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Phytoavailability control based management for paddy soil contaminated with Cd and Pb: Implications for safer rice production

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ABSTRACT

A metal phytoavailability control based management protocol for a metal contaminated paddy soil was investigated as an alternative to conventional engineering-based remediation methods such as 'clean soil cover' for safer rice crop production. The accumulation of Cd and Pb in rice was monitored following application of three pH change-induced immobilizing agents (dolomite, steel slag, and agricultural lime) and two sorption agents (zeolite and compost) to a Cd and Pb contaminated paddy soil. Changes in the phytoavailable pool of Cd and Pb in soils following the application of each immobilizing agents were also determined using 1 M NH_4NO_3 extraction. Among the immobilizing agents considered, pH change-induced immobilizers were more effective than sorption agents; exhibiting more significant decreases ($p < 0.001$) in phytoavailable Cd and Pb concentrations. The phytoavailable pool of these metals was even lower than those measured in the 'clean soil cover' where the total metal concentrations of the plow layer were reduced via capping the surface with uncontaminated soil. Consequently, the decline in the phytoavailable pool of Cd and Pb in soil induced by immobilizing agents resulted in significantly lower accumulation of these metals in the rice grain (0.02–0.03 mg kg^{-1} for Cd and 0.11–0.16 mg kg^{-1} for Pb) compared to those measured in the rice cultivated in the control (unammended) soil (0.16–0.23 mg kg^{-1} for Cd and 0.19–0.30 mg kg^{-1} for Pb). This indicated that immobilization using pH-change induced immobilizing agents was a feasible approach for safe rice crop production in Cd and Pb contaminated paddy soils.

1. Introduction

Although metals such as Cd and Pb are naturally ubiquitous in the earth's crust, their concentrations in agricultural soils have often been elevated by anthropogenic sources including mining sites, disposal of industrial waste, and treatment with fertilizer and pesticides containing trace metals (Bai et al., 2010; Omwoma et al., 2010). Among these sources, metals released from mine sites through erosion of mine tailings and acid mine drainages have commonly contaminated paddy fields. In Korea, the total number of metal mines reported in 2011 was 2166; out of which 2089 had been abandoned (MIRECO, 2012). In 2012, the Ministry of Environment, Korea conducted intensive investigation for agricultural soils near 60 metal mining sites and found that 26 mine sites had caused elevated metal concentrations in the investigated soils (MoE, 2012). The major concern is that since rice cultivation is still being performed in these contaminated areas, rice produced in such areas may contain significant amounts of metals, potentially threatening human health (Nabulo et al., 2010; Yusuf et al., 2003). For this reason, the Korean government has legislated maximum allowable 'standard limit' concentrations for Cd (<0.2 mg kg^{-1} FW) and Pb (<0.2 mg kg^{-1} FW) for polished rice (KFDA, 2010) which are comparable with other guidelines legislated internationally and nationally (EC, 2001; FAO/WHO-CA, 2001; Yang et al., 2010). The goal of these guidelines was to screen out the metal contaminated rice before it was distributed to the market. However, despite the introduction of these guidelines, health safety issues from consumption of contaminated rice products is still a major concern because monitoring and screening of rice from contaminated paddy field is very limited and local market distribution and consumption of produce from these areas is still occurring. This implies that management approaches during rice cultivation are required to mitigate safety issues from metal contaminated rice produced from contaminated paddy soils.

To date, many engineering-based remediation technologies have been applied to contaminated agricultural sites mainly to decrease the total metal concentrations in soils. This has included excavation and burying followed by re-filling with uncontaminated soils and simply covering the contaminated area with uncontaminated soils to the depth of the tilling layer. Taking into account the wide range of agricultural land affected by mining sites, the economic feasibility of these

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methods is poor because transportation of large amount of soils over an extended distance is prohibitively expensive and it is often hard to obtain the large amounts of clean soil required to treat large areas of agricultural lands. More importantly in terms of environmental preservation, taking significant amounts of bulk soils from a specific area is likely to be linked with significant environmental disruption and destruction of that area. Alternatively, safe food crop production in contaminated soils may be achievable by immobilization of metals using a wide range of amendments taking into consideration that metal uptake from soils by plants relies primarily on metal phytoavailability rather than the total metal concentrations (Geebelen et al., 2003; Ruby et al., 1993). Calcite, dolomite, fly ash, lime, and steel slag have been widely examined as pH-change (or liming effect) induced immobilizing agents (Bolan and Duraisamy, 2003; Dermatas and Meng, 2003; Rangel-Porras et al., 2010) while compost, iron compounds, zeolite, and PO_4 enriched minerals such as apatite have been widely used as sorption agents (Kosobucki et al., 2008; van Herwijnen et al., 2007; Zhou and Haynes, 2010). However, most studies to date have used chemical based extraction methods to evaluate the efficiency of the immobilizing agents by determining the available or mobile pool of metals in soils (Garrido et al., 2005; van Herwijnen et al., 2007). When immobilization efficiency was examined through determination of metal uptake by plants directly, this was generally limited to studies using mainly juvenile plants rather than mature plants (Malandrino et al., 2011; Yang et al., 2010). In comparison evaluation of the immobilization efficiency by determination of the accumulated metal concentration in edible parts of mature crop at the field level has been rare.

