



Lepidolite extraction solid by-product: Mitigation of thallium leaching and utilization of radiogenic strontium isotopes as a tracer

Thai T. Phan^{a,*}, Leah Fulton^a, John Ulkem^a, Steve Aiken^b, Amber Blackwell^b, Joe Walsh^c, Peter Walker^c, Fereidoun Rezanezhad^d

^a Department of Earth and Environmental Sciences, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

^b Knight Piésold Ltd., 1650 Main Street West, North Bay, Ontario P1B 8G5, Canada

^c Lepidico Ltd., 254 Railway Parade West Leederville, WA 6007 Australia

^d Ecohydrology Research Group, Department of Earth and Environmental Sciences and Water Institute, University of Waterloo, Waterloo, ON, Canada

ARTICLE INFO

Keywords:

Thallium
Lepidolite
Solid waste
Metal leaching
Blended residue
Radiogenic strontium isotopes

ABSTRACT

The emerging growth of lithium-ion battery usage necessitates the development of unconventional resources for battery grade lithium carbonate. Extraction of lithium from micas such as lepidolite produces several marketable by-products as well as a silt-sized gypsum rich blended residue containing elevated level of thallium (Tl). The goal of this study was to assess the alternative use of the blended residue as fill material for mine reclamation. Bulk elemental analysis and shake flask extraction of the blended residue showed that radionuclide and heavy metal levels of the solid blended residue and its leachate were within the guidelines for soil and its leachates. However, Tl concentration (24.7 ± 0.9 mg/kg), possibly in the forms of water-soluble salts in the blended residue, was much higher than the general level of Tl in naturally uncontaminated soil (<1 mg/kg). Thus, the efficiency of four easily accessible amendments (peat, clay, biochar, and topsoil) in mitigating the release of Tl was evaluated using a modified SPLP procedure. In addition, the usefulness of radiogenic Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) as a tracer of the leachate plumes derived from the blended residue was assessed. Results from SPLP experiments showed that Tl was released from the blended residue under a wide range of pH values, especially under acidic conditions. Mixing proportions of the blended residue and amendment (1:9 or 1:1) did not appreciably affect the high Tl removal efficiencies (68 – 89%) of clay, biochar, and topsoil. While mixing time did not affect the Tl removal efficiencies of clay and topsoil, Tl removal efficiency of biochar proportionally increased with mixing time and was at the highest value (~95%) among four amendments, if the mixing time was at least 7 days. Peat was not an effective amendment because its acidity possibly enhanced the release of Tl. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in leachates of the blended residue (0.792 – 0.810) and its amendment mixtures were significantly higher than those in surface and groundwaters, soil leachates, and coal mine drainage. Thus, when the blended residue is used as fill material for mine reclamation, $^{87}\text{Sr}/^{86}\text{Sr}$ can be a powerful naturally occurring tracer in distinguishing Tl from the blended residue from other major sources of Tl in the environment. Overall, this study recommends clay and soils as the most promising amendments in mitigating the release of Tl in well-drained systems, and biochar for poor drainage conditions.

1. Introduction

Emerging growth of the usage of lithium (Li) ion batteries drastically increases the significance of Li resources (Grosjean et al., 2012). Li has been widely extracted from Li rich brines because its existence as a dissolved species eases the cost of extraction (Munk et al., 2016). Li also exists in high abundance in economically viable micas such as spodumene, petalite, and lepidolite (Meshram et al., 2014; Peerawattuk and Bobicki, 2018). Pure Li carbonate from mineral extraction has been commercially produced primarily in Canada and Aus-

tralia (Dessemond et al., 2019; Kavanagh et al., 2018). Among several chemical processes such as high temperature roasting and acid leaching (Kavanagh et al., 2018), a low energy consumption hydro-metallurgical process using sulfuric acid has been successfully applied to extract high purity Li from lepidolite (Zhang et al., 2019) such as the L-Max® process developed by Lepidico Ltd. This process yields solid by-products that are referred to as “blended residue” in this study.

The blended residue is a fine white alkaline solid containing ~60% gypsum by weight and measurable levels of trace metals including cadmium (Cd), lead (Pb), zinc (Zn), aluminum (Al), thallium (Tl), and beryl-

* Corresponding author.

E-mail address: thai.phan@uwaterloo.ca (T.T. Phan).

lium (Be) which are potentially harmful to the environment. Among these trace metals, Tl is of environmental concern due to its high toxicity (Memon et al., 2008) and elevated levels in the blended residue. Increasing production of Li from mineral extraction will lead to generating great amounts of solid by-product that requires proper characterization and treatment, if needed, to mitigate the potential release of contaminants during storage, disposal, or reuse as fill material in post-mining land reclamation. So far, no study has been reported to properly characterize the extent of the release of potentially toxic metals and radionuclides from the solid by-products derived from lepidolite extraction. This necessitates the work presented in this study.

Tl content in the Earth's crust ranges from 0.1 to 1.7 mg/kg (Peter and Viraraghavan, 2005). In natural soils, Tl varies in a wide range from 1.7 to 55 mg/kg, which is mainly controlled by the levels of sulfide minerals in the parent bedrocks (Tremel et al., 1997). Anthropogenic sources of Tl are mainly from processing of sulfide ores of zinc, copper, and lead as well as coal smelting and combustion (Cabala and Teper, 2007; Karbowska, 2016; Liu et al., 2020c). Thousands of tons of Tl are released into the environment from industrial processes annually (Karbowska, 2016). In Slave River, Alberta, Canada, elevated Tl concentration in its tributaries (total Tl = 0.03 µg/L, dissolved Tl = 0.01 µg/L) are linked to the upstream oil sands operations (Kelly et al., 2010; Sanderson et al., 2012). However, this level is unlikely to pose a concern to human health from drinking the water or fish consumption due to the bio-dilution behavior of Tl in the food web (Jardine et al., 2019). In contrast, many riverine waters and sediments, agricultural soils, and vegetables from different areas worldwide accumulate high level of Tl due to industrial activities such as steel-making plants and Pb-Zn smelters (Cabala and Teper, 2007; Karbowska, 2016; Liu et al., 2020b; Liu et al., 2020c; Vaněk et al., 2018; Xiao et al., 2004; Xiao et al., 2012). For example, elevated Tl with distinct isotope compositions in soil profiles near coal-fired power plants in a Czech–Polish–German tripoint area (Vaněk et al., 2016) and a Zn smelter in Poland reflects the on-going and historical contamination occurring many years ago (Vaněk et al., 2018). This highlights that the Tl accumulated in soils can be preserved for such a long time that is potentially taken up by vegetation (Liu et al., 2020b) and leached into groundwater aquifer by meteoric water (Santonastaso et al., 2018).

The radiogenic Sr isotope system ($^{87}\text{Sr}/^{86}\text{Sr}$) is one of the most powerful environmental tracers that has been widely used in a variety of applications. These include understanding water-rock interactions during hydraulic fracturing Cui et al., 2020; (Phan et al., 2018; Phan et al., 2020), solid and water pollution sources (Geeza et al., 2018; Wang et al., 2020), and many other earth surface processes due to its conservative behavior during mineral dissolution and precipitation (Capo et al., 1998). Complex processes controlling the fate and transport of heavy metals including Tl in mine tailings and drainage have been also unraveled using $^{87}\text{Sr}/^{86}\text{Sr}$ (Petrini et al., 2016; Salifu et al., 2018). Thus, $^{87}\text{Sr}/^{86}\text{Sr}$ can be a useful and unique tool in distinguishing Tl containing leachates from the blended residue with other common sources of Tl in the environment.

In an aqueous environment, Tl is commonly in highly mobile and soluble Tl^+ form over a wide pH range (Kaplan and Mattigod, 1998) making its removal especially difficult (Liu et al., 2019). The most common removal methods for Tl in wastewater treatment include oxidative precipitation (Davies et al., 2016) and adsorption (Li et al., 2018; Tang et al., 2019). These methods are found to be very effective, but each method is unable to completely remove Tl alone and must often be combined or repeated for better efficiency. Some of these methods also require expensive reagents and/or infrastructures to be effective, which may not be feasible or practical (Davies et al., 2016), especially for treatment of the Tl contaminated solid waste or soils. Phytoremediation (Anderson et al., 1999; Wei et al., 2020) and biochar and mineral amendments (Liu et al., 2020a; O'Connor et al., 2018) significantly decrease Tl mobility in contaminated soils, subsequently decreasing the risk of surface and groundwater contamination. Thus, the goal of this

study was to evaluate the role of four easily accessible materials in controlling the release of Tl from the blended residue when used as fill material for mine reclamation. Four amendments (peat, topsoil, biochar, and clay) were selected based on availability, cost effectiveness, and evidence from past research indicating their potential as effective sorbents. *Sphagnum* peat moss has been found to be an effective adsorbent for heavy metals (Kalmykova et al., 2008; Sharma and Forster, 1993) due to its high adsorption capacity and solute transport attenuation (Rezanezhad et al., 2016). The wide availability of soil makes it a convenient candidate for its use as a heavy metal adsorbent (Das and Mondal, 2011) and clays are also widely available with high specific surface area, cation exchange capacity, and are good adsorbents for heavy metals (especially montmorillonite) (Bhattacharyya and Gupta, 2008). Biochar has also been used for remediation of heavy metal polluted soils (He et al., 2019; Li et al., 2017; O'Connor et al., 2018; Rajapaksha et al., 2018). In addition, the usefulness of $^{87}\text{Sr}/^{86}\text{Sr}$ as a tracer of the leachate plume was assessed because monitoring of the movement of the plume is crucial for future field applications.

2. Materials and methods

A flowchart summarizing all physical and chemical characterization and laboratory experiments to assess the extent of Tl release from the blended residue and roles of four amendments in mitigation the Tl release is shown in Fig. S1 (Supporting Materials).

2.1. Blended residue and amendments

The blended residue material used in this study was provided by Lepidolite Ltd. The residue is a gypsum-based by-product from a lepidolite extraction process which is a blend of the solid waste streams of the L-Max® process. Peat (*Sphagnum* peat moss, Fafard), topsoil (Organic garden soil, Miracle-Gro), biochar (SoilMatrix Biochar, AirTerra), and clay (Montmorillonite, Ceratosil® WG) were used as amendments. The blended residue material was an initially wet and plasticky white semi solid in which a portion of the material was dried at 110 °C for 72 h, crushed, and sieved to obtain particles less than 0.5 mm. Similarly, the amendments were dried at 80°C for 24 h, and then ground and sieved to obtain particles less than 0.5 mm. The blended residue was initially characterized for its physical properties (Table S1) such as moisture content (ASTM D2216), specific gravity (ASTM D854), grain size distribution (ASTM D6913 and D7928), mineralogical composition (Table S2) by SGS Canada Inc. (Lakefield, ON, Canada), and radionuclide levels (Table S3) by the SRC Environmental Analytical Labs (Saskatoon, Canada). The total carbon, nitrogen, and sulfur in the blended residue were measured on a CHNS Carbo Erba analyzer (method detection limit = 0.1% dry). Bulk elemental concentrations were analyzed by ICP-OES and ICP-MS following sodium peroxide fusion at Activation Laboratories (ActLabs), Canada. Elemental concentrations in the blended residue and amendments are shown in Table S4.

2.2. Shake flask extraction: evaluation of trace metal and radionuclide release

Shake flask extraction testing (ASTM D3987) on the blended residue was performed by SGS Canada, Inc. to evaluate the potential release of metals and radionuclides of environmental concern. A 1:3 mass ratio of bulk rock to deionized water was used for this testing. The elemental concentrations in the leachates were analyzed by SGS Canada whereas analysis for radionuclides was done by the SRC Environmental Analytical Labs (Saskatoon, SK, Canada). Specifically, gamma spectroscopy was performed for ^{228}Ra , ^{40}K , ^{234}Th , and ^{235}U and Alpha spectroscopy was used for ^{228}Th and ^{230}Th . Liquid scintillation was performed for ^{230}Pb , and Radon emanation was used for ^{226}Ra . The results are presented in the Table S5 (Supporting Materials).

