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Phosphorus Recovery and Reuse Potential from Smouldered Sewage Sludge Ash

T. Fournie, T.L. Rashwan, C. Switzer, J.I. Gerhard

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

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

c Department of Civil and Environmental Engineering, University of Strathclyde, G1 1XQ Glasgow, UK

1 Present address

*Corresponding author
Abstract

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

Phosphorus, Smouldering, Sewage sludge, Potentially Toxic Elements, Land application, Recovery
1.0 Introduction

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

However, recovery and reuse of phosphorus from sludge remains a challenge for numerous reasons. For example, several concerns arise when considering the direct application of sewage sludge as a fertilizer. High water and organic matter content, pathogens, and numerous compounds of concern in the sludge can require sludge processing prior to such use (Donatello
Thermal processes for managing sewage sludge are now common in the industry. For example, incinerating allows for volume reduction and contaminant destruction (Adam et al., 2009). However, the pre-drying required to facilitate sludge incineration makes the treatment process energy intensive and expensive (Khiari et al., 2004; Werther and Ogada, 1999).

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

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

A recent study identified that smouldered sewage sludge ash is likely safe for landfilling (Feng et al., 2020). However, landfilling ignores the recovery potential of limited resources such as phosphorus (Donatello and Cheeseman, 2013b; Fang et al., 2020). Moreover, recovering potential toxic elements (PTEs) – such as chromium and zinc – from sewage sludge ash has a twofold benefit of removing these PTEs from a pathway into the environment and providing...
value-added recovery (Westerhoff et al., 2015), especially from compounds present in high
concentrations (Bosshard et al., 1996).

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

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

2.0 Materials and Methods

2.1. Smouldering Experiments

2.1.1. Treatment System

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

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

For the sludge/sand test, the sludge was batch dried in an oven at 105°C, achieving a moisture content of 3.81% (ASTM-D267-17). Coarse silica sand (1.180 ≤ mean grain diameter ≤ 2.000 mm, porosity = 0.37, bulk density = 1670 kg/m³, Number 12, Bell & Mackenzie) was mixed with processed sludge as is typical for industrial smouldering treatments. For this experiment, 8.53 kg of sludge was mechanically mixed with 218 kg of coarse silica sand to achieve a sand-to-sludge ratio of 25.5:1 on a dry-mass basis. If the sludge had not been dried, the sand-to-sludge ratio would have been 6.5:1 on a wet-mass basis which has been shown to result in self-sustaining smouldering (Rashwan et al., 2021a) The mixture was prepared in small batches of ~22 kgs in a mechanical mixer before being transferred to sealed 19 L buckets for storage prior to loading. This methodology provided a homogeneous sludge sample that was stable over time.
On the experiment day, the sludge mixture was carefully added into the reactor in a way that ensure homogeneity and limited material compaction (SM, Section S1). The emptied buckets were reweighed to account for any material retained during packing. A clean sand cap (3 – 6 cm thick) was added on top of the sludge pack as done in commercial applications. Air was injected into the reactor base at a Darcy flux of 5.0 cm/s throughout the test via a mass flux controller (8290B045PDB67 ASCO Numatics). An inline air heater (F074736 36 kW SureHeat® MAX, Osram Sylvania), operated at 300 – 400°C from the beginning of the test, provided convective ignition of smouldering as is done in the field (Solinger et al., 2020). The experiment required ~61 min for ignition (~34 min to increase the heater temperature and an additional ~27 min preheat). Smouldering of the sludge was confirmed when the first thermocouple within the contaminant pack peaked at 480°C (see SM, Figure S1-2). Following ignition, the heater was turned off and ambient air was injected into the reactor, supporting a self-sustaining smouldering reaction propagating up the reactor. The reaction velocity was 0.38 cm/s ± 10% and the average centreline peak temperature was 525°C ± 4%, which are representative of laboratory and field applications (Torero et al., 2020; Wyn et al., 2020). The experiment was complete and self-terminated once the smouldering front reached the end of the contaminant pack (after 180 minutes). The emissions data aligned with what is typically observed during smouldering (Wyn et al., 2020) and showed that smouldering was robust, and the fuel was fully oxidized. These results were confirmed upon excavation.

