



## Modified sequential extraction for biochar and petroleum coke: Metal release potential and its environmental implications



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### HIGHLIGHTS

- Modified four step sequential extraction method suitable for pyrolyzed materials.
- Untreated biochar may easily release alkaline earth and transition metals.
- Wood biochar releases metals more readily than does sewage sludge biochar.

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### ABSTRACT

A modified Community Bureau of Reference (CBR) sequential extraction method was tested to assess the composition of untreated pyrogenic carbon (biochar) and oil sands petroleum coke. Wood biochar samples were found to contain lower concentrations of metals, but had higher fractions of easily mobilized alkaline earth and transition metals. Sewage sludge biochar was determined to be less recalcitrant and had higher total metal concentrations, with most of the metals found in the more resilient extraction fractions (oxidizable, residual). Petroleum coke was the most stable material, with a similar metal distribution pattern as the sewage sludge biochar. The applied sequential extraction method represents a suitable technique to recover metals from these materials, and is a valuable tool in understanding the metal retaining and leaching capability of various biochar types and carbonaceous petroleum coke samples.

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## 1. Introduction

Biochar is a solid material obtained in an oxygen-limited environment through the thermochemical transformation (pyrolysis) of biomass, such as wood, leaves, or sewage sludge (Glaser et al., 2002). It can be used on a larger scale to sequester carbon, to remediate water and wastewater, and can be an important soil amendment in agriculture (e.g., terra preta) (Yuan et al., 2011a; Lee et al., 2013; Alam et al., 2016). However, during pyrolysis, contaminants which are present in the feedstock can be retained and their concentrations amplified several times due to the relative organic mass decrease or gasification (Koppolu et al., 2003; Kim et al., 2012). Although regulatory agencies normally consider the total metal content of materials in setting regulatory guidelines, it is essential to assess metal speciation and distribution within those

materials. For instance, understanding the extractability, and therefore availability of metals in biochar is particularly important when using biochar for remediation purposes or as a soil amendment. Biochar will be potentially degraded through abiotic and biological processes, with estimated half-lives of 10–100,000 years (Spokas, 2010), releasing its metals into the surrounding environment. An assessment of the extractability of those metals would aid in estimating how easily certain macronutrients (e.g., Ca, K, Mg) and micronutrients (e.g., B, Mn, Fe, Cu, Zn) might be released or whether the biochar might act as a heavy metal source (e.g., for Ni, As, Pb).

To estimate the leaching and contaminant release potential of biomass, sequential extraction techniques are typically applied, which allow for the differentiation of various substrate components that can act as metal sinks (Rao et al., 2008). The results of these techniques are useful to operationally define the metal extractability, to give initial insights into how strongly metals are retained in the tested substrate, and to provide estimates of how

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environmentally stable (prone to being released into the environment) and bioaccessible they might be (Rao et al., 2008).

Various sequential extraction procedures have been applied to soils amended with biochar (Rao et al., 2008; Park et al., 2011; Lu et al., 2017). Yet surprisingly little work has been done on contaminants in different fractions of untreated biochar by itself, which is important in assessing its potential uses. The widely-used sequential extraction method of Tessier et al. (1979) may not be suitable for metals extraction from biochar, because of problems arising from the low material density, which makes separation through centrifugation difficult. Other issues are; the low extractant volumes used to perform the extraction process, high water retention of biochar that makes it challenging to separate the extraction solutions after incubation, and high salt concentrations of extraction solutions that can make instrumental analysis of metals difficult. Yuan et al. (2011b) characterized the metal holding components of liquefaction residues of sewage sludge, a solid product which has similarities to biochar. The authors used a four-step Community Bureau of Reference (CBR) sequential extraction to differentiate between the following fractions: (1) acid soluble/exchangeable, (2) reducible, (3) oxidizable, and (4) residual (Quevauviller et al., 1993). This method uses lower extractant concentrations (but longer incubation times) and higher extraction volumes. Centrifugation steps are still required for the separation of extraction solutions, which does not work well with very light and hydrophobic biochar (particularly wood-derived types). Additionally, the use of nitric acid, perchloric acid, and hydrogen peroxide for the final digestion step might not be sufficient for the total digestion of very resilient carbonaceous residues of biochar.

The objectives of this study were to; (1) apply a modified CBR sequential extraction method on well-characterized biochar and a liquid petroleum coke to determine their metal content and release potential, and (2) test total digestion methods that avoid the use of hazardous chemicals and that might be used to characterize the residual fraction of the sequential extraction process.