2.3. Synthetic precipitation leaching procedure

The Synthetic Precipitation Leaching Procedure (SPLP; EPA 1312), developed by the United States Environmental Protection Agency (EPA) was used to quantify groundwater contamination potential by granular solid wastes (U.S. EPA, 1994). This procedure was modified and used to evaluate the extent of Tl release from the blended residue and four amendments (peat, topsoil, biochar, and clay). A pH 4.2 solution was prepared by mixing a 60/40 ratio of H₂SO₄ and HNO₃ (EPA 1320) with ultrapure water (18.2 MΩ-cm) to mimic rainwater compositions that would cause metal leaching in the field. In each experiment, 2 grams of sieved and homogenized solids (blended residue, peat, topsoil, biochar or clay) was reacted with 40 mL liquid (solid:liquid ratio = 1:20) in a 50 mL polypropylene centrifuge tube in a rotary shaker. To evaluate the role of amendments, each amendment was mixed with the blended residue at two different ratios: (1) 10% blended residue and 90% amendment (1:9) and (2) 50% blended residue and 50% amendment (1:1). Amending the blended residue at a 1:9 ratio is not a practical approach for the purpose of land reclamation due to the immense quantity of amendment that would be required. However, due to high level of Tl in the blended residue (24.7 ± 0.9 mg/kg; see Section 3.1), the blended residue is required to mix with the amendment at a maximal ratio of 1:6 to meet provincial regulation for disposal. Thus, experiments were performed in two ratios (1:9 and 1:1) to compare the effect of mixing proportion. The blended residue and amendments were also leached separately to determine the metals leaching from the blended residue itself and potential contribution from the amendment. Blank experiments (without solids) were also conducted to determine the potential contribution of metals released from the experimental apparatus. A summary of experimental details is shown in Table S6. The SPLP experiments were conducted for nine different reaction times: 2, 6, 12, 24, 48, 96 h and 7, 14, 35 days. When the leaching time was due, the tubes were centrifuged at 5,000 rpm for 10 min and the leachates were immediately collected and analyzed for electrical conductivity (EC) and pH using handheld meters (LAQUA Twin meters, model Horiba B-213). The remaining leachates were filtered through a 0.2 μm membrane filter (Thermo Scientific Polysulfone syringe filter) and were acidified to pH 2 using trace metal grade HNO₃ prior to the elemental concentration and radiogenic Sr isotope analyses (see 2.4).

2.4. Elemental concentration and radiogenic Sr isotope ratio analyses

Elemental concentration and radiogenic strontium isotope analyses were performed at the Metal Isotope Geochemistry Laboratory (University of Waterloo, Canada). The concentrations of major (Na, K, Ca, Mg, Si) and minor (Al, P, Sr, Tl) elements in SPLP leachate samples were analyzed using an Agilent 8800 QQQ-ICP-MS (Table S7). The analysis was performed under kinetic energy discrimination mode to reduce polyatomic ion and double charge interferences to less than 1.5%. In each analytical session, four reference surface water samples (T227, P67, M220 from USGS and SLRS-6 from NRC, Canada) were frequently analyzed for data quality control. Based on repeated measurements of these reference water standards, the accuracy of elemental concentration data was estimated to be within 10% for all reported elements.

Sr isotopes were separated from sample matrix, particularly from Rb to minimize the interference on the measured ⁸⁷Sr/⁸⁶Sr, using a high throughput vacuum assisted system (Wall et al., 2013). Selected leachate samples were analyzed for ⁸⁷Sr/⁸⁶Sr and the results are reported in Table S8. The ⁸⁷Sr/⁸⁶Sr was measured by a Nu Plasma MC-ICP-MS. Multiple reference materials including seawater (NASS-7, NRC Canada), marine sediment (HISS-1, NRC Canada), and USGS rock reference standards such as BCR-2, BHVO-2, and AGV-2 were processed together with the leachate samples for quality control. The measured ⁸⁷Sr/⁸⁶Sr was corrected for instrumental mass fractionation using an exponential law (Russell et al., 1978) and corrected for the interferences of ⁸⁷Rb on ⁸⁷Sr using ⁸⁵Rb and ⁸⁶Kr on ⁸⁶Sr using ⁸³Kr, respectively. Dur-

ing each analytical session, NIST SRM 987 was measured after every four unknown samples, giving ⁸⁷Sr/⁸⁶Sr = 0.71031 ± 00006 (n=17). The unknown samples were measured in duplicate and the average value was then normalized to ⁸⁷Sr/⁸⁶Sr = 0.710240 of NIST SRM-987 Sr standard as in previous studies (Phan et al., 2019; Phan et al., 2020). The ⁸⁷Sr/⁸⁶Sr values analyzed in this study agreed well with published literature (Neymark et al., 2014; Raczek et al., 2003) when their measured values were corrected to the normalized SRM-987 value (0.71024).

2.5. Normalization of concentration data to facilitate the comparison

When the blended residue is amended, two factors impact the overall Tl concentration in the bulk rock and leachate. The most apparent factor is dilution from the addition of the amendment. The second is adsorption and/or precipitation, where Tl ions bind to the exposed surface or precipitate with anions released from the amendment. Leachate concentration data of experiments on a mixture of the blended residue and amendment were normalized to facilitate the comparison of the effectiveness of each amendment. Note that the contribution of Tl from the amendments was negligible for Tl (Table S4). When the concentration was below the detection limit (<0.001 μg/g), half of the detection limit (0.0005 μg/g) was used. Eq. (1) below was used to normalize concentration data:

$$[X]_N = \frac{[X]_{mix} - (1 - a) \times [X]_{100\% \text{ amendment}}}{a} \quad (1)$$

where $[X]_N$ is normalized elemental concentration of X, $[X]_{mix}$ is measured elemental concentration of X in the mixture, a is the fraction of the blended residue in the mixture, and $[X]_{100\% \text{ amendment}}$ is the measured elemental concentration of X in the experiment on 100% amendment. In this normalization method, lower normalized concentration than in experiments on pure solid (either the blended residue or amendment) suggests that the release of the element is suppressed in the mixture. In contrast, if it is higher, this means the release of the element is enhanced in the mixture. The Tl removal efficiency (suppression of the release of Tl into the aqueous phase) of each amendment at a specific mixing time was calculated using:

$$\text{Tl removal efficiency (\%)} = \frac{[\text{Tl}]_{N-Mix}}{[\text{Tl}]_{BR}} \times 100 \quad (2)$$

where $[\text{Tl}]_{N-Mix}$ is the normalized elemental concentration of Tl calculated using the Eq. (1) and $[\text{Tl}]_{BR}$ is the concentration of Tl in the leachates of 100% blended residue at the corresponding time.

2.6. Two endmember mixing model

A two-component mixing model (Capo et al., 1998; Faure and Mensing, 2005) was used to provide a framework of using ⁸⁷Sr/⁸⁶Sr as a tracer of the blended residue leachate plume. The concentration and isotopic composition of the mixture was defined as:

$$C_{mix} = C_1 \cdot f_1 + C_2 \cdot (1 - f_1) \quad (3)$$

$$R_{mix} = \frac{R_1 \cdot (C_1 \cdot f_1)}{C_{mix}} + \frac{R_2 \cdot C_2 \cdot (1 - f_1)}{C_{mix}} \quad (4)$$

where C_{mix} and R_{mix} are concentration and isotopic composition in the mixture, respectively, C_1 and R_1 are concentration and isotopic composition in end member 1, respectively, C_2 and R_2 are concentration and isotopic composition in end member 2, respectively, and f_1 is the fraction of end member 1 in the mixture. The Sr/Na in endmember was used to calculate the ⁸⁷Sr/⁸⁶Sr because Sr and Na were expected to behave conservatively and that Sr/Na in the blended residue leachate was distinct from natural sources of Sr in the aqueous environment.

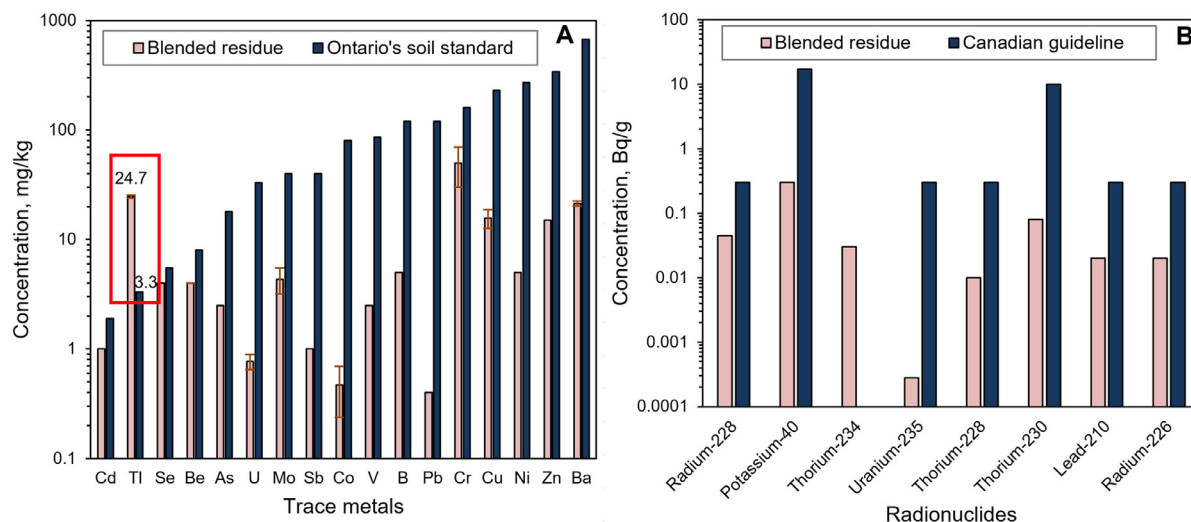


Fig. 1. Comparison of trace metal levels in the blended residue with the Ontario's standard for a non-potable groundwater area (Ontario Ministry of the Environment, 2011) (A) and radionuclide levels with the Canadian Guidelines for the Management of Naturally Occurring Radioactive Materials (NORM), Health Canada, 2011 (B). The error bars are two standard deviations of triplicate measurements.

3. Results and discussion

3.1. Mineralogy and elemental concentrations of the blended residue

The moisture content and specific gravity of the blended residue were 74% and 2.51 g/cm³, respectively. Grain size distribution analysis showed that the blended residue was 83% silt, 14% sand, and 3% clay sized particles based on The Unified Soil Classification System (Table S2, Supporting Materials). Total organic carbon in the blended residue was 0.37% by dry mass which is much lower than the average organic carbon in soils (4%) (Sparling, 1992). Total nitrogen and sulfur contents were 0.5% and 15.4%, respectively. The blended residue was approximately 60% gypsum, 17% ettringite, 6% calcite and 6% plagioclase feldspar (by mass). The remaining 11% was comprised of quartz, talc, mica/illite, and other minerals (Table S2, Supporting Materials). Under anoxic condition, sulfate derived from gypsum in the blended residue can be biologically reduced by sulfate reducing bacteria to form H₂S (Shen and Buick, 2004) which its levels are regulated under occupational health and safety guidelines due to the potential effects to human health.

Radionuclide levels in the blended residue (Table S3, Supporting Materials) are not an environmental concern because they are below the guideline from the Canadian Guidelines for the Management of Naturally Occurring Radioactive Materials (NORM; see Fig. 1A). Likewise, bulk rock analysis showed that most trace metal concentrations in the blended residue (Table S4, Supporting Materials) are below the Ontario's standard for soil in a non-potable groundwater area except Tl (Fig. 1A). The Tl content in bulk blended residue was 24.7 ± 0.9 (2SD) mg/kg which is about seven times higher than the Ontario's soil standard (3.3 mg/kg). At this level, the blended residue is required to mix with the amendment at a maximal blended residue vs. amendment ratio of 1:6, presuming the amendment does not contain Tl, to meet the provincial regulation of Ontario, Canada. The Tl level in the blended residue is considerably higher than Tl in background soils (<1 mg/kg) in Canada, England, Scotland, and France (Alloway, 2012) and in a similar range of Tl in contaminated soils nearby coal combustion, ore processing, and metal mining and smelting areas: 35 – 269 mg/kg in soils in the southwest Guizhou Province of Southwest China (Sun et al., 2012; Xiao et al., 2004), 8.8 – 27.8 mg/kg in Wiesloch, Germany (Schoer and Nagel, 1980), up to 30 mg/kg in top soils nearby a Zn mining and smelting area in Poland (Vaněk et al., 2018).

