Abstract

Biologically available phosphorus supports plant growth but can also cause environmental contamination. Sequential extraction methods, such as Hedley fractionation, are the most widely used to assess available phosphorus from solids. However, such methods exhibit numerous deficiencies. The USEPA Leaching Environmental Assessment Framework (LEAF) is a tiered system developed to evaluate releases of Potentially Toxic Elements (PTEs) from solids. This study compared the Hedley fractionation method to the LEAF pH-dependent, parallel batch tests (Method 1313) and dynamic leaching column test (Method 1314) to assess the bioavailability of phosphorus. The three methods were applied to wastewater treatment plant sludge before and after thermal treatment. Both methods revealed similar qualitative trends, namely that thermal treatment transformed phosphorus into less immediately available forms. However, the Hedley and LEAF methods were inconsistent in the forms and amounts of available phosphorus recovered from the solids. The Hedley method left 40% of phosphorus unextracted from sludge and 20% from ash, suggesting that it may be less appropriate for organic materials. Moreover, only 2 of the 6 Hedley phosphorus pools were within environmentally relevant pH conditions. Furthermore,
the Hedley method overpredicted the readily available phosphorus. In contrast, the LEAF methods allowed for a more detailed analysis of phosphorus availability - while simultaneously assessing PTEs - across a controlled pH range. Moreover, LEAF used simpler procedures and provided more easily interpreted results. Thus, LEAF facilitates more robust and valuable assessment of organic and inorganic solids being considered for land application.
1. Introduction

Land application of solids, such as manure, inorganic fertilizers, and wastewater treatment plant (WWTPs) sludge, are valuable sources of phosphorus and other nutrients. However, accumulation of phosphorus within soils can increase leaching (1) as previously studied with applied manures (2,3) and inorganic fertilizers (1,4). Released phosphorus is transported through the subsurface or via runoff to surface waters (5); contributing to eventual eutrophication (6). Determining the biologically available (i.e., bioavailable) phosphorus in land applied solids is important for developing application guidelines, maximizing beneficial use, and establishing regulatory compliance.

Numerous methods have been developed to quantify phosphorus, especially bioavailable phosphorus, in a wide range of solids. Most literature and analytical methods focus on soils and the Hedley sequential fractionation method (7) dominates the field (8–10). Hedley uses progressively stronger chemical extractants to recover increasingly recalcitrant forms of phosphorus (11), inferring potential sources and sinks of phosphorus based on phosphorus quantity within various fractions. Bioavailable phosphorus is typically divided into several “pools” ranging from highly available to unavailable (12).

Hedley forms the basis for many related sequential fractionation methods (13–16). Common modifications to the Hedley method include (i) an initial deionized water step prior to anion exchange resin (15), (ii) excluding quantification of microbial phosphorus (16), (iii) eliminating sonication during the extraction of moderately-bound phosphorus (13), and (iv) using heated digestion to quantify residual (unavailable) phosphorus (14). Sequential phosphorus fractionation methods vary significantly in the type of chemical extractant and molarity used to quantify each pool (a summary of published methods can be found in Appendix A of the Supplementary Materials). Since phosphorus dissolution is highly pH dependent (17), extraction methods are likely to yield different results for available phosphorus depending on chosen extractants and procedure order (18,19). Furthermore, strong extractants can
change the chemical structure of phosphorus species (20–23). As a consequence, conclusions on phosphorus availability from studies using fractionation methods are inconsistent (18,24) and sometimes contradictory (25).

Studies assessing phosphorus availability in other solids including animal manure and sewage sludge have used modified versions of Hedley and soil phosphorus test procedures (15,26–29). Only a few studies have attempted to fractionate phosphorus in sewage sludge (15,27,30,31). Such evaluations are anticipated to suffer from the same problems identified for sequential fractionation of phosphorus in soils.

Following decades of development, the USEPA released the Leaching Environmental Assessment Framework (LEAF) in 2010. LEAF is a characterization-based leaching framework combining experimental data on relevant intrinsic leaching behaviour with scenario-specific information for environmental assessments (32). USEPA Method 1313 from LEAF consists of a series of parallel batch experiments to produce a liquid-solid partitioning curve of the material of interest as a function of pH (33). The complementary USEPA Method 1314 involves a column percolation experiment to obtain eluate concentrations and/or cumulative release as a function of the liquid-to-solids ratio (34). LEAF has been used to assess leaching behaviour of potentially toxic elements (PTEs) from coal fly ash (e.g., 33); municipal solid waste (MSW) incinerator ash (e.g., 34); concrete waste (37); and sewage sludge compost (38). Using LEAF to assess phosphorus is less common and has been used for inorganic phosphorus from mining waste (39,40). The methodology seems promising to evaluate bioavailable phosphorus for a wide range of organic/inorganic matrices.