The post-treatment bed consisted of coarse silica sand (conserved during treatment) and sewage sludge ash. Dry sieving separated them, with sand grains quantified as >0.250 mm (#60 ASTM
sieve) and ash quantified as the finer inert mass. The sand summed to 26.5 kg while ash comprised 0.56 kg (97.9% and 2.1% of post-treatment materials, respectively).

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

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

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

Ignition by convection was completed in 58 min (~39 min to increase the heater temperature and an additional ~19 min preheat). The heating period caused moisture loss via evaporation and boiling, only in the bottom ~2 cm of the 45 cm tall bed. As expected, – and in contrast to the sludge/sand test – the front did not migrate up the column. Instead, the self-sustained reaction
slowly consumed the base of the pack – since it was nearly entirely smoulderable – and the pack
steadily shrunk downwards. The experiment was complete after 280 minutes, when the fuels
were completely consumed (SM, Figure S1-3). The average centreline temperature was 812°C ±
4%. The post-treatment ash was 20% of the initial mass of the mixture (i.e., 13.5 kg), and was
estimated to comprise 87% sludge ash and 13% woodchip ash. Since a single post-treatment ash
was produced, no sieving was required prior to analysis. The top sand cap was not used in this
experiment.

2.2. Analytical Materials and Methods

The chemical composition of the solids and elemental concentrations in all extracts were
determined using an Agilent 720 Inductive Coupled Plasma Optical Emission Spectrometer (ICP-
OES) (Agilent Technologies). Analyses were conducted in accordance with standard procedures,
including quality control/quality assurance, outlined by USEPA Method 6010D (Element Symbol
CAS Number, 2007). Solids were analyzed after acid extraction with a 3:1 ratio of concentrated
nitric acid (HNO₃) and hydrochloric acid (HCl), assisted by microwave digestion (170 °C for 10 min
in a CEM MARS 6® Microwave Accelerated Reactor System, MFR) according to USEPA Method
3051A (Element, 2007).

Inorganic phosphorus was measured as dissolved orthophosphate (PO₄³⁻), the most reactive form
of inorganic phosphorus, which is readily soluble and therefore easily utilized by plants (Johnston
et al., 2014). High-Performance Liquid Chromatography (HPLC) was used to quantify PO₄³⁻ via
direct injection using a Water® 515 pump following the standard procedure outlined by USEPA
Method 300 (Pfaff, 1993).
Elements analyzed by ICP-OES included phosphorus, aluminum, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, lead, and zinc, all of which are regulated at WWTPs in Ontario, Canada. For reuse applications, cadmium, cobalt, chromium, copper, molybdenum, nickel, lead, and zinc are also regulated under Ontario Regulation 338/09 (O. Reg. 338) from the Nutrient Management Act (2002). O. Reg. 338 classifies sewage sludge as a category 3 non-agricultural source material (NASM) and sets guideline values for reuse applications. CM1 is the most stringent set of NASM guideline values in the O. Reg. 338 guideline.

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

This study conducted a series of batch extractions on 5 pre- and post-treatment materials following USEPA Method 1313, measuring phosphorus and 12 other PTEs in the extracts. USEPA Method 1313 consists of 9 parallel batch extractions to produce a liquid-solid partitioning curve of the material of interest over eluate pH range $2 \leq \text{pH} \leq 13 \pm 0.5$ (USEPA, 2012a). Briefly, for each extraction, 10 g of material was combined with 100 mL of extraction solution that consisted of deionized water with varied amounts of either 2 N nitric acid ($\text{HNO}_3$) or 1 N potassium hydroxide (KOH) to achieve the 9 specified target pH values. All extractions took place over 24 hours to achieve equilibrium between the solid and liquid phases. The pH and electrical conductivity of the supernatants were measured, and eluate samples were filtered and preserved for further analysis.

