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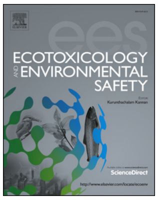

Release of cadmium in contaminated paddy soil amended with NPK fertilizer and lime under water management

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ABSTRACT

Agricultural soils contaminated with cadmium (Cd) pose a risk to receiving surface water via drainage or runoff. A 90-day laboratory incubation experiment was conducted to investigate the release characteristics and transformation of Cd from contaminated paddy soil amended with agrochemical (NPK fertilizer) and lime (L) under water management regimes of continuous flooding (F) and drying-wetting cycles (DW). The result showed that the dissolved Cd concentrations in overlying water of the fertilizer treatment under flooding (NPK + F) and drying-wetting (NPK + DW) reached up to 81.0 μg/L and 276 μg/L, and were much higher than that from the corresponding controls without NPK fertilizer addition at the end of experiment. The Cd concentration showed significantly negative correlation with overlying water pH, but positive correlation with soil redox potential and concentrations of dissolved total nitrogen, sulfate and manganese in overlying water ($P < 0.05$), indicating that drying-wetting cycles and N fertilizer addition may enhance soil Cd release. The Cd concentrations in overlying water from all treatments except NPK + L + F treatment exceeded the Cd threshold limit of Chinese Environmental Quality Standards for Surface Water (10 μg/L Grade V) and poses potential risk to surface water quality. Meanwhile, the proportion of Cd in the acid-soluble fraction from all incubated soil except NPK + L + F treatment increased compared to before incubation. The results indicated that continuous flooding was a reasonable water management candidate coupled with lime addition for immobilizing soil Cd.

1. Introduction

Cadmium (Cd), a potential toxic element, has long been identified as major human health hazard (Ye et al., 2014; Xue et al., 2017). The main anthropogenic sources of Cd are activities such as non-ferrous metal mining and refining, but atmospheric sedimentation, wastewater irrigation, and application of chemical fertilizers and pesticides also result in high level of Cd accumulating in soils (Janoš et al., 2010; Liu et al., 2017). Agricultural soils contaminated with Cd may pose a risk to human health via the food chain due to its high mobility and toxicity (Zhu et al., 2014), and may also lead to contamination of surface water and groundwater through runoff and infiltration (Schipper et al., 2008; Wang et al., 2011). Unfortunately, soil Cd contamination occurs widely in paddy fields of subtropical China, especially in Hunan province (Zeng et al., 2015). This problem has recently received considerable attention because the increasing input flux of Cd poses a major threat to food safety and downstream surface water quality (Zhang et al., 2015).

Cadmium availability and mobility in soil is influenced by many factors including water management, pH, redox potential (Eh), agricultural measures (Kashem and Singh, 2002, 2004; Ye et al., 2018). Soil moisture regime is one of the most important factors affecting the physical, chemical, and biological properties of soil and may indirectly influence Cd transformation (Zheng and Zhang, 2011; Li and Xu, 2017a). For instance, the availability of Cd in soils decreased and redistributed from exchangeable fraction to iron-manganese (Fe-Mn) oxide-bound fraction after submergence due to its adsorption on hydrous Mn and Fe oxides (Zhu et al., 2012). Chemical fertilizer, as a basic agricultural input for crop growth, is another important factor affecting Cd mobility by directly reacting with Cd or altering soil properties such as pH and surface charge (Tu et al., 2000). Application of nitrogen (N), phosphorus (P) and potassium (K) fertilizer increased the solubility and exchangeable fraction of Cd in soil (Kashem and Singh, 2002; Chen et al., 2006). Lime, a calcareous material obtained very easily and inexpensively, is the most widely used stabilizer of soil Cd by increasing soil pH (Haddad et al., 2017).

Wetland rice ecosystems, widely distributed in Asian countries such as China, India, Japan and Korea (Zeng et al., 2015), are generally in flooded and unflooded conditions by rotation to meet rice's needs for growth (Zhu et al., 2012). Paddy soil maintained under long-term flooding conditions before harvest may induce an array of abiotic and

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biotic reduction processes (Boivin et al., 2002). These processes largely modify soil physiochemical properties during periods of flooding and subsequent drainage (Caetano et al., 2003) and can affect the mobility of Cd directly via changes in its speciation or indirectly through related changes in pH, dissolved organic carbon (DOC), and the redox chemistry of Fe, Mn, and sulfur (S) (Frohne et al., 2011; Shaheen et al., 2014a, 2014b). Previous study using column leaching tests have focused on the influence of different water management regimes on soil Cd release to groundwater. Soil submersion decreased the Cd concentration in leachate due to the increased pH (Yun and Yu, 2015). Lime addition also can increase pH and accordingly reduce Cd concentration in column leachate (Ash et al., 2015). However, current knowledge is still limited about how the dynamics of redox chemistry combined with agro-measures to affect the release and transformation of Cd in soils during incubation experiments (Pan et al., 2016). In this study, a 90-day static laboratory incubation test was conducted using Cd contaminated paddy soil amended with NPK fertilizer and lime under water regimes of continuous flooding and alternating drying-wetting cycles. The objectives of the study were to: 1) investigate the release characteristics of dissolved Cd in soil to overlying water; 2) elucidate the relationships between Cd concentration and soil Eh, and concentrations of dissolved total N (TN), total P (TP), sulfate (SO_4^{2-}), Fe, Mn and pH in the overlying water; and 3) determine the transformation characteristics of soil Cd affected by water management combined with application of NPK fertilizer and lime. This study will extend the knowledge to understand the potential risk of Cd release from soils to surface water as induced by agricultural measures.

