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SHORT COMMUNICATION

Effects of Natural and Calcined Oyster Shells on Antimony Solubility in Shooting Range Soil

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Abstract Waste oyster shells (OS) and calcined oyster shells (COS) were used to treat metal-contaminated shooting range soil, where antimony (Sb) leachability was assessed. Changes in soil pH induced by the amendments strongly influenced Sb leachability. Sb was immobilized by COS most likely due to calcium antimonate precipitation. This is the first time to our knowledge to report that COS can effectively immobilize Sb in the soil.

Keywords calcination · immobilization · soil pH · waste oyster shells

There has been a recent increase in interest in the distribution, cycling, and mobility of antimony (Sb) in the environment (Okkenhaug et al., 2011). Shooting range soils in particular are important and critical sources of Sb and lead (Pb) contamination. For example, Johnson et al. (2005) reported a maximum soil Sb concentration of 17,500 mg kg^{-1} at a shooting range in Switzerland. USEPA has added Sb to its list of priority pollutants due to its potential toxicity (Smichowski, 2008). Sb has a similar chemistry to arsenic (As) where it exists mainly in two oxidation states: Sb(III) and Sb(V). Despite its widespread use in bullets and its substantial toxicity, very little is known about the geochemistry and leaching behavior of Sb at shooting range (Ok et al., 2011a). The high leachability of Sb at shooting ranges is mainly due to bullet fragmentation upon impact and weathering (Ahmad et al., 2012a). Unlike cationic Pb which is less mobile in soil, the metalloid Sb exists mainly as anionic Sb(V) which is produced by the weathering of metallic Sb in firing range soils and is more susceptible to dissolution in soil systems (Johnson et al., 2005; Griggs et al., 2011). Sb leaching at shooting ranges negatively impacts groundwater quality and nearby soil biota. Therefore, an effective remediation technology is urgently needed for Sb contaminated soils at shooting range. Use of naturally occurring waste materials for Sb remediation at shooting ranges would be an advancing innovative research.

In our previous studies, we explored the use of naturally occurring waste materials comprising mainly of $CaCO_3$ as innovative soil amendments to remediate metal-contaminated soils (Ok et al., 2011b; Ok et al., 2011c; Ahmad et al., 2012b). Waste eggshells, oyster shells and mussel shells were used successfully as amendments (Yang et al., 2007; Moon et al., 2011; Ahmad et al., 2012c). These studies focused on immobilization of Pb, Cd, and As, and revealed that changes in soil pH induced by the waste amendments could control the mobility of metals in soils. The present study is an extension of our previous work (Ahmad et al., 2012d; Ahmad et al., 2012e), where we first assessed the utilization of eggshells, oyster shells and mussel shells for the

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Table 1 Selected soil properties and total metal contaminant levels in shooting range (SR) soil and the bullet crust (BC)

Soil	pH[a]	Texture	OM[a,b] (g kg^{-1})	Available P[a] (mg kg^{-1})	CEC[a,c] (cmol$_{(+)}$ kg^{-1})	Co mg kg^{-1}	Cu[a]	Fe	Mn	Ni[a]	Pb[a]	Sb[a]	Ti	V	Zn
SR	6.66	Sandy loam	10.10	8.65	5.29	12.51	225.45	32843.70	390.11	31.15	4626.39	22.96	1350.59	60.64	65.47
BC						13.75	2442.84	32533.85	406.68	25.13	35075.79	641.11	1329.09	57.46	401.64

[a] Data obtained from Ahmad et al. (2012b)

[b] Organic matter

[c] Cation exchange capacity

immobilization of Pb in a shooting range soil, and then predicted the mechanism of Pb immobilization by eggshell and calcined eggshell using an integrated mechanistic approach. It was depicted that eggshells, oyster shells, and mussel shells effectively reduced (up to 45%) water-soluble Pb at an application rate of 2.5% compared to untreated soil (Ahmad et al., 2012b). This Pb immobilization effect associated with waste shells was related to an increase in soil pH (from 6.6 to 8.0). Here we report, for the first time to our knowledge, the effects of waste oyster shell and calcined oyster shell on Sb leachability at a Korean military shooting range soil using a standard batch-leaching procedure.