The aim of this research was to evaluate analytical procedures for assessing bioavailable phosphorus from sewage sludge before and after thermal treatment. The two procedures chosen for comparison were the widely used Hedley fractionation method and USEPA LEAF. This study demonstrates that the LEAF provides a more consistent method for analyzing phosphorus bioavailability in sludges and suggests that
it may be more widely applicable to soils and other solids under consideration for land application. This study also illustrates how the LEAF methods provide valuable quantification of PTEs that may be present in these materials with no further analytical steps required.

2. Materials and Methods

The sludge utilized in this study was collected from Greenway Wastewater Treatment Plant (Greenway), London, Ontario, Canada. At Greenway, sludge is produced as a by-product of primary and secondary treatment. Primary clarification removes settleable solids (i.e., primary sludge). Following aerobic digestion and thickening, secondary clarification settles out waste activated sludge via dissolved air flotation units and rotating drums. Centrifugation with polymer addition is used to dewater a combined slurry of primary and waste activated sludge to produce a cake sludge. All sludge was collected as cake sludge in a single batch on July 26th, 2018, to minimize compositional variability.

2.1. Sample Preparation and Storage

Sludge was oven-dried to prevent decomposition and moulding. Prior to subsequent analyses, the oven-dried sludge was pulverized into a homogenous powder using an immersion blender and mortar and pestle. Batches of ~100 g of dried sludge were placed in large crucibles and heated in a muffle furnace at 950°C for 2 hours to produce incinerated sewage sludge ash (herein referred to as ash). The ash appeared to be a relatively homogenous powder; no further grinding was done. All materials were stored in sealed 20 L pails at 5°C prior to use.

2.2. Preliminary Analysis

Moisture content, volatile matter, ash content, and fixed carbon of the sludge were determined following EPA Method 1684 (41), with three replicates analyzed for each. The sludge had an average moisture content of 73 ± 0.2%, volatile matter content of 18 ± 0.3%, ash content of 7 ± 0.1%, and fixed carbon
content of 2 ± 0.4%, all on a wet-mass basis. Laboratory incineration at 950°C resulted in mass loss of ~93%.

Pseudo-total elemental concentrations (herein referred to as total concentrations) were determined for aluminum, cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, phosphorus, lead, and zinc within sludge and ash. Elements were extracted from the solid phase through microwave assisted acid digestion following USEPA Method 3051A (42). Acid digestions were performed in triplicate.

2.3. Hedley Method

In the Hedley method, inorganic and organic phosphorus fractions are extracted using progressively stronger chemical reagents. Figure 1a illustrates the series of 6 extracts (H1 – H6). In each extraction, 1 g dried sample was added to a 250 mL polyethylene bottle. An anion exchange resin bag (Dowex™ resin, Sigma-Aldrich Canada Co., within 41 µm nylon mesh, Fisher Scientific Co Ltd.) and 30 mL deionized water were added and shaken at 170 RPM on a rotary shaker for 16 hours. Phosphorus was removed from the resin with 20 mL 0.5 M hydrochloric acid (HCl) (H1). The supernatant was decanted and disposed of followed by the addition of 30 mL 0.5 M sodium bicarbonate (NaHCO₃). The bottle was shaken for 16 hours, then the supernatant was collected (H2). This process was repeated, adding 30 mL 0.1 M sodium hydroxide (NaOH) (H3), 20 mL 0.1 M NaOH with 2 min sonication (H4), and 30 mL 1 M HCl (H5). Following the resin extraction procedure, a repeat sample was used to determine the microbial biomass phosphorus by spiking the solid material with 1 mL concentrated chloroform (CHCl₃), leaving the sample to fumigate for 16 hours, then extracting the phosphorus with 30 mL 0.5 M NaHCO₃. The microbial biomass phosphorus is calculated as the difference between the total labile phosphorus extracted with only NaHCO₃ and pretreated with CHCl₃ (43). The residual phosphorus is determined by digesting (H5) in 10 M sulfuric acid (H₂SO₄) (H6). Importantly, pH is not dictated in this method. Instead, following each procedure step, eluate samples were analyzed for pH and conductivity using a Fisher Scientific accumet™
AB200 pH/mV/Conductivity meter (Waltham, MA, USA), then preserved for further analysis of inorganic and total phosphorus. Concentrations of organic phosphorus were calculated as the difference between total and inorganic phosphorus in each extract. All extractions were performed in triplicate with results presented as averages including standard error.