2.4. Column Percolation Tests (USEPA Method 1314)

Percolation tests were also conducted on 3 materials to measure phosphorus and 12 other PTEs using the USEPA Method 1314. This method uses a percolation column experiment to evaluate
constituent release from the material of interest as a function of the liquid-to-solid ratio (L/S) (USEPA, 2012b). A full description of the process has been described elsewhere (Fournie et al., 2021). Briefly, 300 g of pulverized, air-dried sample is packed into a 30 cm tall glass column. Deionized water was injected using a Masterflex® L/S® digital peristaltic pump with flow moving upwards through the column. Prior to continuous percolation, the column was rested for 24 hours in a fully saturated state. After the rest period, the flow rate of the water through the column was maintained at 0.75 ± 0.5 L/S per day to collect the nine eluate samples (T01-T09) at 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. Each eluate sample was analyzed for pH and conductivity using a Fisher Scientific Accumet® AB200 pH/mV/Conductivity meter within one hour of sample collection. Subsamples were filtered and preserved with 1 N nitric acid for further analysis.

2.5. Extraction Potential

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

Subsequently, each element was identified as either solubility- or availability-limited by plotting cumulative element release as a function of the liquid-to-solid ratio measured in Method 1314 on a log-log scale (Kosson et al., 2017).

**3.0 Results and Discussion**

**3.1. Material Characterization**

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

For the co-smouldering test, the woodchips comprised 23% of the pre-treatment mixture, sludge was 59%, and water was 18%. This test experienced higher energy smouldering (due to increased fuel loading), with average peak temperatures of 812°C ± 4% (SM, Figure S1-3). The temperatures...
were more similar to temperatures observed during sludge incineration. The post-treatment mixture (herein referred to as ‘mixed ash’) was 20% of the initial mass (i.e., 20% ash content).

Initial phosphorus was 19,000 mg/kg-dry starting material in the co-smouldering test, diluted in comparison to the test with sand because of much higher water content and addition of woodchips. After the higher energy combustion, 22% of phosphorus (split 32/68 ± 13% organic/inorganic) was retained in mixed ash and 78% was recoverable from process emissions.

Concentrations of the 12 quantified PTEs are presented in Table 2. The PTE concentrations are presented on a dry-mass basis for direct comparison to the O. Reg. 338 NASM CM1. All 12 PTEs were detected in all materials. However, PTE concentrations within sand were very low, 1 – 4% of the concentration originally present in the sludge. Concentrations in ash were often higher than those in virgin sludge (aluminum, cobalt, chromium, copper, magnesium, manganese, molybdenum, nickel, lead, and zinc) on this basis because smouldering reduced total mass by nearly 80%, which had a concentrating effect on elements not released to emissions or retained by sand. With negligible PTE content in the sand prior to smouldering, the observed PTE concentrations were likely contributed by ash retention within the sand fraction during dry sieve separation and/or condensation onto sand surfaces. However, because of its large mass in the system, sand provided an important sink for some elements such as lead, nickel, and chromium (SM, Table S2-2), reducing their total content in ash. The PTE concentrations in the mixed ash were lower than the virgin sludge for 10 of the 12 elements (aluminum, cadmium, cobalt, chromium, copper, iron, molybdenum, nickel, lead, and zinc) by 30 – 70%. The reduced PTE concentrations in the mixed ash were likely due to dilution by the woodchips and release to emissions via the higher energy smouldering.
When considered on a dry-sludge basis, total elemental contents between the materials are similar (see SM, Figure S2-1). Essentially complete retention of aluminum, cobalt, chromium, manganese, nickel, and lead by bottom ash (i.e., material retained in the reactor) was observed with 100% retained in ash and sand (SM, Table S2-2). Less than complete retention was observed for cadmium (87%), copper (67%), iron (60%), magnesium (74%), molybdenum (56%), phosphorus (69%), and zinc (93%), suggesting availability for recovery via emissions. For the mixed ash, low retention in the bottom ash is observed for all elements; aluminum (15%), cadmium (15%), cobalt (28%), chromium (14%), copper (25%), iron (14%), magnesium (29%), manganese (27%), molybdenum (11%), nickel (17%), phosphorus (22%), lead (6%), and zinc (22%) (SM, Table S2-3). These elements are available for recovery via emissions capture, which is commonly employed for incinerators (Cieślik and Konieczka, 2017). Lower retention in mixed ash was likely the result of (1) increased volatilization due to the higher energy smouldering (see Table 1), and (2) physical mobilization of elements in the exhaust gas.

