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Abstract

Soybean stover derived biochar was used to immobilize Pb in military firing range soil at a mass application rate of 0 to 20 wt% and a curing period of 7 days. The toxicity characteristic leaching procedure (TCLP) was performed to evaluate the effectiveness of the treatment. The mechanism responsible for Pb immobilization was evaluated by scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) and X-ray absorption fine structure (XAFS) spectroscopy analyses. The treatment results showed that TCLP Pb leachability decreased with increasing biochar content. A reduction of over 90% in Pb leachability was achieved upon treatment with 20 wt% soybean stover derived biochar. SEM-EDX, elemental dot mapping and XAFS results in conjunction with TCLP leachability revealed that effective Pb immobilization was probably associated with the pozzolanic reaction products, chloropyromorphite and Pb-phosphate. The results of this study demonstrated that soybean stover derived biochar was effective in immobilizing Pb in contaminated firing range soil.

Keywords Pb · Immobilization · Biochar · Soybean · Firing range soil

Introduction

Lead (Pb), known as one of the most toxic elements to human health, represents a widespread contaminant in military and civilian firing range sites. In 2006, more than 70,000 tons of Pb was used in the USA for ammunition production including shots and bullets (USGS 2007). Pb can cause a variety of adverse effects that harm the brain, red blood cells, blood vessels, kidneys and the nervous system (Lin et al. 1996; Long and Zhang 1998). Typical military-grade bullets are mainly composed of Pb alloy slugs enclosed within Cu alloy jackets (Dermatas et al. 2004). Moreover, a bullet pellet typically consists of more than 90% Pb (Chrastný et al. 2010; Dermatas et al. 2006; Robinson et al. 2008; Sorvari et al. 2006). Pb concentrations in military firing range soils are often higher than 1,000 mg kg^{-1} (Lin et al. 1995; Cao et al. 2003a) while levels well over 20,000 mg kg^{-1} have been reported (Lin 1996; Stansley and Roscoe 1996; Dermatas et al. 2006). More than 3,000 and 1,400 active small arms firing ranges are estimated to exist in the USA (USEPA 2005), and in Korea (MOE 2005), respectively. Bullet fragments and Pb particulates originating from multiple impacts with berm surfaces during range operations can lead to significant accumulations in military firing range soils. Remedial action for Pb contaminated military firing range soils is imperative for preventing ground- and surface-water pollution, minimizing environmental risks (Craig et al. 1999; Knechtenhofer et al. 2003) and preventing Pb from entering the trophic chain via plants and vegetative matter growing in the vicinity of firing ranges (Cao et al. 2003b; Robinson et al. 2008).

In this study, a stabilization/solidification (S/S) process is applied as a remedial technique to immobilize Pb in firing range soils. The S/S process has been widely used to immobilize heavy metals in contaminated particulate matrices including soils, sediments, and sludges. By applying the stabilization process, Pb can be converted to forms which are much less soluble, mobile and toxic. Also, Pb can be incorporated into a monolithic solid with reduced surface area by employing the solidification process. A variety of S/S agents are used including cement, lime, fly ash, etc.. In this study, biochar, also known as biomass-derived black carbon is used to immobilize Pb in military firing range soil. Currently, biochar is recognized as a multifunctional material associated with various applications including carbon sequestration, metal immobilization by cation exchange and fertilization in soils (Awad et al. 2012; Chen et al. 2011; Uchimiya et al. 2010). Although the use of biochar as a S/S agent for Pb immobilization is rather limited, its affordable cost makes it a very attractive option.

The objective of this study is to evaluate the Pb immobilization effectiveness in contaminated firing range soil using biochar. The treatment effectiveness is evaluated using the toxicity characteristic leaching procedure (TCLP) test following stabilization treatment. The Pb immobilization mechanism is investigated using scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) and X-ray absorption fine structure (XAFS) spectroscopy analyses.

Experimental methodology

Contaminated firing range soil

Heavy metal contaminated soil from a military firing range was collected from Busan Metropolitan City in Korea at a depth of 0-30 cm below the ground surface. The total Pb concentrations based on extraction by aqua regia [1 ml of HNO_3 (65%, Merck) and 3 ml of HCl (37%, J.T. Baker)] were approximately 11,885 mg kg^{-1}. The TCLP

Pb concentration of the control sample was approximately 696 mg kg^{-1}. The initial pH value of the contaminated soil was 6.94. The collected firing range soil was sieved through a #10 mesh (2 mm) to remove large particles and improve soil homogeneity. Physicochemical characterization data for the contaminated firing range soil is presented in Table 1. The elemental composition of the contaminated firing range soil was determined using X-ray fluorescence (XRF) and the results are presented in Table 2.