Thus, in the present study, a rice cultivation experiment was carried out to investigate the feasibility of chemical immobilization for safer rice production in Cd and Pb contaminated paddy soils.

2. Materials and methods

2.1. Soils and immobilizing agents

A bulk soil contaminated with Cd and Pb was collected from a paddy field located nearby abandoned metal mines. The main minerals mined in this region included Au, Ag, and Zn. The collected soil was fertilized by adding nitrogen, phosphorus and potassium at the following rates 9 kg N per 1000 m^2, 3 kg P_2O_5 per 1000 m^2, and 3 kg K_2O per 1000 m^2, and then thoroughly homogenized by mixing prior to being incorporated with each immobilizing agent. The collected paddy soil was considered to be moderately contaminated with Cd and Pb as it only slightly exceeded the local guideline values. The total metal concentrations and selected physicochemical properties of the soil were summarized in Table 1.

In order to decrease Cd and Pb phytoavailability in paddy soils, five different immobilizing agents were examined including dolomite ($CaMg(CO_3)_2$), agricultural lime (hereafter named as agri-lime), steel slag, zeolite, and pig-manure based compost (hereafter referred to as compost). Phytoavailability of the cationic metals can be controlled by the soil pH and sorption substance existing in soils (Kim et al., 2012). From this consensus, dolomite, agri-lime, and steel slag were included as representative examples of pH change-induced immobilizer while zeolite and compost were included as representative examples of common sorption agents. Generally, these candidate immobilizing agents were all inexpensive and locally available. They were also previously demonstrated to have high trace metal immobilization efficiency under upland conditions (Kim et al., 2012).

Table 1
Selected physicochemical properties and trace metal concentrations of the upland soil and the uncontaminated soil used for the clean soil treatment.

	Contaminated soil	Clean soil
pH (1:5)	6.4	6.1
EC (dS m^{-1})	0.12	0.11
Organic matter (%)	2.1	1.6
CEC (cmol kg^{-1})	10.2	9.5
Particle size (%)		
Sand	66	68
Silt	26	25
Clay	8	7
Trace metal (mg kg^{-1})		
Cd (4)	5	1.2
Pb (200)	328	160

The numbers in parenthesis represent the legislated guideline, the warning levels in Soil Environmental Conservation Act 2009 (MoE, 2015).

2.2. Plot installation and treatments

Twenty one (21) plastic containers (rectangular rubbish bin like shape; 0.3 m × 0.3 m × 0.6 m) were buried in a paddy field at ground level (3 rows and 7 columns) 0.3 m apart from each container and filled with soils composed of each treatment. Each 150 kg of collected soil (as it was moistened) was treated with dolomite and steel slag at 2% (*w*/*w*), agri-lime at 1% (*w*/*w*), and with zeolite and compost at 3% (*w*/*w*). Preliminary laboratory scale experiments were carried out to determine the treatment amounts of pH change induced immobilizing agents required to adjust the final soil pH to 7.5–8.0. For the sorption agents, incorporation level was simply determined to provide enough for cationic metal adsorption. Although moistened soils were used during the incorporation of immobilizing agents, the amount of immobilizing agents added were calculated on a dry soil weight basis. Each treated soil was then thoroughly mixed and divided into three aliquots prior to placing the soils in the buried growth containers. A conventional 'clean soil cover' treatment was also included for comparison. For this treatment, three growth containers were filled with untreated contaminated paddy soil to a depth of 20 cm and covered with a 30 cm layer of clean soil, not contaminated with heavy metals, so that the total depth remained 50 cm. The clean paddy soil was also collected from the area where the contaminated paddy soil was collected so that both soils would have similar if not identical soil properties. The final three containers were each filled with 50 kg of contaminated paddy soil as a control treatment. All treatments were prepared in triplicate in a random block design. The treated soils were aged under saturated moisture conditions for 2 months and rice cultivation commenced in May 2013.

2.3. Plant cultivation

This study used the rice cultivar, *Oryza sativa* L. Ilmi because this was the cultivar most widely grown in the region. Two stands (3–4 plants for a stand) of 50 day old seedlings were obtained from a local rice nursery. Prior to transplantation of seedlings, each growth container was flooded via irrigation with non-contaminated local ground water commonly used for the irrigation of paddy fields. Preliminary investigations had indicated that the groundwater contained only trace metal concentrations (data not shown). During rice cultivation water was supplied using only the local ground water or natural precipitation with appropriate management, such as weed control and pesticide treatment being practiced as necessary until the rice was harvested.

2.4. Soil and plant sample preparation

Soil samples from each growth container were collected twice; initially before cultivation in April 2013 and subsequently after rice cultivation in October 2013. Consistent sampling conditions were ensured by using an augur (5 cm in diameter, 20 cm in depth) to collect soil samples from each growth container. The collected soils were air-dried and passed through a 2 mm sieve and then stored in plastic bottles until further analysis.

At harvest rice plants were removed from each growth chamber and the grains or each plant separated from the straw prior to measuring the fresh weight of each. The collected rice grains were dried until the