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RESEARCH ARTICLE

Use of flue gas desulfurization gypsum for leaching Cd and Pb in reclaimed tidal flat soil

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Abstract A soil column leaching experiment was conducted to eliminate heavy metals from reclaimed tidal flat soil. Flue gas desulfurization (FGD) gypsum was used for leaching. The highest removal rates of Cd and Pb in the upper soil layers (0–30 cm) were 52.7 and 30.5 %, respectively. Most of the exchangeable and carbonate-bound Cd and Pb were removed. The optimum FGD gypsum application rate was 7.05 kg·m^{-2}, and the optimum leaching water amount for the application was 217.74 L·m^{-2}. The application of FGD gypsum (two times) and the extension of the leaching interval time to 20 days increased the heavy metal removal rate in the upper soil layers. The heavy metals desorbed from the upper soil layers were re-adsorbed and fixed in the 30–70 cm soil layers.

Keywords Cadmium · Lead · Reclaimed tidal flat soil · Fluidized gas desulfurization gypsum · Leaching · Soil column

Introduction

The reclamation of tidal flat soil is one of the main methods to replace arable land. However, due to adsorption and sedimentation in coastal areas, tidal flats are also one of the key sinks for heavy metals (Williams et al. 1994). The high salinity of coastal tidal flat sediments can enhance heavy metal mobility through complexation with salt anions and ion exchange between cations and metal ions (Du Laing et al. 2008). In the Pearl River estuary area, which is highly contaminated with heavy metals, Cd and Pb concentrations in soil are usually high. The chemical fractions of Cd and Pb in reclaimed tidal flat soils are mainly found in exchangeable forms, accounting for 38.3 and 43.2 % of the total amount, respectively (Li et al. 2007a, b).

Soil washing is one of the few treatments to permanently remove metal contaminants from soil. In soil washing, reagents are used to extract metals from solid soil to an aqueous solution. Four reagent types (i.e., acids, salts and high-concentration chloride solutions, chelating agents, and surfactants) are frequently used in leaching. Acids generally rely on the ion exchange and dissolution of soil components/discrete metal compounds to extract metals. In the experiments of Steele and Pichtel (1998), the removal rates of Cd and Pb are 56 and 35 %, respectively, when soil is leached using HCl. During the leaching of heavy metal contaminated soils by salts and high-concentration chloride solutions, Cl^- concentration in soils can form stable compounds, such as $CdCl^+$, $CdCl_2^0$, $PbCl^+$, $PbCl_2^0$, and $PbCl_3^-$, which increase Cd and Pb mobility (Norvell et al. 2000; Usman et al. 2005). Chelating agents and surfactants can efficiently remove heavy metals. Several reagents, such as ethylenediaminetetraacetic acid, can promote high metal complexation and extraction but have comparably low biodegradability in natural environments (Nowack 2002). Previous studies (Arwidsson et al. 2010) proposed [S,S]-ethylenediamine disuccinic acid and methylglycinediacetic acid as ecologically friendly and safe chelating agents.

The addition of wet limestone is commonly applied in coal-fired power plants to reduce sulfur emissions because of the high desulfurization performance, reliability, and low utility consumption of this process (Kikkawa et al. 2002).

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Consequently, a large amount of relatively pure flue gas desulfurization (FGD) gypsum is produced as a co-product. For instance, domestic coal-fired power plants in the USA produce 11.95 million tons of gypsum per year through FGD (ACAA 2006). In 2003, 15.2 million tons of FGD gypsum was produced in 17 European countries (Huller and Kersten 2005). By the end of 2005, the annual FGD gypsum production in China exceeded 6.5 million tons (Wang et al. 2008). However, large amounts of FGD gypsum are not utilized; instead, these large amounts of FGD gypsum are deposited at waste disposal sites (Tesárek et al. 2007). Therefore, the use of FGD gypsum should be investigated to obtain economic and environmental benefits.

Ca^{2+} can be used to remove heavy metals from contaminated soils. The presence of double-charged cations, such as Ca^{2+}, can increase the rate of metal release (Du Laing et al. 2008). Cd desorption is higher in the presence of Ca^{2+} than in the presence of Na^{+} possibly because of the stronger competition for adsorption sites by Ca^{2+} than by Na^{+} (Mustafa et al. 2004). The key element of FGD gypsum is $CaSO_4{\cdot}2H_2O$, which indicates that FGD gypsum can be used to remove Cd and Pb from soils.

This study aimed to evaluate the ability of FGD gypsum to leach Cd and Pb from the upper rooting zone of reclaimed tidal flat soils and to determine the optimal leaching scheme.

Materials and methods

Collections of soils and FGD gypsum

The test soil with a depth of 0–70 cm in an area of 1.5 × 1.5 m was obtained from a reclaimed farmland in Zhongshan City, Southern China. The local average water table is 1.0 m due to deep ditch draining in the field. The taxonomic classification of the soil was Tidalic Fluvisol (Aric): FL-td-ai (World reference base for soil resources 2014). The upper 20 cm of topsoil is a silt loam (21 % clay) transitioning to a silty clay loam (30 % clay) below 40 cm with a mixed micaceous and kaolinitic mineralogy. The soil was equally divided into seven layers. Each layer was independently stored in polyethylene bags and sequentially loaded in a plexiglass tube on the basis of the original depth in the laboratory. The tube measured 100 cm in length and 20 cm in diameter; one end of the tube was wrapped with a clean coarse cloth and capped with a layer of sand. The soil was kept in the same volume ratio as natural soil. The depth of the soil column was 70 cm. A container was placed under the soil column to collect the leachate. FGD gypsum, a byproduct from the Huangpu Power Plant, was used as an active agent. We evaluated the concentrations of Cd, Pb, Zn, Cu, Ni, and Cr, which were below the detection limit, in FGD gypsum. These detection limits were 0.05, 0.2, 0.5, 1, 5, and 5 mg/kg, respectively.

