



ELSEVIER

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradisoEffects of low molecular weight organic acids on ^{137}Cs release from contaminated soilsPo Neng Chiang^a, Ming Kuang Wang^{b,*}, Pan Ming Huang^{b,1}, Jeng Jong Wang^c^a The Experimental Forest, National Taiwan University, Nantou 557, Taiwan^b Department of Agricultural Chemistry, National Taiwan University, Taipei 106, Taiwan^c Institute of Nuclear Energy Research, Taoyuan 325, Taiwan

ARTICLE INFO

Article history:

Received 19 August 2009

Received in revised form

14 February 2011

Accepted 23 February 2011

Available online 2 March 2011

Keywords:

 ^{137}Cs

Complexation

Low molecular weight organic acids (LMWOAs)

Parabolic diffusion

ABSTRACT

Radio pollutant removal is one of several priority restoration strategies for the environment. This study assessed the effect of low molecular weight organic acid on the lability and mechanisms for release of ^{137}Cs from contaminated soils. The amount of ^{137}Cs radioactivity released from contaminated soils reacting with 0.02 M low molecular weight organic acids (LMWOAs) specifically acetic, succinic, oxalic, tartaric, and citric acid over 48 h were 265, 370, 760, 850, and 1002 Bq kg⁻¹, respectively. The kinetic results indicate that ^{137}Cs exhibits a two-step parabolic diffusion equation and a good linear relationship, indicating that the parabolic diffusion equation describes the data quite well, as shown by low p and high r^2 values. The fast stage, which was found to occur within a short period of time (0.083–3 h), corresponds to the interaction of LMWOAs with the surface of clay minerals; meanwhile, during the slow stage, which occurs over a much longer time period (3–24 h), desorption primarily is attributed to inter-particle or intra-particle diffusion. After a fifth renewal of the LMWOAs, the total levels of ^{137}Cs radioactivity released by acetic, succinic, oxalic, tartaric, and citric acid were equivalent to 390, 520, 3949, 2061, and 4422 Bq kg⁻¹ soil, respectively. H⁺ can protonate the hydroxyl groups and oxygen atoms at the broken edges or surfaces of the minerals, thereby weakening Fe–O and Al–O bonds. After protonation of H⁺, organic ligands can attack the OH and OH₂ groups in the minerals easily, to form complexes with surface structure cations, such as Al and Fe. The amounts of ^{137}Cs released from contaminated soil treated with LMWOAs were substantially increased, indicating that the LMWOAs excreted by the roots of plants play a critical role in ^{137}Cs release.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Radiocesium, which is one kind of artificial radionuclide, is one of the priority radionuclide contaminants of major concern in the environment. Release of radiocesium into the environment largely results from nuclear weapons tests, or from accidents related to nuclear facility operation processing, like those involving reactors, evaporation ponds, liquid-storage tanks, and burial grounds (Avery, 1996; Hansen et al., 2001; Nabyvanets et al., 2001; Zachara et al., 2002). Cesium contributes a major portion of the radioactivity found at many sites associated with nuclear weapons production (Riley et al., 1992); as such, it is a key contaminant that must be considered in ecosystem restoration strategies.

Whether Cs⁺ can be sorbed onto the surface of clays in soil environments, particularly micaceous clay minerals, has been

* Corresponding author. Tel.: +886 2 3366 4808; fax: +886 2 2366 0751.

E-mail address: mkwang@ntu.edu.tw (M.K. Wang).¹ Permanent address: Department of Soil Science, University of Saskatchewan, Saskatoon, SK, Canada S7H 4A5.

studied widely, as reviewed by Cornell (1993). Tamura and Jacobs (1960) reported that non-expanding layer silicates, namely illite and mica, sorb more Cs from solution than the expanding layer silicates of vermiculite and montmorillonite. Frayed edge sites (FES) are reportedly responsible for highly selective Cs sorption by illite (Sawhney, 1972). Frayed edge sites are formed during mineral edge weathering, when K⁺ ions are replaced by hydrated cations like Na⁺. Poorly hydrated alkali metal ions are selectively sorbed to FES with easily dehydration and cause partial collapse of interlayer space near the phyllosilicate edge, and hence fixation by layer silicates.