Each extract is associated with a phosphorus pool and mechanism of phosphorus binding to solid surfaces, as illustrated in Figure 1a. Whether each of the chemical extractants can accurately dissociate the target phosphorus compounds from the solids is not fully understood, and it is likely that each pool contains a combination of compounds (44).

2.4. USEPA LEAF Methods 1313 and 1314

USEPA LEAF Method 1313 consists of 9 parallel batch extractions (Figure 1b) to produce a liquid-solid partitioning curve of the material of interest over eluate pH range 2 ≤ pH ≤ 13. For each extraction, 10 g of material was combined with 100 mL of extraction solution consisting of deionized water with either 2 N nitric acid (HNO₃) or 1 N potassium hydroxide (KOH) to achieve 9 target pH values ± 0.5 for each (Figure 1b). The liquid-to-solids ratio was 10 mL/g-dry. Quantities of HNO₃ or KOH were determined after measuring the native pH of the material using deionized water. Mixtures were prepared in 125 mL HDPE bottles, sealed, and shaken end-over-end at 170 RPM for 24 hours. Following shaking, bottles were centrifuged. pH was measured to confirm the final solution remained within target ranges; electrical conductivity was also measured. Eluate samples were filtered, preserved, and analyzed for total and inorganic phosphorus. Additionally, cadmium, cobalt, chromium, copper, molybdenum, nickel, lead, and zinc were analyzed because they are typically monitored and/or regulated at WWTPs.

USEPA LEAF Method 1314 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). The L/S is computed as the quantity of solution (mL) passed through the fixed quantity of solid material (g) within the column. A glass column
(DWK Life Sciences, KIMBLE®) of 5 cm outer diameter and 30 cm height was used for each test. A 5 cm layer of acid-washed, air-dried sand (Number 12, Bell & Mackenzie) was packed into the base of the column. Dried material (sludge or ash) was added to the column in successive layers (~60 g), tamping each using a glass rod, until 300 g of sample was added. A second 5 cm layer of acid-washed sand was added to the top of the material pack to minimize material loss from the column. Deionized water (neutral pH) was pumped using a Masterflex® L/S® digital peristaltic pump (Cole-Parmer Instrument Company, IL, USA) upwards at a L/S of 1.0 mL/g/day until breakthrough occurred. The pump was stopped, letting the saturated column rest for 24 hours. After resting, water flow was reintroduced and maintained at rate of 0.75 ± 0.5 mL/g/day to collect the nine eluate samples (T01-T09) at specified L/S of 0.2, 0.5, 1.0 ± 0.1, and 1.5, 2.0, 4.5, 5.0, 9.5, and 10.0 ± 0.2 mL/g-dry matter. The pH and electrical conductivity of each eluate sample were measured within an hour of collection. Eluate samples were filtered through 0.45 µm filters (Whatman 0.45 µm celluacetate filters, VWR International) via a vacuum pump. Filtered samples were preserved with concentrated HNO$_3$ and analyzed for total and inorganic phosphorus as well as cadmium, cobalt, chromium, copper, molybdenum, nickel, lead, and zinc.

2.5 Analytical Methods

Total elemental concentrations in the microwave extracts, Hedley method extracts, and LEAF Method 1313 and 1314 samples, were analyzed using an Agilent 720 Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES) following USEPA Method 6010D (45).

Total phosphorus in the Hedley method extracts and USEPA method 1313 and 1314 samples was measured using ICP-OES to avoid interferences that affect colorimetric analysis (46). Inorganic phosphorus was measured as dissolved orthophosphate (PO$_4^{3-}$) by High-Performance Liquid Chromatography (HPLC) using direct injection by a Water® 515 pump following USEPA Method 300 (47).
All extracts were run at dilution factors of 1:1 – 1:100 (1:10 – 1:100 for digested samples) on both ICP-OES and HPLC to ensure all elements were within detection ranges for every sample. Triplicates, method blanks, and spiked extracts were also run on both ICP-OES and HPLC to ensure quality assurance and quality control.