Soil properties, such as pH, field moisture capacity (FMC), cation exchange capacity (CEC), exchangeable Ca and Mg concentration, and heavy metal concentration, were determined (Table 1). Compared with the soil in Guangdong Province with the corresponding background values (0.056 mg/kg Cd, 36.0 mg/kg Pb), the tested soil was severely polluted with Cd and slightly polluted with Pb (China Environmental Monitoring Station 1990). FGD gypsum contained 85–90 % $CaSO_4{\cdot}2H_2O$. The measured solubility of FGD gypsum was $2.5\ g{\cdot}L^{-1}$.

Soil column leaching experimental design

As per the original depth, 63 organic glass columns (diameter = 20 cm and height = 1 m) were filled with soil to simulate natural field conditions. The bulk density of the soil columns was identical to that of the natural soil. A nylon sieve was attached to the bottom of the columns, and coarse sand was placed on the sieve. Under each soil column, a tank was placed to collect the leachate. In each sand column, FGD gypsum was mixed with the upper soil layer (0–30 cm). Water was then added to the soil surface at the selected time intervals. The total amount of leaching water was determined by the FGD gypsum dosage to enable the complete dissolution of FGD gypsum. Twenty-one treatments (T1–T21, which belonged to four experiment groups) were prepared and analyzed. Each treatment was repeated thrice.

FGD gypsum application rates and times

The amount of FGD gypsum needed to replace the exchangeable cation besides Ca adsorbed in soil completely was defined as the theoretical application rate, which was $7.05\ kg{\cdot}m^{-2}$. Ten treatments (T1–T10) with different FGD gypsum application rates, i.e., 10–100 % of the theoretical application quantity (TAQ) in increments of 10 %, were then performed. All the required FGD gypsum was then mixed at once in soil at 0–30 cm depth. The soil was then leached with $186.63\ L{\cdot}m^{-2}$ of water (120 % FMC in 0–30 cm soil) 2–15 times at a leaching interval of 10 days (d).

FGD gypsum was applied once, twice, and thrice in treatments T11, T12, and T13, respectively. In T12 and T13, the total amounts of FGD gypsum (100 % TAQ) were equally separated into two and three portions, respectively, and then added in the respective soils. The leaching water amount and intervals were the same as those in the 10 treatments using different gypsum application rates. The soils were leached 15 times using water.

Leaching water amount and intervals

Four treatments, i.e., 110 % (T14), 120 % (T15), 130 % (T16), and 140 % (T17) FMC in the 0–30 cm soil layer of the soils

Table 1 Test soil properties before leaching

Depth/cm	pH	CEC/cmol·kg^{-1}	Ca content/ cmol·kg^{-1}	Mg content/cmol·kg^{-1}	FMC/%	Total soluble salt/%	Organic matter/%	Cd/mg·kg^{-1}	Pb/mg·kg^{-1}
0–10	6.39	12.31	0.476	0.2328	43.83	0.361	2.12	2.766	42.1
10–20	6.66	12.12	0.542	0.2162	45.68	0.244	2.09	2.741	35.01
20–30	6.45	11.83	0.452	0.2208	44.27	0.306	1.75	2.524	30.34
30–40	7.74	10.88	0.681	0.3399	56.43	0.276	1.53	2.037	35.13
40–50	6.83	10.22	1.321	0.512	59.72	0.263	1.22	1.759	20.34
50–60	6.92	10.83	1.235	0.5343	52.49	0.331	0.98	1.647	30.19
60–70	6.99	10.73	0.647	0.2293	39.86	0.361	0.54	1.467	25.24

equivalent to 171.08, 186.63, 202.19, and 217.74 L·m^{-2} of tap water, respectively, were conducted with different leaching water amounts. In each treatment, 7.05 kg·m^{-2} (100 % TAQ) of FGD gypsum was added to the soil once. Water was added in the soil at a time interval of 10 days. The soils in these four treatments were leached 17, 15, 14, and 13 times.

In addition, four treatments (i.e., T18–T21) were performed with different time intervals, i.e., 10–25 days in increments of 5 days. In each treatment, 7.05 kg·m^{-2} (100 % TAQ) of FGD gypsum was added once in the soil. The soils were subsequently leached with 186.63 L·m^{-2} water 15 times.

After the leaching process, the soils were removed from the columns in seven layers.

The removal rates of Cd and Pb at different FGD gypsum application rates (a), application times (b), water amount each time (c), and time intervals (d) are shown in Fig. 1. The heavy metal removal rates in each treatment were calculated along with their average concentration in the 0–10, 10–20, and 20–30 cm soil layers.

Analytical methods

The soils used for the analyses were air dried at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris. The soils were then thoroughly mixed to ensure uniformity and crushed with a pestle and mortar until all particles passed a 100-mesh nylon sieve.

The salinity and pH of the soil samples were measured using the filtrate of a 1/5 soil/distilled water suspension (Dewis and Freiras 1976). CEC, total organic carbon of soil samples, and FMC were determined using the method of Dewis and Freiras (1976).

