPA Method
240 3051A (Element, 2007).

241 Inorganic phosphorus was measured as dissolved orthophosphate (PO_4^{3-}), the most reactive form
242 of inorganic phosphorus, which is readily soluble and therefore easily utilized by plants (Johnston
243 et al., 2014). High-Performance Liquid Chromatography (HPLC) was used to quantify PO_4^{3-} via
244 direct injection using a Water[®] 515 pump following the standard procedure outlined by USEPA
245 Method 300 (Pfaff, 1993).

246 Elements analyzed by ICP-OES included phosphorus, aluminum, cadmium, cobalt, chromium,
247 copper, iron, magnesium, manganese, molybdenum, nickel, lead, and zinc, all of which are
248 regulated at WWTPs in Ontario, Canada. For reuse applications, cadmium, cobalt, chromium,
249 copper, molybdenum, nickel, lead, and zinc are also regulated under Ontario Regulation 338/09
250 (O. Reg. 338) from the Nutrient Management Act (2002). O. Reg. 338 classifies sewage sludge as
251 a category 3 non-agricultural source material (NASM) and sets guideline values for reuse
252 applications. CM1 is the most stringent set of NASM guideline values in the O. Reg. 338 guideline.

253 *2.3. pH-dependent Leaching Tests (USEPA Method 1313)*

254 This study conducted a series of batch extractions on 5 pre- and post-treatment materials
255 following USEPA Method 1313, measuring phosphorus and 12 other PTEs in the extracts. USEPA
256 Method 1313 consists of 9 parallel batch extractions to produce a liquid-solid partitioning curve
257 of the material of interest over eluate pH range $2 \leq \text{pH} \leq 13 \pm 0.5$ (USEPA, 2012a). Briefly, for each
258 extraction, 10 g of material was combined with 100 mL of extraction solution that consisted of
259 deionized water with varied amounts of either 2 N nitric acid (HNO_3) or 1 N potassium hydroxide
260 (KOH) to achieve the 9 specified target pH values. All extractions took place over 24 hours to
261 achieve equilibrium between the solid and liquid phases. The pH and electrical conductivity of
262 the supernatants were measured, and eluate samples were filtered and preserved for further
263 analysis.

264 *2.4. Column Percolation Tests (USEPA Method 1314)*

265 Percolation tests were also conducted on 3 materials to measure phosphorus and 12 other PTEs
266 using the USEPA Method 1314. This method uses a percolation column experiment to evaluate

267 constituent release from the material of interest as a function of the liquid-to-solid ratio (L/S)
268 (USEPA, 2012b). A full description of the process has been described elsewhere (Fournie et al.,
269 2021). Briefly, 300 g of pulverized, air-dried sample is packed into a 30 cm tall glass column.
270 Deionized water was injected using a Masterflex® L/S® digital peristaltic pump with flow moving
271 upwards through the column. Prior to continuous percolation, the column was rested for 24
272 hours in a fully saturated state. After the rest period, the flow rate of the water through the
273 column was maintained at 0.75 ± 0.5 L/S per day to collect the nine eluate samples (T01-T09) at
274 liquid-to-solid ratios of 0.2, 0.5, 1.0 ± 0.1 , and 1.5, 2.0, 4.5, 5.0, 9.5, 10.0 ± 0.2 mL/g-dry matter.
275 Each eluate sample was analyzed for pH and conductivity using a Fisher Scientific Accumet®
276 AB200 pH/mV/Conductivity meter within one hour of sample collection. Subsamples were
277 filtered and preserved with 1 N nitric acid for further analysis.

278 *2.5. Extraction Potential*

279 For this study, extraction potential was defined as the elemental concentration in the extracted
280 supernatant divided by the total elemental concentration within the solids. Extractions were
281 performed following the procedures outlined in section 2.3, under three pH conditions: native,
282 acidic (pH 2 ± 0.5), and alkaline (pH 13 ± 0.5). Water washing was used for the extraction under
283 native pH conditions, 2 N HNO₃ for acid extraction, and 1 N KOH for alkaline extraction. The total
284 elemental contents for each material were determined according to section 2.2. Extraction
285 potentials, initially determined as percentages, were converted to a mass of potentially
286 extractable element per mass of material (results presented in SM, Table S2-1). This was done
287 using a mass balance of the pre- and post-treatment materials. All extraction potential results

288 were normalized in terms of kg of virgin sludge to allow comparison between samples.
289 Subsequently, each element was identified as either solubility- or availability-limited by plotting
290 cumulative element release as a function of the liquid-to-solid ratio measured in Method 1314
291 on a log-log scale (Kosson et al., 2017).

292 **3.0 Results and Discussion**

293 *3.1. Material Characterization*

294 Smouldering resulted in the $75 \pm 3\%$ mass reduction of sludge (i.e., $25 \pm 3\%$ ash content and the
295 rest organic material that was oxidized). For the sludge/sand test, sand comprised 85% of the
296 pre-treatment mixture by mass (sludge was 15%) and the sand mass was conserved during
297 smouldering. The average temperature during 180 minutes of smouldering was $525^\circ\text{C} \pm 4\%$ (SM,
298 Figure S1-2). The post-treatment mixture comprised 98% sand and 2% ash. The phosphorus
299 content initially present in the sludge was 26,000 mg/kg-dry sludge, split 57/43 ($\pm 5\%$) as
300 organic/inorganic. Following smouldering of the sludge/sand, 78% of phosphorus was retained
301 by solids and the other 22% was recoverable from process emissions. In the solids, 39% of
302 phosphorus was retained in ash, split 7/93 ($\pm 11\%$) organic/inorganic, and 30% retained in sand,
303 split 49/51 ($\pm 6\%$) organic/inorganic. When smouldering sludge with sand, total phosphorus was
304 not conserved. Inorganic phosphorus seems to be conserved and potentially increased by
305 transformation of organic phosphorus.

306 For the co-smouldering test, the woodchips comprised 23% of the pre-treatment mixture, sludge
307 was 59%, and water was 18%. This test experienced higher energy smouldering (due to increased
308 fuel loading), with average peak temperatures of $812^\circ\text{C} \pm 4\%$ (SM, Figure S1-3). The temperatures

309 were more similar to temperatures observed during sludge incineration. The post-treatment
310 mixture (herein referred to as 'mixed ash') was 20% of the initial mass (i.e., 20% ash content).
311 Initial phosphorus was 19,000 mg/kg-dry starting material in the co-smouldering test, diluted in
312 comparison to the test with sand because of much higher water content and addition of
313 woodchips. After the higher energy combustion, 22% of phosphorus (split 32/68 ± 13%
314 organic/inorganic) was retained in mixed ash and 78% was recoverable from process emissions.