Early in 1990, the Institute of Nuclear Energy Research (INER, Taiwan) accidentally discharged radionuclide wastewater into an irrigation ditch and contaminated the agricultural ecosystem. Part of the agricultural soil contaminated by radionuclide was removed by INER in 1994 and 1995 (Atomic Energy Council, 1995). Contaminated soil with radioactivity in the range of 20,000–60,000 Bq kg⁻¹ soil was stored at INER.

Plants have a remarkable ability to absorb and accumulate metals and organic compounds from soil, water, and air. There has been increasing interest in developing plant-based technology

(phytoremediation) to remediate soils contaminated with heavy metals and radionuclides (Cunningham et al., 1995; Chiang et al., 2005; Fuhrmann and Lanzirrotti, 2005). The uptake mechanisms of radiocesium and the interrelationships of species and soil parameters have been well demonstrated (Lasat et al., 1998; Wang et al., 2000; White and Broadley, 2000; Zhu and Smolders, 2000; Fuhrmann et al., 2002; Gil-García et al., 2008; Velasco et al., 2008). However, phytoremediation application in the field to remediate local ^{137}Cs contaminated soil takes an estimated 10–58 years, based upon concentration ratios and plant biomasses observed in field experiments. Recently, radionuclide desorption by phytoremediation with chelating reagents has been recognized as a major advance in the restoration of radiocesium contaminated soils (Fuhrmann and Lanzirrotti, 2005). A variety of natural and synthetic chelating agents can elute contaminants from soil and enhance their uptake into plants. Low molecular weight organic acids (LMWOAs) are natural products of root exudates, microbial secretions, and plant and animal residue decomposition in soil (Strom, 1997; Ebbs and Kochian, 1998; Wang et al., 2004). In recent studies, they have been implicated in altering the bioavailability and phytoremediation efficiencies of heavy metals and radionuclides in soils (Huang et al., 1997; Lee et al., 1997; Yang et al., 1997; Cieśliński et al., 1998; Onyatta and Huang, 2003; Krishnamurti et al., 2005). Metal chelation and/or complexing with LMWOAs for mobilization of mineral nutrients influence metal release from soils and enhance the metal uptake by plants. Chiang et al. (2005) investigated the role of organic acids in rape tolerance to Cs^+ and found that organic acids can chelate with Fe^{2+} and Al^{3+} and enhance Cs^+ accumulation in rape. Huang et al. (1997) investigated the effect of organic acids amendment of uranium-contaminated soils and found that citric acid significantly increases metal availability and enhances uranium accumulation many-fold in the shoots of selected plants. Although the effects of several organic acids on radionuclide sorption and desorption from various clay minerals and/or oxides have been studied (Wending et al., 2004, 2005), there is limited information on desorption behavior of radionuclides from contaminated soils by organic acids. The characterization of Cs release from contaminated soil will provide insight regarding Cs restoration strategies, in particular, the potential applicability of phytoremediation for the removal of Cs from contaminated soils. Thus, this study assessed the effect of low molecular weight organic acid release-ability and the mechanism of ^{137}Cs release from contaminated soils.

2. Materials and methods

2.1. Study site

The study area is located in the Ta-Han River valley, about 30 km south of Taipei in Tau-Yuan County, Taiwan, as described by Nabyvanets et al. (2001). Highly radioactive contaminated soils were removed and transferred to INER in 1994 and 1995. Large quantities of soil were put in storage at INER, not be disposed until they have decayed to a point at which they exhibit a natural background value. For testing the effect of LMWOAs ability of ^{137}Cs from contaminated soil, these stored contaminated materials were used for this experiment. These soils were classified as kaolinitic, alluvial, hyperthermic, and Typic Hapludox (Soil Survey Staff, 2006).