## 2. Materials and methods

### 2.1. Used materials and their characterization

In this study, five biochar samples and one oil sands fluid petroleum coke sample (SPC) were used (Table 1). The investigated biochar can be separated into wood-derived biochar, “Pin Chips Wood” (PW), “Bamboo Wood” (BW), and “Oak Wood” (OW), and sewage sludge derived biochar, “Sewage Sludge Biochar” (SSBC 300 and SSBC 700), respectively. All samples were dried at 60 °C, ground and sieved (<1 mm). PW obtained from the Alberta Biochar

Initiative (ABI) and SPC was obtained from an oil sand processing plant in the Athabasca Oil sands. OW, BW, SSBC 300 and SSBC 700 were obtained from the Korea Biochar Research Center. The detailed characterization of all samples is described in the [Supplementary information \(SI\)](#). Briefly, all samples were characterized by determining pH, ash content and the C, N, H, and O contents. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method and the surfaces were characterized by scanning electron microscopy (SEM) and attenuated total reflection Fourier–transform infrared (ATR-FTIR) spectroscopy.

### 2.2. Total digestion methods

Three digestion methods were applied: (1) aqua regia digestion – a 3:1 mixture of hydrochloric and nitric acids, (2) total digestion with hydrofluoric acid (HF) with hydrogen peroxide and nitric acid pretreatment, and (3) sodium peroxide alkaline fusion to determine the Si concentration. Before digestion, the samples were ashed at 500 °C. All three digestion methods are described in detail in [SI](#).

### 2.3. Sequential extraction

Sequential extraction was performed in triplicates according to a modified CBR method by Yuan et al. (2011b). A detailed description can be found in the [SI](#). Briefly, 0.5 g of biochar and petroleum coke were stepwise extracted by 0.1 M acetic acid (16 h, 25 °C), 0.1 M hydroxylamine chloride (16 h, 25 °C), 30% hydrogen peroxide (1 h 25 °C + 1 h 85 °C) and 1 M ammonium acetate (30 min, 25 °C), followed by an ashing step as described before and a total digestion with HF. To separate the solids after each step, the suspensions were centrifuged at 10,000g and the supernatant filtered through 0.2 µm nylon membranes. The remaining solids were flushed with ultrapure water in a vacuum filtration unit and used for the next extraction step. All liquids were filtered through 0.2 µm nylon membranes (Agilent Technologies) and analyzed using inductively coupled plasma – triple quadrupole mass spectrometry (Agilent Technologies 8800 ICP-QQQ). More details on the measurement conditions can be found in the [SI](#).

## 3. Results and discussion

### 3.1. Sample characterization and stability

Characterization results are summarized in [Table 1](#). The samples PW, OW, BW, and SPC, all with O:C ratios <0.2, are expected to have a relatively high half-life in the environment, 1000 years

**Table 1**  
Biochar and petroleum coke samples used in this study: sample descriptions and characterization results.

	PW	OW <sup>1</sup>	BW	SSBC 300	SSBC 700	SPC <sup>3</sup>
Source	Pin chips mixture	Oak wood	Bamboo wood	Sewage sludge <sup>2</sup>	Sewage sludge <sup>2</sup>	Oil sands
Country of origin	Canada	South Korea	Japan	South Korea <sup>2</sup>	South Korea <sup>2</sup>	Canada
Pyrolysis temperature (°C)	500	400	Unknown	300 <sup>2</sup>	700 <sup>2</sup>	350
pH	9.70	10.17	10.23	6.76 <sup>2</sup>	8.13 <sup>2</sup>	5.83
%C	84.60	82.30	81.38	30.70	22.10	78.68
%H	2.10	1.12	1.08	3.10	0.50	1.83
%O	9.40	9.02	8.11	11.10	7.09	3.08
%N	0.20	0.34	0.60	4.11	1.73	1.74
Molar H:C	0.30	0.16	0.16	1.20	0.26	0.28
Molar O:C	0.08	0.08	0.07	0.27	0.24	0.04
Surface area (m <sup>2</sup> /g)	224.00	270.76	76.65	4.50	54.80	5.68
Ash content (%)	3.70	5.03	3.47	56.63 <sup>2</sup>	76.55 <sup>2</sup>	5.33

<sup>1</sup> Ahmad et al. (2012).

<sup>2</sup> Kim et al. (2015).