Stabilization agents

Soybean stover was used as a raw feedstock to produce biochar. Soybean stover was collected from a local agricultural field in Chungju-city, Korea. The raw feedstock was dried in an air-forced oven at 60 °C for 3 days and grinded to a size less than 1 mm. The grinded soybean stover was placed in a ceramic crucible with a lid and then pyrolyzed in a muffle furnace (MF 21GS, Jeio Tech, Seoul, Korea) at 7 °C min^{-1} under limited oxygen conditions. Carbonization was performed at 700 °C for 3 hours followed by cooling to room temperature inside the furnace. Subsequently, the resulting biochar was stored in air-tight containers. The initial pH of the biochar was 10.5. The elemental composition of the biochar is listed in Table 2.

Treatment conditions

The contaminated military firing range soil was stabilized with soybean stover derived biochar at 1 wt% - 20 wt%

at a liquid to solid (L:S) ratio of 0.2. All the treated samples were prepared in duplicate and cured for 7 days. The specific treatment conditions based on the percent biochar/soil ratio (dry basis) are presented in Table 3.

Physicochemical analyses

The soil and biochar pH values were obtained in accordance with the KST method (MOE 2002) at a liquid to solid ratio of 5:1. The TCLP test, conducted in accordance with the U.S. EPA protocol (EPA 1992), was used to evaluate the effectiveness of the stabilization treatment for the contaminated military firing range soil. In order to analyze the total Pb concentration, soil samples (0.25 g) were mixed with aqua regia [1 ml of HNO_3 (65%, Merck) and 3 ml of HCl (37%, J.T. Baker)] (Ure 1995). The mixture was then heated to 70°C, shaken for 1 hour, and diluted with 6 ml of distilled water to obtain a final L:S ratio of 20:1 (Ure 1995). The extracted solution was then filtered through a 0.45-µm micropore filter, after which the soluble Pb concentrations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500ce, USA). All sample analyses were performed in triplicate and averaged values were reported only if the individual measurements were within an error of 10%. Two control standards (sodium arsenite and sodium arsenate) and recovery spikes were used to monitor the accuracy and performance of the equipment.

SEM-EDX analyses

Prior to SEM analyses, untreated and treated air-dried sub-samples were prepared using double-sided carbon tape coated with platinum (Pt). SEM analyses were performed using a Hitachi S-4800 SEM instrument equipped with an ISIS 310 EDX system.

X-ray absorption fine structure (XAFS) spectroscopy analyses

The XAFS spectroscopy analyses were conducted in order to investigate the existence of different Pb species in untreated and treated soil samples. The spectroscopic measurements were made at the beamline 7D at the Pohang Accelerator Laboratory (PAL) in Korea. The selected soil samples were grinded to a size <100 µm, and were mounted on a sample holder using Kapton adhesive tape. The Pb L-III absorption edge at 13035 eV and a Si(111) double crystal monochromator were used to collect the extended X-ray absorption fine structure (EXAFS) spectra in fluorescence mode. A number of Pb reference standards were also analyzed at the same beamline. These Pb references include massicot (PbO), plattnerite (PbO_2), cerussite ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), Pb-phosphate ($PbHPO_4$), Pb-acetate ($(CH_3COO)_2Pb$), Pb-citrate ($C_{12}H_{10}O_{14}Pb_3$), Pb-oxalate (PbC_2O_4), Pb-hydroxide ($Pb(OH)_2$), chloropyromorphite ($Pb_5(PO_4)_3Cl$), Pb sorbed to birnessite, gibbsite, goethite, humic acid and kaolinite. The EXAFS data were interpreted by the Athena software ver. 0.8.061 (Ravel and Newville 2005). After normalization and background correction, the χ_k function was used to isolate the scattering portion of the spectra. The EXAFS spectra were weighted to k_2 up to 10 Å^{-1}.

The linear combination fitting (LCF) analysis was performed on the k_2-weighted EXAFS spectra to determine the quantitative estimation of the Pb species in soil samples. A fitting range of 2 to 8 $Å^{-1}$ was used. The effectiveness of the fit was evaluated by the normalized sum of the squared residuals of the fit (R-factor) and reduced χ^2 values. At first, the complete dataset of Pb references was used to identify the Pb species in soil samples. The Pb reference spectra were then narrowed down to a maximum of four based on the lowest R-factor value.