2. Materials and methods

2.1. Soil physicochemical properties

Surface soil (0–20 cm depth) was collected from an abandoned paddy field near a lead and zinc smelting plant in Hengyang city, Hunan Province, Southern China. The soil sample was air-dried, ground, and sieved through a 2-mm nylon screen before testing. The selected physiochemical properties of the soil were as follows: pH, 4.98; available nitrogen (N) content, 95.4 mg/kg; available phosphorous (P) content, 3.2 mg/kg; available potassium (K) content, 20.2 mg/kg; organic matter content, 27.3 g/kg. The contents of free Fe_2O_3 and amorphous Fe_2O_3 were 15.9 and 3.51 g/kg, respectively. The total Cd content was 11.5 mg/kg and far exceeded the recommended Cd content (0.3 mg/kg) for acid soil as described in the Chinese Environmental Quality Standard for Soils (GBl5618-1995) (Grade II for soil $pH < 6.5$) (MEPPRC, 1995).

2.2. Experimental design and laboratory incubation

Air-dried soil samples (500 g) were placed in individual plastic pots (14 cm in height and 11 cm in diameter). The NPK fertilizer consisted of urea ($CO(NH_2)_2$), calcium dihydrogen phosphate ($Ca(H_2PO_4)_2$) and potassium chloride (KCl) and was added to the soil with 0.2 g N/kg, 0.1 g P_2O_5/kg and 0.2 g K_2O/kg soil. Lime (L) using calcium hydroxide ($Ca(OH)_2$) was added at 2 g/kg soil. A treatment without fertilizer and lime addition was used as a control (CK). The treatment soils and controls were then incubated under two water regimes of continuous flooding (F) and alternating drying-wetting cycles (DW) using deionized water. Therefore, the treatments included (i) controls of CK + F and CK + DW, (ii) NPK fertilizer addition treatments of NPK + F and NPK + DW, and (iii) NPK fertilizer addition combined with lime treatments of NPK + L + F and NPK + L + DW. Each treatment was in duplicates. All chemicals of NPK fertilizer and lime were analytical reagent grade.

On day 1 of an experiment, deionized water was added to all treatments to submerge the soil under 2.0 ± 0.5 cm depth of water. In the continuous flooding treatments, pots sprayed daily by measuring weight to maintain an approximate 2.0 cm depth of surface water. In the drying-wetting experiments, the soils were incubated without water addition until the day before sampling when they were re-submerged under 2.0 cm depth water for 24 h. The overlying water (approximate 140 mL) in each treatment was removed carefully by pipette for analysis and collected on day 5, 15, 30, 60 and 90. Soil samples from each pot were collected at 30 and 90 days incubation to determine Cd fractions using sequential extractions. The incubation experiments were conducted in a thermostatic incubator maintained at 25 ± 1 °C and a relative humidity of 80%.

The pH of each water sample was measured immediately, then the water was passed through a 0.45-μm membrane filter. Some of the filtrate was analyzed for concentrations of dissolved TN, TP and SO_4^{2-}. The remainder of each filtered water sample was acidified to $pH < 2.0$ using concentrated nitric acid (HNO_3) prior to being analyzed for dissolved Cd, Fe and Mn concentrations.

2.3. Sample analysis

Selected soil properties were determined according to the general methods described by Lu (1999). Soil pH was measured using a glass electrode (Mettler Toledo 420) at a soil: water ratio of 1:2.5. Soil organic matter was determined using a volumetric method of potassium dichromate ($K_2Cr_2O_7$) heating. The content of free iron oxide (Fe_2O_3) in soil was determined following extraction using a dithionite citrate system buffered with sodium bicarbonate; amorphous Fe_2O_3 was extracted using ammonium and oxalate under dark conditions. Soil Eh was measured using mini platinum-electrodes (Falkenberg, ELANA Ltd, Germany). The electrodes were horizontally installed and exactly positioned at the measurement depth of 5 cm below the soil surface. The pH of overlying water was determined using a glass electrode. The concentrations of dissolved TN and TP in water samples were digested with alkaline potassium persulfate and determined by UV spectrophotometric method, and the SO_4^{2-} concentration was determined by barium chromate spectrophotometry as described by Lu (1999).

The fractionation of Cd in soils was achieved using the sequential extraction procedure of European Community Bureau of Reference (BCR) method (Rauret et al., 1999). The method basically consisted of three extraction steps: (i) acid-soluble fraction (Aci-Cd) was extracted with acetic acid; (ii) the Cd combined with Fe/Mn oxides (reducible fraction, Red-Cd) was extracted with hydroxylamine hydrochloride; (iii) the Cd bound to organic matter and sulfides was extracted with hydrogen peroxide and ammonium acetate (oxidizable fraction, Oxi-Cd). Soil samples and residual fractions (Res-Cd) were digested in a mixture of HNO_3 and H_2O_2 to determine the content of Cd (USEPA, 1996).

The concentrations of dissolved Cd, Fe and Mn in overlying water samples, extracting solution and digested solutions were determined using mass spectrometry with inductively coupled plasma (ICP-MS, Agilent 7500 Series). The accuracy of the digestion procedure and analytical method was checked with certified soil reference material (GBW-08303) obtained from China National Center, yielding analytical error < 10%. The recovery efficiency of the sequential extraction was calculated as: Recovery (%) = [(Step1 + Step2 + Step3 + Residual)/(pseudo-total)] × 100, and the recovery values were found to be in the range of 90–105%.

2.4. Statistical analysis

Statistical analyses were performed using Microsoft Excel 2013 and SPSS 19.0. One-way analysis of variance (ANOVA) was used to examine statistically significant differences among the Cd concentrations of overlying water and soils in different treatments. A probability level of 0.05 was considered to be statistically significant.