Due to differences in the sludge versus post-treatment ash, all results were normalized in terms of the starting material: mass of element per mass of initial dry sludge (mg/kg–DS). Results in terms of dry matter (i.e., mg/kg–dm) can be found in Supplementary Materials (Appendix C).
Figure 1: Procedural schematics for a. the Hedley et al. (1982) fractionation procedure and b. USEPA Method 1313 parallel batch extraction. The 6 steps of the Hedley procedure (H1-H6) are outlined in a, including the chemical extractant and molarity used for to quantify each phosphorus pool. The phosphorus pools are assumed to decrease in plant availability from step (H1) being immediately available to step (H6) being unavailable. H1 is associated with readily soluble inorganic phosphorus (14). H2 is correlated to labile inorganic phosphorus from P-esters bound to surfaces of aluminum and iron (9). H3 and H4 are moderately-labile phosphorus pools assumed to contain phosphorus chemisorbed to amorphous and some crystalline aluminum and iron oxides/hydroxides (13). H5 is assumed to be non-labile phosphorus bound to calcium-species (9). The pH ranges corresponding to Hedley method pools and USEPA Method 1313 samples are provided in c. and compared to typical environmental pH conditions.
3. Results and Discussion

3.1. Phosphorus Analysis

3.1.1. Hedley Method

Figure 2 presents Hedley method results for sludge and ash. In the immediately soluble phosphorus pool (H1), 1100 mg/kg – dry sludge (i.e., mg/kg–DS) was extracted from both sludge and ash, comprising 2 and 5% of total phosphorus, respectively. Majority was from unavailable pools (H3 – H6): 57% and 79% for sludge and ash, respectively. The fraction of total phosphorus released from non-labile (H5) and residual (H6) pools increases from 32% in sludge to 62% in ash. Thermal treatment seems to have transformed a fraction of phosphorus to less available forms.

Hedley assumes organic phosphorus is the difference between total and inorganic phosphorus. The sludge seems to have larger proportions of organic phosphorus compared to the ash. Phosphorus in the sludge extracted by Hedley consists of 32% organic phosphorus distributed as 54% labile (H2), 16% loosely bound (H3), 10% moderately bound (H4), and 85% non-labile (H5). In contrast, only 10% of phosphorus in the ash is present as organic, distributed as 14% labile (H2), <1% loosely bound (H3), 10% moderately bound (H4), and <1% non-labile (H5). This reduction in organic phosphorus during thermal treatment is also evident when comparing microbial phosphorus: ~310 mg/kg–DS of microbial phosphorus for sludge versus negligible for ash. This is due to the destruction of any microbial biomass present in the sludge which would cause subsequent release of any microbially-bound phosphorus.

Phosphorus recovered from all steps of Hedley accounted for only 60% of total phosphorus extracted by microwave digestion from sludge and 80% from ash (Figure 2). This is consistent with unextracted phosphorus of 20-70% in other studies (13,48). Hedley was developed for use in soils that have
significantly less organic matter than sludges. In sludges, the optimal application of Hedley may be to compare the relative changes to functional phosphorus pools between samples.

Figure 2: Results from the Hedley method on sludge and ash presented in orange and gray, respectively. The different P-pools are shown on the x-axis and labelled with numbers corresponding to the respective extraction steps shown in the Hedley procedural schematic (Figure 1a.). The full bar represents the total-P in that fraction. The bars are subdivided into inorganic- and organic-P which are shown with diagonal stripes and dots, respectively. The P concentration is given in mg of P per kg of dry sludge. The cumulative percentage of P extracted by the Hedley method compared to the total-P for the sludge and ash are plotted as lines on the secondary axis.

3.1.2. USEPA Method 1313

USEPA Method 1313 was used to quantify pH-dependent phosphorus availability (Figure 3). Sludge is slightly acidic while ash is slightly alkaline with native pH of 5.8 and 8.0, respectively. At native pHs, phosphorus availabilities were at a minimum from both sludge and ash; increasing significantly under strongly acidic and alkaline conditions.