Results and Discussion

Stabilization of Pb in contaminated firing range soil

The TCLP Pb leachability and associated pH results obtained from the samples treated with soybean stover derived biochar are presented in Fig. 1. The TCLP Pb leachability of approximately 696 mg L^{-1} established for the control sample decreased with increasing biochar content. A 50% reduction in TCLP Pb leachability was observed for the sample treated with 10% biochar. However, a drastic reduction of greater than 91% in TCLP Pb leachability (corresponding to 57.67 mg L^{-1}) was attained for the sample treated with 20% biochar. The treatment pH of the 20% biochar treated sample was about 10.2. Elevated pH would induce the solubilization of Al and Si from the clay in the sample (Keller 1964), which would be available to form cementious hydrates (pozzolanic reaction products) such as calcium aluminum hydrate (CAH) and calcium silicate hydrate (CSH) (Gougar et al. 1996). Therefore, the formation of CSH/CAH at the high pH condition induced by the high content of biochar may play a key role in immobilizing Pb in the contaminated soil. It has been reported that Pb could be incorporated within the CSH structure based on the hydration of tricalcium silicate which is a main compound in Portland cement (Rose et al. 2000). Moulin et al (1999) also suggested that Pb can be retained through the Si-O-Pb bond.

On the other hand, studies where soils are subjected to phosphates have showed that Pb immobilization proceeds via the formation of lead phosphate compounds such as pyromorphite-like phases ($Pb_5(PO_4)_3X$, X=F, Cl, OH) (Cao et al. 2002; Scheckel and Ryan 2002; Zhang and Ryan 1999). Therefore, the phosphate content of biochar may play a key role in Pb immobilization. In fact, it may be theorized that Pb immobilization in soil samples treated with a biochar content in the range of 1 - 10 wt% and treatment pH values of 7.42 to 9.61 may be controlled by the formation of lead phosphate compounds. Moreover, in the case of the soil sample treated with a higher biochar content (20 wt%) where the treatment pH is high (10.2), the formation of pozzolanic reaction products may be responsible for effectively immobilizing Pb. Therefore, the drastic reduction in TCLP Pb leachability upon 20 wt% biochar treatment was most probably caused by the combinatory effect of lead phosphate precipitation and pozzolanic stabilization.

The TCLP pH values increased in the range of 3.6-4.2 with increasing biochar content. The highest TCLP pH value of 4.2 was obtained for the sample treated with 20% biochar.

SEM-EDX analyses

SEM-EDX results for the control sample presented in Fig. 2a indicate a lack of Phosphorus (P). However, P is clearly evident in the sample treated with a 20 wt% biochar content (Fig. 2b). The elemental dot map results show that Pb immobilization was strongly associated with P (Fig. 2c). This indicates that pyromorphite-like phases may be the key compounds responsible for effective Pb immobilization (Zhang and Ryan 1999; Cao et al. 2002; Scheckel and Ryan 2002). Moreover, Fig. 2d shows that Pb is associated with Al, Si and O which is indicative of the key role of pozzolanic reaction products such as CSH/CAH in the immobilization of Pb under high pH conditions. Therefore, pyromorphite-like phases and pozzolanic reaction products may have simultaneously contributed to the immobilization of Pb in the sample treated with 20 wt% biochar, where significant reduction in TCLP Pb leachability was obtained.

Lead LIII XAFS spectroscopy

The quantitatively computed proportions of different Pb species in the untreated and biochar treated military firing range soil are presented in Fig. 3. The LCF analysis demonstrated the transformation of Pb species in the treated soils. The results indicate that Pb in the untreated soil is mainly present as Pb sorbed to humic acid (31.5%) followed by hydrocerussite (23.3%) and Pb-sorbed to ferrihydrite (19.0%). In the sample treated with 1% biochar, the hydrocerussite proportion increased to 50.7%, while Pb sorbed to humic acid decreased to 21.6% compared to the control sample. Likewise, for the sample treated with 5% biochar, the hydrocerussite portion increased to 40.4% compared to the control sample. This increased proportion of hydrocerussite may be related to its relatively high stability in soil under alkaline conditions (pH 7.7 to 10.1; Cao et al., 2003). Additionally, Pb-hydroxide (21.5%) and chloropyromorphite (19.0%) are predicted in the 5% biochar treated soil sample. Precipitation of Pb-hydroxide under alkaline soil conditions is commonly reported (Ahmad et al., 2012; Ok et al., 2011). Formation of chloropyromorphite, which is one of the most stable Pb species in soil, is attributed to the presence of phosphate in biochar as indicated by the XRF analysis (Table 2). By increasing the application of biochar to 10%, the proportion of hydrocerussite is decreased to 19.3%, compared to the samples treated with 1% and 5% biochar, probably due to Pb-phosphate (22.4%) formation. The increased phosphate content of the sample treated with 10% biochar facilitates the formation of Pb-phosphate and chloropyromorphite. Several studies have also reported the formation of stable chloropyromorphite in P-treated soils (Hashimoto et al. 2009; Cao et al. 2002). Biochar addition results in an increase in soil pH that also favored the sorption of Pb to kaolinite. Grafe et al. (2007) pointed out that Pb can form polymeric complexes via edge sharing to the more negatively charged kaolinite under increased pH conditions (Puls et al. 1991).