<sup>3</sup> Alam et al. (2016).

or more based on predictions by Spokas (2010). On the other hand, the sewage sludge derived biochar samples have ratios  $>0.2$  and are estimated to have smaller half-lives of only a few hundred years. Lower O:C ratios can also be an indicator of lower hydrophilicity (Shen et al., 2012). This would mean that the sewage sludge-derived biochar would be the most hydrophilic of the tested samples. This higher affinity for water might also be a reason for potentially shorter residence time in the environment. Lower H:C ratios are often related to an increased unsaturated nature (higher aromaticity) of carbon in the biochar (Shen et al., 2012). BW and OW, having the lowest H:C ratios, most probably have a high abundance of aromatic carbon, making them less susceptible to biological degradation. On the other hand, SSBC 300, with a relatively high ratio of 1.2, should have a higher fraction of aliphatic groups. The studied materials have very different surface areas, which can be used as an approximation for surface reactivity (Shen et al., 2012). For example, OW would be the most surface reactive biochar ( $271 \text{ m}^2/\text{g}$ ), followed by PW ( $224 \text{ m}^2/\text{g}$ ). The least reactive would be SSBC 300 and SPC, with values between 5 to  $6 \text{ m}^2/\text{g}$ . Based on the molar H:C and O:C ratios and considering the surface area, the order of stability for the six samples is estimated (highest to lowest): SPC  $>$  BW  $>$  PW, OW, SSBC 700  $>$  SSBC 300. FTIR spectra and SEM images were collected to further classify the biochar samples and corroborate the aforementioned findings (SI).

### 3.2. Total metal concentrations

Total digestion of biochar with aqua regia (Table S2), HF (Table S3) and alkaline fusion (for Si; Table S3) revealed large differences in metal content between the plant-sourced biochar and the ones produced from sewage sludge. Typically, plant-derived biochar was less enriched in metals as compared to the sewage sludge biochar samples. Dominant elements were Si (3–15 mg/g), K (5–24 mg/g), Ca (0.8–13 mg/g), and Fe (0.7–3 mg/g). A special case was PW, which had higher concentrations of Cr (186  $\mu\text{g/g}$ ), Ni (78  $\mu\text{g/g}$ ), Cu (631  $\mu\text{g/g}$ ), and Zn (297  $\mu\text{g/g}$ ). The sewage sludge biochar contained elevated concentrations of Al (59–83 mg/g), Mg (7–10 mg/g), Si (112–175 mg/g), K (14–20 mg/g), Fe (29–41 mg/g), Zn (1–2 mg/g), and Ba (0.9–1 mg/g), but contained only traces of As (10–15  $\mu\text{g/g}$ ), Cd (2–3  $\mu\text{g/g}$ ), Pb (53–72  $\mu\text{g/g}$ ), and U (24–34  $\mu\text{g/g}$ ). SSBC 700, because of the higher pyrolysis temperature, generally had higher concentrations of metals than SSBC 300 (concentrating effect during pyrolysis) by an average factor of 1.5 ( $\pm 0.4$ ).

Aqua regia was not strong enough to extract the entire elemental load in the case of Al, Si, Ca, Cr, and Mg, of which Al, Si, Ca and Cr dominate in the residual fractions of the biochar (see below). However, the results of all tested digestion methods for other metals were similar (comparing Table S2 and Table S3), suggesting that aqua regia digestion might be a useful method to evaluate the total amount of transition metals (excluding Cr), As, Sr, Ba, and Pb in biochar. This is important because it is less dangerous than performing digestions with HF or perchloric acid.

### 3.3. Sequential extraction

The plant-derived biochar (PW, OW, BW), the sewage sludge biochar (SSBC 300, SSBC 700), and the petroleum coke (SPC) showed different metal distribution patterns (Fig. 1; details in Tables S4–S9). The exchangeable/acid soluble fraction contained a large portion of metals in the wood biochar, especially for Mg, K, Ca, Mn, Zn, and Sr. Those elements are likely present as mono- and divalent cations weakly sorbed to the biochar matrix (Tessier et al., 1979; Forghani et al., 2012); they might be easily released under the influence of irrigation, and could be useful in plant