The total heavy metal content of the prepared soils was determined using HCl–HNO$_3$–HF–HClO$_4$ extraction. All soil samples were analyzed for the speciation of heavy metals using the Tessier sequential extraction procedure (Tessier et al. 1979). Solution concentrations were determined by flame atomic absorption spectrometry (FAAS, Shimadzu AA-7000, Japan). For the samples in which FAAS was inadequately sensitive, metal concentrations were determined using a graphite furnace atomic absorption spectrometry (Shimadzu AA-7000, Japan). Two soil standard reference materials, i.e., GBW07401 (GSS-1) and GBW07404 (GSS-4), were used through digestion and analyzed as part of the quality control protocol. The analyzed results were only accepted when the measured concentrations in the reference materials were within one standard deviation of their certified values. SPSS 19.0 was used to perform statistical analyses.

Results and discussion

Heavy metal removal in soil through FGD gypsum leaching

The removal rates of Cd and Pb in the 0–30 cm soil layer tended to increase from T1 to T10 (Fig. 1a). In T10, Cd and Pb proportion detached from the 0 to 30 cm soil layer increased to 45.5 and 23.7 % in comparison with 20.1 and 11.0 % in T1, respectively. In the treatment with a low FGD gypsum application rate (T1), the decrease in Cd and Pb concentrations was mainly caused by the removal of heavy metals from the pore water of the soil (Li et al. 2011) and the carbonate fraction. In T2–T10, the desorption of Cd^{2+} and Pb^{2+} was mainly due to Ca^{2+} competition for adsorption sites. The removal rate of Cd increased continuously as the FGD gypsum application rate increased. The Pb removal rate also gradually increased as the FGD gypsum application rate increased. These phenomena occurred because the ionic radius of Cd^{2+} (97 pm) is similar to that of Ca^{2+} (i.e., 99 pm); as such, Cd^{2+} likely exchanges with Ca^{2+}; by contrast, the ionic radius of Pb^{2+} (i.e., 120 pm) is different from that of Ca^{2+} (i.e., 99 pm), thereby causing a reduced or gradual exchange.

After the FGD gypsum was applied at different times, the order of the removal rates of Cd was T11 < T12 < T13; the order of the removal rates of Pb was T11 < T12 = T13 (Fig. 1b). The removal rates of Cd in T11 and T13 were 45.3 and 52.7 %, respectively. The removal rates of Pb in T12 and T11 were 30.5 and 23.2 %, respectively. This treatment aimed to mix the FGD gypsum and soil homogeneously to increase the gypsum utilization rate. The result showed that this treatment is an efficient method, especially for Pb removal. A portion of Cd was only removed after the FGD gypsum was applied thrice. This finding might be due to the low Cd concentration. Nedwed and Clifford (2000) reported that heavy metals are adsorbed tightly on soil particles at low concentrations.

The removal rates increased as the amounts of the applied freshwater increased at each time (Fig. 1c). The removal rates of Cd and Pb increased from 22.6 and 14.9 % in T14 to 46.0 and 23.7 % in T17, respectively. The amount of freshwater added at each time strongly influenced the removal of Cd and Pb. Although the total amount of leaching water was the same, the amount of consumed leaching water at each time increased from T14 to T17. High amounts of water were used in each successive treatment, resulting in the removal of more heavy metals from the upper soil layers. Bradl (2004) indicated that metal ions desorbed from soil are continuously transported to the subsequent layer; thus, ion exchange occurs constantly. Therefore, the application of high amounts of water promoted the release of heavy metals in soil.

Figure 1d shows that the removal rate of Cd increased from T18 to T21. However, the Cd removal rate (i.e., 44.5 and 48.1 %) slightly increased. The removal rate of Pb significantly increased from T18 to T20 (i.e., 16.8–26.2 %) but decreased from T20 to T21 (i.e., 26.2–21.9 %). Hence, most of the Cd was removed in 10, and 20 days were required for Pb removal. Bahçecİ (2009) indicated that a time interval of several days was required to leach water through a soil profile. Therefore, the frequent addition of excessive water may reduce the utilization rate and cause FGD gypsum seepage. A sufficient time interval is required for the release of heavy metals from soil. Arwidsson et al. (2010) reported a positive correlation between heavy metal removal rate and contact time. Juwarkar et al. (2007) revealed that Cd was more readily mobilized than Pb and that Cd removal rate was two times that of Pb at the beginning of their experiment. Consequently, the removal rate of Cd at 10 days was considerably high in our study, and 20 days were required to remove Pb sufficiently. If the interval time is extremely long, heavy metals desorbed from soil will not be removed in time. Metal ions, such as Pb^{2+}, may be re-absorbed to soil, and this may cause a decrease in Pb removal rate from T20 to T21.

Heavy metal concentration changes in vertical soil profiles

The heavy metal (i.e., Cd and Pb) concentrations in vertical soil profiles after leaching with different FGD gypsum application rates are listed in Table 2. After leaching, the concentrations of heavy metals (i.e., Cd and Pb) in the 0–30 cm soil layer decreased, and the concentrations of Cd in 40–60 cm and Pb in the 30–40 cm soil layer increased in comparison with natural soil (CK). The concentrations of Cd in the 60–70 cm soil layer and Pb in the 40–70 cm soil layer remained almost