315 Concentrations of the 12 quantified PTEs are presented in Table 2. The PTE concentrations are
316 presented on a dry-mass basis for direct comparison to the O. Reg. 338 NASM CM1. All 12 PTEs
317 were detected in all materials. However, PTE concentrations within sand were very low, 1 – 4%
318 of the concentration originally present in the sludge. Concentrations in ash were often higher
319 than those in virgin sludge (aluminum, cobalt, chromium, copper, magnesium, manganese,
320 molybdenum, nickel, lead, and zinc) on this basis because smouldering reduced total mass by
321 nearly 80%, which had a concentrating effect on elements not released to emissions or retained
322 by sand. With negligible PTE content in the sand prior to smouldering, the observed PTE
323 concentrations were likely contributed by ash retention within the sand fraction during dry sieve
324 separation and/or condensation onto sand surfaces. However, because of its large mass in the
325 system, sand provided an important sink for some elements such as lead, nickel, and chromium
326 (SM, Table S2-2), reducing their total content in ash. The PTE concentrations in the mixed ash
327 were lower than the virgin sludge for 10 of the 12 elements (aluminum, cadmium, cobalt,
328 chromium, copper, iron, molybdenum, nickel, lead, and zinc) by 30 – 70%. The reduced PTE
329 concentrations in the mixed ash were likely due to dilution by the woodchips and release to
330 emissions via the higher energy smouldering.

331 When considered on a dry-sludge basis, total elemental contents between the materials are
332 similar (see SM, Figure S2-1). Essentially complete retention of aluminum, cobalt, chromium,
333 manganese, nickel, and lead by bottom ash (i.e., material retained in the reactor) was observed
334 with 100% retained in ash and sand (SM, Table S2-2). Less than complete retention was observed
335 for cadmium (87%), copper (67%), iron (60%), magnesium (74%), molybdenum (56%),
336 phosphorus (69%), and zinc (93%), suggesting availability for recovery via emissions. For the
337 mixed ash, low retention in the bottom ash is observed for all elements; aluminum (15%),
338 cadmium (15%), cobalt (28%), chromium (14%), copper (25%), iron (14%), magnesium (29%),
339 manganese (27%), molybdenum (11%), nickel (17%), phosphorus (22%), lead (6%), and zinc (22%)
340 (SM, Table S2-3). These elements are available for recovery via emissions capture, which is
341 commonly employed for incinerators (Cieřlik and Konieczka, 2017). Lower retention in mixed ash
342 was likely the result of (1) increased volatilization due to the higher energy smouldering (see
343 Table 1), and (2) physical mobilization of elements in the exhaust gas.

344 The O. Reg. 338 NASM CM1 (Government of Ontario, 2009) PTE thresholds for land application
345 are given in Table 2. Based on the guidelines, copper, molybdenum, nickel, and zinc were
346 exceeded in the sludge, ash, or both. Conversely, cadmium, cobalt, chromium, and lead were not
347 exceeded in any material. Only copper and molybdenum were exceeded in the mixed ash. Sludge
348 and ash exceeded the guideline values for copper, molybdenum, zinc, and ash additionally
349 exceeded for nickel. The current land application guidelines under O. Reg. 338 specify the
350 maximum quantity of total regulated PTEs that can be added to a specific area of soil in a 5-year
351 period (Government of Ontario, 2009). If the amount of ash required for land application is
352 lowered because of well-regulated phosphorus, these exceedances may be avoidable. The

353 following sections discuss reuse options for the smouldered ash via land application and
354 alternatively, extraction of elements from the ash to subsequently recycle.

355 *3.2. Suitability for Land Application*

356 *3.2.1. Phosphorus Availability and Release*

357 Phosphorus release during column percolation, and pH-dependent availability from sludge, ash,
358 and sand are shown in Figure 1. The values have been normalized in terms of mg of elemental
359 release per kg of dry sludge (mg/kg – DS) so that all materials are weighted consistently based on
360 starting material.

361 A large slug of phosphorus (60% of total release, 98% organic, <0.1% of total content) was
362 immediately released from the sludge (Figure 1a). This initial release was followed by a significant
363 decline, reaching a steady release after an L/S of 2 mL/g-dry. Most of the available phosphorus
364 in the sludge was released early in the experiment, at low L/S. Of the cumulative phosphorus
365 released from the sludge, 0.08% of total phosphorus, 74% was organic phosphorus and 26% was
366 inorganic. Released phosphorus appears to be availability-limited as it reached an equilibrium
367 within the duration of the experiment, which means that more phosphorus will not become
368 available with additional water percolation alone (SM, Figure S3-1).

369 In contrast, a smaller initial slug, 81% organic, was released from the ash representing <0.001%
370 of total phosphorus content in ash and <1% of total release (Figure 1a). The release profile
371 transitioned to 36-59% inorganic phosphorus later in the test. Release never reached an
372 equilibrium and seemed likely to continue releasing primarily inorganic phosphorus beyond the

373 cumulative L/S of 10 mL/g-dry. Therefore, smouldering transformed phosphorus species into
374 more solubility-limited forms (SM, Figure S3-1). Of the cumulative phosphorus released from the
375 ash, 0.09% of total phosphorus, 41% was organic phosphorus and 59% was inorganic. Over time,
376 ash became a better source of inorganic phosphorus that is more valuable to plants. The available
377 phosphorus from the ash was also primarily inorganic, composing 70-100% and varying with pH
378 (Figure 1b). At native pH, ash had less available total and inorganic phosphorus compared to
379 sludge at its native pH, i.e., pH 7.82 for the ash and 5.8 for the sludge. As pH changes, availability
380 from ash increased by 4400 mg/kg – DS at pH 1.57 or 1800 mg/kg – DS at pH 13.