The molecular level spectroscopic investigations in conjunction with TCLP leachability indicate that the formation of chloropyromorphite and the precipitation of Pb-phosphate in soil treated with biochar may result in the immobilization of Pb in military firing range soil, thereby contributing to the low leachability and bioavailability of Pb.

Conclusions

Biochar derived from soybean stover was used for the immobilization of Pb in contaminated firing range soil. The effectiveness of immobilization is evaluated using the TCLP test. The Pb immobilization mechanism is investigated based on SEM-EDX, elemental dot mapping and XAFS analyses. The treatment results show that a reduction of more than 90% in TCLP Pb leachability is obtained upon a treatment regimen of 20% soybean derived biochar. The SEM-EDX, elemental dot mapping and XAFS results in conjunction with TCLP leachability indicate that pozzolanic reaction products, chloropyromorphite and Pb-phosphate formation may simultaneously contribute to the immobilization of Pb in the sample treated with 20 wt% soybean stover biochar. This study showed that the soybean stover derived biochar treatment was effective in immobilizing Pb in contaminated firing range soil.

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Table 1 Physicochemical properties of the contaminated firing range soil

Soil properties	Firing range soil
Soil pH	6.94±0.22
Organic matter content (%)[a]	5.94
Cation exchange capacity (meq 100mg^{-1})[b]	7.92
Composition (%)[c]	
Sand	85.07
Silt	12.28

Clay	2.87
Texture[d]	Loamy sand

[a] Organic matter content (%) was calculated from measured loss-on-ignition (LOI) (Ball 1964; FitzPatrick 1983)

[b] Cation exchange capacity (CEC) measured by USEPA method 9081 (USEPA 1986)

[c] Sand, 50-2,000 µm; silt, 2-50 µm; clay, < 2 µm

[d] Soil texture suggested by the United States Department of Agriculture (USDA)

Table 2 Elemental composition of firing range soil and soybean stover derived biochar

Element	Firing range soil (wt%)		Soybean stover derived biochar (wt%)
SiO_2	60.15	C	85.3
Al_2O_3	15.9	Na	0.0314
TiO_2	0.40	Mg	0.9
Fe_2O_3	4.31	Al	0.149
MnO	0.09	Si	0.436
MgO	0.44	P	0.914
CaO	1.32	S	0.244
Na_2O	0.72	Cl	0.075
K_2O	4.37	K	6.63
P_2O_5	0.06	Ca	4.63
SO_3	0.22	Fe	0.199

Table 3 Test matrix for untreated and treated samples

Sample ID	Firing range soil	Soybean stover derived biochar (wt%)	L:S ratio
Control	√	0	0.2
Soy biochar1	√	1	0.2
Soy biochar2	√	2	0.2
Soy biochar3	√	3	0.2
Soy biochar4	√	4	0.2
Soy biochar5	√	5	0.2
Soy biochar10	√	10	0.2
Soy biochar20	√	20	0.2

Table 4 Proportions of the Pb species in the firing range untreated soil (control) and treated with soybean derived biochar (BC) as determined by linear combination fittings (LCF) on EXAFS spectra.

	Hydrocerussite	Pb-humic acid	Pb-ferrihydrite	Pb-kaolinite	Pb-hydroxide	Chloro-pyromorphite	Pb-phosphate	Total	R[†]
				%					
Control	23.3	31.5	19.0	-	-	-	-	73.8	0.33
1% BC	50.7	21.6	-	14.9		-	-	87.2	0.17
5% BC	40.4	-	-	9.4	21.5	19.0	-	90.3	0.13
10% BC	19.3	-	-	12.3		11.3	22.4	65.3	0.14

[†] Normalized sum of the squared residuals of the fit

Fig. 1 TCLP Pb leachability and TCLP pH results for the contaminated firing range soil upon treatment with soybean stover derived biochar

Fig. 2 SEM-EDX results of the control (a), 20 wt% biochar treated sample (b) and SEM elemental dot maps of 20 wt% biochar treated sample, showing that Pb is associated with P and O (c) and SEM elemental dot maps of the 20 wt% biochar treated sample, showing that Pb is associated with Al, Si and O (d)

Fig. 3 Pb L-III edge EXAFS spectra for firing range untreated soil (a, control) and treated soil with biochar derived from soybean stover with an application rate of 1% (b), 5% (c) and 10% (d), along with standards giving the best linear combination fit (LCF). Circles: LCF fit.