The O. Reg. 338 NASM CM1 (Government of Ontario, 2009) PTE thresholds for land application are given in Table 2. Based on the guidelines, copper, molybdenum, nickel, and zinc were exceeded in the sludge, ash, or both. Conversely, cadmium, cobalt, chromium, and lead were not exceeded in any material. Only copper and molybdenum were exceeded in the mixed ash. Sludge and ash exceeded the guideline values for copper, molybdenum, zinc, and ash additionally exceeded for nickel. The current land application guidelines under O. Reg. 338 specify the maximum quantity of total regulated PTEs that can be added to a specific area of soil in a 5-year period (Government of Ontario, 2009). If the amount of ash required for land application is lowered because of well-regulated phosphorus, these exceedances may be avoidable. The
following sections discuss reuse options for the smouldered ash via land application and alternatively, extraction of elements from the ash to subsequently recycle.

3.2. Suitability for Land Application

3.2.1. Phosphorus Availability and Release

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

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

In contrast, a smaller initial slug, 81% organic, was released from the ash representing <0.001% of total phosphorus content in ash and <1% of total release (Figure 1a). The release profile transitioned to 36-59% inorganic phosphorus later in the test. Release never reached an equilibrium and seemed likely to continue releasing primarily inorganic phosphorus beyond the
cumulative L/S of 10 mL/g-dry. Therefore, smouldering transformed phosphorus species into
more solubility-limited forms (SM, Figure S3-1). Of the cumulative phosphorus released from the
ash, 0.09% of total phosphorus, 41% was organic phosphorus and 59% was inorganic. Over time,
ash became a better source of inorganic phosphorus that is more valuable to plants. The available
phosphorus from the ash was also primarily inorganic, composing 70-100% and varying with pH
(Figure 1b). At native pH, ash had less available total and inorganic phosphorus compared to
sludge at its native pH, i.e., pH 7.82 for the ash and 5.8 for the sludge. As pH changes, availability
from ash increased by 4400 mg/kg – DS at pH 1.57 or 1800 mg/kg – DS at pH 13.

Release from the sand fraction showed similar patterns to both sludge and ash (Figure 1a). Initial
phosphorus release from the sand, 88% organic, represents 0.2% of total phosphorus content in
sand and 7% of total release. The normalized release from the sand was immediately higher than
the ash and rapidly exceeded the release from the sludge between an L/S of 1 and 1.5 mL/g-dry.
Of the cumulative phosphorus released from the sand (i.e., 2.4% of its total content), 90% was
organic phosphorus and 10% was inorganic, suggesting a condensation effect on the sand. Some
of the organic phosphorus that was volatilized during smouldering may condense within the
cooler fixed sand bed ahead of the reactions, retaining a portion of it within the sand that would
otherwise be released in the emissions. This was consistent throughout the experiment (88 –
90% organic and 10 – 12% inorganic) and further observed from the pH-dependent availability
results (89 – 94% organic) (Figure 1b). Based on the release profile, sand seemed likely to
continue to release phosphorus beyond the highest L/S in Figure 1a, thereby demonstrating a
solubility-limited process similar to the ash. Furthermore, sand has minimal pH-dependence
(Figure 1b), achieving a limited range of phosphorus availability, 440-770 mg/kg – DS, over environmental relevant pH conditions (3.55<pH<10.98).

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

3.2.2. Potentially Toxic Elements

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

Ash exhibited lower releases of 6 of 8 PTEs (Figure 2). Initial releases of cadmium, cobalt, copper, nickel, lead, and zinc from sludge exceeded those from ash by 93-99%, and cumulative releases from sludge exceeded ash by 50-96%. Of these, cobalt, copper, and nickel were availability-limited in the sludge (Figure 3). The lower relative pH of the sludge (pH 5.8) compared to the ash (pH 7.8), may explain the higher initial release of the availability-limited PTEs from the sludge since chemical changes would influence the release of these elements more than increased percolation (SM, Figure S3-2). While ash had higher total elemental concentrations compared to sludge (Table 2), higher total elemental concentrations did not translate to higher element releases. The relatively higher release of the other PTEs from the sludge than ash could be the result of mineralization during smouldering.
Releases of chromium and molybdenum, the two elements where release from ash exceeded that from sludge, were low from both materials. These two PTEs and lead were similar to or slightly more available from the ash than sludge under environmentally relevant conditions (i.e., pH 5.5–8.5; Figure 3). In contrast, availabilities of cobalt, copper, nickel, and zinc from sludge exceeded their availabilities from ash across the pH range most relevant to land application.

