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# Remediation of Pb-contaminated soils by washing with hydrochloric acid and subsequent immobilization with calcite and allophanic soil

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## Abstract

Removal of heavy metals from contaminated soil is not popular because of its high cost. Reducing the bioaccessible heavy metals content to an allowable level by washing with inorganic acids and subsequent immobilization of remained metals may be a low cost option for soil remediation. The applicability of this combined treatment was investigated using three different types of soil, a kaolinitic, a smectitic and an allophanic soil, which were artificially contaminated with Pb. The effectiveness of the treatment was evaluated using two main criteria: (i) reduction of the HCl extractable Pb (bioaccessible Pb) below 150 mg $kg^{-1}$, reduction of water extractable Pb below the concentration of 0.01 mg $L^{-1}$. These values correspond to allowable levels suggested by the Japanese Ministry of Environment. The soils were washed batch-wise at a solution to soil ratio of 5 L $kg^{-1}$ successively with 1 mol $L^{-1}$ HCl and 0.1 mol $L^{-1}$ $CaCl_2$ solutions. The two solutions were separated by filtration from one batch and reused for washing the next batch of soil without processing. The Pb concentration in the solutions increased after repeated use and removal efficiency gradually declined. The efficiency of the treatment was highly dependent on the type of soil. In the kaolinitic soil, HCl extractable Pb content of the soil from the first batch was about 50 mg $kg^{-1}$ and it exceeded 150 mg $kg^{-1}$ in that from sixth batch. But the combined soils from 1st to 10th batches gave bioaccessible Pb content barely below 150 mg $kg^{-1}$. For the smectitic soil having higher cation exchange capacity, the acceptable number of times of reuse was estimated to be 4. For the allophanic soil, treatment with the HCl solution was efficient only for the first batch of the soil, and the reuse of the acid solution was found to be ineffective.

The application of 50 g $kg^{-1}$ of calcite or slacked lime was effective for reducing the water extractable Pb content. To keep soil pH near neutral and secure long term stability, the application of 50 g $kg^{-1}$ of calcite and 100 g $kg^{-1}$ of allophanic soil was chosen as the best method. This combination of amendments could reduce the water extractable Pb to almost undetectable levels after 3 days of aging.

*Keywords:* Allophane; Heavy metal removal; Immobilization; Lead; Soil washing

## 1. Introduction

The disposal of waste in landfills should be the last option in the waste management. Actually, however, the excavation and disposal in landfills is the most frequently employed countermeasure for soils contaminated with toxic heavy metals. According to a statistics by the Japanese Ministry of Environment [1], the disposal of excavated soil was practiced in 356 out of 527 soil pollution cases in 2002. It is technically difficult and costly to reduce the heavy metal content of soils to an extremely low level. But decontamination may be much easier and economical if a more realistic clean up goal is set. Such a goal may be to remove only the soluble fraction of heavy metals or, more particularly, to remove the bioaccessible fraction, i.e., the fraction of metals that is soluble in the gastrointestinal tract. It is noted that the Japanese Ministry of Environment has adopted a 1 mol $L^{-1}$ HCl extraction procedure for simulating the dissolution in the acidic environment of the gastrointestinal tract, and has established maximum allowable levels for some contaminants in terms of this procedure [2]. Whatever decontamination goal is set, the immobilization of heavy metals that remain after the decontamination treatment is indispensable in order to prevent the leaching of the metals from backfilled soils and pollution of surface and ground waters.

Several technologies including soil washing [3] and electrokinetic methods [4,5] have been developed and tested, but no all-round technology that can treat all types of contaminated soils at a reasonable cost has been established. The soil washing can be practiced in two ways, i.e., mixing a soil and washing solution followed by soil-solution separation (batch-washing) and passing the solution through a packed soil column (column-washing). The latter technology is often termed soil flushing.

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According to a compilation by Abumaizer and Smith [3], various extraction agents including acids, neutral salts and chelating agents have been employed. In recent years, many researches have been focusing on the use of chelating agents such as EDTA, SCMC (s-carboxymethyl-cysteine), etc. [6–8] and organic acid [9]. Some chelating agents have been proven to be effective in removing cationic heavy metals because they form stable anionic chelate compounds which exhibit lower tendency to be retained on the surface of soil particles via ion exchange and surface complexation mechanisms. However, they are disadvantageous in terms of cost of chemicals, toxicity of some chelating agents and increased mobility of the chelated heavy metals that may remain after the treatment. On the other hand the immobilization of heavy metals after washing with inorganic acids is easier because most cationic heavy metals forms sparingly soluble hydroxides or are adsorbed onto soil minerals when soil is neutralized. For these reasons, washing of contaminated soils with inorganic acid or alkali and subsequent immobilization are still worth further study. Unexpectedly, however, there is little published report on the combination of acid-washing and stabilization.