Soil samples were collected from a military shooting range at Icheon City located in the southeastern part of Gyeonggi Province, Korea. Waste oyster shells were processed to a homogenous powder after cleaning, drying, crushing, and sieving. Calcination of the sieved oyster shell powder was performed in a furnace at 900°C for 4 h (Ok et al., 2010). The soil and amendments were characterized for selected physicochemical parameters. A detailed description of the soil and amendment characteristics are given in reports of Ahmad et al. (2012b) and Ok et al. (2010), respectively. The standard batch-leaching test described in the DIN 38414 S4 guidelines was adopted to assess the efficiency of natural and calcined oyster shells for Sb immobilization (Ahmad et al., 2012b). Oyster shells (OS) and calcined oyster shells (COS) were mixed with 10 g of dried soil at rates of 0% (control), 2.5%, and 25%, respectively, based on dry soil weight. The low and high application rates were selected to identify marked differences in amendment efficiency. Subsequently, 100 mL of de-ionized water was added to each treatment, maintaining a liquid/solid ratio of 10:1. The mixture was tumbled for 24 h, and the supernatant was filtered through a 0.45-μm membrane filter and analyzed for Sb. An inductively coupled plasma spectrometer (Perkin Elmer, USA), equipped with a hydride generator, was used for the Sb analysis. SAS ver. 9.1 (USA) was used to calculate Pearson correlation coefficient (R) and probability value (P).

The selected shooting range soil was sandy loam with a pH value of 6.66. Soil had relatively low contents of organic matter (10.10 g kg^{-1}) and available P (8.65 mg kg^{-1}) than average values in Korean upland soil (20–30 g kg^{-1} for organic matter and 300–500 mg kg^{-1} for available P) (Jo and Koh, 2004). Total Sb concentration in the shooting range soil was 22.96 mg kg^{-1} (Table 1), which was over 4-fold higher than the standard acceptable limit (5 mg kg^{-1}) in Swiss cultured soil (Olive, 2006). No regulatory values are available for Sb in Korean soils; therefore, 5 mg kg^{-1} was used as a target standard in the present study. Additionally, high Pb concentration (4,626 mg kg^{-1}) was observed in the soil, which was 6.6-fold greater than the Korean Standard Warning Level of total Pb (700 mg kg^{-1}) for military sites. The high Sb and Pb concentrations in the bullet crust (641and 35,076 mg kg^{-1}, respectively) indicated that bullet fragments were the source of these metals.

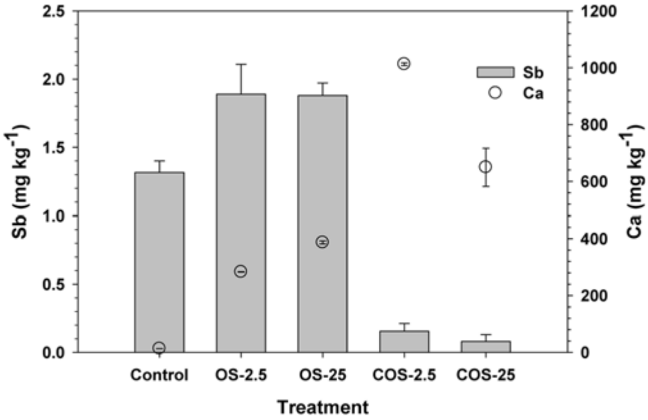

Fig. 1 Water-soluble Sb and Ca (1:10 soil/water ratio) in shooting range soil treated with oyster shells (OS, 2.5 and 25 wt%) and calcined oyster shells (COS, 2.5 and 25 wt%). Bars indicate Sb concentrations, and circles represent Ca concentrations.