At pH < 7, phosphorus availability was greater in ash than sludge, whereas at pH > 7, the opposite was true. Under acidic conditions (pH < 6), the concentration of total available phosphorus in ash increased from 370 to 3800 mg/kg–DS and from 150 to 1300 mg/kg–DS in sludge under the same conditions. Organic
phosphorus accounts for an important fraction of available phosphorus in both materials in these
conditions: 15 – 80% in sludge and 17 – 83% in ash. Most of the available organic phosphorus in ash
becomes available at pH = 4, whereas, in sludge, available organic phosphorus varies more with pH. This
difference likely reflects the absence of organic matter in ash.

Above pH 7, the concentration of available phosphorus in sludge increases almost linearly with increasing
pH. In slightly alkaline conditions (7.5 ≤ pH ≤ 9.5), available phosphorus from ash was 0.4% of available
phosphorus from sludge. As alkalinity increased (pH > 9.5), available phosphorus increased linearly in both
sludge and ash. Available phosphorus in ash remained 20 – 40% of that available in sludge (3100 – 17,000
mg/kg–DS and 650 – 6400 mg/kg–DS in sludge and ash, respectively). Organic phosphorus accounts for a
significantly larger fraction of available phosphorus in sludge than ash in alkaline conditions: 29 – 68%
versus 0 – 61%.

In summary, sludge shows generally higher concentrations of immediately available phosphorus across
environmentally relevant pH conditions (3.5 < pH < 8.5) while ash contains higher available phosphorus
under increasingly acidic conditions (pH ≤ 4). Thermal treatment of sludge is likely transforming a portion
of immediately available phosphorus at native pH into more recalcitrant forms (27). This transformation
may have important benefits since, after land application, immediately available phosphorus may be
flushed rapidly from the system causing eutrophication of nearby surface waters. Conducting dynamic
leaching tests (Method 1314) allows this potential impact to be directly studied.
Figure 3: Comparison of the available-P as a function of pH for a. sludge and b. ash using the results of the EPA leaching method 1313 and the Hedley fractionation procedure. Method 1313 results are plotted along the curves while the Hedley results are plotted as discrete points using square markers. The extraction steps corresponding to each of the points are labelled as 1-6 (see Figure 1 for the full procedure). Total phosphorus is presented as the dotted line. The native pH of each material is outlined in a box.
3.1.3. USEPA Method 1314

USEPA Method 1314 dynamic leaching tests evaluate constituent release from materials as a function of increasing L/S ratio. The highest concentration of phosphorus is released immediately from both sludge and ash (Figure 4); however, important differences were observed between their release profiles.

In sludge, an initial slug of 9.5 mg/kg–DS of phosphorus was released (L/S = 0.2) followed by diminishing rates. Phosphorus rapidly becomes availability – limited as minimal release occurs with additional percolation (0.5 ≤ L/S ≤ 10), leading to a cumulative release of 19.7 mg/kg–DS. Of the total eluted phosphorus, 48% is released immediately. This behaviour is consistent with applications of sludge to soil where a rapid initial release of phosphorus, which can be linked to eutrophication (5).

In ash, the initial slug of phosphorus leached was smaller - 92% less than in sludge - and released more slowly (0.8 mg/kg–DS over 0.2 ≤ L/S ≤ 2.0). Organic phosphorus accounted for 37% of this initial slug as compared to 95% of the initial slug in sludge. Total and inorganic phosphorus then exhibited a continued slow release for the remainder of the ash experiment (2.0 ≤ L/S ≤ 10), exhibiting solubility-limited behaviour. Importantly, approximately 81% of total eluted phosphorus from ash was in the inorganic form, compared to 52% from sludge.

Early washout of soluble ions did not have a substantial impact on eluate pH in either material, although thermal treatment affected the initial pH (Figure 4). The elevated temperatures of incineration are associated with processes such as denaturation of organic acids and combustion of organic materials that have been observed to cause similar increases in soil pH (49). Combustion of organic matter within sludge resulted in about 50% of phosphorus being released through volatilization (see Supplementary Materials Appendix A), illustrating an important mechanism for recovery during thermal treatment. Most of what remained within the ash was likely transformed into more crystalline forms (50). The net result was a decrease in immediate phosphorus leaching, agreeing with the Method 1313 results at native pH.
Figure 4: The USEPA method 1314 column percolation experiments for sludge (orange) and ash (grey). The concentrations of released phosphorus are shown in mg of phosphorus per kg dry sludge. The darker solid lines and lighter broken lines show total- and inorganic-P release, respectively. The pH changes over the column leaching experiment are plotted as dotted lines on the secondary y-axis.
3.2. Potentially Toxic Element Availability and Leaching