381 Release from the sand fraction showed similar patterns to both sludge and ash (Figure 1a). Initial
382 phosphorus release from the sand, 88% organic, represents 0.2% of total phosphorus content in
383 sand and 7% of total release. The normalized release from the sand was immediately higher than
384 the ash and rapidly exceeded the release from the sludge between an L/S of 1 and 1.5 mL/g-dry.
385 Of the cumulative phosphorus released from the sand (i.e., 2.4% of its total content), 90% was
386 organic phosphorus and 10% was inorganic, suggesting a condensation effect on the sand. Some
387 of the organic phosphorus that was volatilized during smouldering may condense within the
388 cooler fixed sand bed ahead of the reactions, retaining a portion of it within the sand that would
389 otherwise be released in the emissions. This was consistent throughout the experiment (88 –
390 90% organic and 10 – 12% inorganic) and further observed from the pH-dependent availability
391 results (89 – 94% organic) (Figure 1b). Based on the release profile, sand seemed likely to
392 continue to release phosphorus beyond the highest L/S in Figure 1a, thereby demonstrating a
393 solubility-limited process similar to the ash. Furthermore, sand has minimal pH-dependence

394 (Figure 1b), achieving a limited range of phosphorus availability, 440-770 mg/kg – DS, over
395 environmental relevant pH conditions ($3.55 < \text{pH} < 10.98$).

396 Mixed ash was not evaluated for its applicability for land application because of its low retention
397 of phosphorus (22%) (SM, Table S2-3), which translated to a low phosphorus availability (SM,
398 Figure S3-5).

399 *3.2.2. Potentially Toxic Elements*

400 Understanding the availability and leaching behaviour of PTEs is important for assessing the
401 environmental impacts of disposal and/or reuse options for sludge and ash. Releases of 8
402 commonly regulated PTEs from the column percolation experiments are shown in Figure 2, and
403 pH-dependent availabilities are shown in Figure 3.

404 Ash exhibited lower releases of 6 of 8 PTEs (Figure 2). Initial releases of cadmium, cobalt, copper,
405 nickel, lead, and zinc from sludge exceeded those from ash by 93-99%, and cumulative releases
406 from sludge exceeded ash by 50-96%. Of these, cobalt, copper, and nickel were availability-
407 limited in the sludge (Figure 3). The lower relative pH of the sludge (pH 5.8) compared to the ash
408 (pH 7.8), may explain the higher initial release of the availability-limited PTEs from the sludge
409 since chemical changes would influence the release of these elements more than increased
410 percolation (SM, Figure S3-2). While ash had higher total elemental concentrations compared to
411 sludge (Table 2), higher total elemental concentrations did not translate to higher element
412 releases. The relatively higher release of the other PTEs from the sludge than ash could be the
413 result of mineralization during smouldering.

414 Releases of chromium and molybdenum, the two elements where release from ash exceeded
415 that from sludge, were low from both materials. These two PTEs and lead were similar to or
416 slightly more available from the ash than sludge under environmentally relevant conditions (i.e.,
417 pH 5.5 – 8.5; Figure 3). In contrast, availabilities of cobalt, copper, nickel, and zinc from sludge
418 exceeded their availabilities from ash across the pH range most relevant to land application.

419 Although sand meets land application guidelines for PTEs (Table 2), a large mass of sand would
420 be required to meet plant nutrient requirements, which would be labour intensive and costly.
421 Moreover, operational challenges make direct land application of the sand infeasible. Wet sieving
422 of sand to recover phosphorus is more practical and sequesters other PTEs, primarily lead, nickel,
423 and chromium which are retained in the sand fraction. Therefore, the release and availability of
424 other PTEs in the sand were not assessed here, but more information is available in the
425 Supplementary Materials.

426 *3.3. Extraction Potential*

427 The extraction potential of phosphorus from the sludge/sand test was determined for the post-
428 treatment ash and sand using three different extractants and compared to virgin sludge (Table
429 3). A 10:1 L/S acidic extraction from ash and sand recovered 42% of initial phosphorus (10,900
430 mg/kg – initial sludge [IS]). The extractant solution was also enriched with iron (30%, 15,900
431 mg/kg – IS), magnesium (65%, 2730 mg/kg – IS), and aluminium (32%, 1730 mg/kg – IS) and
432 contained measurable amounts of copper (60%, 290 mg/kg – IS), manganese (73%, 190 mg/kg –
433 IS), zinc (22%, 140 mg/kg – IS), lead (32%, 35 mg/kg – IS), chromium (14%, 17 mg/kg – IS) and
434 nickel (18%, 8.5 mg/kg – IS). The additional PTEs present in the extractant solution would likely

435 require subsequent separation. All other measurable elements are below 15 mg/kg – IS.
436 Phosphorus released from ash and sand were both solubility-limited (Figure 1); increasing the L/S
437 above 10:1 could further increase the amount of phosphorus recovered from ash and sand.
438 However, increasing the L/S would also increase PTE content in the solution, especially of
439 cadmium, cobalt, lead, and zinc, which were all identified as solubility-limited (see Table 2).

440 Acidic extraction from sludge recovered only 5% of initial phosphorus (1300 mg/kg – IS) and is
441 therefore not suitable on its own for phosphorus recovery. However, its high yields of PTEs from
442 the initial sludge (magnesium (72%, 3020 mg/kg – IS), zinc (100%, 630 mg/kg – IS), and
443 manganese (75%, 190 mg/kg – IS)) may make it attractive as a pre-treatment prior to smouldering
444 or another recovery method. Phosphorus released from sludge is availability-limited (Figure 1),
445 so increasing L/S would not provide much additional benefit.

446 Alkaline extraction from ash and sand recovered 19% of initial phosphorus (4940 mg/kg – IS) and
447 was also enriched with aluminium (19%, 1030 mg/kg – IS). It also contained measurable amounts
448 of iron (0.1%, 53 mg/kg – IS), copper (11%, 53 mg/kg – IS), and magnesium (0.4%, 17 mg/kg – IS).
449 Although the phosphorus recovery was somewhat poor, the low abundance of other extractable
450 elements may make it an attractive step in a more complex recovery effort.

451 Alkaline extraction from sludge recovered 68% of initial phosphorus (17,700 mg/kg – IS) and was
452 also enriched with iron (11%, 5830 mg/kg – IS) and aluminium (60%, mg/kg – IS). The extractant
453 solution also contained measurable amounts of magnesium (7%, mg/kg – IS), zinc (37%, 230
454 mg/kg – IS), copper (44%, 210 mg/kg – IS), manganese (16%, 42 mg/kg – IS), lead (27%, 30 mg/kg
455 – IS), chromium (10%, 12 mg/kg – IS), nickel (26%, 12 mg/kg – IS), and molybdenum (55%, 12

456 mg/kg – IS). Subsequent separation of PTEs would likely be required, similar to acidic extraction
457 from the ash. Water extraction was not a viable method for any material.