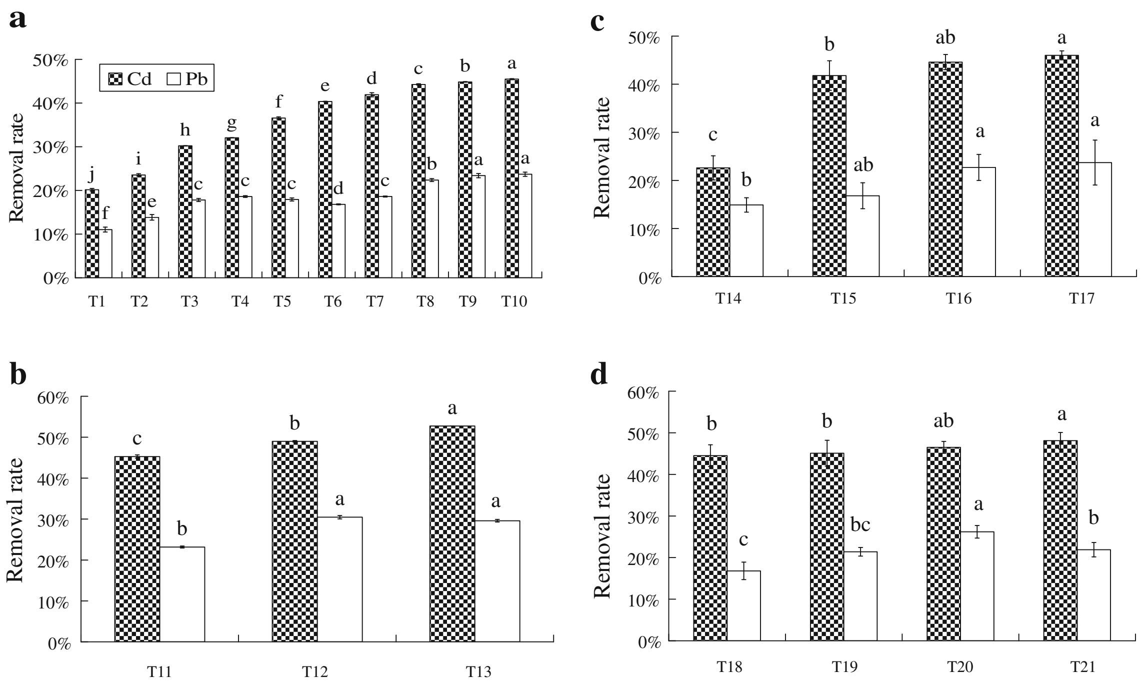

Fig. 1 Removal rates of Cd and Pb in the 0–30 cm soil layer. **a** Different FGD gypsum application rates (T1 to T10), from 10 to 100 % of the theoretical application quantity (TAQ) in increments of 10 %. **b** Different FGD gypsum (100 % TAQ) application times, once (T11), twice (T12), and thrice (T13). **c** Different leaching water amounts, 110 % field moisture capacity (FMC) (T14), 120 % FMC (T15), 130 % FMC (T16), and 140 % FMC (T17), **d** Different elution time intervals (T18–T21), from 10 to 25 days in increments of 5 days. The *letters* "*a*" to "*j*" mean significant difference ($p < 0.05$), and each figure shows the contrast between the same element only

Table 2 Cd and Pb concentrations in vertical soil profiles after applying different FGD gypsum rates (mg·kg^{-1})

Depth/cm	CK	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Cd											
0–10	2.77 ± 0.02	2.21 ± 0.01a	2.05 ± 0.00b	1.73 ± 0.01c	1.72 ± 0.02c	1.70 ± 0.00c	1.61 ± 0.00d	1.60 ± 0.02d	1.54 ± 0.00e	1.53 ± 0.01e	1.54 ± 0.01e
10–20	2.74 ± 0.01	2.16 ± 0.01a	2.06 ± 0.01b	2.03 ± 0.00c	1.95 ± 0.01d	1.68 ± 0.00e	1.61 ± 0.01f	1.53 ± 0.01 g	1.46 ± 0.01 h	1.45 ± 0.00hi	1.44 ± 0.01i
20–30	2.52 ± 0.00	2.04 ± 0.01a	2.03 ± 0.01a	1.85 ± 0.01b	1.79 ± 0.01c	1.72 ± 0.01d	1.57 ± 0.00e	1.54 ± 0.02e	1.47 ± 0.00f	1.46 ± 0.01f	1.40 ± 0.01 g
30–40	2.04 ± 0.01	2.31 ± 0.11a	2.30 ± 0.10a	2.27 ± 0.14a	2.24 ± 0.09ab	2.16 ± 0.09abc	2.11 ± 0.07abc	2.04 ± 0.09abc	1.84 ± 0.12c	1.94 ± 0.07bc	1.86 ± 0.07c
40–50	1.76 ± 0.01	2.11 ± 0.13b	2.27 ± 0.12b	2.69 ± 0.13a	2.84 ± 0.11a	2.85 ± 0.08a	2.74 ± 0.14a	2.99 ± 0.11a	2.83 ± 0.10a	3.00 ± 0.19a	2.89 ± 0.14a
50–60	1.65 ± 0.02	2.09 ± 0.13a	2.12 ± 0.09a	2.15 ± 0.09a	2.34 ± 0.18a	2.68 ± 0.16a	2.44 ± 0.18a	2.44 ± 0.43a	2.71 ± 0.16a	2.59 ± 0.23a	2.79 ± 0.15a
60–70	1.47 ± 0.01	1.58 ± 0.10a	1.48 ± 0.02a	1.64 ± 0.00a	1.57 ± 0.07a	1.58 ± 0.11a	1.56 ± 0.05a	1.55 ± 0.11a	1.55 ± 0.07a	1.59 ± 0.05a	1.58 ± 0.07a
Pb											
0–10	42.15 ± 0.49	36.09 ± 0.09a	34.53 ± 0.04b	32.39 ± 0.10d	32.46 ± 0.27d	32.39 ± 0.08d	33.42 ± 0.11c	31.98 ± 0.09d	30.24 ± 0.33f	31.07 ± 0.06e	29.78 ± 0.04f
10–20	35.00 ± 0.28	31.89 ± 0.24a	30.35 ± 0.34b	28.78 ± 0.21 cd	27.97 ± 0.35e	28.96 ± 0.21c	28.81 ± 0.06 cd	28.18 ± 0.07de	27.90 ± 0.04e	26.65 ± 0.09f	26.83 ± 0.15f
20–30	30.35 ± 0.21	27.64 ± 0.09ab	27.75 ± 0.18a	27.15 ± 0.16c	27.06 ± 0.23c	26.86 ± 0.02c	27.18 ± 0.03bc	27.32 ± 0.06abc	25.31 ± 0.03d	24.63 ± 0.21e	25.40 ± 0.18d
30–40	35.10 ± 0.57	40.26 ± 0.02i	44.15 ± 0.01 h	47.69 ± 0.07 g	48.66 ± 0.08f	49.17 ± 0.03e	52.44 ± 0.08a	49.13 ± 0.04e	51.23 ± 0.02c	50.24 ± 0.01d	52.12 ± 0.03b
40–50	20.35 ± 0.21	20.19 ± 0.06f	20.03 ± 0.01 g	22.29 ± 0.00b	21.02 ± 0.05e	21.51 ± 0.06d	18.47 ± 0.01i	19.93 ± 0.02 g	22.03 ± 0.03c	22.86 ± 0.05a	19.79 ± 0.05 h
50–60	30.20 ± 0.42	28.69 ± 0.05c	27.32 ± 0.01 g	28.06 ± 0.00e	27.89 ± 0.11f	29.09 ± 0.01b	28.06 ± 0.00e	28.23 ± 0.05d	28.78 ± 0.00c	27.94 ± 0.04ef	30.82 ± 0.04a
60–70	25.25 ± 0.35	24.12 ± 0.07e	26.20 ± 0.02b	24.67 ± 0.01d	23.07 ± 0.01 g	26.55 ± 0.01a	23.38 ± 0.00f	23.43 ± 0.04f	22.68 ± 0.01 h	25.94 ± 0.04c	26.57 ± 0.01a