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

3.3. Extraction Potential

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

Phosphorus released from ash and sand were both solubility-limited (Figure 1); increasing the L/S above 10:1 could further increase the amount of phosphorus recovered from ash and sand. However, increasing the L/S would also increase PTE content in the solution, especially of cadmium, cobalt, lead, and zinc, which were all identified as solubility-limited (see Table 2).

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

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

Alkaline extraction from sludge recovered 68% of initial phosphorus (17,700 mg/kg – IS) and was also enriched with iron (11%, 5830 mg/kg – IS) and aluminium (60%, mg/kg – IS). The extractant solution also contained measurable amounts of magnesium (7%, mg/kg – IS), zinc (37%, 230 mg/kg – IS), copper (44%, 210 mg/kg – IS), manganese (16%, 42 mg/kg – IS), lead (27%, 30 mg/kg – IS), chromium (10%, 12 mg/kg – IS), nickel (26%, 12 mg/kg – IS), and molybdenum (55%, 12
mg/kg – IS). Subsequent separation of PTEs would likely be required, similar to acidic extraction from the ash. Water extraction was not a viable method for any material.

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

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

3.4. Discussion of Land Application and Recovery Opportunities
3.4.1. Sludge smouldered in an inert porous media

The best opportunity to create a valuable product for land application is smouldering sludge with sand which resulted in 78% phosphorus retention in the bottom ash. Furthermore, the ash contained more inorganic phosphorus than either the sludge or sand fraction which is more beneficial to plants. This inorganic phosphorus was released more slowly than the phosphorus from sludge, which experienced early washout, losing 60% of total released content almost immediately. Following the early release, remaining phosphorus species within the sludge were less available and therefore less useful to plants without additional weathering or solubilization by plants and microbes, which can be slow and often insufficient for plant needs (Arcand and Schneider, 2006). Interpreting column percolation (Figure 1a) and pH-dependent availability (Figure 1b) results together suggests that the sludge was already more acidic when applied and therefore its phosphorus was already more available in the immediate term. Early washout of available phosphorus from sludge can (1) contribute to eutrophication and (2) require sludge to be applied more frequently to meet plant nutrient needs. Comparatively, the phosphorus from the ash became more available with decreasing pH (relative to starting pH), which means a steadier supply of phosphorus to plants as pH becomes slightly more acidic with repeated plant growth cycles. With a high abundance of desirable, inorganic phosphorus in the ash, significantly less ash is likely to be needed for land application relative to sludge. Release of most retained PTEs was already lower from the ash and applying less ash would further reduce PTE release. The behaviour of phosphorus release and availability for the sand, supports the idea that a small amount of ash was retained in the sand fraction during dry sieving. Since sand comprises 98% of the mass of post-treatment materials (2% ash), mechanical separation of the ash and sand would
make land application of the ash more practical and economically feasible. Moreover, although sand meets land application guidelines for PTEs (Table 2), a large mass of sand would be required to meet plant nutrient requirements, which would be labour intensive and costly. Since the sand retained 30% of phosphorus (90% organic), wet sieving could be used to fully remove ash from the sand fraction and potentially recover some of the additional phosphorus retained on the sand while removing other PTEs (most notably lead, nickel, and chromium). Future work involving plant growth studies and multiple growth cycles may be beneficial to (1) optimize amounts of ash required to support plant growth and (2) determine the phosphorus flux from ash.

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

3.4.2. Co-smouldering sludge with organic waste

Of the alternatives assessed, the best opportunity for direct recovery of phosphorus is smouldering sludge with woodchips (or another low-impurity, high-energy fuel) and capturing the gases (SM, Table S3-3). While emissions recovery was not rigorously quantified in this research, it is an important source of recoverable phosphorus that will be explored in future work on smouldering systems. The remaining phosphorus in the resultant mixed ash can be recovered easily with an acidic extractant (pH 2). Between the emissions capture (78%) and extraction from ash (21% at pH 2), close to 100% of phosphorus could be recovered from sludge (and woodchips).