458 For the post-treatment materials (i.e., ash and sand): in addition to phosphorus recovery using
459 either acidic or alkaline solutions, 30% of phosphorus could be recovered from the emissions
460 stream. Emissions recovery could bring total phosphorus recovery from post-treatment materials
461 to 70% with acidic extraction, and 50% with alkaline extraction.

462 For co-smouldering sludge and woodchips, the largest fraction of potentially recoverable
463 phosphorus is from process emissions (78%). Both acidic and alkaline extractions from mixed ash
464 provided some further recovery (SM, Figure S3-5). In particular, acidic extraction yielded a further
465 21% of initial phosphorus (2,500 mg/kg of initial sludge/woodchip content [IS/WC]), bringing
466 total phosphorus recovery to nearly 100%. Acidic extraction of mixed ash was also enriched in
467 magnesium (32%; 850 mg/kg – IS/WC), iron (<1%; 190 mg/kg – IS/WC), zinc (24%; 72 mg/kg –
468 IS/WC), aluminum (2.5%; 72 mg/kg – IS/WC), manganese (31%; 69 mg/kg – IS/WC), and copper
469 (12%; 24 mg/kg – IS/WC). All other measurable elements were below 10 mg/kg – IS/WC. In
470 contrast, alkaline extraction yielded only 2% additional phosphorus, making the total potentially
471 recoverable phosphorus 80%. Alkaline extraction of mixed ash requires less additional separation
472 of other elements. Only aluminum had significant presence in the extractant (3%; 96 mg/kg –
473 IS/WC). All other PTEs were < 2 mg/kg – IS/WC. However, this benefit is small given its poor
474 phosphorus yield at high pH. Therefore, the optimal method of phosphorus recovery from the
475 mixed ash is via the process emissions combined with acidic extraction of the bottom ash.

476 *3.4. Discussion of Land Application and Recovery Opportunities*

477 3.4.1. Sludge smouldered in an inert porous media

478 The best opportunity to create a valuable product for land application is smouldering sludge with
479 sand which resulted in 78% phosphorus retention in the bottom ash. Furthermore, the ash
480 contained more inorganic phosphorus than either the sludge or sand fraction which is more
481 beneficial to plants. This inorganic phosphorus was released more slowly than the phosphorus
482 from sludge, which experienced early washout, losing 60% of total released content almost
483 immediately. Following the early release, remaining phosphorus species within the sludge were
484 less available and therefore less useful to plants without additional weathering or solubilization
485 by plants and microbes, which can be slow and often insufficient for plant needs (Arcand and
486 Schneider, 2006). Interpreting column percolation (Figure 1a) and pH-dependent availability
487 (Figure 1b) results together suggests that the sludge was already more acidic when applied and
488 therefore its phosphorus was already more available in the immediate term. Early washout of
489 available phosphorus from sludge can (1) contribute to eutrophication and (2) require sludge to
490 be applied more frequently to meet plant nutrient needs. Comparatively, the phosphorus from
491 the ash became more available with decreasing pH (relative to starting pH), which means a
492 steadier supply of phosphorus to plants as pH becomes slightly more acidic with repeated plant
493 growth cycles. With a high abundance of desirable, inorganic phosphorus in the ash, significantly
494 less ash is likely to be needed for land application relative to sludge. Release of most retained
495 PTEs was already lower from the ash and applying less ash would further reduce PTE release. The
496 behaviour of phosphorus release and availability for the sand, supports the idea that a small
497 amount of ash was retained in the sand fraction during dry sieving. Since sand comprises 98% of
498 the mass of post-treatment materials (2% ash), mechanical separation of the ash and sand would

499 make land application of the ash more practical and economically feasible. Moreover, although
500 sand meets land application guidelines for PTEs (Table 2), a large mass of sand would be required
501 to meet plant nutrient requirements, which would be labour intensive and costly. Since the sand
502 retained 30% of phosphorus (90% organic), wet sieving could be used to fully remove ash from
503 the sand fraction and potentially recover some of the additional phosphorus retained on the sand
504 while removing other PTEs (most notably lead, nickel, and chromium). Future work involving
505 plant growth studies and multiple growth cycles may be beneficial to (1) optimize amounts of ash
506 required to support plant growth and (2) determine the phosphorus flux from ash.

507 The maximum recoverable phosphorus from smouldering sludge mixed with sand was around
508 70% with approximately 30% from emissions and 40% from ash and sand with acidic extractant
509 (pH 2). The lower observed phosphorus recovery using an alkaline extractant (19%) is
510 unsurprising, as it has been observed consistently among other studies (Biswas et al., 2009;
511 Petzet et al., 2012; Stark et al., 2006). The phosphorus yield using an acidic extractant may be
512 improved further with more extractant volume. Furthermore, because the ash was the most
513 concentrated source of retained phosphorus after treatment (50%) but only 2% of the post-
514 treatment mass, extraction from the ash alone at low pH could minimize extractant volume
515 requirements (0.69 m³/tonne virgin sludge) while only slightly reducing phosphorus recovery
516 (32% from ash alone). Comparatively, a significantly larger extractant volume would be required
517 for a 10:1 L/S extraction ratio from both the sand and ash (66 m³/tonne virgin sludge), or from
518 the sludge (10 m³/tonne virgin sludge). Reduced extractant requirements also results in less
519 processing solution waste which can be expensive and challenging to dispose of (Donatello and
520 Cheeseman, 2013b). Therefore, when considering phosphorus recovery, it would make more

521 economical sense to physically separate the ash and sand and reuse the sand in future
522 smouldering applications.