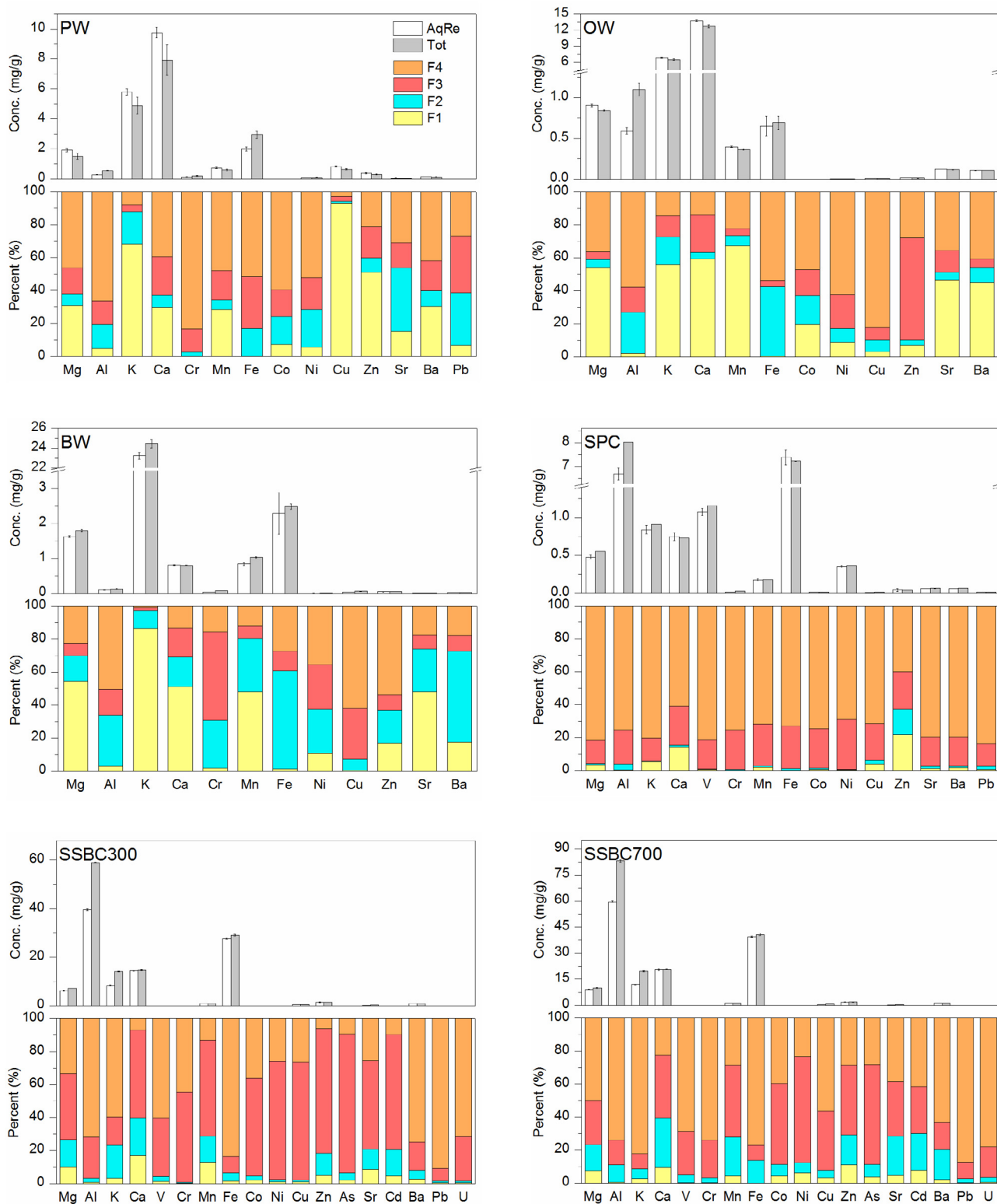
growth. The wood biochar, which had the highest surface area ( $180\text{--}270 \text{ m}^2/\text{g}$ ) of all 6 investigated samples, also had the highest metal concentrations in the exchangeable/acid soluble fraction. OW, with a surface area of  $270 \text{ m}^2/\text{g}$ , contained relatively large amounts of metals in this fraction, with sometimes more than 50% of the total amount (e.g., Mg, K, Ca, Mn). In the sewage sludge biochar, the first fraction held less than 15% of any metal. This result is very similar for the petroleum coke, with the exception of Zn (more than 20%). Therefore, surface area may be a reasonable indicator of the importance of the exchangeable/acid soluble fraction of a biochar or petroleum coke sample. At the same time, surface area is a key difference between plant and non-plant biochar types.