Interesting results were observed for Sb in the soil after OS and COS treatments (Fig. 1). Sb leachability decreased significantly for the COS treated soil. Sb concentration decreased from 1.32 mg kg^{-1} for control to 0.08 mg kg^{-1} for the 25% treatment. This could be attributed to formation of calcium antimonate precipitation ($Ca(Sb(OH)_6)_2$) as described by Johnson et al. (2005). In the case of COS treatment, calcium was quickly released into the soil with concentration up to 1,012 mg kg^{-1} (Fig. 1), allowing abundant dissolved calcium to react with Sb and form calcium antimonate, which is a relatively stable phase with a solubility product ($\log_{10}K$) of −12.5 (Table 2). Similarly, Johnson et al. (2005) reported that precipitation of calcium antimonate under elevated Ca concentrations in soil controls antimony solubility in soil. Cornelis et al. (2011) also found that romeite or calcium antimonate

Table 2. Equilibrium constants for antimony complexes at 25°C

Antimony complex	Equilibrium reaction	$\text{Log}_{10}K^a$
Antimonic acid	$Sb(OH)_5+H_2O\leftrightarrow Sb(OH)_6^-+H^+$	2.85
Antimonite ion	$Sb(OH)_6^-+Ca^{2+}\leftrightarrow CaSb(OH)_6^+$	2.15
Oxycalcioromeite	$Ca_2Sb_2O_7+2H^++5H_2O\leftrightarrow 2Ca^{2+}+2Sb(OH)_6^-$	-6.70
Calcium antimonate hydrated	$Ca_{1.13}Sb_2O_6(OH)_{0.26}\cdot 0.74H_2O+0.87Ca^{2+}\leftrightarrow Ca_2Sb_2O_7+1.74H^+$	-12.50

[a]Data obtained from Cornelis et al. (2011)

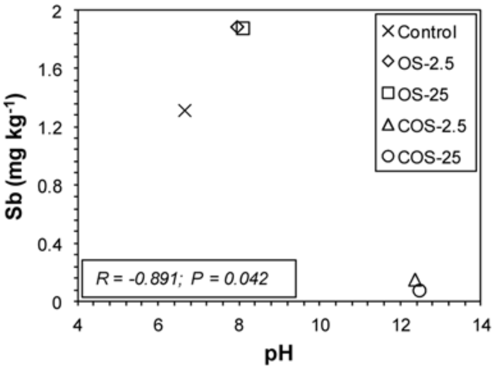

Fig. 2 Water-soluble Sb as a function of soil pH in shooting range soil treated with oyster shells (OS, 2.5 and 25 wt%) and calcined oyster shells (COS, 2.5 and 25 wt%).

synthesized in cementitious alkaline matrix (pH 12) is more stable than that synthesized at pH 6.5.

Sb also has a strong interaction with ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), which is a possible mineral phase at pH >12 potentially causing Sb reduced leachability in the COS treated soil (Cornelis et al., 2006). Therefore, pH is also an important factor controlling Sb mobility in soil. A negative correlation ($R = -0.891$ at $P = 0.042$) was observed between soil pH and Sb concentrations upon application of soil amendments (Fig. 2), indicating decreased Sb leachability from pH 8 to 12. However, Sb concentration increased from 1.32 to 1.89 mg kg^{-1} for the OS treatment. Johnson et al. (2005) reported that desorption of Sb from soil particles may occur under alkaline conditions (pH ~8), which may explain the increased Sb solubility in soils treated with OS where pH was measured at 8.19 (Fig. 2). Cornelis et al. (2008) observed maximum and minimum Sb leachability at pH 7 at pH 13, respectively. These findings are in agreement with the present study related to the impact of pH on Sb leachability for the treated shooting range soils. However, these findings are preliminary, and a more detailed study using X-ray absorption near edge structure (XANES) spectroscopy is needed to understand the mechanistic evidence for Sb mobilization or immobilization by OS and COS in shooting range soil.

In conclusion, the leachability of Sb in contaminated shooting range soils was significantly influenced by waste OS and COS. The two different forms of oyster shells impacted Sb leachability differently. OS increased Sb leachability, whereas COS decreased Sb leachability; dissolved calcium in addition to soil pH strongly impacted the treatment. The decreased leachability of Sb in the COS-treated soil was attributed to the formation of calcium antimonate precipitate at high pH. Our results suggest that anionic metal species such as Sb require special attention when treated with soil amendments, due to geochemical transformations at different soil pHs. A comprehensive study should be conducted to determine the effects of soil amendment in multi-metal contaminated soil (specifically Pb and Sb in shooting range) before application in the field.

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