The column shows the average value ± standard deviation. CK indicates the values before the leaching of soil with different FGD gypsum (100 % TAQ) application rates, such as 10 % (T1), 20 % (T2), 30 % (T3), 40 % (T4), 50 % (T5), 60 % (T6), 70 % (T7), 80 % (T8), 90 % (T9), and 100 % (T10). In the same row, different letters denote significant difference ($p < 0.05$)

Table 3 Cd and Pb concentrations in vertical soil profiles after different FGD gypsum application times (mg·kg^{-1})

Depth/cm	CK	T11	T12	T13
Cd				
0–10	2.77 ± 0.02	1.53 ± 0.01a	1.39 ± 0.02b	1.23 ± 0.02c
10–20	2.74 ± 0.01	1.45 ± 0.02a	1.33 ± 0.00b	1.25 ± 0.02c
20–30	2.52 ± 0.00	1.41 ± 0.00a	1.38 ± 0.01b	1.31 ± 0.00c
30–40	2.04 ± 0.01	2.25 ± 0.17b	2.67 ± 0.14b	3.36 ± 0.25a
40–50	1.76 ± 0.01	2.60 ± 0.20a	2.72 ± 0.19a	2.70 ± 0.14a
50–60	1.65 ± 0.02	2.24 ± 0.00c	2.47 ± 0.01b	2.62 ± 0.03a
60–70	1.47 ± 0.01	1.77 ± 0.12a	1.64 ± 0.13a	1.68 ± 0.15a
Pb				
0–10	42.15 ± 0.49	30.70 ± 0.14a	27.15 ± 0.35b	27.75 ± 0.21b
10–20	35.00 ± 0.28	26.55 ± 0.07a	24.50 ± 0.42b	24.95 ± 0.49b
20–30	30.35 ± 0.21	25.25 ± 0.49a	23.05 ± 0.35b	22.95 ± 0.35b
30–40	35.10 ± 0.57	36.65 ± 0.07c	38.45 ± 0.07b	46.55 ± 0.07a
40–50	20.35 ± 0.21	37.20 ± 0.14c	37.90 ± 0.00b	42.70 ± 0.14a
50–60	30.20 ± 0.42	33.25 ± 0.07a	29.00 ± 0.00c	29.20 ± 0.00b
60–70	25.25 ± 0.35	23.45 ± 0.07b	23.05 ± 0.07c	24.70 ± 0.00a

The column shows the average value ± standard deviation. CK indicates the values before the leaching of soil with different FGD gypsum (100 % TAQ) application times, such as once (T11), twice (T12), and thrice (T13). In the same row, different letters denote significant difference ($p < 0.05$)

unchanged compared with those in the natural soil (CK). Evidently, the wash down from the upper layers fixed Cd in the 40–60 cm soil layer, and Pb was fixed in the 30–40 cm soil layer, consistent with the design. Cd migrated faster than Pb.

The heavy metal (i.e., Cd and Pb) concentrations in vertical soil profiles after leaching with different FGD gypsum application rates are listed in Table 3. After leaching, the concentrations of heavy metals (i.e., Cd and Pb) in the 0–30 cm soil layer decreased, and the concentration of Cd in the 30–60 cm soil layer and Pb in the 30–50 cm soil layer increased. The concentration of Cd in the 60–70 cm soil layer and Pb in the 50–70 cm soil layer changed slightly. The concentrations of Cd and Pb in the 30–40 cm soil layer increased from T11 to T13. Thus, after the FGD gypsum was applied twice or thrice, the vertical transport of heavy metals was inhibited. This phenomenon may be because the utilization of gypsum increased in the upper layers; thus, the downward transport of Ca^{2+} was reduced and the competitive adsorption in the 30–70 cm soil layer was decreased.