In the present study, laboratory scale batch-washing with dilute hydrochloric acid (HCl) is applied to three artificially lead (Pb)-contaminated soils to reduce the Pb content. The decontamination goal is set at reducing the amount of bioaccessible Pb below 150 mg $kg^{-1}$, which is the maximum allowable level according to the Japanese Law [2]. Then, the unextracted Pb is immobilized by application of some amendments. Since the present decontamination goal is moderate and the soils are still acidic after washing, they may contain significant amounts of water soluble Pb. The objective of the present study is twofold. One is to find out suitable amendments that can effectively reduce the lability of the remaining Pb. Another objective is to test the possibility of reducing the volume of waste solution by recycled use of the acid. In soil washing, it is difficult to drastically reduce the cost for agitation, solid–liquid separation and mixing amendments. But it is possible to reduce the cost for waste water processing by reducing the volume of washing solution.

The experimental results showed that the washing solution can be recycled several times and that the combined application of calcite and allophanic soil can effectively reduce the solubility of the remained Pb.

## 2. Materials and methods

### 2.1. Soil sample preparation and characterization

Three soil samples that differ in chemical and mineralogical properties were collected in Japan. The soil samples were air-dried and passed through a 2 mm sieve. The soil samples were analyzed for pH, organic carbon content, and exchangeable cation content following the standard methods [10]. The content of allophane plus imogolite was determined by the oxalate-oxalic acid dissolution method [11,12]. Clay content and clay mineralogy was determined by the method described by Wada and Umegaki [13]. The values of the measured properties are listed in Table 1. The Yoshiki soil was taken from the subsurface layer of a soil derived from saprolite of granite. It has relatively low organic matter content and effective cation exchange capacity (ECEC), i.e., the summed amount of exchangeable cations. The Chikugo soil was taken from the surface layer of a soil developed on an alluvial sediment rich in smectite and it is characterized by high ECEC. The Goshi soil was taken from the surface layer of a humus-rich soil derived from volcanic ash. It contains large amount of humus as well as allophane. The content of allophane determined by the selective dissolution was 162 g $kg^{-1}$.

The soil samples were spiked with 1000 mg $kg^{-1}$ of Pb(II) with $Pb(NO_3)_2$. Four hundred and eighty milliliter of 0.01 mol $L^{-1}$ $Pb(NO_3)_2$ solution was sprayed onto 1 kg of an air-dried soil sample spread on a shallow plastic vat with frequent mixing with plastic spoon. The spiked soil sample was aged for 3 months at a room temperature without cover and stored in a plastic bag after grinding to pass through a 2 mm screen. The total Pb contents of the prepared samples are listed in the last column of Table 1. The extractability of Pb in the contaminated soil samples was characterized by a simplified sequential extraction with water, 1 mol $L^{-1}$ $MgCl_2$ and hot 6 mol $L^{-1}$ HCl [5].

### 2.2. Batch-washing

Thirty grams portions of a contaminated air-dried and sieved soil sample were placed in 10 250 mL plastic bottles with fitted stoppers and numbered from 1 to 10. A 150 mL portion of a 1 mol $L^{-1}$ HCl was added to the first bottle and it was shaken for 1 h. The reacted soil suspension was transferred onto a 0.45 μm-membrane filter and the extract was collected by suction. A small amount of the extract was drawn for measurements of its pH and Pb concentration and the remaining extract was applied to the second bottle and fresh HCl solution was added to compensate the volume of the extracting solution. All 10 batches of the soil were washed with this manner. At each extraction, the amounts of recovered solution and added HCl solution were estimated by weighing.

To remove a part of remaining Pb and reduce the acidity of the soil, the soil left on the filter was washed by suction with 150 mL of a 0.1 mol $L^{-1}$ $CaCl_2$ solution. The $CaCl_2$ solution was used because it is effective in extracting exchangeable Pb retained on layer silicate minerals. Mori and Wada [14] reported that a part of Pb released from surface complexes is re-adsorbed on cation exchange sites of layer silicate minerals having permanent negative surface charge. Also in $CaCl_2$ washing, the filtrate from the first batch was reused for washing the second batch and so on in a similar way as in HCl washing.

The Pb concentration of the filtrates was determined by atomic absorption spectroscopy, the pH was determined with glass electrode.

The soil samples after $CaCl_2$ washing were air-dried and the content of 1 mol $L^{-1}$ HCl extractable Pb was determined by the method specified by the Ministry of Environment of Japan [2]. In the procedure, a soil sample was shaken with 1 mol $L^{-1}$ HCl for 2 h at a soil to solution ratio of 0.030 kg $L^{-1}$ and the extracted Pb was determined after filtration through a 0.45 μm