High Tl level is also found in natural soils in which geogenic Tl is commonly concentrated in sulfide minerals such as galena, sphalerite, and realgar (Xiao et al., 2012). For example, soils in the Swiss Jura Mountains area formed above dolomite rocks hosting weathered hydrothermal Tl-As-Fe sulfide contain up to thousands of mg/kg of Tl (Vaněk et al., 2020). Even though most Tl is found in the residual fraction of these soils, likely in silicates and incorporated in the interlayer of clay minerals, the Tl leachable (reducible and oxidizable) fraction contributes up to 20% of total Tl (Vaněk et al., 2020). As the blended residue is the solid by-product from hydrometallurgical processes, Tl speciation and subsequent environmental factors controlling the mobility of Tl in the blended residue are not expected to be similar as those found in soil. Diluting/mixing the blended residue with amendment lowers the bulk Tl level which is easily achieved to meet local environmental guideline. However, understanding the conditions and geochemical reactions that lead to the release of Tl from the blended residue will help save the cost of disposal. For example, the proportion of the amendment and selection of the most effective amendment in mitigating the release of Tl can be optimized to reduce the cost associated with monitoring and management. Therefore, the discussions below are focused on Tl mobility through characterizations of the leachates from the blended residue and its mixture with a variety of amendments.

3.2. Thallium and radionuclide release from the shake flask extraction

The leachates from shake flask extraction tests of the blended residue represent the metals associated with water soluble salts. The results (Table S5, Supporting Materials) showed that water soluble Tl contributes about 11% of total Tl in the blended residue. This suggests that Tl is primarily associated with other mineralogical reservoirs such as gypsum and ettringite, which are not easily dissolved under circumneutral pH. Regarding radionuclides, the concentrations of all analyzed radionuclides in the leachate are much lower than the guideline by Health Canada (Table S4, Supporting Materials). Notably, significant amount of K (~81%) is readily dissolved in water, suggesting that dissolved K in the blended residue can be a significant source of nutrition for vegetation when the blended residue is amended with topsoil to reclaim open mine pits. To further evaluate the extent release of Tl under acidic condition, the results from SPLP experiments were used to emulate the exposure of the blended residue to rainwater (see Section 3.3).

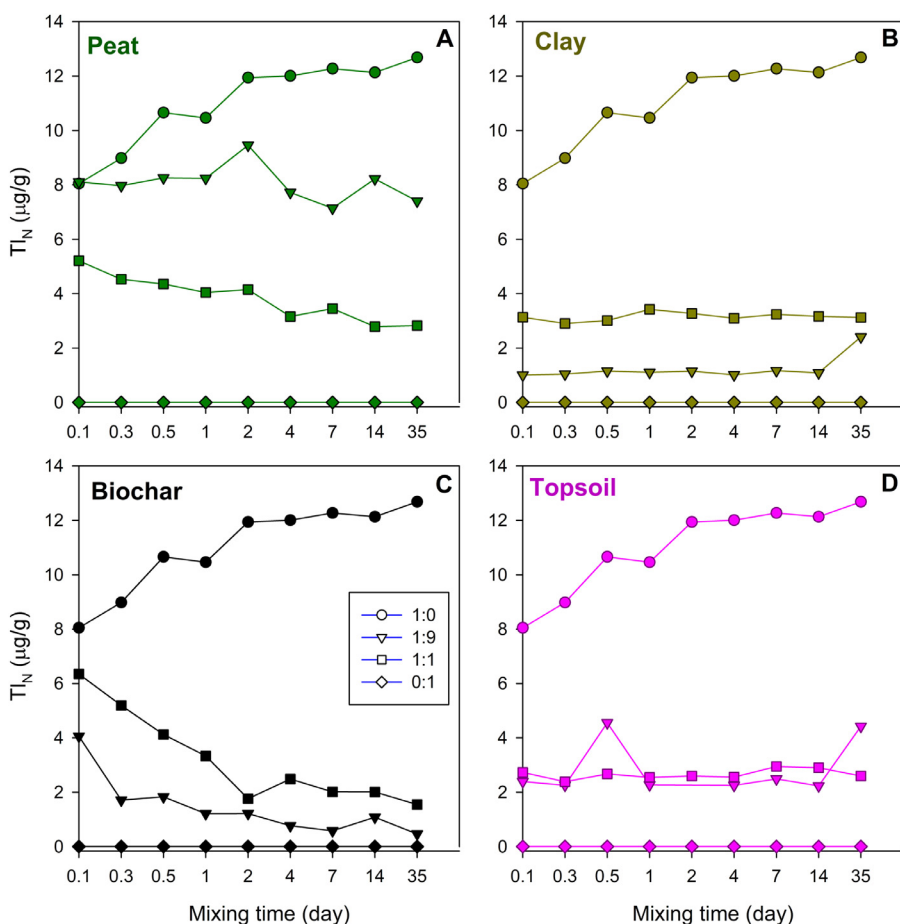


Fig. 2. Temporal Tl concentration changes in SPLP experiments of the blended residue and its mixtures with peat (A), clay (B), biochar (C), and topsoil (D). The ratios in the legend (in D) represent the mass ratios of the blended residue and the amendment. The concentration is normalized to the mass of the blended residue in the mixture using the Eq. (1) (Section 2.5) which is the amount (μg) of Tl leached per g of the blended residue. Relative standard deviations of measured concentrations of Tl are generally less than 5%.

3.3. Thallium leaching from the blended residue under acidic condition

The elemental concentration data (Sr, Ca, Al, Si, Tl) from the SPLP experiments are shown in Table S7. The carbonate minerals in the blended residue rapidly neutralized the acid as shown by a rapid increase in pH from 4.2 to 8.4 after 2 h of reactions (Fig. S2, Supporting Materials). As shown in Fig. 2, about $8 \mu\text{g/g}$ of Tl ($\sim 33\%$ of Tl in bulk blended residue) was rapidly dissolved in the acidic leachate within this 2 h period which is three times greater than the Tl leached by $18.2 \text{ M}\Omega\text{-cm}$ water ($\sim 11\%$) at circumneutral pH in the shake flask experiments. This suggests that acidic solution enhances the dissolution of Tl from the blended residue. After 2 h, acidic dissolution was expected to cease because the pH of the solution increased and remained within the circumneutral range ($\text{pH} = 6 - 8$; Fig. S2). However, Tl continues to gradually increase to as much as 50% of total Tl during the experimental duration (35 days).

Correlations between Tl and major mineral forming elements (Si, Al, K, Na, Mg, Sr, and Ca) were determined using a Data Analysis tool pack in Microsoft Excel to evaluate the potential sources of Tl in the blended residue. The results showed that Tl exhibits strong correlations with Na and K ($r^2 = 0.99$ and 0.98 , respectively) and moderate correlations with Si, Sr, and Mg ($r^2 = 0.73$, 0.65 , 0.60 , respectively). This observation implies that Tl could be likely released concurrently with the dissolution of Na and K containing minerals such as illite and plagioclase feldspars, which are present at observable levels in the blended residue. Even though substitution of K^+ in K-feldspars by Tl^+ is thermodynamically possible due to their similarity in ionic radii and hydration enthalpy (Peter and Viraraghavan, 2005; Wick et al., 2018), the dissolution of il-

lite and feldspar can be ruled out as potential sources of Tl. It is because previous studies (Gomez-Gonzalez et al., 2015; Vaněk et al., 2010) also showed that Tl associated with aluminosilicate minerals is not easily extracted following a BCR procedure (Tessier et al., 1979). Moreover, the results showed that Tl continued leaching out under circumneutral pH values. Thus, dissolution of illite and chemically resistant feldspar is not likely a source of Tl. This also corroborates with a previous study (Welch and Ullman, 1996) showing that the rate of feldspar dissolution at neutral pH is very low. Negative correlation between Tl and Ca ($r^2 = -0.70$) suggests that temporarily increasing Tl is not due to the dissolution of minerals containing only Ca such as calcite (CaCO_3) and gypsum (CaSO_4), two main minerals found in the blended residue (Table S2). Overall, acidic water enhances the release of Tl via acidic dissolution, but Tl is still progressively leached under circumneutral pH conditions. Up to 50% of total Tl was leached after 35 days. This largely leachable amount suggests that Tl dissolved in leachates is not likely due to the dissolution of major minerals (gypsum, ettringite, calcite, or feldspars) found in the blended residue. It is very likely that Tl is associated with water soluble salts. However, identification of the specific form of Tl in the blended residue can be a challenge given its trace level (ppm) in the blended residue. The soluble Tl could be due to the presence of the lanmuchangite mineral ($\text{TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; Daiyan et al. (2003), a soluble hydrated Tl sulfate formed during metallurgical processes. This important observation demonstrates that the blended residue could be leached by mildly acidic water to extract as much as 50% of Tl, then the remaining gypsum rich residue will be less susceptible to Tl leaching when it is mixed with amendment for field applications such as soil or mine reclamation.

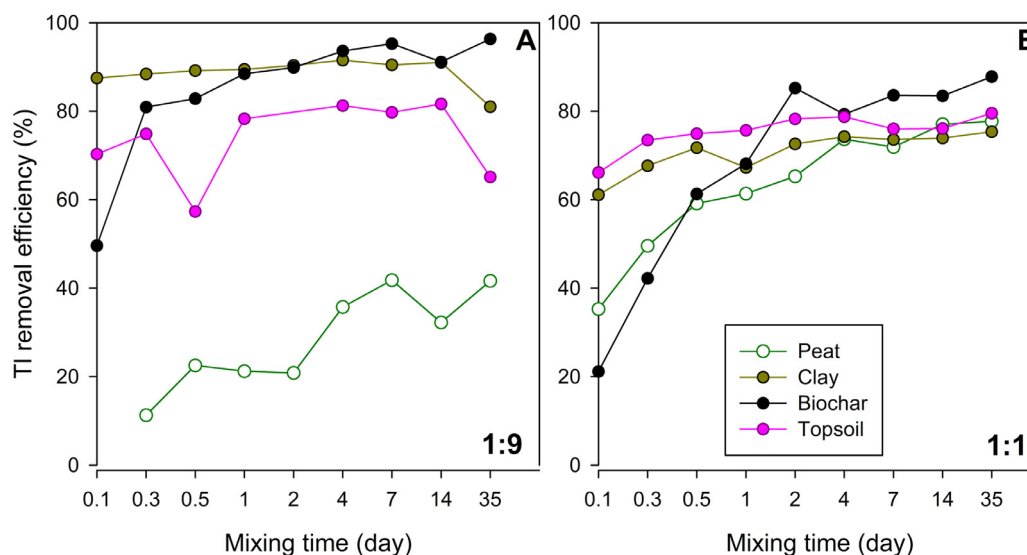


Fig. 3. Temporal changes in Tl removal efficiency of four amendments when mixed with the blended residue in different proportions: 1:9 denotes 10% blended residue and 90% amendment (A) and 1:1 denotes 50% blended residue and 50% amendment (B).

3.4. The effects of amendments on thallium release from the blended residue

Since the acidic condition enhanced the release of Tl from the blended residue, which also occurs slowly under circumneutral pH range (Fig. 2), the amendment additions are expected to have high surface areas to facilitate adsorption, and to be somewhat basic to neutralize acidic rainwater. Saturation states of minerals calculated using the Visual MINTEQ program (thermo.vdp database) showed that all Tl minerals such as Tl(OH) and Tl₂O are undersaturated in all experimental fluids in which Tl is present as Tl⁺. Thus, precipitation of Tl minerals did not likely occur, suggesting that the decrease of Tl⁺ in experiments are fully attributed to adsorption. To evaluate the overall effects of the amendments on the suppression of the Tl release, the removal efficiency was calculated using Equation 2.

3.4.1. Proportion of amendments

The contribution of Tl from the leachates of any of the amendments is negligible (below detection limits; Table S7) in comparison to Tl release from the blended residue itself (Fig. 2). As shown in Fig. 3, this study evaluated two mixing proportions: 10% blended residue and 90% amendment (1:9) and 50% blended residue and 50% amendment (1:1). For both mixing proportions (1:9 and 1:1), the mixing time did not generally affect the Tl removal efficiencies of clay and topsoil. However, the Tl removal efficiencies of peat and biochar appreciatively increase over time (see Fig. 3). It is hypothesized that relatively higher surface areas of clay and soil (Jacobson et al., 2005; Martin et al., 2018) than that of biochar and peat facilitate Tl sorption. Thus, Tl is quickly retained right after leaching out from the blended residue. This observation implies that the most effective control on the release of Tl in field applications is to create a low drainage soil condition (e.g., compact or use low hydraulic conductivity soils) to increase the mixing time between rainwater and the solid mixtures with either biochar or peat, particularly for mixtures containing larger portion of the blended residue. Except peat, Tl removal efficiencies of clay and biochar in 1:9 mixture are significantly higher by 18% and 15% than those in 1:1 mixture, respectively ($p < 0.05$; t-test). For topsoil, Tl removal efficiencies of 1:9 and 1:1 mixtures did not differ significantly ($p > 0.05$; t-test). Overall, the results showed that mixing proportion does not greatly affect the Tl removal efficiencies of clay, biochar, and topsoil (Fig. 4). However, high level of peat in the mixture (e.g., 1:9 ratio) promotes acidic condition which

apparently enhances the release of Tl, thus, decreases the removal efficiency. This is discussed in detail in Section 3.4.2.