Table 4 shows a decrease in Cd concentration in the 30–40 cm soil layer and an increase in the 40–60 cm soil layer from T14 to T15. From T15 to T17, the Cd concentrations decreased in the 50–60 cm soil layer and increased in the 60–70 cm soil layer. For Pb, an increase was observed in the 30–40 cm soil layer from T14 to T15. From T15 to T17, the Pb concentrations changed slightly in the 30–40 cm soil layer. In the 40–70 cm soil layer, the concentrations of Pb in T15, T16, and T17 were approximately the same as those in T14. As the amount of applied freshwater increased, the accumulated Cd in the 30–40 cm soil layer decreased, and Pb was retained in the soil.

Table 5 shows that the concentration of Cd in the 30–40 cm soil layer and the concentration of Pb in the 40–50 cm soil layer increased from T18 to T21; the concentration of Pb in the 60–70 cm soil layer decreased from T18 to T21. The

Table 4 Cd and Pb concentrations in vertical soil profiles after applying different freshwater amounts (mg·kg^{-1})

Depth/cm	CK	T14	T15	T16	T17
Cd					
0–10	2.77 ± 0.02	2.05 ± 0.07a	1.70 ± 0.08b	1.53 ± 0.09b	1.35 ± 0.05c
10–20	2.74 ± 0.01	2.10 ± 0.11a	1.53 ± 0.09b	1.55 ± 0.08b	1.54 ± 0.07b
20–30	2.52 ± 0.00	2.00 ± 0.07a	1.57 ± 0.08b	1.43 ± 0.07b	1.41 ± 0.07b
30–40	2.04 ± 0.01	3.00 ± 0.23a	1.90 ± 0.14b	1.88 ± 0.15b	1.85 ± 0.09b
40–50	1.76 ± 0.01	2.23 ± 0.11a	2.77 ± 0.15a	2.49 ± 0.52a	2.60 ± 0.21a
50–60	1.65 ± 0.02	1.83 ± 0.09c	3.01 ± 0.11a	2.27 ± 0.10b	2.17 ± 0.12b
60–70	1.47 ± 0.01	1.72 ± 0.12ab	1.60 ± 0.10b	1.82 ± 0.12ab	1.89 ± 0.13a
Pb					
0–10	42.15 ± 0.49	34.73 ± 0.45a	35.41 ± 0.41a	34.95 ± 2.79a	35.32 ± 2.12a
10–20	35.00 ± 0.28	28.92 ± 2.25a	23.54 ± 1.24b	22.12 ± 0.38b	23.62 ± 1.23b
20–30	30.35 ± 0.21	28.71 ± 0.49a	28.81 ± 0.71a	27.71 ± 0.79a	25.93 ± 0.74b
30–40	35.10 ± 0.57	37.89 ± 1.11b	45.69 ± 3.27a	44.90 ± 0.89a	41.79 ± 3.44a
40–50	20.35 ± 0.21	22.39 ± 0.63a	20.96 ± 0.54b	24.19 ± 1.97a	22.75 ± 1.56a
50–60	30.20 ± 0.42	31.14 ± 2.80a	27.59 ± 0.63b	29.91 ± 0.51ab	30.20 ± 1.13a
60–70	25.25 ± 0.35	26.67 ± 0.59ab	27.36 ± 2.15a	24.40 ± 0.69b	26.89 ± 0.70a

The column shows the average value ± standard deviation. CK indicates the values before the leaching of soil with different leaching water amounts, such as 110 % FMC (T14), 120 % FMC (T15), 130 % FMC (T16), and 140 % FMC (T17). In the same row, different letters denote significant difference ($p < 0.05$)

Table 5 Cd and Pb concentrations in vertical soil profiles after the application of FGD gypsum at different time intervals (mg·kg^{-1})

Depth/cm	CK	T18	T19	T20	T21
Cd					
0–10	2.77 ± 0.02	1.63 ± 0.08a	1.60 ± 0.10a	1.41 ± 0.05b	1.39 ± 0.05b
10–20	2.74 ± 0.01	1.58 ± 0.10a	1.56 ± 0.11ab	1.47 ± 0.10ab	1.34 ± 0.08b
20–30	2.52 ± 0.00	1.35 ± 0.07a	1.39 ± 0.02a	1.37 ± 0.03a	1.34 ± 0.07a
30–40	2.04 ± 0.01	1.90 ± 0.13c	2.31 ± 0.17cb	2.73 ± 0.27b	3.45 ± 0.31a
40–50	1.76 ± 0.01	2.64 ± 0.14a	2.92 ± 0.26a	2.87 ± 0.21a	2.92 ± 0.10a
50–60	1.65 ± 0.02	2.92 ± 0.14a	2.78 ± 0.28a	2.71 ± 0.16a	2.74 ± 0.12a
60–70	1.47 ± 0.01	1.48 ± 0.11a	1.51 ± 0.10a	1.44 ± 0.07a	1.44 ± 0.09a
Pb					
0–10	42.15 ± 0.49	31.24 ± 0.44b	30.82 ± 0.55bc	28.74 ± 0.93c	34.05 ± 1.38a
10–20	35.00 ± 0.28	28.85 ± 0.91a	30.33 ± 0.23a	28.71 ± 1.32a	30.04 ± 1.15a
20–30	30.35 ± 0.21	28.01 ± 0.50a	23.92 ± 1.69b	21.73 ± 0.94b	18.79 ± 1.45c
30–40	35.10 ± 0.57	46.37 ± 3.95a	50.04 ± 2.66a	52.00 ± 3.75a	51.96 ± 3.75a
40–50	20.35 ± 0.21	22.14 ± 1.84b	23.51 ± 0.19b	27.11 ± 1.10a	26.58 ± 1.21a
50–60	30.20 ± 0.42	29.08 ± 2.98a	28.04 ± 1.00a	30.41 ± 2.67a	29.04 ± 2.41a
60–70	25.25 ± 0.35	28.13 ± 2.22a	26.31 ± 0.98ab	24.10 ± 1.48b	23.09 ± 1.97b