523 3.4.2. Co-smouldering sludge with organic waste

524 Of the alternatives assessed, the best opportunity for direct recovery of phosphorus is
525 smouldering sludge with woodchips (or another low-impurity, high-energy fuel) and capturing
526 the gases (SM, Table S3-3). While emissions recovery was not rigorously quantified in this
527 research, it is an important source of recoverable phosphorus that will be explored in future work
528 on smouldering systems. The remaining phosphorus in the resultant mixed ash can be recovered
529 easily with an acidic extractant (pH 2). Between the emissions capture (78%) and extraction from
530 ash (21% at pH 2), close to 100% of phosphorus could be recovered from sludge (and woodchips).
531 The significant phosphorus volatilization observed during co-smouldering of sewage sludge is
532 commonly observed during incineration (Cieślik and Konieczka, 2017). Similar to chemical
533 extraction, recovering phosphorus from the emissions stream would require additional
534 processing to separate out other PTEs. To minimize disposal requirements from processing, the
535 extraction waste and emissions waste could be combined and recycled for other purposes such
536 as an additive in construction materials (Cieślik and Konieczka, 2017). Co-smouldering presents
537 both operational and procedural advantages. Since both the sludge and woodchips are
538 combustible, only inert ash remains (20% initial mass) making phosphorus recovery simpler and
539 more economical. Phosphorus extraction from the mixed ash would require 1.3 m³ extractant
540 solution/tonne virgin sludge which is 88% less extractant volume than would be required for
541 virgin sludge. Another advantage of treating fully organic waste beds is their capacity to be

542 straightforwardly designed as continuous or semi-continuous smouldering systems, where fuel
543 (e.g., sludge/woodchips) is continuously added to the reactor with potential to remove ash from
544 the base. A system of this nature could eliminate time and costs of reignition. Furthermore,
545 continuous smouldering would behave similarly to current incinerator configurations at WWTPs,
546 making adaptation of the process highly feasible.

547 **4.0 Conclusions**

548 Smouldering enables phosphorus recovery from wastewater treatment sludge in several
549 potentially beneficial forms. The best opportunity to create a valuable soil amendment with
550 sufficient phosphorus available to plants in the longer term is smouldering with sand. The
551 resulting ash retained 78% of the total phosphorus of the parent sludge and contained higher
552 quantities of inorganic phosphorus in sorbed and mineral phases, providing beneficial slow
553 phosphorus release and avoiding early washout. Furthermore, land application of ash is more
554 favourable than sludge since it reduces co-dissolution of 6 of 8 commonly regulated PTEs.
555 Although total elemental concentrations of sludge and ash exceeded O. Reg. 338 land application
556 guidelines for some PTEs, release profiles suggest that smouldering treatment provides
557 important benefits by creating a resource of high-quality phosphorus while sequestering other
558 potentially more harmful elements. Since sand provided an important sink for phosphorus (30%
559 of retained phosphorus, 90% organic), mechanical separation and washing at low L/S should be
560 applied to recover this additional phosphorus from the large sand mass.

561 Considering extraction as an alternative to direct land application, no single extraction from any
562 material is ideal for phosphorus recovery, before or after smouldering. However, co-smouldering

563 sludge with woodchips could enable close to 100% phosphorus recovery when extraction from
564 the post-treatment ash (21% phosphorus at pH 2) is combined with emissions capture (78%
565 phosphorus). Further separation of phosphorus and PTEs would still be required from the
566 emissions stream which contained >70% of PTEs originally present in the parent sludge. Overall,
567 co-smouldering sewage sludge with woodchips (or another low-impurity, high-energy fuel) has
568 numerous benefits, including (1) treating multiple waste streams, (2) producing a single post-
569 treatment ash, (3) being apt for continuous operation, and (3) increasing treatment
570 temperatures, which may provide further opportunities for treating additional persistent
571 contaminants in the parent sewage sludge.

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590 **Supplementary Materials**

591 Supplementary data associated with this article can be found, in the online version, at:

592

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769 *Table 1: Material composition and experimental data*

Experiment		Units	Sludge & Sand		Sludge & Woodchips		
Proximate Analysis							
			Sludge	Mixture	Sludge	Woodchips	Mixture
Moisture Content ^a		%	3.81	3.22	74.8	10.9	65.4
Volatile Matter ^b		% (dry basis)	61.0	-	62.7	77.6	-
Ash Content ^c		% (dry basis)	27.5	26.6	28.8	10.7	20.0
Fixed Carbon ^d		% (dry basis)	11.4	-	8.53	11.8	-
Experimental Data							
			Sand: Sludge		Woodchips: Extra Water ^e : Sludge		
Mixture	Wet Basis	(g/g)	6.5: 1		0.4: 0.3: 1		
Ratio	Dry Basis	(g/g)	25.5: 1		-		
Mass of	Sludge	kg	8.5		39.4		
Materials	Sand	kg	217.7		-		
Added	Woodchips	kg	-		16.0		
	Water	kg	-		12.1		
Air Flux		cm/s	5.5		2.5 – 5.0		
Average Centreline Temperature		°C	525 ^f		812 ^f		

770 ^a Determined according to ASTM-D267-17

771 ^b Determined according to ASTM-D5832-98

772 ^c Determined according to ASTM-D2866-11

773 ^d Calculated as the difference

774 ^e Water was added to the fuel mixture to reduce treatment temperatures

775 ^f The thermocouple temperature results have an associated error of $\pm 4\%$