Fig. 1

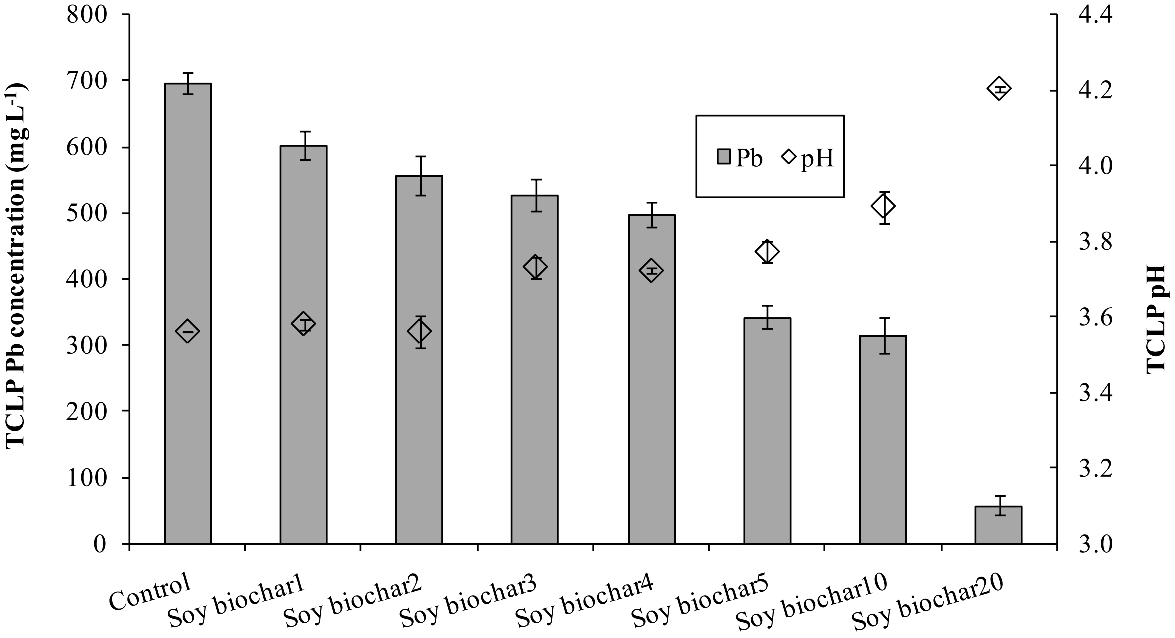
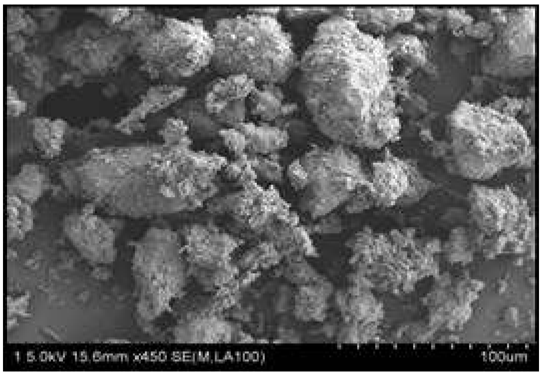
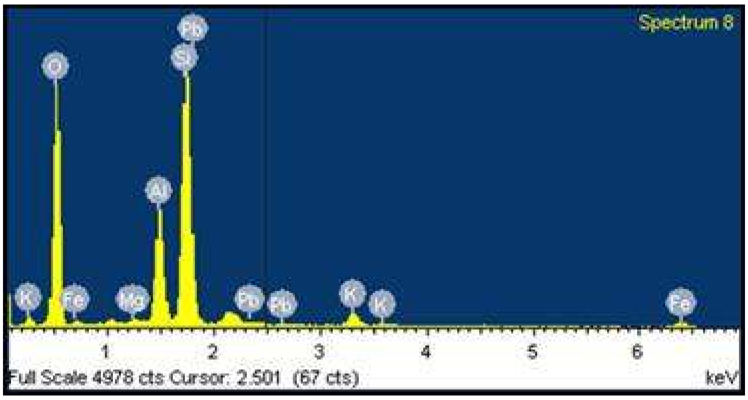