The column shows the average value ± standard deviation. CK indicates the values before the leaching of soil with different elution time intervals (T18–T21), such as 10–25 days in increments of 5 days. In the same row, different letters denote significant difference ($p < 0.05$)

concentration of Cd in the 40–70 cm soil layer and the concentration of Pb in the 30–40 cm and 50–60 cm soil layers were not affected. The vertical transport of Cd and Pb was inhibited. In areas with a high groundwater level, gypsum can be applied twice or thrice and the interval time can be extended to reduce the effect on groundwater.

Effect of soil leaching on the distribution of heavy metal fractions

Table 6 lists the chemical speciation of Cd and Pb in soil from CK and T10. Before leaching occurred, Cd was associated with exchangeable, residual, and carbonate-bound fractions. The predominant chemical partitioning of Pb was in the exchangeable, residual, and reducible fractions. After leaching, Cd in the exchangeable and carbonate-bound fractions reduced from 1.03 to 0.05 mg·kg^{-1} and from 0.49 to 0.01 mg·kg^{-1}, respectively. Pb in the exchangeable and carbonate-bound fractions decreased from 15.47 to 1.93 mg·kg^{-1} and from 2.08 to 0.12 mg·kg^{-1}, respectively. The contents of Cd in the oxidizable and residual fractions and Pb in the reducible and residual fractions remained constant during leaching. Pb in the oxidizable fraction increased after leaching.

Speciation analysis demonstrated that FGD gypsum played a key role in the removal of exchangeable heavy metals, although only a few exchangeable heavy metals can be rinsed by leaching with freshwater (Li et al. 2011). Ca^{2+} is responsible for the release of Cd and Pb from soil particles (as discussed in the Introduction). Many studies have demonstrated that carbonates in saline soil are dissolved during leaching with freshwater (Chen et al. 1996; Hinrich and Clark 1985; Turner and Clark 1956). The anaerobic microorganisms in soils produce certain organic acids that may accelerate carbonate dissolution in reduced surroundings (Jiang et al. 2006). An

Table 6 Chemical fractionation of heavy metals in soil before and after leaching (mg·kg^{-1}, dry weight)

	Exchangeable	Carbonate bound	Reducible	Oxidizable	Residual
Cd					
CK	1.03 ± 0.21a	0.49 ± 0.23a	0.18 ± 0.09a	0.02 ± 0.06a	0.96 ± 0.17a
T10	0.05 ± 0.00b	0.01 ± 0.00b	0.08 ± 0.00b	0.05 ± 0.02a	1.15 ± 0.21a
Pb					
CK	15.47 ± 3.19a	2.08 ± 0.82a	5.16 ± 2.11a	1.36 ± 0.97b	11.75 ± 1.40a
T10	1.93 ± 0.07b	0.12 ± 0.00b	5.37 ± 0.08a	4.00 ± 0.18a	12.63 ± 0.39a

The column shows the average value ± standard deviation. CK indicates the values before the leaching of soil. T10 was performed with 100 % TAQ of desulfurization gypsum, once applications, leaching water (120 % FMC in 0–30 cm soil), and leaching interval of 10 days. In the same row, different letters denote significant difference ($p < 0.05$) and show the contrast between the same elements increase in oxidizable Pb may cause precipitation reactions. As per the theory of hard and soft acids and bases, Pb^{2+} forms borderline acids, Cd^{2+} forms soft acids, and organic acids form hard acids; organic acids only react with Pb^{2+}, thereby generating complex precipitates.

Many studies (Chlopecka and Adriano 1996; Li et al. 1998; Maiz et al. 2000; Wang et al. 2002) have indicated that the concentration of heavy metals associated with exchangeable and carbonate-bound fractions in soils correlates well with the contents of those elements in plants. Heavy metals in these fractions are readily bioavailable (Hseu 2006). In this study, the majority of Cd and Pb in exchangeable and carbonate-bound forms were removed. Therefore, health risks from heavy metals in food crops grown on reclaimed tidal flat soil can be effectively reduced through FGD gypsum leaching. Given that a great proportion of the removal is from exchangeable and carbonate-bound fractions, the effect on crop uptake may be greater than the observed reduction in total Cd and Pb contents (52.7 and 30.5 %, respectively) in the upper 30 cm soil layer. However, further investigation should be conducted.