3.4.2. Type of amendments and mixing time

Despite relatively high carbonate minerals in the blended residue, the pH of the leachates of mixtures with peat remains acidic (pH < 4) after five weeks of reactions, particularly on 1:9 mixtures (Fig. S2). For clay, biochar, and topsoil, the leachate pH values increased to circumneutral range after 2 h (Fig. S2). The Tl removal efficiencies of peat in both 1:9 and 1:1 mixing proportions are 22% and 63%, respectively, which are the lowest among four studied amendments (Fig. 4). This could be a result of a combination of enhanced acidic dissolution and low adsorption of Tl under acidic conditions. This observation is consistent with previous works showing that higher Tl adsorption occurred under basic conditions (Li et al., 2018; Tang et al., 2019), e.g., adsorption on peat was at the highest under pH 10 (Robalds et al., 2013). Thus, peat is not an effective amendment due to its acidic properties.

Mixing time is an important factor affecting the design for field applications to maximize the removal efficiency. The results show that the average removal efficiencies of clay, biochar, and topsoil are in a similar range (68 – 89%; Fig 4) for both mixing proportions. The removal efficiencies of clay and topsoil are relatively unchanged with the mixing time whereas the Tl removal efficiency of biochar proportionally increased with time, reaching its highest value of about 95% and 85% after 7 days in 1:9 and 1:1 mixing proportions, respectively. This observation implies that biochar is the most effective amendment if the rainwater has enough time (at least 7 days) to interact with the blended residue – biochar mixture. Given that typical soil water residence time ranging from days to months (Stewart and McDonnell, 1991), the condition should favor the application of biochar as an amendment. Under well drained systems, clay and topsoil are the most promising contenders due to their high Tl removal efficiencies that are independent with the mixing time.

3.5. Radiogenic Sr isotopes as a tracer of solutes in leachates of the blended residue

An important question in applying the blended residue as fill material in mine reclamation is how to trace the movement of the leachate plume and subsequently Tl. Leachates from the blended residue exhibited high values of ⁸⁷Sr/⁸⁶Sr (0.792 – 0.810; Table S8) which is

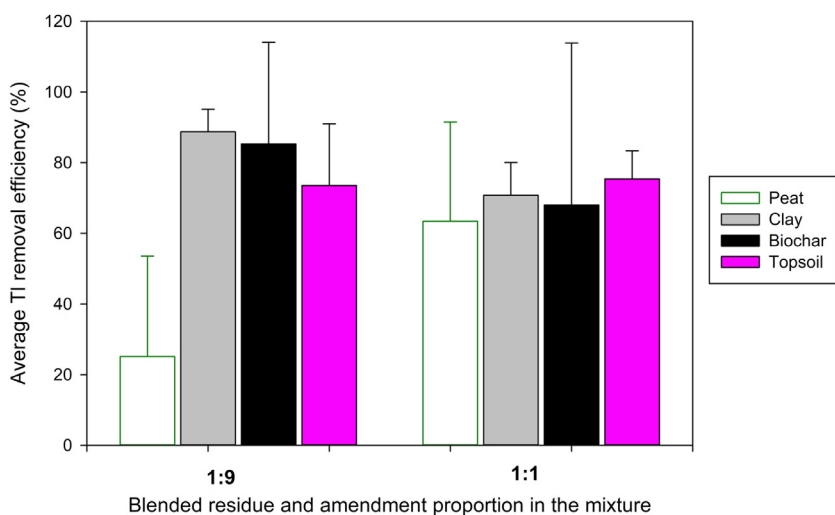


Fig. 4. Average Tl removal efficiency for all experiments on two mixing proportions between the blended residue and amendment (1:9 and 1:1). The error bars (2SD) represent the deviation of the removal efficiency with mixing time.

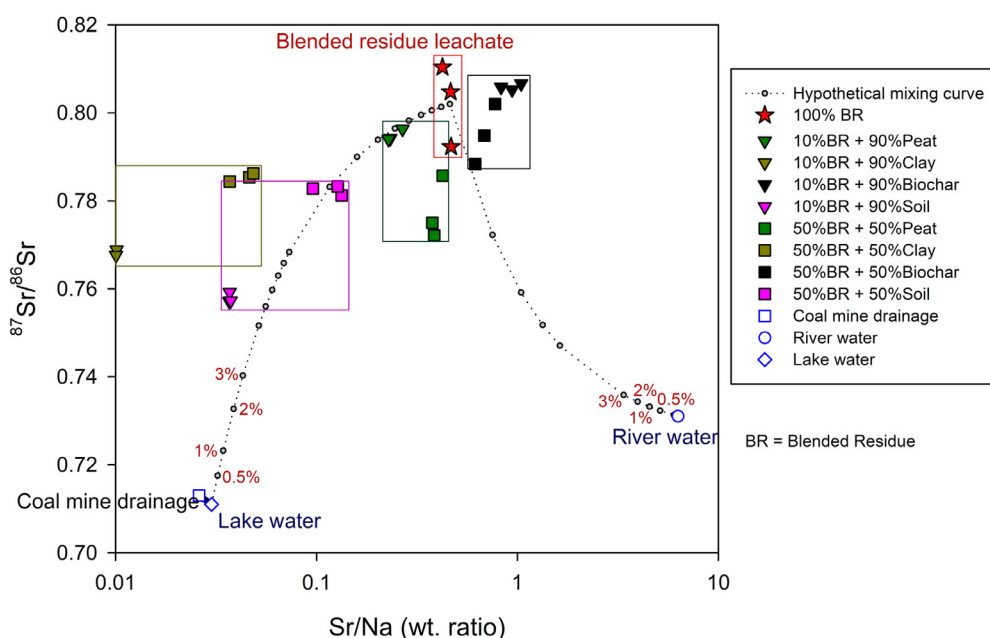


Fig. 5. Variation in $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Sr/Na (wt. ratio) of all leachates of the blended residue and its mixtures with four amendments. Rectangular box outlines the range of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Na in the leachates of each mixture. All leachates of the blended residue with any amendments are distinguishable in Sr/Na and $^{87}\text{Sr}/^{86}\text{Sr}$ from lake water and riverine water. The mixing curves for two hypothetical surface waters: lake water and riverine water, being impacted by the leachates of the blended residue (100%). The numbers next to the curve indicate the percent flux of the blended residue leachate added to the hypothetical lake water and riverine water. A very small portion of the blended residue leachate (0.5%) added to the stream can produce a large shift in $^{87}\text{Sr}/^{86}\text{Sr}$ which is easily detected because it is much larger than analytical uncertainty for $^{87}\text{Sr}/^{86}\text{Sr}$. Analytical error bars (2SE) of $^{87}\text{Sr}/^{86}\text{Sr}$ are within the size of the symbols. In contrast, coal mine drainage, a major source of Tl, is indistinguishable with lake water.

much higher than $^{87}\text{Sr}/^{86}\text{Sr}$ range (0.703 – 0.739) in Canadian riverine waters (Wadleigh et al., 1985), groundwaters of Silurian-Devonian carbonate aquifers (0.708–0.709) in Great Lakes region (McIntosh and Walter, 2006), groundwaters from the East Bull Lake pluton, Superior Province, east of Sudbury, Ontario, Canada (0.711 – 0.720; McNutt et al., 1987). In the central Ontario, $^{87}\text{Sr}/^{86}\text{Sr}$ in precipitation (0.709 – 0.711), lake waters (0.710 – 0.716), and soil leachates (0.709 – 0.718) are all lower than those from the blended residue leachates (Watmough, 2018). Mass-dependent fractionation occurring during water-rock interactions or analysis is corrected by normalizing to measured $^{88}\text{Sr}/^{86}\text{Sr}$. Thus, $^{87}\text{Sr}/^{86}\text{Sr}$ in aqueous phase is expected to inherit $^{87}\text{Sr}/^{86}\text{Sr}$ in weathered minerals (Capo et al., 1998). Groundwaters in equilibrium with carbonate (0.707 – 0.709) and granite (0.715 – 0.725) aquifers (McArthur et al., 2001) are expected to have similar $^{87}\text{Sr}/^{86}\text{Sr}$ with the host rocks which are all lower than $^{87}\text{Sr}/^{86}\text{Sr}$ in the leachates of the blended residue. Despite the mixing proportions, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ in the leachates of all mixtures (0.757) is still much higher than the above natural sources of Sr (Fig. 5). In addition, the Sr/Na ratio of the blended residue leachate (~ 0.45) is much higher than this in peat ($\sim 10^{-6}$), clay ($\sim 10^{-4}$), biochar ($\sim 10^{-2}$), and topsoil

($\sim 10^{-3}$) leachates. Sr and Na are expected to be conservative tracers and the distinguishing characteristic of the leachate suggests that $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Na can be a powerful tool for identifying and distinguishing the blended residue leachates from other possible solute sources. Discharges from coal fired power plants, coal mines, and gold mines are major sources of Tl in the environment (Cheam, 2001; Vaněk et al., 2018; Vaněk et al., 2016). Thus, to develop a framework for using $^{87}\text{Sr}/^{86}\text{Sr}$ as a tracer of the blended residue leachates, several endmembers were considered. Two endmembers (“Lake water” and “River water”) represent two types of unimpacted freshwaters that drain Precambrian Shield bedrock but are distinct in Sr/Na and $^{87}\text{Sr}/^{86}\text{Sr}$. A “coal mine drainage” represents a major source of Tl in aquatic environment. Lastly, “Blended residue leachate” represents the leachates from SPLP experiments on the blended residue (100%). The $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Na values of these endmembers (Chapman et al., 2012; Rosa et al., 2012; Stevenson et al., 2018; Watmough, 2018) are summarized in Table S9. Hypothetical mixing curves were constructed for the lake and riverine waters impacted by the leachate of the 100% blended residue (Fig. 5). As shown in Fig. 5, even small additions of the blended residue leachate to a lake water or river water could strongly affect the $^{87}\text{Sr}/^{86}\text{Sr}$. For example, mixing in

only 0.5% of blended residue leachate would increase the $^{87}\text{Sr}/^{86}\text{Sr}$ in lake water by about 0.007 which is two orders of magnitude higher than typical analytical uncertainty ($2\text{SD} \approx 0.00005$). In contrast, mixing lake water with at least 30% of coal mine drainage water is required to shift a detectable increase in $^{87}\text{Sr}/^{86}\text{Sr}$.

It is also worth noting that the effectiveness of using a tracer depends on the distinction in the isotope composition and concentration of the tracer between all potential sources. Thus, it depends on the location in which the blended residue will be used as fill material. Many studies have shown that $^{87}\text{Sr}/^{86}\text{Sr}$ in surface waters such as riverine waters are strongly controlled by the lithology of the drainage bedrocks (Stevenson et al., 2018; Yang et al., 1996). Tracing the leachate plume using $^{87}\text{Sr}/^{86}\text{Sr}$ would be most effective in areas of young rock types such as limestones and basalts. Because the leachate of the blended residue is very high in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.792–0.810), this study demonstrates that the $^{87}\text{Sr}/^{86}\text{Sr}$ is a sensitive tracer of the blended residue leachate with strong potential as a tool for verification of safe use of this residue as fill material for mine reclamation in a wide range of hydrochemically and geologically complex areas.

4. Conclusion

This study reports the potential release of Tl and the roles of amendments in mitigating the release of Tl from the gypsum rich blended residue, a solid by-product from the metallurgical extraction of lepidolite for lithium. In addition, radiogenic Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) were evaluated for their usefulness as a tracer of the leachates when the blended residue is used as fill material in the environment. This study found that heavy metal (e.g., As, Cd, Pb) and radionuclide levels in the blended residue are below the Canadian guidelines for the management of NORM and soil standards for soil in a non-potable groundwater area, except Tl concentration which was about seven times higher than the guideline's level. Because most Tl (up to 50%) can be extracted using mildly acidic water, pre-leach of the blended residue before using it as fill material will significantly mitigate the risk of Tl release into groundwater aquifers. This highly soluble fraction of Tl may easily be transported to groundwater aquifers if low Tl⁺ sorption occurs throughout the soil column. Thus, the blended residue must be treated properly prior to disposal.