TCLP Pb concentration (mg L-1)
TCLP pH
0
100
200
300
400
500
600
700
800
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
Pb
pH
Control
Soy biochar1
Soy biochar2
Soy biochar3
Soy biochar4
Soy biochar5
Soy biochar10
Soy biochar20

Fig. 2

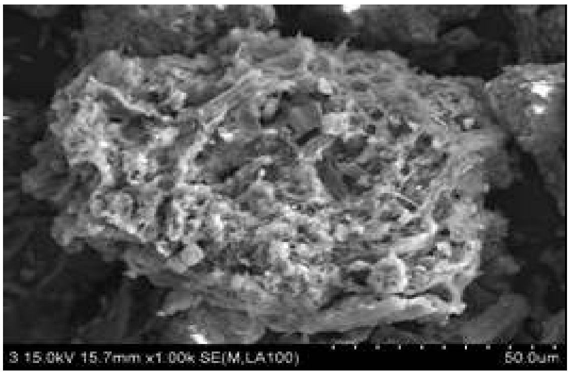
(a)

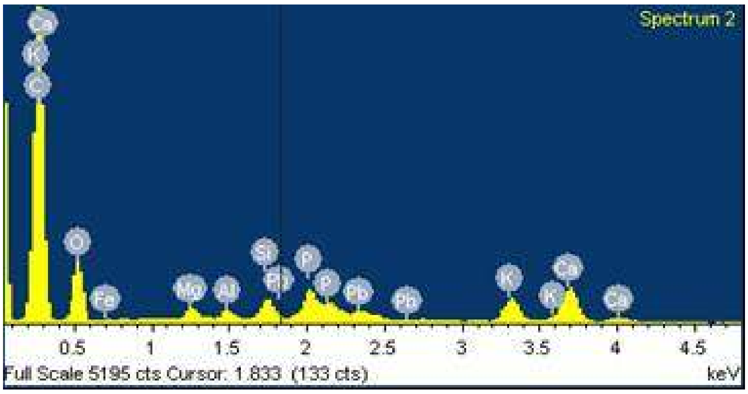




Element	Atomic%
O K	77.21
Mg K	0.28
Al K	5.97
Si K	14.85
K K	0.87
Fe K	0.73
Pb M	0.08

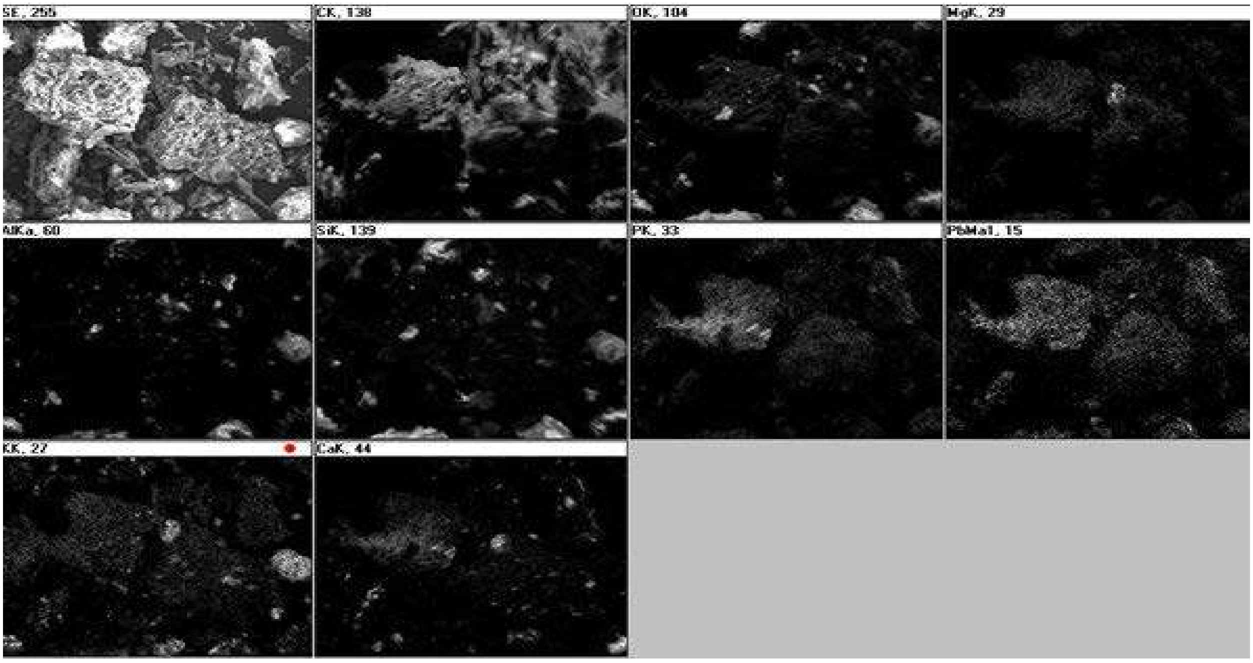
(b)