The reducible fraction (amorphous Mn and Fe oxides) in the plant-derived biochar holds over 20% of V, Ni, Sr, and Pb in PW; V, Co, and Fe in OW; and many elements in BW (Fig. 1). For BW, the reason for high metal diversity might result from the high abundance of Mn in the sample, possibly providing adsorption sites in the form of Mn oxides (Tessier et al., 1979). The reducible fraction played only a minor role in the sewage sludge and the petroleum coke samples. It held more than 15% of all metal mass for K and Ca in SSBC 300, and for Ca, Mn, Zn, and Sr in SSBC 700. In SPC only Zn was found in significant amounts in the reducible fraction.

Despite the large amount of organic carbon present in biochar, the easily oxidizable fraction does not play the largest role in metal release, indicating that either the organics found in biochar are very resilient and/or that the easily oxidizable fraction does not contain a high amount of metals. Nonetheless, over 20% of Mg, Al, Fe, Co, Ni, As, Ba, Sr, and Pb were found in this fraction in PW. This was also the case for Ni, Zn, and Pb in OW; and V, Cr, Ni, and Pb in BW. In the sewage sludge samples, the oxidizable fraction is far more important. More than 50% of V, Co, Cu, Zn, and As were found in this fraction in SSBC 300, and nearly half of the Cr, Ni, Cd, and U were in this fraction as well. In SSBC 700, the higher pyrolysis temperature resulted in a reduction of metal amounts in the oxidizable fraction, where only Ni and As were dominant ( $>50\%$ ).

Considerable amounts of metals in all biochar samples were associated with the residual fraction. This was especially the case for Al, Si, Ca, Cr, and As in the plant-derived biochar, and most of the analyzed elements in the other biochar samples. This residual fraction likely represents silicates and recalcitrant organic compounds which are not prone to hydrogen peroxide attack.

Based on the factors discussed earlier, the biochar samples might be ordered by the long-term stability as follows: SPC  $>$  BW  $>$  PW, OW, SSBC 700  $>$  SSBC 300. Once in the environment, the various materials are likely to have different fates. Despite the high metal loads in SPC, this material is likely to retain the metals over a long period of time - this is supported by the low amount of metals in extraction fractions 1 and 2. The wood biochar can also be expected to have a relatively long lifetime, providing long term containment for heavy metals in the residual fraction; however, high amounts of metals may be released fairly rapidly under temperate environmental conditions from fractions 1 and 2. The samples PW, OW, and BW should readily release macronutrients and micronutrients, such as Mg, K, Ca, Mn, Cu, Zn, Co and Ba. Under reductive and oxidative influence (bacterial decomposition, photo-oxidation), these biochar types may also act as a source of Cr, V, Fe, As, Ni, and Pb. The sewage sludge biochar samples had lower metal concentrations associated with the exchangeable/acid soluble and the reducible fractions. Metals, including Al, Fe, Zn, As, Ba, and Pb are therefore more strongly retained in the biochar matrix compared to the plant-derived biochar samples, and stronger biochar degradation would be necessary to release those nutrients/contaminants. Nonetheless, the lifetime of sewage sludge biochar is expected



**Fig. 1.** Sequential extraction results. Sequential extraction results showing the contributions of fractions 1–4 to the total metals concentrations. The digestion results are shown above each graph. AqRe: aqua regia. Tot: total digestion with HF. F1: exchangeable/acid soluble fraction. F2: reducible fraction. F3: oxidizable fraction. F4: residual fraction. The error bars represent standard deviations (n = 3).

to be shorter than that of the investigated wood biochar, and hence, incorporated metals are likely being released over a shorter period of time. This is a particularly critical consideration for the presence of potential contaminants (e.g., As, Cd, Pb, and U) in

those biochar types. The petroleum coke SPC is very poor in macronutrients and is highly loaded with V and Ni. Other potentially hazardous metals are present in concentrations lower than in the sewage sludge biochar, allowing this material to be used

as an adsorbent for water treatment purposes (e.g., Alam et al., 2016).

#### 4. Conclusions

The modified CBR method was successful for characterizing the metal release potential of several types of biochar and a petroleum coke. Untreated biochar was shown to contain high concentrations of metals. However, the release of those metals is related to both the predicted recalcitrant nature of the biochar itself, and the extraction fractions in which the metals are found. For example, wood-derived biochar is expected to not only have a relatively long half-life, but also higher concentrations of weakly bound metals. The modified method simplifies the assessment of the metal leaching potential from biochar and petroleum coke.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.03.162>.

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