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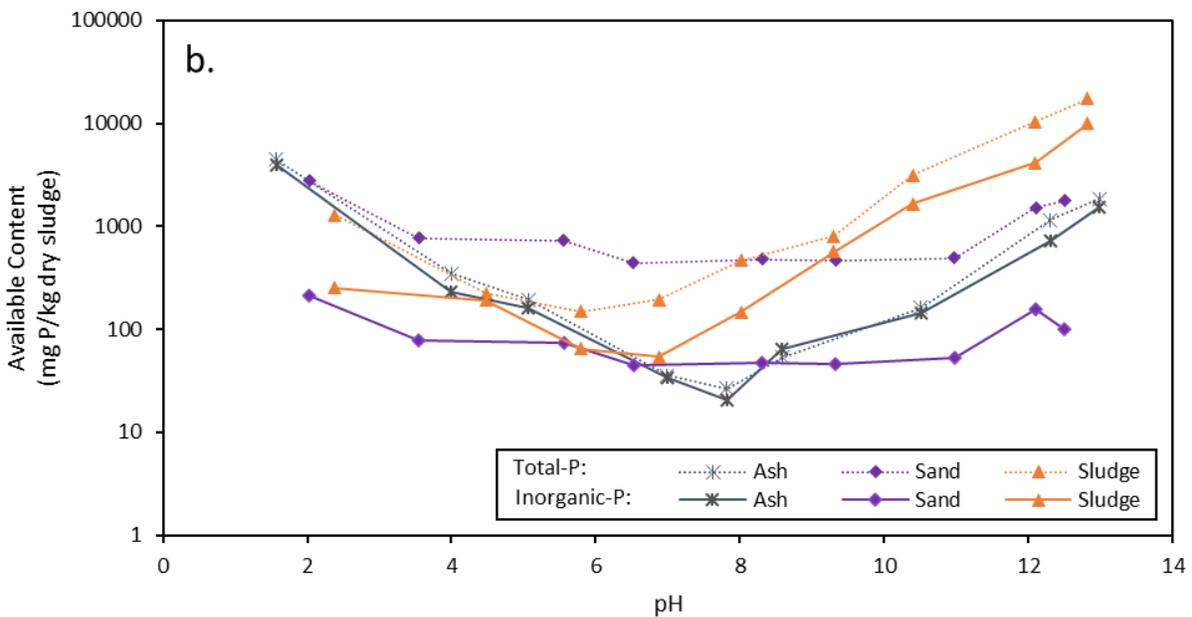
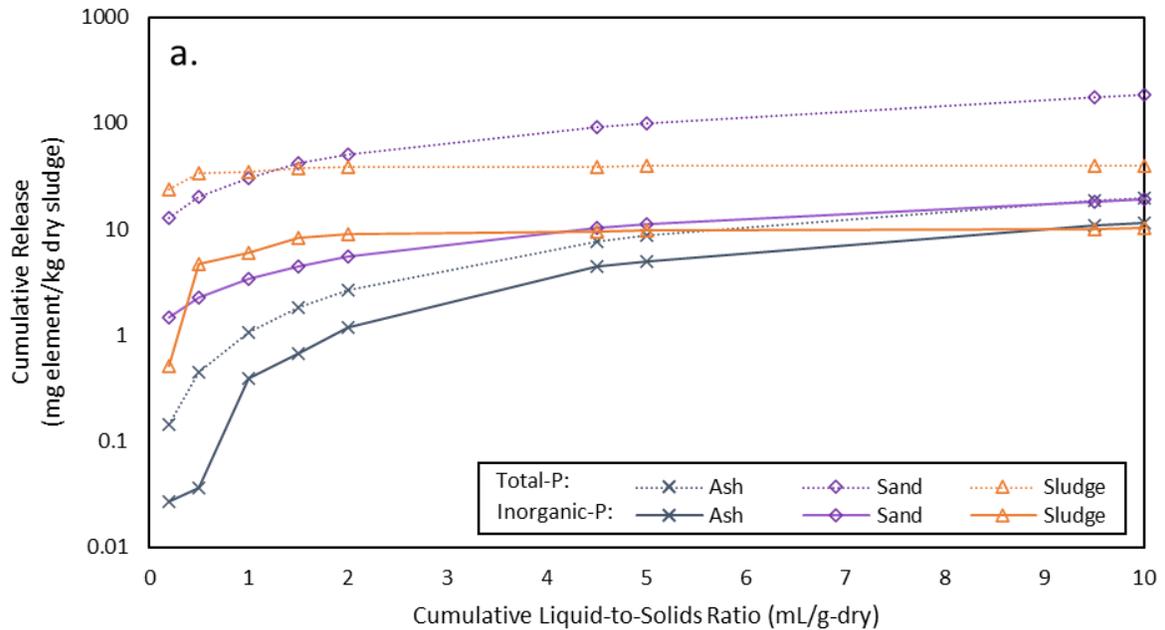
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781 *Table 2: Total elemental concentrations*