The significant phosphorus volatilization observed during co-smouldering of sewage sludge is commonly observed during incineration (Cieślik and Konieczka, 2017). Similar to chemical extraction, recovering phosphorus from the emissions stream would require additional processing to separate out other PTEs. To minimize disposal requirements from processing, the extraction waste and emissions waste could be combined and recycled for other purposes such as an additive in construction materials (Cieślik and Konieczka, 2017). Co-smouldering presents both operational and procedural advantages. Since both the sludge and woodchips are combustible, only inert ash remains (20% initial mass) making phosphorus recovery simpler and more economical. Phosphorus extraction from the mixed ash would require 1.3 m$^3$ extractant solution/tonne virgin sludge which is 88% less extractant volume than would be required for virgin sludge. Another advantage of treating fully organic waste beds is their capacity to be
straightforwardly designed as continuous or semi-continuous smouldering systems, where fuel (e.g., sludge/woodchips) is continuously added to the reactor with potential to remove ash from the base. A system of this nature could eliminate time and costs of reignition. Furthermore, continuous smouldering would behave similarly to current incinerator configurations at WWTPs, making adaptation of the process highly feasible.

4.0 Conclusions

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

Considering extraction as an alternative to direct land application, no single extraction from any material is ideal for phosphorus recovery, before or after smouldering. However, co-smouldering
sludge with woodchips could enable close to 100% phosphorus recovery when extraction from the post-treatment ash (21% phosphorus at pH 2) is combined with emissions capture (78% phosphorus). Further separation of phosphorus and PTEs would still be required from the emissions stream which contained >70% of PTEs originally present in the parent sludge. Overall, co-smouldering sewage sludge with woodchips (or another low-impurity, high-energy fuel) has numerous benefits, including (1) treating multiple waste streams, (2) producing a single post-treatment ash, (3) being apt for continuous operation, and (3) increasing treatment temperatures, which may provide further opportunities for treating additional persistent contaminants in the parent sewage sludge.

5.0 Acknowledgements

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column percolation test assistance provided by Brendan Evers, and data analysis assistance provided by Reagan Campbell, and additional project support from Gudgeon Thermfire International (particularly from Justin Barfett and Randy Adamski), London Ontario’s Greenway Wastewater Treatment Centre (especially from Randy Bartholomew, Michael Wemyss, and Anthony Van Rossum), Dr. Gavin Grant, Cody Murray, Megan Green, Joshua Brown, Thomas Mathias, and Dillon McIntyre.

**Supplementary Materials**

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


Kijo-Kleczkowska, A., Środa, K., Kosowska-Golachowska, M., Musiał, T., Wolski, K., 2016. Experimental research of sewage sludge with coal and biomass co-combustion, in pellet


Pfaff, J.D., 1993. Method 300.0 Determination of inorganic anions by ion chromatography.


smoldering treatment of waste oil sludge: Proof of concept and sensitivity to key design parameters: https://doi.org/10.1177/0734242X20904430 38, 554–566.
https://doi.org/10.1177/0734242X20904430