Conclusions

The results of the simulated in situ remediation were consistent with our expectations. After remediation occurred, the removal rates of Cd and Pb in the 0–30 cm soil layer were 52.7 and 30.5 %, respectively. This result was mainly due to the leaching of the exchangeable and carbonate-bound heavy metals. Most of these heavy metals were accumulated in the 30–70 cm soil layer. The heavy metal removal rate exhibited a high positive correlation with FGD gypsum application rate and the amount of leaching water applied. The removal rate also improved when a suitable number of FGD gypsum applications and leaching intervals were used. Based on the best performance in each specific soil column leaching experiment, we proposed a combination across several sets of treatments as the optimum application: 100 % TAQ of FGD gypsum application rate ($7.05\ kg\cdot m^{-2}$), 140 % FMC of water application rate ($217.74\ L\cdot m^{-2}$), two times gypsum application, and 20-day interval. The results of this study can be used as the basis of the remediation of soils contaminated with Cd and Pb and the utilization of FGD gypsum. However, this recommendation does not correspond with any one specific treatment that was tried in this experiment. Its real performance in field needs further investigation.

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References

ACAA (2006) CCP Survey <http://www.acaa-usa.org/PDF/2005_CCP_Production_and_Use_Figures_Released_by_ACAA.pdf>. American Coal Ash Association

Arwidsson Z, Elgh-Dalgren K, von Kronhelm T, Sjöberg R, Allard B, van Hees P (2010) Remediation of heavy metal contaminated soil washing residues with amino polycarboxylic acids. J Hazard Mater 173:697–704

Bahçeci̇ İ (2009) Determination of salt leaching and gypsum requirements with field tests of saline–sodic soils in central Turkey. Irrig Drain 58:332–345

Bradl HB (2004) Adsorption of heavy metal ions on soils and soils constituents. J Colloid Interface Sci 277:1–18

Chen W, Chen B, Fang M (1996) Studies on the increasing of pH value and alkalization of seashore saline soil during its desalting in Liaodong Peninsula. J Nanjing Agric Univ 21:59–64

China Environmental Monitoring Station (1990) Natural background values of soil elements in China. China Environmental Science Press, Beijing, pp 334–366 **(In Chinese)**

Chlopecka A, Adriano DC (1996) Mimicked in-situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. Environ Sci Technol 30:3294–3303

Dewis J, Freiras F (1976) Physical and chemical methods of soil and water analysis. Food and Agricultural Organization United Nations, Rome

Du Laing G, De Vos R, Vandecasteele B, Lesage E, Tack FMG, Verloo MG (2008) Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuar Coast Shelf Sci 77:589–602

Hinrich LB, Clark JS (1985) Soil chemistry. Wiley, New York

Hseu Z-Y (2006) Extractability and bioavailability of zinc over time in three tropical soils incubated with biosolids. Chemosphere 63:762–771

Huller R, Kersten H (2005) FGD gypsum—a product for the gypsum industry. VGB PowerTech 85:66–69

Jiang M, Lu X, Yang Q, Tong S (2006) Iron biogeochemical cycle and its environmental effect in wetlands. Acta Pedol Sin 43:493–499

Juwarkar AA, Nair A, Dubey KV, Singh SK, Devotta S (2007) Biosurfactant technology for remediation of cadmium and lead contaminated soils. Chemosphere 68:1996–2002

Kikkawa H, Nakamoto T, Morishita M, Yamada K (2002) New wet FGD process using granular limestone. Ind Eng Chem Res 41:3028–3036

Li F, Shan X, Zhang T, Zhang S (1998) Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis. Environ Pollut 102:269–277

Li Q, Chu B, Shi L, Fang J, Cai S (2007a) Heavy metal distribution in tidal wetland soils and its effect on reclamation in the pearl river estuary. J Agro-Environ Sci 26:1422–1426

Li Q, Wu Z, Chu B, Zhang N, Cai S, Fang J (2007b) Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. Environ Pollut 149:158–164

Li Q, Liu Y, Du Y, Cui Z, Shi L, Wang L et al (2011) The behavior of heavy metals in tidal flat sediments during fresh water leaching. Chemosphere 82:834–838

Maiz I, Arambarri I, Garcia R, Millán E (2000) Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. Environ Pollut 110:3–9

Mustafa G, Singh B, Kookana RS (2004) Cadmium adsorption and desorption behaviour on goethite at low equilibrium concentrations: effects of pH and index cations. Chemosphere 57:1325–1333

Nedwed T, Clifford DA (2000) Feasibility of extracting lead from lead battery recycling site soil using high-concentration chloride solutions. Environ Prog 19:197–206

Norvell WA, Wu J, Hopkins DG, Welch RM (2000) Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. Soil Sci Soc Am J 64:2162–2168

Nowack B (2002) Environmental chemistry of aminopolycarboxylate chelating agents. Environ Sci Technol 36:4009–4016

Steele M, Pichtel J (1998) Ex-situ remediation of a metal-contaminated superfund soil using selective extractants. J Environ Eng 124:639–645

Tesárek P, Drchalová J, Kolísko J, Rovnaníková P, Černý R (2007) Flue gas desulfurization gypsum: study of basic mechanical, hydric and thermal properties. Constr Build Mater 21:1500–1509

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51: 844–851

Turner RC, Clark JS (1956) The pH of calcareous soils. Soil Sci 82:337–342

Usman ARA, Kuzyakov Y, Stahr K (2005) Effect of immobilizing substances and salinity on heavy metals availability to wheat grown on sewage sludge-contaminated soil. Soil Sediment Contam Int J 14: 329–344

Wang Z, Shan X-Q, Zhang S (2002) Comparison between fractionation and bioavailability of trace elements in rhizosphere and bulk soils. Chemosphere 46:1163–1171

Wang SJ, Chen CH, Xu XC, Li YJ (2008) Amelioration of alkali soil using flue gas desulfurization byproducts: productivity and environmental quality. Environ Pollut 151:200–204

Williams TP, Bubb JM, Lester JN (1994) Metal accumulation within salt marsh environments: a review. Mar Pollut Bull 28:277–290