Element	Atomic%
C K	76.73
O K	18.75
Mg K	0.38
Al K	0.22
Si K	0.57
P K	0.71
K K	0.90
Ca K	1.51
Fe K	0.13
Pb M	0.10

(c)


SE, 255
CK, 138
OK, 104
MgK, 29
AlKa, 60
SiK, 139
PK, 33
PbMa1, 15
KK, 27
CaK, 44

(d)

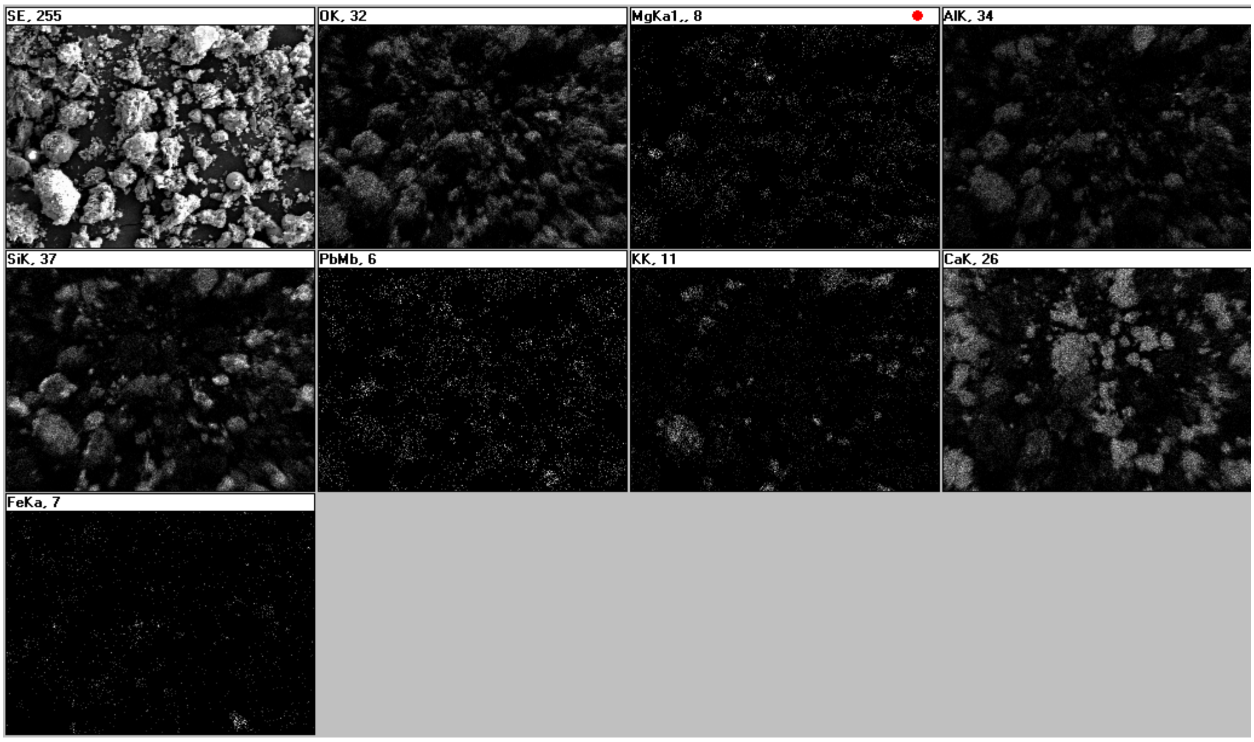
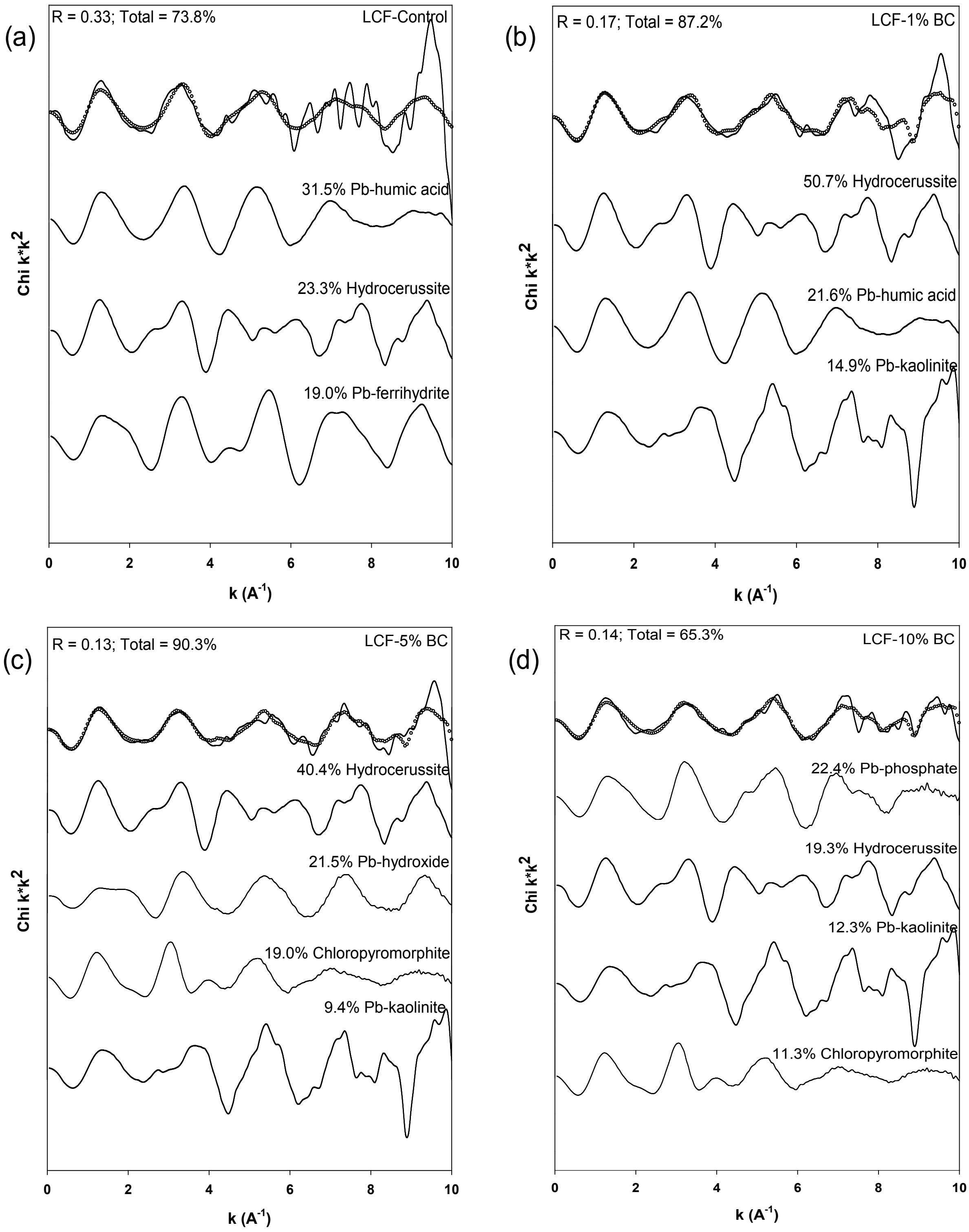

SE, 255
OK, 32
MgKa1,, 8
AlK, 34
SiK, 37
PbMb, 6
KK, 11
CaK, 26
FeKa, 7

Fig. 3



(a)
R = 0.33; Total = 73.8%
LCF-Control
31.5% Pb-humic acid
23.3% Hydrocerussite
19.0% Pb-ferrihydrite
Chi k*k^2
0
2
4
6
8
10
k (A^{-1})
(b)
R = 0.17; Total = 87.2%
LCF-1% BC
50.7% Hydrocerussite
21.6% Pb-humic acid
14.9% Pb-kaolinite
Chi k*k^2
0
2
4
6
8
10
k (A^{-1})
(c)
R = 0.13; Total = 90.3%
LCF-5% BC
40.4% Hydrocerussite
21.5% Pb-hydroxide
19.0% Chloropyromorphite
9.4% Pb-kaolinite
Chi k*k^2
0
2
4
6
8
10
k (A^{-1})
(d)
R = 0.14; Total = 65.3%
LCF-10% BC
22.4% Pb-phosphate
19.3% Hydrocerussite
12.3% Pb-kaolinite
11.3% Chloropyromorphite
Chi k*k^2
0
2
4
6
8
10
k (A^{-1})