### Table 1: Material composition and experimental data

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Units</th>
<th>Sludge &amp; Sand</th>
<th>Sludge &amp; Woodchips</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Moisture Content&lt;sup&gt;a&lt;/sup&gt;</td>
<td>%</td>
<td>3.81</td>
<td>3.22</td>
</tr>
<tr>
<td>Volatile Matter&lt;sup&gt;b&lt;/sup&gt;</td>
<td>% (dry basis)</td>
<td>61.0</td>
<td>-</td>
</tr>
<tr>
<td>Ash Content&lt;sup&gt;c&lt;/sup&gt;</td>
<td>% (dry basis)</td>
<td>27.5</td>
<td>26.6</td>
</tr>
<tr>
<td>Fixed Carbon&lt;sup&gt;d&lt;/sup&gt;</td>
<td>% (dry basis)</td>
<td>11.4</td>
<td>-</td>
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<tr>
<td><strong>Experimental Data</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Mixture Ratio</td>
<td>Wet Basis</td>
<td>Sand: Sludge 6.5: 1</td>
<td>Woodchips: Extra Water&lt;sup&gt;e&lt;/sup&gt;: Sludge 0.4: 0.3: 1</td>
</tr>
<tr>
<td></td>
<td>Dry Basis</td>
<td>(g/g)</td>
<td>(g/g)</td>
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<td>Mass of Materials Added</td>
<td>Sludge</td>
<td>kg</td>
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</tr>
<tr>
<td></td>
<td>Sand</td>
<td>kg</td>
<td>217.7</td>
</tr>
<tr>
<td></td>
<td>Woodchips</td>
<td>kg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>kg</td>
<td>-</td>
</tr>
<tr>
<td>Air Flux</td>
<td>cm/s</td>
<td>5.5</td>
<td>2.5 – 5.0</td>
</tr>
<tr>
<td>Average Centreline Temperature</td>
<td>°C</td>
<td>525&lt;sup&gt;f&lt;/sup&gt;</td>
<td>812&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined according to ASTM-D267-17
<sup>b</sup> Determined according to ASTM-D5832-98
<sup>c</sup> Determined according to ASTM-D2866-11
<sup>d</sup> Calculated as the difference
<sup>e</sup> Water was added to the fuel mixture to reduce treatment temperatures
<sup>f</sup> The thermocouple temperature results have an associated error of ± 4%
Table 2: Total elemental concentrations

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/kg-dry matter) ± SE&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Regulatory standard O. Reg. 338: NASM CM1 (mg/kg-dry mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge</td>
<td>Woodchips</td>
</tr>
<tr>
<td>Target</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>26000 ± 3000</td>
<td>480 ± 90</td>
</tr>
<tr>
<td>PTEs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>5400 ± 300</td>
<td>1100 ± 400</td>
</tr>
<tr>
<td>Cd</td>
<td>2.6 ± 0.2</td>
<td>0.3 ± 0.4</td>
</tr>
<tr>
<td>Co</td>
<td>3.8 ± 0.3</td>
<td>0.4 ± 0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>120 ± 10</td>
<td>34 ± 2</td>
</tr>
<tr>
<td>Cu</td>
<td>480 ± 40</td>
<td>16 ± 4</td>
</tr>
<tr>
<td>Fe</td>
<td>53000 ± 5000</td>
<td>2100 ± 600</td>
</tr>
<tr>
<td>Mg</td>
<td>4200 ± 400</td>
<td>1600 ± 300</td>
</tr>
<tr>
<td>Mn</td>
<td>260 ± 30</td>
<td>200 ± 40</td>
</tr>
<tr>
<td>Mo</td>
<td>22 ± 2</td>
<td>1.4 ± 0.6</td>
</tr>
<tr>
<td>Ni</td>
<td>47 ± 6</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>Pb</td>
<td>110 ± 10</td>
<td>70 ± 10</td>
</tr>
<tr>
<td>Zn</td>
<td>630 ± 90</td>
<td>64 ± 30</td>
</tr>
</tbody>
</table>

<sup>a</sup> Standard error calculated as $\frac{\sigma}{\sqrt{n}}$

<sup>b</sup> Ash is considered all materials from smouldering experiments of sand mixed with sludge finer than 0.250 mm (< #60 sieve)

<sup>c</sup> Post-treatment ash from co-smouldering experiments consisted of sludge mixed with woodchips