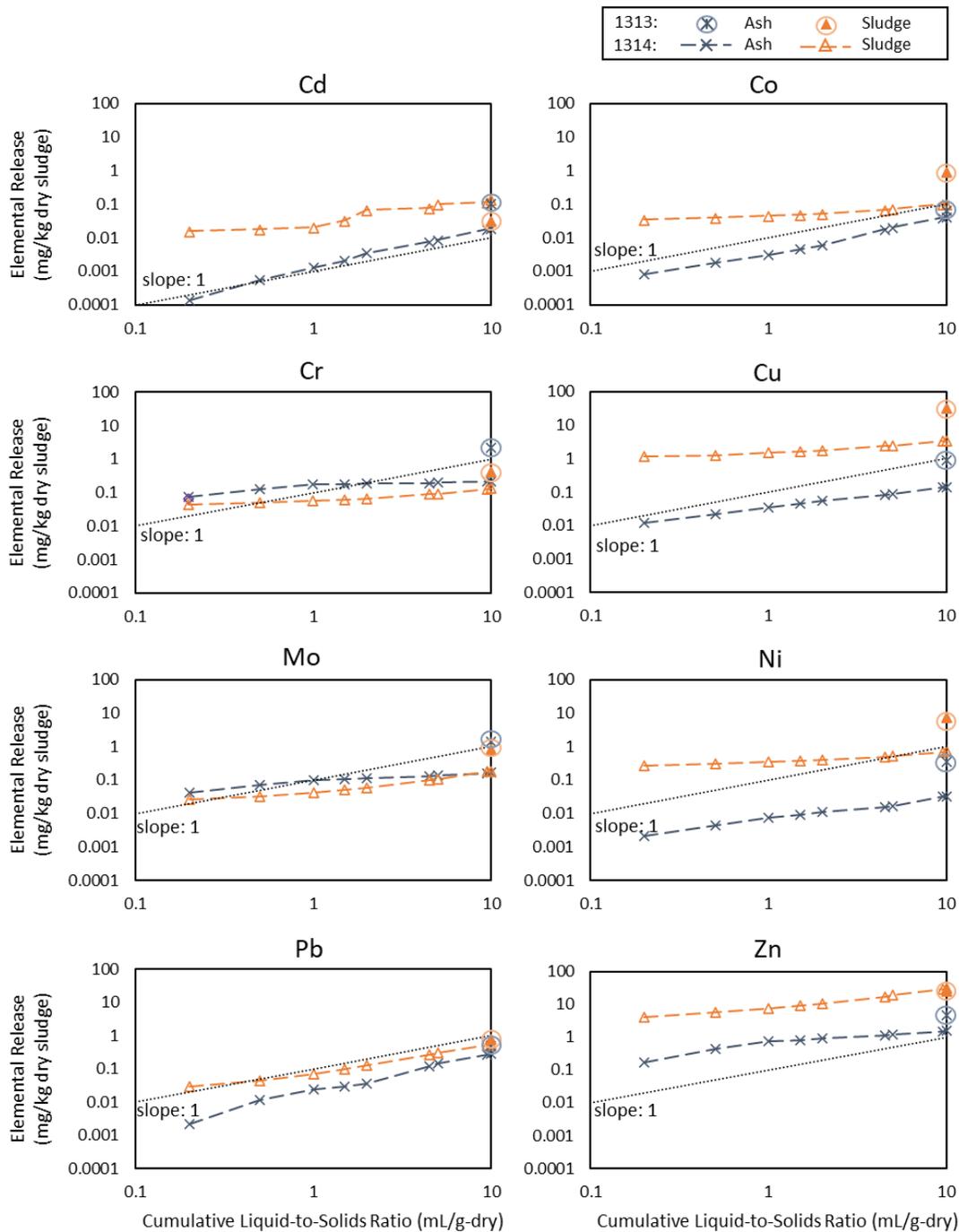
Element	Concentration (mg/kg-dry matter) \pm SE ^a						Regulatory standard O. Reg. 338: NASM CM1 (mg/kg-dry mass)
	Sludge	Woodchips	Ash ^b	Mixed Ash ^c	Woodchip Ash ^d	Sand ^e	
Target							
P	26000 \pm 3000	480 \pm 90	43000 \pm 6000	13000 \pm 20	970 \pm 20	290 \pm 50	
PTEs							
Al	5400 \pm 300	1100 \pm 400	13000 \pm 1000	2400 \pm 90	3200 \pm 600	300 \pm 100	
Cd	2.6 \pm 0.2	0.3 \pm 0.4	2.0 \pm 0.8	1.0 \pm 0.1	1.2 \pm 0.05	0.06 \pm 0.01	3
Co	3.8 \pm 0.3	0.4 \pm 0.4	5.7 \pm 1	2.8 \pm 0.3	2.8 \pm 0.3	0.15 \pm 0.01	34
Cr	120 \pm 10	34 \pm 2	160 \pm 40	53 \pm 2	13 \pm 10	4.2 \pm 0.7	210
Cu	480 \pm 40	16 \pm 4	1500 \pm 400	290 \pm 7	23 \pm 8	3.5 \pm 2	100
Fe	53000 \pm 5000	2100 \pm 600	56000 \pm 20000	18000 \pm 1000	4200 \pm 800	620 \pm 200	
Mg	4200 \pm 400	1600 \pm 300	9000 \pm 1000	4200 \pm 90	2900 \pm 500	37 \pm 13	
Mn	260 \pm 30	200 \pm 40	690 \pm 50	330 \pm 9	540 \pm 30	4.1 \pm 1	
Mo	22 \pm 2	1.4 \pm 0.6	26 \pm 2	6.2 \pm 0.3	3.7 \pm 1	1.9 \pm 0.3	5
Ni	47 \pm 6	13 \pm 2	87 \pm 10	25 \pm 1	25 \pm 4	1.7 \pm 0.2	62
Pb	110 \pm 10	70 \pm 10	110 \pm 60	31 \pm 4	29 \pm 4	8.4 \pm 0.2	150
Zn	630 \pm 90	64 \pm 30	1400 \pm 500	350 \pm 10	77 \pm 7	7.8 \pm 3	500

782 ^a Standard error calculated as $\frac{\sigma}{\sqrt{n}}$ 783 ^b Ash is considered all materials from smouldering experiments of sand mixed with sludge finer than 0.250 mm (< #60 sieve)784 ^c Post-treatment ash from co-smouldering experiments consisted of sludge mixed with woodchips785 ^d Woodchip ash generated in the lab according to ASTM-D2866-11786 ^e The sand is considered all materials from smouldering experiments of sand mixed with sludge coarser than 0.250 mm (> #60 sieve)