One of the barriers to land application of sludge, with or without further treatment, is potential release of PTEs. LEAF Methods 1313 and 1314 provide additional data to evaluate their potential release. Figure 5 shows Method 1313 plots of 8 elements of concern identified in Ontario Regulation 338/09 (O. Reg. 338 CM1 NASM) from the Nutrient Management Act (2002) (see Supplementary Materials for PTE results from Method 1314).

All elements generally had higher availabilities from sludge compared to ash. The exceptions typically occurred in limited circumstances not relevant to conditions for land application (pH = 4). Cadmium, molybdenum, and lead all had similar availabilities from sludge and ash under neutral to acidic conditions and higher availabilities from sludge than ash under alkaline conditions. To understand how availability translates to potential release behaviour upon potential land application, results from Methods 1313 and 1314 must be viewed together.

Cumulative releases of all elements apart from molybdenum were higher from sludge than ash, often significantly higher (see Figure C2, Supplementary Materials). Importantly, although lead had higher available concentration at neutral pH (Figure 5), lead release from ash was small and 5% of lead released from sludge (Figure C2, Supplementary Materials). Among the other 6 PTEs, similar release trends were observed; cumulative releases from ash were <1-10% of the cumulative releases from sludge, usually because of a relatively large initial slug released from the sludge. The thermal treatment process appears to affect the availability and leaching of PTEs in the resulting material, similar to phosphorus.
Figure 5: pH-dependent leaching curves for 8 PTEs of concern from O. Reg. 338 CM1 NASM for both sludge and ash, following USEPA Method 1313. Values have been normalized per kg dry sludge.
3.3. Discussion: Comparing Hedley and LEAF Methods

LEAF methods are easier to execute than sequential fractionation procedures. Hedley uses 6 different chemical extractants of varying molarities while Method 1313 requires only 2 and Method 1314 only 1 (deionized water). Method 1313 consists of 9 parallel batch extractions that are performed simultaneously, yielding independent results. Although Method 1314 is technically also a series extraction from the percolation column, compared to sequential fractionation the sample collection is simplistic. Sample quantity may also influence results. Hedley indicates 1 g dried sample which may not fully represent material characteristics. Method 1313 utilizes 10 g (or more) dried sample for each extraction and Method 1314 uses at least 300 g dried sample in the column. Although likely more characteristic, the larger sample sizes used in LEAF may also be a drawback compared to Hedley if sample amount is limited.

Quantifying release of phosphorus from each material is important to evaluate what plants may receive. Inconsistencies between Hedley and LEAF methods have important implications. Hedley soluble (H1) and labile (H2) pools typically correspond to points between T04 and T08 in Method 1313 (Figure 1c). In this work, soluble (H1) and labile (H2) pools correspond to T07 (pH = 5.5) and T05 (pH = 8), respectively, in the sludge and to T06 (pH = 7) and T04 (pH = 9), respectively, in the ash (Figure 1c). Phosphorus released at native pH in Method 1313 is inconsistent with soluble (H1) pool from Hedley, releasing ~6% and <1% from the sludge and ash, respectively (Figure 3). Furthermore, in sludge, soluble (H1) pool exceeds available phosphorus determined by Method 1313 at 3.5 < pH < 9.5 (i.e., samples T04 – T08) making it only comparable at pH extremes, which is not relevant to land application. Similarly, in ash, soluble (H1) pool only matches the magnitude of available phosphorus from Method 1313 determined in more extreme conditions (pH <5 or pH >11). Additional discrepancies arise considering Method 1314 results. Cumulative inorganic phosphorus released from Method 1314 was <1% of the quantity released in soluble (H1) pool for both sludge and ash, even when differences in L/S ratios between methods were considered.
This lack of alignment is problematic. Readily soluble phosphorus is the primary concern for receiving waters (5). Overestimation of this pool could result in insufficient phosphorus being applied to crops whereas underestimation risks contributing to eutrophication. The discrepancy between the LEAF and Hedley results for readily soluble phosphorus is probably caused by the Hedley’s use of anion exchange resin, which likely extracts low-leachability phosphorus bound to solids (51,52).