<sup>d</sup> Woodchip ash generated in the lab according to ASTM-D2866-11

<sup>e</sup> The sand is considered all materials from smouldering experiments of sand mixed with sludge coarser than 0.250 mm (> #60 sieve)
Figure 1: a. column percolation experimental results (following USEPA Method 1314), b. pH-dependent leaching (following USEPA Method 1313) of phosphorus from the virgin sludge and post-treatment ash and sand. The total phosphorus is shown with dotted lines and inorganic phosphorus with solid lines. All values have been normalized to mg of P per kg of dry sludge, and the release is presented as a function of the cumulative liquid-to-solids ratio.
Figure 2: column percolation experimental results (following USEPA Method 1314) for 8 commonly regulated 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. A slope of an element release curve near 1 demonstrates solubility-limited processes governing elemental release while a slope less than 1 demonstrates that availability-limited processes.
Figure 3: pH-dependent leaching (following USEPA Method 1313) of 8 potentially toxic elements from the virgin sludge compared to the post-treatment ash and sand. All values have been normalized to mg of phosphorus per kg of dry sludge.
<table>
<thead>
<tr>
<th>Element</th>
<th>Initial Content (mg/kg-dry matter) ± SE</th>
<th>Percentage extracted from total content in sludge ± SE (%)</th>
<th>Water b</th>
<th>pH 2 c</th>
<th>pH 13 c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sludge</td>
<td>Sand + Ash d</td>
<td>Sludge</td>
</tr>
<tr>
<td>Target</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>26000 ± 300</td>
<td>0.6 ± 0.06 AL</td>
<td>1.8 ± 0.4 SL</td>
<td>5 ± 0.5</td>
<td>42 ± 8</td>
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<tr>
<td>High Recoverable Content (&gt; 100 mg /kg-dry sludge)</td>
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<td></td>
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<td></td>
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<tr>
<td>Fe</td>
<td>53000 ± 5000</td>
<td>0.1 ± 0.01 SL</td>
<td>0.3 ± 0.1 SL</td>
<td>5 ± 0.4</td>
<td>30 ± 9</td>
</tr>
<tr>
<td>Al</td>
<td>5400 ± 300</td>
<td>0.04 ± 0.01 AL</td>
<td>0.2 ± 0.1 SL</td>
<td>4 ± 0.2</td>
<td>32 ± 11</td>
</tr>
<tr>
<td>Mg</td>
<td>4200 ± 400</td>
<td>16 ± 2 SL</td>
<td>31 ± 15 AL</td>
<td>72 ± 7</td>
<td>65 ± 24</td>
</tr>
<tr>
<td>Zn</td>
<td>630 ± 90</td>
<td>4 ± 1 SL</td>
<td>0.3 ± 0.1 SL</td>
<td>100 ± 14</td>
<td>22 ± 6</td>
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<tr>
<td>Cu</td>
<td>480 ± 40</td>
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<td>61 ± 27</td>
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<tr>
<td>Mn</td>
<td>260 ± 30</td>
<td>5 ± 1 AL</td>
<td>7 ± 3 AL</td>
<td>75 ± 7</td>
<td>74 ± 33</td>
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<tr>
<td>Low Recoverable Content (&lt; 40 mg /kg-dry sludge)</td>
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<td></td>
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<tr>
<td>Cr</td>
<td>120 ± 10</td>
<td>0.3 ± 0.02 AL</td>
<td>2 ± 1 AL</td>
<td>2 ± 0.2</td>
<td>14 ± 5</td>
</tr>
<tr>
<td>Pb</td>
<td>110 ± 10</td>
<td>0.7 ± 0.1 SL</td>
<td>1.2 ± 0.6 SL</td>
<td>2 ± 0.3</td>
<td>32 ± 18</td>
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<tr>
<td>Ni</td>
<td>47 ± 6</td>
<td>16 ± 2 AL</td>
<td>1.4 ± 0.8 AL</td>
<td>25 ± 3</td>
<td>18 ± 12</td>
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<tr>
<td>Mo</td>
<td>22 ± 2</td>
<td>4 ± 0.4 SL</td>
<td>9 ± 6 AL</td>
<td>2 ± 0.2</td>
<td>7 ± 4</td>
</tr>
<tr>
<td>Co</td>
<td>3.8 ± 0.3</td>
<td>25 ± 2 AL</td>
<td>1 ± 1 SL</td>
<td>90 ± 7</td>
<td>42 ± 10</td>
</tr>
<tr>
<td>Cd</td>
<td>2.6 ± 0.2</td>
<td>1.3 ± 0.1 SL</td>
<td>1.2 ± 0.4 SL</td>
<td>13 ± 1</td>
<td>18 ± 5</td>
</tr>
</tbody>
</table>

a Standard error calculated as \( \frac{\sigma}{\sqrt{n}} \)

b Extraction at native pH where samples were mixed with only deionized water (pH 6 for sludge, 7 for sand, and 8 for 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)
Material identified as ‘solubility-limited’ based on the column percolation results following USEPA Method 1314

Material identified as ‘availability-limited’ based on the column percolation results following USEPA Method 1314