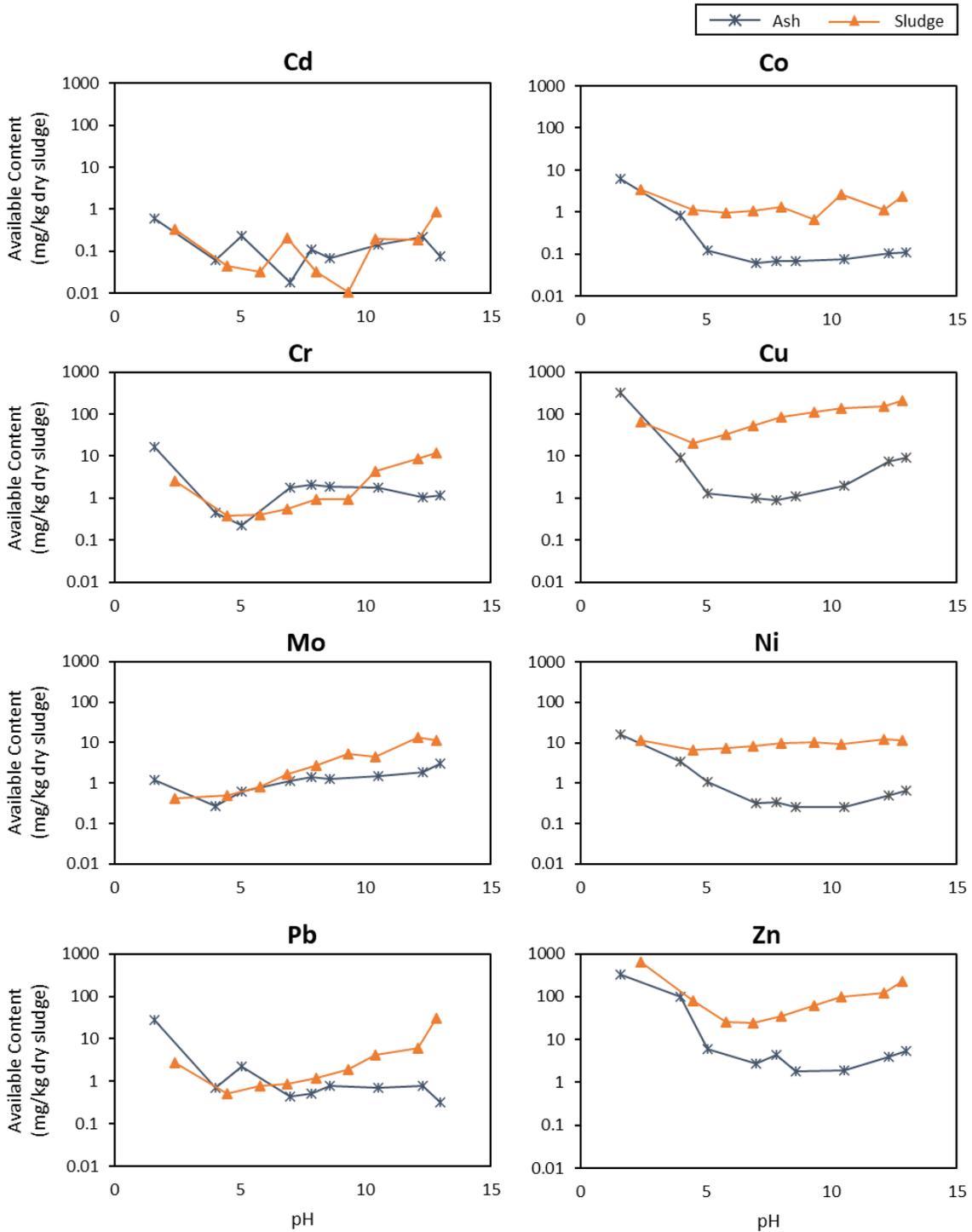


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788 *Figure 1: a. column percolation experimental results (following USEPA Method 1314), b. pH-*
 789 *dependent leaching (following USEPA Method 1313) of phosphorus from the virgin sludge and*
 790 *post-treatment ash and sand. The total phosphorus is shown with dotted lines and inorganic*
 791 *phosphorus with solid lines. All values have been normalized to mg of P per kg of dry sludge, and*
 792 *the release is presented as a function of the cumulative liquid-to-solids ratio.*



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 794 *Figure 2: column percolation experimental results (following USEPA Method 1314) for 8*
 795 *commonly regulated potentially toxic elements from the virgin sludge and post-treatment ash*
 796 *and sand. The elemental release is shown as cumulative release as a function of the liquid-to-solid*
 797 *ratio. The values have been normalized to mg of element per kg of dry sludge. The available*
 798 *content of the materials from USEPA Method 1313 at native pH has been plotted at an L/S of 10*
 799 *mL/g-dry. A dotted line with a slope of 1 has been added to each plot. A slope of an element*
 800 *release curve near 1 demonstrates solubility-limited processes governing elemental release while*
 801 *a slope less than 1 demonstrates that availability-limited processes.*



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803 *Figure 3: pH-dependent leaching (following USEPA Method 1313) of 8 potentially toxic elements*
 804 *from the virgin sludge compared to the post-treatment ash and sand. All values have been*
 805 *normalized to mg of phosphorus per kg of dry sludge.*

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807 Table 3: Extraction Potential from the Sludge and Sand with Ash

Element	Initial Content (mg/kg-dry matter) ± SE ^a	Percentage extracted from total content in sludge ± SE ^a (%)					
		Water ^b		pH 2 ^c		pH 13 ^c	
	Sludge	Sludge	Sand + Ash ^d	Sludge	Sand + Ash ^d	Sludge	Sand + Ash ^d
Target							
P	26000 ± 3000	0.6 ± 0.06 ^{AL}	1.8 ± 0.4 ^{SL}	5 ± 0.5	42 ± 8	68 ± 7	19 ± 3
High Recoverable Content (> 100 mg /kg-dry sludge)							
Fe	53000 ± 5000	0.1 ± 0.01 ^{SL}	0.3 ± 0.1 ^{SL}	5 ± 0.4	30 ± 9	11 ± 1	0.1 ± 0.1
Al	5400 ± 300	0.04 ± 0.01 ^{AL}	0.2 ± 0.1 ^{SL}	4 ± 0.2	32 ± 11	60 ± 3	19 ± 7
Mg	4200 ± 400	16 ± 2 ^{SL}	31 ± 15 ^{AL}	72 ± 7	65 ± 24	7 ± 1	0.4 ± 0.1
Zn	630 ± 90	4 ± 1 ^{SL}	0.3 ± 0.1 ^{SL}	100 ± 14	22 ± 6	36 ± 5	0.7 ± 0.2
Cu	480 ± 40	7 ± 1 ^{AL}	5 ± 4 ^{AL}	14 ± 1	61 ± 27	43 ± 3	11 ± 8
Mn	260 ± 30	5 ± 1 ^{AL}	7 ± 3 ^{AL}	75 ± 7	74 ± 33	16 ± 2	0.4 ± 0.2
Low Recoverable Content (< 40 mg /kg-dry sludge)							
Cr	120 ± 10	0.3 ± 0.02 ^{AL}	2 ± 1 ^{AL}	2 ± 0.2	14 ± 5	10 ± 1	3 ± 1
Pb	110 ± 10	0.7 ± 0.1 ^{SL}	1.2 ± 0.6 ^{SL}	2 ± 0.3	32 ± 18	27 ± 3	0.9 ± 0.3
Ni	47 ± 6	16 ± 2 ^{AL}	1.4 ± 0.8 ^{AL}	25 ± 3	18 ± 12	25 ± 3	4 ± 2
Mo	22 ± 2	4 ± 0.4 ^{SL}	9 ± 6 ^{AL}	2 ± 0.2	7 ± 4	54 ± 6	30 ± 19
Co	3.8 ± 0.3	25 ± 2 ^{AL}	1 ± 1 ^{SL}	90 ± 7	42 ± 10	62 ± 5	2 ± 2
Cd	2.6 ± 0.2	1.3 ± 0.1 ^{SL}	1.2 ± 0.4 ^{SL}	13 ± 1	18 ± 5	34 ± 3	3 ± 1

808 ^a Standard error calculated as $\frac{\sigma}{\sqrt{n}}$

809 ^b Extraction at native pH where samples were mixed with only deionized water (pH 6 for sludge, 7 for sand, and 8 for ash)

810 ^c The actual sample pH values are within ± 0.5 pH units of the specified value

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

812 ^{SL} Material identified as 'solubility-limited' based on the column percolation results following USEPA Method 1314

813 ^{AL} Material identified as 'availability-limited' based on the column percolation results following USEPA Method 1314

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