Hedley is also inconsistent with Method 1313 for the labile (H2), loosely bound (H3), and moderately bound (H4) phosphorus pools (Figure 3), whereas non-labile (H5) and residual (H6) pools were in line with Method 1313 results; however, pH values in Hedley are outside the range of Method 1313 (Figure 1c). For sludge, the quantities of labile (H2) and loosely bound (H3) phosphorus are consistently lower than available phosphorus from corresponding Method 1313 points, opposite to the case for readily soluble (H1) phosphorus (Figure 3). The resin used in soluble (H1) pool may have extracted some phosphorus that would otherwise appear in these subsequent pools, as was observed by (19). For ash, an order of magnitude more phosphorus is released in Hedley labile (H2) fraction than by Method 1313 at the same pH. The phosphorus concentrated in ash following thermal treatment of sludge may have exceeded the capacity of the resin used in soluble (H1), enabling release into subsequent pools. Consistent with sludge, phosphorus concentrations in Hedley loosely bound (H3) and moderately bound (H4) pools in ash are lower than corresponding points in Method 1313. The large portion of sorbed phosphorus removed within labile (H2) pool may have caused only more strongly bound phosphorus to remain, reducing the proportion of phosphorus extracted within the loosely bound (H3) pool. These discrepancies demonstrate an important drawback to Hedley and other sequential fractionation procedures: pools quantified in each extraction step influence pools quantified in subsequent steps (19,44). Incorporating mineralogy into phosphorus analyses has the potential to improve our interpretation and understanding of these results (27,31). Phosphorus mineralogy of virgin sewage sludge is challenging (53) and research in this area is limited. Minerals such as hydroxyapatite, brushite, monetite, and others have been identified in sludges...
Mineral phases seem to depend on source materials; wastewater treatment processes and operating conditions; and subsequent sludge handling processes. For examples, phosphorus mineral transformations have been observed after low temperature drying processes \cite{53}. High temperature treatment likely causes further transformations \cite{27,31}. This work provides important groundwork for future research exploring phosphorus mineralogy of sewage sludge and transformations brought about by thermal treatment.

4. Conclusions

Hedley and LEAF methods provide trends in available phosphorus that are qualitatively consistent. In this study, both suggest that thermal treatment of the sludge changes phosphorus minerals into forms that are more strongly bound to the solid surfaces. Therefore, phosphorus is less likely to leach from the ash in the short term, providing a more regulated source of gradual inorganic phosphorus with less potential harm to downstream water bodies.

However, Hedley and LEAF methods provide quantitative differences and LEAF is concluded to be superior for the following reasons. First, more incomplete phosphorus extraction from sludge than ash using Hedley suggests that it may be less appropriate for organic materials; this is consistent with previous studies and limits its applicability. Second, Hedley phosphorus pools were mostly at extreme pH conditions while LEAF (Method 1313) provided results across a range of controlled pH conditions relevant to land application. Third, Hedley overpredicted readily available phosphorus and underpredicted less soluble forms. Moreover, Hedley overpredicted the amount that would rapidly leach as inferred by LEAF (Method 1313) and directly quantified in LEAF (Method 1314). LEAF avoids the problem of sequential fractionation procedures where pools quantified in each extraction step influence pools quantified in subsequent steps. Fourth, LEAF was found to be practically simpler to execute and, while requiring more sample, the results may be more representative. Fifth, LEAF additionally provides analysis of PTEs, which
are valuable for decision-making. In this study, smaller initial releases, lower availability in environmentally relevant conditions, and lower total contents in ash are promising indicators that land application of ash would likely result in less PTE release to soil compared to land application of sludge. Although these elements could be analyzed in the Hedley extracts, that method was not designed for such purposes.

This analysis shows the value of the USEPA LEAF Methods in understanding phosphorus availability from materials such as sewage sludge before and after treatment. Land application of a material will change soil pH, which influences phosphorus availability and leaching of PTEs. LEAF was shown to provide valuable and superior insights into the effects of fluctuations in pH, dynamic leaching, and availability of PTEs. This information is essential for assessing material reuse and land application options. It is expected that LEAF will be similarly beneficial, relative to sequential fractionation methods (e.g., Hedley), when applied to soils and other relevant matrices.

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Supplementary Materials

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