Mixing the blended residue with amendments used in this study was not only to meet the guideline for Tl in soil but also help suppress the release of Tl through increasing Tl adsorption capacity. Mixing proportion did not greatly affect the Tl removal efficiencies of clay, biochar, and topsoil. However, high level of peat in the mixture promotes acidic conditions which apparently enhances the release of Tl, thus decreasing the removal efficiency. Thus, peat is not recommended as a suitable amendment for Tl removal. Biochar is the most effective amendment in removing Tl if adequate mixing time is provided (~ 7 days), while quickly achieved high Tl removal efficiencies of clay and topsoil make these two the most promising contenders under well drained condition.

The greatly distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the leachates of the blended residue and its mixtures with surface waters demonstrates that $^{87}\text{Sr}/^{86}\text{Sr}$ can be one of the most effective tracers of the leachate plume. Future studies can use the sequential extraction methods to determine the distribution of Tl in different mineralogical reservoirs of the blended residue. Such information provides valuable insights into the extent of Tl release under varying environments (e.g., changes in redox condition, temperature) under which the blended residue might be used.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This study was funded by a research contract grant from Lepidoco Ltd. to Rezanezhad and Phan and was supported in part by the Natural Sciences and Engineering Research Council Partnership Grants with Knight Piésold Ltd (Engage Grant to Rezanezhad: EGP-533973 - 18) and the University of Waterloo starter grant to Phan. We would like to acknowledge the lab supplies provided by the Canada Excellence Research Chair program in Ecohydrology and facilities in the Metal Isotope Geochemistry Laboratory at the University of Waterloo. We also thank Marianne Vandergriendt for technical support throughout the experiments. We thank Dr. Su Shiung Lam for careful handling of the manuscript as an associate editor and anonymous reviewers for their constructive comments.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2021.100035.

References

- Alloway, B.J., 2012. Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability. Springer Science & Business Media.
- Anderson, C., Brooks, R., Chiarucci, A., LaCoste, C., Leblanc, M., Robinson, B., Simcock, R., Stewart, R., 1999. Phytomining for nickel, thallium and gold. *J. Geochem. Explorat.* 67, 407–415.
- Bhattacharyya, K.G., Gupta, S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in colloid and interface science* 140, 114–131.
- Cabala, J., Teper, L., 2007. Metalliferous constituents of rhizosphere soils contaminated by Zn–Pb mining in southern Poland. *Water Air Soil Pollut.* 178, 351–362.
- Capo, R.C., Stewart, B.W., Chadwick, O.A., 1998. Strontium isotopes as tracers of ecosystem processes: theory and methods. *Geoderma* 82, 197–225.
- Chapman, E.C., Capo, R.C., Stewart, B.W., Kirby, C.S., Hammack, R.W., Schroeder, K.T., Edenborn, H.M., 2012. Geochemical and strontium isotope characterization of produced waters from Marcellus Shale natural gas extraction. *Environ. Sci. Technol.* 46, 3545–3553.
- Cheam, V., 2001. Thallium contamination of water in Canada. *Water Q. Res. J.* 36, 851–877.
- Cui, X., Zheng, Z., Zhang, H., Zhang, C., Li, X., Zhu, P., Chen, Z., 2020. Impact of water-rock interactions on indicators of hydraulic fracturing flowback fluids produced from the Jurassic shale of Qaidam Basin, NW China. *J. Hydrol.* 590, 125541.
- Daiyan, C., Guanxin, W., Zhenxi, Z., Yuming, C., 2003. Lanmchangite, a new thallium (hydrated) sulphate from Lanmchang, Guizhou Province, China. *Chinese J. Geochem.* 22, 185–192.
- Das, B., Mondal, N.K., 2011. Calcareous soil as a new adsorbent to remove lead from aqueous solution: equilibrium, kinetic and thermodynamic study. *Univ. J. Environ. Res. Technol.* 1, 515–530.
- Davies, M., Figueroa, L., Wildeman, T., Bucknam, C., 2016. The oxidative precipitation of thallium at alkaline pH for treatment of mining influenced water. *Mine Water Environ.* 35, 77–85.
- Dessemond, C., Lajoie-Leroux, F., Soucy, G., Laroche, N., Magnan, J.-F., 2019. Spodumene: The lithium market, resources and processes. *Minerals* 9, 334.
- Faure, G., Mensing, T.M., 2005. *Isotopes: Principles and Applications*. Wiley-Blackwell.
- Geeza, T.J., Gillikin, D.P., McDevitt, B., Van Sice, K., Warner, N.R., 2018. Accumulation of Marcellus Formation oil and gas wastewater metals in freshwater mussel shells. *Environ. Sci. Technol.* 52, 10883–10892.
- Gomez-Gonzalez, M.A., Garcia-Guinea, J., Laborda, F., Garrido, F., 2015. Thallium occurrence and partitioning in soils and sediments affected by mining activities in Madrid province (Spain). *Sci. Total Environ.* 536, 268–278.
- Grosjean, C., Miranda, P.H., Perrin, M., Poggi, P., 2012. Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. 16, 1735–1744.
- He, L., Zhong, H., Liu, G., Dai, Z., Brookes, P.C., Xu, J., 2019. Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China. *Environ. Pollut.* 252, 846–855.
- Jacobson, A.R., McBride, M.B., Baveye, P., Steenhuis, T.S., 2005. Environmental factors determining the trace-level sorption of silver and thallium to soils. *Sci. Total Environ.* 345, 191–205.
- Jardine, T.D., Doig, L.E., Jones, P.D., Bharadwaj, L., Carr, M., Tendler, B., Lindenschmidt, K.-E., 2019. Vanadium and thallium exhibit biodilution in a northern river food web. *Chemosphere* 233, 381–386.
- Kalmykova, Y., Strömvall, A.-M., Steenari, B.-M., 2008. Adsorption of Cd, Cu, Ni, Pb and Zn on Sphagnum peat from solutions with low metal concentrations. 152, 885–891.
- Kaplan, D.I., Mattigod, S.V., 1998. Aqueous geochemistry of thallium. *Adv. Environ. Sci. Technol.* New York 29, 15–30.
- Karbowska, B., 2016. Presence of thallium in the environment: sources of contaminations, distribution and monitoring methods. *Environ. Monit. Assess.* 188, 640.