2.2. Soil analysis

Contaminated surface soil (0–15 cm) was removed by mechanical excavator, homogenized, and stored at INER, Taiwan (Nabyvanets, et al., 2001). Two kilograms of contaminated soil were air dried, crushed, and passed through a 2 mm sieve. Soil pH was measured in a

1:1 weight-to-volume suspension of soil in both distilled water and 2 M KCl after 30 min reacted time period. Cation-exchange capacity (CEC) and exchangeable cations were determined by 1 M ammonium acetate (pH 7.0) replacement method (Rhodes, 1982). Organic matter content was determined by elemental analyzer (Vario EL, Elementar Analysen-systeme GmbH, Hanau, Germany). Particle size analysis and soil texture were separated into clay, silt, and sand fractions by sedimentation and centrifugation (Jackson, 1979). Semi-quantitative clay fractions were estimated from the peak area of X-ray diffraction (Brindley, 1980). Free Al- and Fe-oxides were extracted with dithionite-citrate-bicarbonate (DCB) solutions (Mehra and Jackson, 1960). X-ray non-crystalline Al- and Fe-oxides were extracted with 0.2 M ammonium oxalate (pH 3.0) solutions (McKeague et al., 1971). The frayed edge site capacity measurement was employed a modification of the method developed by Wauters et al. (1996). Soil samples were pre-treated with 100 mM $\text{CaCl}_2/0.5$ mM KCl mixed solution, then equilibrated with 100 mM $\text{CaCl}_2/0.5$ mM KCl/0.05 mM CsCl mixed solution. Following equilibration with 100 mM CaCl_2 , the soil samples were extracted with 1 M NH_4Cl . Frayed-edge sites were defined as the sum of Cs^+ and K^+ extracted from the soil samples by NH_4Cl . The radioactivity of ^{137}Cs in soil samples was determined by γ -ray spectrometry. The γ -ray spectrometry system was based upon a high-purity Ge detector (CANBERRA GC-4020, FWHM 1.82 keV at 1.33 MeV) coupled to a computerized data acquisition system (CANBERRA Series 95, 4096-channels pulse height analyzer). Total counting time was 80,000 s. Counting efficiency was calibrated using a standard multi- γ -ray source, mixed in agar. The minimum detectable radioactivity of ^{137}Cs was calculated to be 0.33 Bq kg^{-1} soil for contaminated soils.

2.3. Kinetics of radiocesium released from the contaminated soils

Each 10 g portion of contaminated soil was placed in a 100 mL polypropylene cup, and then 100 mL of 0.02 M acetic, succinic, oxalic, tartaric, and citric acid solution were added. Subsequently, all samples were agitated continuously at a speed of 150 strokes per min at 298 K. After 0.083, 0.25, 0.5, 0.75, 1, 2, 3, 4, 8, 12, 24, or 48 h of agitating, the soil suspensions were filtered through Whatman No. 41 filter paper, rinsed filter paper several times with distilled water, and finally re-filtered through $0.22 \mu\text{m}$ cellulose acetate membrane filters to collect filtrate. Make to 100 mL final volume with dishwater. All experiments were performed in triplicate. An approximately 100 mL aliquot of the filtrate was measured for ^{137}Cs in a cylindrical acrylic container (130 mm ϕ , 90 mm high) placed directly on the γ -ray detector. Concentrations of Al, Fe, and Si in the filtrate after contaminated soil reacted with LMWOAs were determined using Inductively Coupled Plasma Optical Emission Spectrometry (Perkin Elmer 2000 DV, ICP-OES). Minimum detection limits (MDL) were 0.09, 0.19, and $0.06 \text{ mmol kg}^{-1}$ for Al and Fe, respectively. The kinetic results were fitted with a parabolic diffusion equation, as follows:

$$Q = a + Dt^{0.5}$$

where Q is the quantity of ^{137}Cs released to solution from contaminated soil at time t , a is a constant, and D is the overall diffusion coefficient.

2.4. Effect of renewing organic acid solutions on radiocesium release

After the first 2 h of the extraction, the soil suspensions were filtered through Whatman No. 41 paper filters and finally re-filtered through $0.22 \mu\text{m}$ membrane filters. Soils that remained on the filters were placed back into a polypropylene cup, and then fresh LMWOAs were replenished. This treatment was repeated

Download English Version:

<https://daneshyari.com/en/article/1877853>

Download Persian Version:

<https://daneshyari.com/article/1877853>

[Daneshyari.com](https://daneshyari.com)