- Kavanagh, L., Keohane, J., Garcia Cabellos, G., Lloyd, A., Cleary, J., 2018. Global lithium sources—industrial use and future in the electric vehicle industry: a review. *Resources* 7, 57.
- Kelly, E.N., Schindler, D.W., Hodson, P.V., Short, J.W., Radmanovich, R., Nielsen, C.C., 2010. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. *Proc. Natl. Acad. Sci.* 107, 16178–16183.
- Li, H., Dong, X., da Silva, E.B., de Oliveira, L.M., Chen, Y., Ma, L.Q., 2017. Mechanisms of metal sorption by biochars: biochar characteristics and modifications. *Chemosphere* 178, 466–478.
- Li, H., Li, X., Chen, Y., Long, J., Zhang, G., Xiao, T., Zhang, P., Li, C., Zhuang, L., Huang, W., 2018. Removal and recovery of thallium from aqueous solutions via a magnetite-mediated reversible adsorption-desorption process. *J. Cleaner Product.* 199, 705–715.
- Liu, J., Luo, X., Sun, Y., Tsang, D.C.W., Qi, J., Zhang, W., Li, N., Yin, M., Wang, J., Lippold, H., Chen, Y., Sheng, G., 2019. Thallium pollution in China and removal technologies for waters: a review. *Environ. Int.* 126, 771–790.
- Liu, J., Ren, J., Zhou, Y., Tsang, D.C.W., Lin, J., Yuan, W., Wang, J., Yin, M., Wu, Y., Xiao, T., Chen, Y., 2020a. Effects and mechanisms of mineral amendment on thallium mobility in highly contaminated soils. *J. Environ. Manage.* 262, 110251.
- Liu, J., Wei, X., Zhou, Y., Tsang, D.C.W., Bao, Z.a., Yin, M., Lippold, H., Yuan, W., Wang, J., Feng, Y., Chen, D., 2020b. Thallium contamination, health risk assessment and source apportionment in common vegetables. *Sci. Total Environ.* 703, 135547.
- Liu, J., Zhou, Y., She, J., Tsang, D.C.W., Lippold, H., Wang, J., Jiang, Y., Wei, X., Yuan, W., Luo, X., Zhai, S., Song, L., 2020c. Quantitative isotopic fingerprinting of thallium associated with potentially toxic elements (PTEs) in fluvial sediment cores with multiple anthropogenic sources. *Environ. Pollut.* 266, 115252.
- Martin, L.A., Wissocq, A., Benedetti, M., Latrille, C., 2018. Thallium (Tl) sorption onto illite and smectite: Implications for Tl mobility in the environment. *Geochim. Cosmochim. Acta* 230, 1–16.
- McArthur, J.M., Howarth, R., Bailey, T., 2001. Strontium isotope stratigraphy: LOWESS version 3: best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical age. *J. Geol.* 109, 155–170.
- McIntosh, J.C., Walter, L.M., 2006. Paleowaters in Silurian-Devonian carbonate aquifers: Geochemical evolution of groundwater in the Great Lakes region since the Late Pleistocene. *Geochim. Cosmochim. Acta* 70, 2454–2479.
- McNutt, R.H., Gascoyne, M., Kaminieni, D.C., 1987. $^{87}\text{Sr}/^{86}\text{Sr}$ values in groundwaters of the East Bull Lake pluton, Superior Province, Ontario, Canada. *Appl. Geochem.* 2, 93–101.
- Memon, S.Q., Memon, N., Solangi, A.R., Memon, J.-u.-R., 2008. Sawdust: A green and economical sorbent for thallium removal. *Water* 140, 235–240.
- Meshram, P., Pandey, B.D., Mankhand, T.R., 2014. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy* 150, 192–208.
- Munk, L.A., Hynek, S.A., Bradley, D., Boutt, D., Labay, K., Jochens, H., 2016. Lithium brines: a global perspective. *Rev. Econ. Geol.* 18, 339–365.
- Neymark, L.A., Premo, W.R., Mel'nikov, N.N., Emsbo, P., 2014. Precise determination of ^{88}Sr in rocks, minerals, and waters by double-spike TIMS: a powerful tool in the study of geological, hydrological and biological processes. *J. Anal. At. Spectrom.* 29, 65–75.
- O'Connor, D., Peng, T., Zhang, J., Tsang, D.C.W., Alessi, D.S., Shen, Z., Bolan, N.S., Hou, D., 2018. Biochar application for the remediation of heavy metal polluted land: A review of in situ field trials. *Water* 10, 815–826.
- Ontario, M.o.t.E., 2011. Soil, ground water and sediment standards for use under Part XV.1 of the Environmental Protection Act. Accessed October 14, 2020. <https://www.ontario.ca/page/soil-ground-water-and-sediment-standards-use-under-part-xv1-environmental-protection-act>.
- Peerawattuk, I., Bobicki, E., 2018. Lithium Extraction and Utilization: A Historical Perspective, Extraction 2018. Springer, pp. 2209–2224.
- Peter, A.L.J., Viraraghavan, T., 2005. Thallium: a review of public health and environmental concerns, pp. 493–501.
- Petrini, R., Cidu, R., Slejko, F.F., 2016. In: Thallium Contamination in the Raibil Mine Site Stream Drainage System (Eastern Alps, Italy), 35. *Mine Water Environ.*, pp. 55–63.
- Phan, T.T., Hakala, J.A., Lopano, C.L., Sharma, S., 2019. Rare earth elements and radiogenic strontium isotopes in carbonate minerals reveal diagenetic influence in shales and limestones in the Appalachian basin. *Chem. Geol.* 509, 194–212.
- Phan, T.T., Hakala, J.A., Sharma, S., 2020. Application of isotopic and geochemical signals in unconventional oil and gas reservoir produced waters toward characterizing in situ geochemical fluid-shale reactions. *Sci. Total Environ.* 714, 136867.
- Phan, Thai, Paukert Vankeuren, Amelia N., Hakala, J. Alexandra, 2018. Role of water-rock interaction in the geochemical evolution of Marcellus Shale produced waters. *International Journal of Coal Geology* 191, 95–111. doi:10.1016/j.coal.2018.02.014.
- Raczek, I., Jochum, K.P., Hofmann, A.W., 2003. Neodymium and strontium isotope data for USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, GSP-1, GSP-2 and eight MPI-DING reference glasses. *Geostandards Newsletter* 27, 173–179.
- Rajapaksha, A.U., Alam, M.S., Chen, N., Alessi, D.S., Igalavithana, A.D., Tsang, D.C.W., Ok, Y.S., 2018. Removal of hexavalent chromium in aqueous solutions using biochar: Chemical and spectroscopic investigations, pp. 1567–1573.
- Rezanezhad, F., Price, J.S., Quinton, W.L., Lennartz, B., Milojevic, T., Van Cappellen, P., 2016. Structure of peat soils and implications for water storage, flow and solute transport: A review update for geochemists. *Chem. Geol.* 429, 75–84.
- Robalds, A., Klavins, M., Dreijalte, L., 2013. Sorption of thallium (I) ions by peat. *Water Sci. Technol.* 68, 2208–2213.
- Rosa, E., Gaillardet, J., Hillaire-Marcel, C., Hélie, J.-F., Richard, L.-F., 2012. Rock denudation rates and organic carbon exports along a latitudinal gradient in the Hudson, James, and Ungava bays watershed. *Canad. J. Earth Sci.* 49, 742–757.
- Russell, W., Papanastassiou, D., Tombrello, T., 1978. Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* 42, 1075–1090.
- Salifu, M., Aiglsperger, T., Hällström, L., Martinsson, O., Billström, K., Ingri, J., Dold, B., Alakangas, L., 2018. Strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes: A tracer for geochemical processes in mineralogically-complex mine wastes. *Appl. Geochem.* 99, 42–54.
- Sanderson, J., Czarnecki, A., Faria, D., 2012. Water and suspended sediment quality of the Transboundary reach of the Slave River, Northwest Territories Report prepared for Aboriginal Affairs and Northern Development Canada. Yellowknife, Northwest Territories.
- Santonastaso, G.F., Erto, A., Bortone, I., Chianese, S., Di Nardo, A., Musmarra, D., 2018. Experimental and simulation study of the restoration of a thallium (I)-contaminated aquifer by Permeable Adsorptive Barriers (PABs). *Sci. Total Environ.* 630, 62–71.
- Schoer, J., Nagel, U., 1980. Thallium in Pflanzen und Böden. *Sci. Nature* 67, 261–262.
- Sharma, D.C., Forster, C.F., 1993. Removal of hexavalent chromium using sphagnum moss peat. *Water* 27, 1201–1208.
- Shen, Y., Buick, R., 2004. The antiquity of microbial sulfate reduction. *Earth-Sci. Rev.* 64, 243–272.
- Sparling, G.P., 1992. Ratio of microbial biomass carbon to soil organic carbon as a sensitive indicator of changes in soil organic matter. *Soil Res.* 30, 195–207.
- Stevenson, R., Pearce, C.R., Rosa, E., Hélie, J.-F., Hillaire-Marcel, C., 2018. Weathering processes, catchment geology and river management impacts on radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$) and stable ($\delta^{88}\text{Sr}/^{86}\text{Sr}$) strontium isotope compositions of Canadian boreal rivers. *Chem. Geol.* 486, 50–60.
- Stewart, M.K., McDonnell, J.J., 1991. Modeling base flow soil water residence times from deuterium concentrations. *Water Resour. Res.* 27, 2681–2693.
- Sun, J., Zou, X., Ning, Z., Sun, M., Peng, J., Xiao, T., 2012. Culturable microbial groups and thallium-tolerant fungi in soils with high thallium contamination. *Sci. Total Environ.* 441, 258–264.
- Tang, J., Wu, W., Yu, L., Fan, X., Liu, G., Yu, Y., 2019. Study on adsorption properties and mechanism of thallium onto titanium-iron magnetic adsorbent. *Sci. Total Environ.* 694, 133625.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace-Metals. *Anal. Chem.* 51, 844–851.
- Tremel, A., Masson, P., Sterckeman, T., Baize, D., Mench, M., 1997. Thallium in French agrosystems—I. Thallium Contents Arable Soils 95, 293–302.
- U.S. EPA, 1994. Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods, EPA SW-846, Office of Solid Waste and Emergency Response (OSWER), Washington, DC (1994).
- Vaněk, A., Grösslová, Z., Mihaljevič, M., Ettler, V., Trubač, J., Chrástný, V., Penížek, V., Teper, L., Cabala, J., Voegelin, A., 2018. Thallium isotopes in metallurgical wastes/contaminated soils: A novel tool to trace metal source and behavior. *J. Hazard. Mater.* 343, 78–85.
- Vaněk, A., Grösslová, Z., Mihaljevič, M., Trubač, J., Ettler, V., Teper, L., Cabala, J., Rohovec, J., Zádorová, T., Penížek, V., Pavlí, L., Holubík, O., Němeček, K., Houška, J., Drábek, O., Ash, C., 2016. Isotopic Tracing of Thallium Contamination in Soils Affected by Emissions from Coal-Fired Power Plants. *Environ. Sci. Technol.* 50, 9864–9871.
- Vaněk, A., Grygar, T., Chrástný, V., Tejnecký, V., Drahot, P., Komárek, M., 2010. Assessment of the BCR sequential extraction procedure for thallium fractionation using synthetic mineral mixtures. *J. Hazard. Mater.* 176, 913–918.
- Vaněk, A., Voegelin, A., Mihaljevič, M., Ettler, V., Trubač, J., Drahot, P., Vaňková, M., Oborná, V., Vejvodová, K., Penížek, V., Pavlí, L., Drábek, O., Vokurková, P., Zádorová, T., Holubík, O., 2020. Thallium stable isotope ratios in naturally Tl-rich soils. *Geoderma* 364, 114183.
- Wadleigh, M.A., Veizer, J., Brooks, C., 1985. Strontium and its isotopes in Canadian rivers: Fluxes and global implications. *Geochim. Cosmochim. Acta* 49, 1727–1736.
- Wall, A.J., Capo, R.C., Stewart, B.W., Phan, T.T., Jain, J.C., Hakala, J.A., Guthrie, G.D., 2013. High throughput method for Sr extraction from variable matrix waters and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope analysis by MC-ICP-MS. *J. Anal. At. Spectrom.* 28, 1338–1344.
- Wang, Z., Coyte, R.M., Dwyer, G.S., Ruhl, L.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2020. Distinction of strontium isotope ratios between water-soluble and bulk coal fly ash from the United States. *Int. J. Coal Geol.* 222, 103464.
- Watmough, S., 2018. An assessment of the Ca weathering sources to surface waters on the Precambrian Shield in central Ontario. *Sci. Total Environ.* 626, 69–76.
- Wei, X., Zhou, Y., Tsang, D.C., Song, L., Zhang, C., Yin, M., Liu, J., Xiao, T., Zhang, G., Wang, J., 2020. Hyperaccumulation and transport mechanism of thallium and arsenic in brake ferns (*Pteris vittata* L.): A case study from mining area. *J. Hazard. Mater.* 388, 121756.
- Welch, S.A., Ullman, W.J., 1996. Feldspar dissolution in acidic and organic solutions: Compositional and pH dependence of dissolution rate. *Geochim. Cosmochim. Acta* 60, 2939–2948.
- Wick, S., Baeyens, B., Marques Fernandes, M., Voegelin, A., 2018. Thallium Adsorption onto Illite. *Environ. Sci. Technol.* 52, 571–580.
- Xiao, T., Guha, J., Boyle, D., Liu, C.-Q., Zheng, B., Wilson, G.C., Rouleau, A., Chen, J., 2004. Naturally occurring thallium: a hidden geoenvironmental health hazard? *Water* 30, 501–507.
- Xiao, T., Yang, F., Li, S., Zheng, B., Ning, Z., 2012. Thallium pollution in China: a geo-environmental perspective. *Sci. Total Environ.* 421, 51–58.
- Yang, C., Telmer, K., Veizer, J., 1996. Chemical dynamics of the “St. Lawrence” riverine system: $\delta\text{D}_{\text{H}_2\text{O}}$, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{34}\text{S}_{\text{sulfate}}$, and dissolved $^{87}\text{Sr}/^{86}\text{Sr}$. *Geochim. Cosmochim. Acta* 60, 851–866.
- Zhang, X., Tan, X., Li, C., Yi, Y., Liu, W., Zhang, L., 2019. Energy-efficient and simultaneous extraction of lithium, rubidium and cesium from lepidolite concentrate via sulfuric acid baking and water leaching. *Hydrometallurgy* 185, 244–249.

SUPPORTING MATERIALS

Lepidolite extraction solid by-product: mitigation of thallium leaching and utilization of radiogenic strontium isotopes as a tracer

Thai T. Phan¹, Leah Fulton¹, John Ulkem¹, Steve Aiken², Amber Blackwell², Joe Walsh³, Peter Walker³, Fereidoun Rezanezhad⁴

¹Department of Earth and Environmental Sciences, University of Waterloo, Canada

²Knight Piésold Ltd

³Lepidico Ltd

⁴Ecohydrology Research Group, Department of Earth and Environmental Sciences and Water Institute, University of Waterloo, Waterloo, ON, Canada

*Corresponding author:

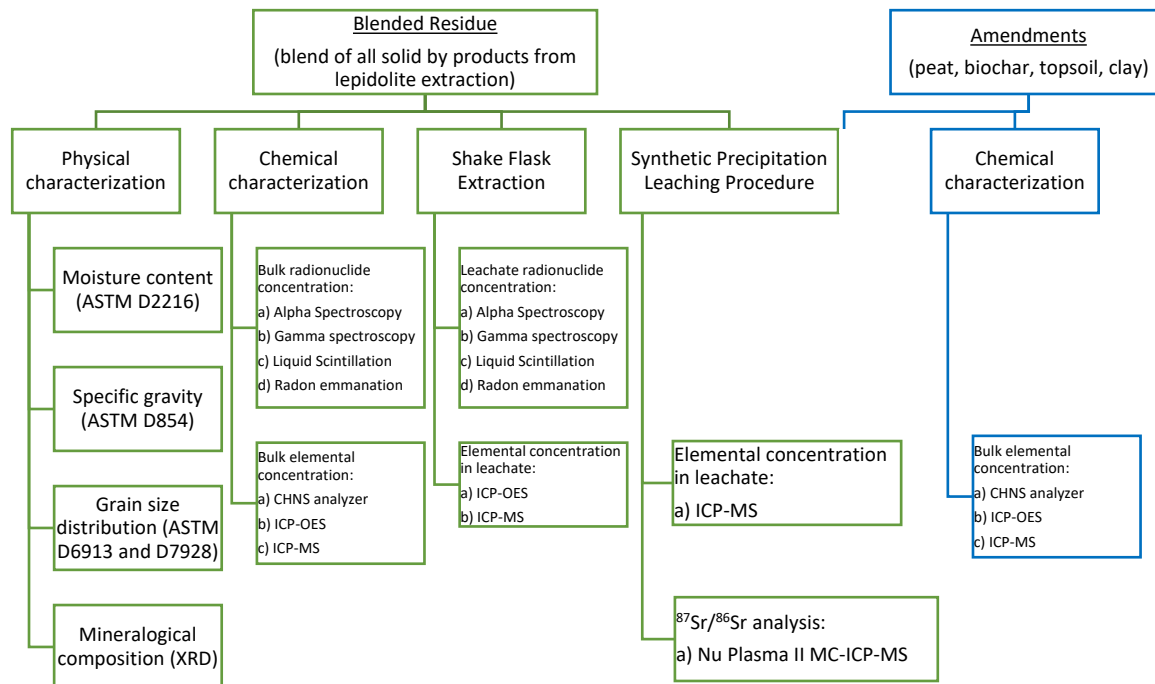
Thai T. Phan

Department of Earth and Environmental Sciences, University of Waterloo,

200 University Avenue West, Waterloo, Ontario, Canada, N2L 3G1

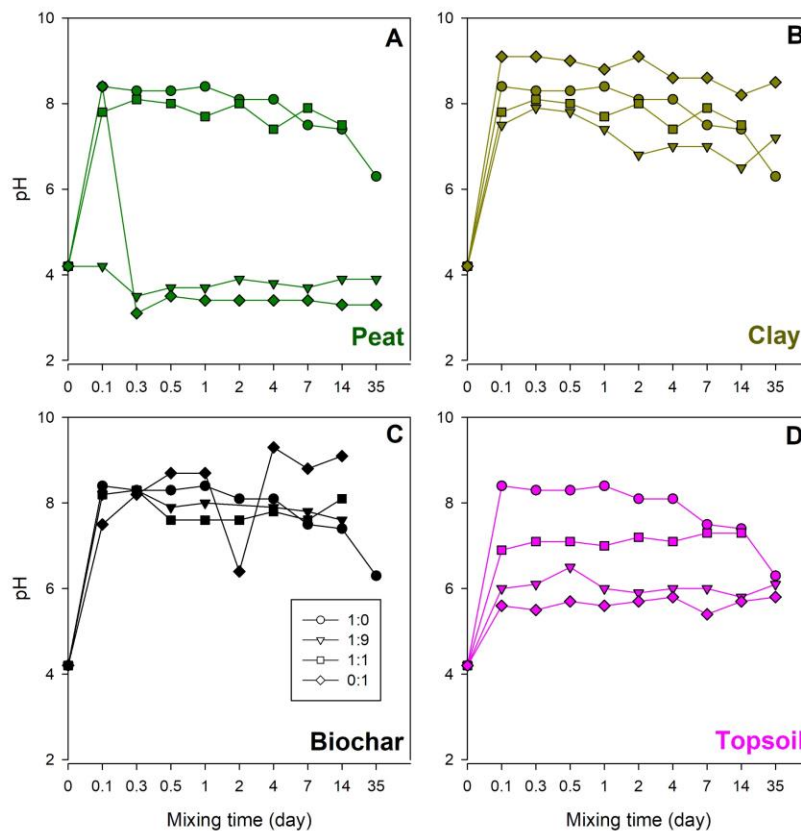
Phone: (519) 888-4567, Ext. 37673, Fax: (519) 746-7484

Email: thai.phan@uwaterloo.ca



41
42
43
44

Figure S1 A flow chart summarizing all experiments and analysis used in this study



45
46
47
48

Figure S2 Temporal change in pH in SPLP leachates of the blended residue and its mixtures with peat (A), clay (B), biochar (C), and soil (D). The ratios in the legend in (C) represent the mass ratios of the blended residue and the amendment (i.e. 1:9 denotes a mixture containing 10% of the blended residue and 90% of the amendment)

Tabl S1 Physical properties of the blended residue

Sample ID ^a	Moisture Content (%)	Specific Gravity	Grain Size Distribution		
			Sand (4.75 to 0.074 mm) (%)	Silt (0.074 to 0.002 mm) (%)	Clay (< 0.002 mm) (%)
Blended Residue 1	-	2.51	15.0	83.0	3.0
Blended Residue 2	74.0	-	-	-	-

a: the blended residues analyzed for physical properties are from different batches with the one used for SPLP leaching experiments

Table S2 Mineralogical composition of the blended residue

Mineral Name	Chemical Formula	Approx. wt % ^a
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	60
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4, \text{CO}_3)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	17
Calcite	CaCO_3	6
Plagioclase Feldspars	$(\text{Na}, \text{Ca})\text{Al}(\text{Si}, \text{Al})_3\text{O}_8$	6
Mica/Illite	$(\text{K}, \text{Na}, \text{Ca})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH}, \text{F})_2$	<5
Quartz	SiO_2	<5
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	<3
"Unidentified"	not applicable	<5

a: the blended residue analyzed for mineralogical composition is from a different batch with the one used for SPLP leaching experiments

Table S3 Radionuclides release from the blended residue and its leachate from the shake flask extraction

	Derived Release Limit - Solid ^a	Unit	Blended residue-solid ^b	Derived Release Limit - Liquid ^a	Unit	Blended residue-leachate ^b
Gamma Spectroscopy						
Radium-228	0.3	Bq/g	<0.09	5	Bq/L	<0.4
Potassium-40	17	Bq/g	0.3			60
Thorium-234		Bq/g	0.03	10	Bq/L	<4
Uranium-235	0.3	Bq/g	0.00028			<0.00006
Alpha Spectroscopy						
Thorium-228	0.3	Bq/g	<0.02	1	Bq/L	<0.1
Thorium-230	10	Bq/g	0.08	5	Bq/L	<0.1
Liquid Scintillation						
Lead-210	0.3	Bq/g	<0.04	1	Bq/L	<0.2
Radon Emanation						
Radium-226	0.3	Bq/g	0.02	5	Bq/L	0.08

a: Terrestrial derived release limit based on values provided by Canadian Guidelines for the Management of Naturally Occurring Radioactive Materials (NORM), Health Canada, 2011.

b: the blended residue used in the shake flask extraction is from a different batch with the one used for SPLP leaching experiments

No values exceeded the NORM guideline levels for the given isotopes

Table S4 Total elemental composition in the blended residue and amendments (clay, biochar, soil, peat)

Element ^a	Unit	Blended residue ^b		Clay	Biochar	Soil	Peat	Ontario's soil standard-Industrial/Commercial/Community Property Use ^c
		mean	±2SD					
Al	%	6.22	0.36	8.13	0.55	0.54	0.08	n/a
Ca	%	21.23	0.31	1.53	2.66	2.37	0.09	n/a
Fe	%	0.12	0.01	0.77	2.66	0.58	< 0.05	n/a
K	%	1.10	0	1.10	0.10	0.40	< 0.1	n/a
Mg	%	0.95	0.01	1.93	0.74	0.55	0.11	n/a
S	%	15.37	0.31	< 0.01	0.05	0.39	0.05	n/a
Si	%	1.17	0.06	> 30.0	1.10	1.56	0.40	n/a
Ti	%	< 0.01		0.09	0.02	0.03	< 0.01	n/a
C (total)	%	0.61		n/a	n/a	n/a	n/a	n/a
C (inorganic)	%	0.24		n/a	n/a	n/a	n/a	n/a
C (organic)	%	0.37		n/a	n/a	n/a	n/a	n/a
N	%	0.05		n/a	n/a	n/a	n/a	n/a
As	mg/kg	< 5		9.00	< 5	< 5	< 5	18
B	mg/kg	< 10		60	20	20	< 10	120
Ba	mg/kg	21.33	1.15	30	100	65	14	670
Be	mg/kg	4.0	0.0	5.00	< 3	< 3	< 3	8
Bi	mg/kg	< 2		< 2	< 2	< 2	< 2	n/a
Cd	mg/kg	< 2		< 2	< 2	< 2	< 2	1.9
Ce	mg/kg	3.03	1.17	79.00	2.80	9.90	0.80	n/a
Co	mg/kg	0.47	0.23	0.90	0.60	1.90	< 0.2	80
Cr	mg/kg	50.00	20	< 30	890.00	< 30	< 30	160
Cs	mg/kg	157.33	4.16	4.80	0.10	0.30	< 0.1	n/a
Cu	mg/kg	15.67	3.06	2.00	23.00	70.00	< 2	230
Dy	mg/kg	0.33	0.12	3.30	< 0.3	0.40	< 0.3	n/a
Er	mg/kg	0.20	0	2.40	< 0.1	0.20	< 0.1	n/a
Eu	mg/kg	< 0.1		0.50	< 0.1	0.10	< 0.1	n/a
Ga	mg/kg	33.70	3.14	16.70	1.10	1.50	0.20	n/a
Gd	mg/kg	0.30	0.2	3.40	0.10	0.60	< 0.1	n/a
Ge	mg/kg	< 0.7		1.60	< 0.7	< 0.7	< 0.7	n/a
Ho	mg/kg	< 0.2		0.70	< 0.2	< 0.2	< 0.2	n/a
Hf	mg/kg	< 10		< 10	< 10	< 10	< 10	n/a
In	mg/kg	0.23	0.12	< 0.2	< 0.2	< 0.2	< 0.2	n/a
La	mg/kg	1.73	0.42	43.30	1.30	5.50	0.40	n/a
Li	mg/kg	645.67	19	152.00	< 3	< 3	< 3	n/a
Mn	mg/kg	501.33	45	564.00	3170.00	233.00	50.00	n/a
Mo	mg/kg	4.33	1.15	3.00	16.00	2.00	< 1	40

Nb	mg/kg	26.03	1.8	14.90	40.00	< 2.4	< 2.4	n/a
Nd	mg/kg	1.67	0.92	22.50	1.10	4.30	< 0.4	n/a
Ni	mg/kg	< 10		< 10	< 10	< 10	< 10	270
Pb	mg/kg	< 0.8		30.80	2.00	2.90	5.20	120
Pr	mg/kg	0.43	0.12	7.40	0.30	1.20	< 0.1	n/a
Rb	mg/kg	750.67	43.5	73.40	3.00	7.00	1.40	n/a
Sb	mg/kg	< 2		< 2	< 2	< 2	< 2	40
Se	mg/kg	< 8		< 8	< 8	< 8	< 8	5.5
Sm	mg/kg	0.33	0.31	3.70	0.10	0.60	< 0.1	n/a
Sn	mg/kg	72.10	9.36	4.00	1.40	< 0.5	< 0.5	n/a
Sr	mg/kg	1060.00	60	148.00	41.00	121.00	11.00	n/a
Ta	mg/kg	0.30	0	1.40	0.40	< 0.2	< 0.2	n/a
Tb	mg/kg	0.10		0.50	< 0.1	< 0.1	< 0.1	n/a
Te	mg/kg	< 6		< 6	< 6	< 6	< 6	n/a
Th	mg/kg	0.57	0.31	35.60	0.30	0.90	0.10	n/a
Tl	mg/kg	24.70	0.87	0.40	< 0.1	< 0.1	< 0.1	3.3
Tm	mg/kg	< 0.1		0.40	< 0.1	< 0.1	< 0.1	n/a
U	mg/kg	0.77	0.12	4.60	0.10	1.40	< 0.1	33
V	mg/kg	< 5		13.00	42.00	10.00	< 5	86
W	mg/kg	14.20	1.11	16.80	19.90	< 0.7	< 0.7	n/a
Y	mg/kg	2.77	0.81	23.80	0.80	2.50	0.40	n/a
Yb	mg/kg	< 0.1		3.80	< 0.1	0.20	< 0.1	n/a
Zn	mg/kg	< 30		30.00	40.00	90.00	< 30	340

n/a = not available

a: analyzed by ICP-OES and ICP-MS at the Activation Laboratories, Canada using sodium peroxide fusion method

b: three separate splits of the homogenized blended residue were digested and analyzed. The blended residue is from the same batch that is used in the SPLP experiments

c: Ontario's soil, ground water and sediment standards effective July 1, 2011 applying for medium and fine textured soils in a non-potable groundwater area

Table S5 Metal release from the blended residue in the shake flash extraction

Parameter	Blended residue-leachate mg/kg ^a	Blended residue-leachate % ^b	Blended residue_solid ^c mg/kg
Initial pH	7.94		
Final pH	9.23		
Sulphate	12000	4.2	288796
Mg	4.38	0.1	4200
Ca	1011	0.5	190000
Na	885	na	na
K	5850	81.3	7200
Hg	<0.00003	na	
Ag	<0.0002	na	0.02
Al	2.148	0.0	42000
As	0.0009	0.1	1.4
Ba	0.1194	1.4	8.3
B	1.32	na	
Be	<0.00002	na	8.6
Bi	<0.00002	na	0.28
Cd	0.00009	0.1	0.12
Co	0.000114	0.0	0.94
Cr	0.0897	0.3	30
Cu	0.00414	0.0	15
Fe	<0.02	<0.003	710
Li	27.18	1.9	1400
Mn	0.00045	0.0	470
Mo	0.1929	17.5	1.1
Ni	0.0003	0.002	17
Pb	0.00009	0.004	2.4
Sb	<0.0006	na	<0.8
Se	0.00066	na	<0.7
Si	1.8	na	
Sn	0.00927	0.0	33
Sr	4.68	6.2	75
Ti	0.00018	0.0	58
Tl	0.828	10.8	7.7
U	0.000018	0.0	0.57
V	0.00102	0.1	2
Zn	<0.006	<0.03	21

a: mg of element leached per kg of the blended residue

b: % of element leached comparing to the concentration of the element in the blended residue

c: the blended residue used in the shake flask extraction is from a different batch with the one used for SPLP leaching experiments

Table S6 Summary of all SPLP leaching experiments

Experiments	Solid in each experiment (wt. %)				
	Blended residue	Peat	Clay	Biochar	Soil
1	100	0	0	0	0
2	0	100	0	0	0
3	0	0	100	0	0
4	0	0	0	100	0
5	0	0	0	0	100
6	10	90	0	0	0
7	10	0	90	0	0
8	10	0	0	90	0
9	10	0	0	0	90
10	50	50	0	0	0
11	50	0	50	0	0
12	50	0	0	50	0
13	50	0	0	0	50

Table S7. Elemental concentrations in leachate samples of the blended residue and its mixtures with varying amendments following SPLP method

Time (hr)	2	6	12	24	48	96	168	336	840
Elements	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Experiment 1: Blended Residue = 100%									
Na	350	433	503	511	610	604	627	628	n/a
Mg	134	160	186	172	177	177	370	491	n/a
Al	77	47	53	49	64	64	19	17	5
Si	0.9	1.5	1.5	1.5	2.0	2.1	2.9	4.0	2.4
P	0.06	0.10	0.06	0.06	0.11	0.14	0.06	0.15	0.06
K	5039	6449	7119	7348	8096	8179	8633	8419	n/a
Ca	8632	8213	9088	8153	7797	7660	6948	6864	n/a
Sr	144	202	269	255	272	281	272	266	193
Tl	8.0	9.0	10.7	10.5	11.9	12.0	12.3	12.1	12.7
Experiment 2: Peat = 100%									
Na	123	139	128	145	147	157	155	171	n/a
Mg	50	59	58	65	71	78	82	85	n/a
Al	2	2	2	2	2	1	1	1	1
Si	34	39	37	41	43	47	52	60	35
P	34	39	43	43	41	16	38	33	24
K	76	105	86	88	87	69	83	82	n/a
Ca	13	16	18	15	13	13	14	15	n/a
Sr	0.16	0.20	0.20	0.21	0.20	0.21	0.22	0.24	0.16
Tl	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Experiment 3: Clay = 100%									
Na	1180	1388	27	1501	1705	1528	1513	1220	2920
Mg	25	34	n/a	26	121	59	95	29	20
Al	73	110	n/a	79	326	147	291	92	73
Si	201	317	259	328	439	357	458	359	1043
P	26	32	30	33	29	33	35	31	99
K	57	66	n/a	71	84	71	71	53	390
Ca	542	577	n/a	624	611	635	575	453	653
Sr	0.90	1.00	n/a	0.98	1.13	1.02	1.06	0.79	0.20
Tl	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Experiment 4: Biochar = 100%									
Na	40	49	32	14	53	23	46	11	81
Mg	25	59	24	8	53	14	29	9	41
Al	52	80	42	64	6	32	82	17	84
Si	1	9	20	7	7	56	29	38	42
P	0.07	0.16	0.88	0.29	0.47	1.70	1.21	1.19	0.48
K	90	126	191	99	221	122	188	41	253
Ca	692	780	330	236	397	334	499	106	739
Sr	1.16	1.29	0.43	0.27	0.67	0.44	0.70	0.16	0.94
Tl	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Experiment 5: Soil = 100%

Na	1768	1823	1820	1782	1881	1738	1805	1689	3102
Mg	1354	1425	1411	1397	1426	1300	1413	1342	2404
Al	29	30	33	33	26	29	27	28	10
Si	18	21	25	26	29	28	27	46	232
P	462	481	468	426	436	448	443	434	1450
K	2101	2127	2130	2171	2260	2106	2150	2069	3858
Ca	2558	2618	2645	2684	2563	2430	2663	2573	4988
Sr	9.9	10.3	10.4	10.3	11.0	10.1	11.1	10.5	20.3
Tl	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002

Experiment 6: Peat = 90%; Blended Residue = 10%

Na	240	241	246	264	293	300	292	299	n/a
Mg	1313	1302	1387	1398	1784	1770	1726	1762	n/a
Al	902	860	1003	976	1298	1216	1219	1285	634
Si	95	86	99	98	133	125	126	137	66
P	29	29	18	14	9	9	9	7	3
K	855	846	889	911	881	813	770	788	n/a
Ca	9710	9617	10277	10014	9613	8513	7858	7440	n/a
Sr	63	65	70	68	74	70	67	68	48
Tl	0.81	0.80	0.83	0.83	0.95	0.77	0.72	0.82	0.74

Experiment 7: Clay = 90%; Blended Residue = 10%

Na	7467	5605	5837	5748	6027	5557	5787	5965	9594
Mg	685	654	705	722	790	738	808	857	1476
Al	27	29	29	29	29	27	27	29	7
Si	62	48	44	40	39	26	31	31	126
P	0	0	0	0	0	0	0	0	1
K	1088	1005	1043	1024	1080	973	997	1027	1506
Ca	8975	9936	10276	10337	10521	9725	9866	10222	19606
Sr	51	55	59	59	58	56	58	60	113
Tl	0.10	0.10	0.12	0.11	0.12	0.10	0.12	0.11	0.24

Experiment 8: Biochar = 90%; Blended Residue = 10%

Na	77	84	71	81	87	65	72	164	108
Mg	67	79	70	81	113	118	125	422	327
Al	66	63	23	13	11	12	14	23	10
Si	0.9	1.4	3.4	3.5	9.9	8.0	8.6	20.2	17.0
P	0.03	0.03	0.44	0.26	0.22	0.21	0.15	0.37	0.12
K	761	799	634	635	763	655	543	1721	1012
Ca	13226	13118	12389	11282	11329	10541	9379	22071	11103
Sr	69	69	67	66	71	67	58	154	73
Tl	0.41	0.17	0.18	0.12	0.12	0.08	0.06	0.11	0.05

Experiment 9: Soil = 90%; Blended Residue = 10%

Na	1664	1763	1798	1773	1920	1657	1750	1644	3129
Mg	2826	3098	3475	3157	3338	2897	3244	3033	6035
Al	28	29	27	28	31	26	27	26	5
Si	14	20	28	34	n/a	44	44	54	242

P	36	35	9	32	n/a	37	36	34	116
K	2741	2826	3505	2908	3104	2729	2845	2645	5132
Ca	13443	12872	17679	12911	12911	11704	12975	12226	27974
Sr	63	65	98	68	67	61	66	61	132
Tl	0.24	0.23	0.46	0.23	n/a	0.23	0.25	0.22	0.44

Experiment 10: Peat = 50%; Blended Residue = 50%

Na	331	364	357	371	418	403	436	444	n/a
Mg	1899	2287	2148	2610	3241	3472	3827	3921	n/a
Al	24	8	34	4	4	4	3	3	1
Si	43	70	85	110	191	181	211	232	118
P	1.95	1.95	2.18	1.95	1.68	1.11	1.22	1.03	0.62
K	2919	3456	3379	3478	3291	3204	3431	3255	na
Ca	9697	9773	10283	10051	9550	8004	8251	8022	n/a
Sr	119	155	149	173	159	155	175	167	124
Tl	2.61	2.27	2.18	2.02	2.08	1.58	1.73	1.39	1.41

Experiment 11: Clay = 50%; Blended Residue = 50%

Na	2706	3242	2680	2822	2916	2797	2801	2860	2869
Mg	341	386	289	301	344	345	432	596	687
Al	20	45	31	29	22	18	15	11	9
Si	1.97	1.58	1.69	2.04	2.66	3.40	4.71	5.90	10.41
P	0.06	0.03	0.06	0.06	0.06	0.06	0.06	0.07	0.22
K	2308	2720	2189	2459	2470	2411	2526	2465	2653
Ca	10977	9561	9646	9836	10350	9734	9863	9947	9298
Sr	105	120	122	127	133	129	133	138	142
Tl	1.57	1.45	1.51	1.71	1.64	1.55	1.62	1.58	1.56

Experiment 12: Biochar = 50%; Blended Residue = 50%

Na	219	127	196	177	205	247	196	253	261
Mg	120	70	118	111	123	138	263	486	659
Al	67	33	39	33	32	16	9	14	11
Si	0.95	0.90	1.90	2.01	3.02	2.85	3.87	5.11	6.10
P	0.03	0.03	0.24	0.22	0.26	0.30	0.29	0.36	0.14
K	2886	1679	3021	2819	3019	3231	3355	3940	4258
Ca	10717	5293	11259	10245	9910	9697	9825	10723	10354
Sr	116	78	180	170	169	169	178	196	197
Tl	3.17	2.60	2.06	1.67	0.88	1.24	1.01	1.00	0.77

Experiment 13: Soil = 50%; Blended Residue = 50%

Na	1241	1206	988	1019	803	955	928	974	910
Mg	2144	2290	1884	2133	1799	2163	2318	2570	2681
Al	31	28	10	12	7	11	11	14	5
Si	4.2	9.0	9.3	13.5	15.3	17.0	23.4	37.3	55.9
P	0.99	1.55	1.15	1.11	0.75	0.86	1.13	1.12	1.46
K	4543	4326	3767	3871	3302	3697	3716	3684	3491
Ca	14094	11205	11528	11944	9979	11184	10434	11528	10413
Sr	113	116	118	122	119	127	118	124	115
Tl	1.36	1.19	1.34	1.27	1.30	1.28	1.47	1.45	1.30

Table S8 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the leachates of the blended residue and its mixtures with the amendments

Leaching time (hr) ^a	Replicate ^b	$^{87}\text{Sr}/^{86}\text{Sr}$ ^c $\pm 2\text{SD}$ (n=2)	Reported value	Source
Experiment 1: Blended Residue = 100%				
	6	0.792298 0.000002		this study
	96	0.804743 0.000061		this study
	336	0.810396 0.000049		this study
Experiment 5: Soil = 100%				
	336	0.710659 0.000011		this study
	6	0.710689 0.000009		this study
	96	0.710667 0.000044		this study
Experiment 6: Peat = 90%; Blended Residue = 10%				
	6	0.796332 0.000062		this study
	96	0.794195 0.000051		this study
	336	0.794012 0.000043		this study
Experiment 7: Clay = 90%; Blended Residue = 10%				
	6	0.769624 0.000074		this study
	96	0.768888 0.000086		this study
	336	0.767651 0.000093		this study
Experiment 8: Biochar = 90%; Blended Residue = 10%				
	6	0.805867 0.000094		this study
	96	0.806649 0.000071		this study
	336	0.805271 0.000047		this study
Experiment 9: Soil = 90%; Blended Residue = 10%				
	6	0.759212 0.000098		this study
	96	0.757194 0.000054		this study
	336	0.757319 0.000141		this study
Experiment 10: Peat = 50%; Blended Residue = 50%				
	6	0.785688 0.000022		this study
	96	0.772158 0.000050		this study
	336	0.775050 0.000042		this study
Experiment 11: Clay = 50%; Blended Residue = 50%				
	6	0.784395 0.000150		this study
	96	0.785317 0.000143		this study
	336	0.786234 0.000072		this study
Experiment 12: Biochar = 50%; Blended Residue = 50%				
	6	0.788381 0.000077		this study
	96	0.794801 0.000054		this study
	336	0.801981 0.000067		this study
Experiment 13: Soil = 50%; Blended Residue = 50%				
	6	0.782781 0.000016		this study
	96	0.781234 0.000016		this study
	336	0.783261 0.000133		this study
Standards				
	AGV-2 Basalt (USGS) A	0.704020 0.000009	0.703968 (Raczek et al., 2003)	
	BCR-2 Basalt (USGS) A	0.705028 0.000005	0.705012 (Neymark et al., 2014)	
			0.704995 (Raczek et al., 2003)	

BHVO-2 Basalt (USGS) A	0.703507	0.000020	0.703461 (Neymark et al., 2014)
			0.703472 (Raczek et al., 2003)
SBC-1 Shale (USGS) A	0.724246	0.000059	
B	0.724113	0.000005	
C	0.724231	0.000062	
D	0.724227	0.000079	
SGR-1B A Shale (USGS) A	0.712141	0.000068	
B	0.712070	0.000000	
GA Granite (Geostandards, CRPG) A	0.713711	0.000001	
B	0.713785	0.000060	
HISS-1 Marine sediment (NRC, Canada) A	0.712726	0.000053	
B	0.712636	0.000029	
NASS-7 Seawater (NRC, Canada) A	0.709180	0.000006	
B	0.709181	0.000001	

a: $^{87}\text{Sr}/^{86}\text{Sr}$ in leachates from peat, clay, and biochar is not reported because the leachates do not contain enough Sr for isotopic analysis

b: replicate of chromatographic column chemistry

c: normalized to $^{87}\text{Sr}/^{86}\text{Sr} = 0.71024$ (NIST SRM987); 2SD are two standard deviation of duplicate measurements by the Nu Plasma II in this study

Table S9 Summary of the endmembers used in the hypothetical mixing curves in Figure 5

Endmember	Description	Sr/Na by weight		$^{87}\text{Sr}/^{86}\text{Sr}$		Source
		Range	Mean	Range	Mean	
Lake water	Lake, lake outflow, and stream waters in central Ontario, Canada	0.01 – 0.06	0.03 (n=29)	0.710 – 0.714	0.711	Watmough, 2018
River water	Rivers draining Precambrian Shield in Quebec, Canada	2.9 - 13.1	6.3 (n=50)	0.727 – 0.734	0.731	Rosa et al., 2012; Stevenson et al., 2018
Coal mine drainage	Western Pennsylvania, USA	0.004 – 0.1	0.026 (n=34)	0.712 – 0.719	0.713	Chapman et al., 2012
100% Blended residue leachate	Leachates from the blended residue	0.41 – 0.54	0.46 (n=9)	0.802	0.802	This study