Determining Optimum Extractants to Evaluate Cd Bioavailability in Paddy Field

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Introduction

❑ **Concerning about Mine Waste Near at the Agricultural Field**

- ➢ Introduction of mine waste from abandoned mine to the environment
- ➢ Adverse effect of transferred heavy metals from soil to plant

❑ **Bioaccumulation of Heavy Metals in plants**

- ➢ Soil properties, crop species, and climate can affect bioavailability of heavy metals
- ➢ No standard method for evaluating bioavailability of heavy metals in soil is available

❑ **Analytical Methods for Assessing Bioavailability of Heavy Metals in Soil**

- ➢ Single Extraction Methods
  - i) Ion Exchange: NH_4Cl, NH_4NO_3, NaCl, NH_4OAc, HCl, HNO_3, $Mg(NO_3)_2$, $CaCl_2$, $NaNO_3$
  - ii) Chelates: EDTA, DTPA, EDDS
  - iii) Low Molecular Weight Organic Acids(LMWOAc)
- ➢ Sequential Extraction Methods: Tessier et al., Krishnamurti et al., Weng et al.

Objective

Remediation of Heavy Metal Polluted Agricultural Field

→ Assessment for Heavy Metal Bioavailability

→ Evaluating Remediation Efficiency and Transfer Factor

Materials & Methods

Table 1. Experimental Setup

Treatments	**Control, Phytostabilization, Lime, Steel Slag, Phytostabilization+Lime, Phytostabilization+Steel Slag**
Heavy Metals	**Cd and Pb**
Extraction Methods	**• Single Extraction: 0.1M HCl, 0.01M $CaCl_2$, 5mM DTPA, 1M NH_4NO_3** **• Sequential Extraction: Tessier et al.(1979)**
Instrument	**Inductively coupled plasma atomic emission spectrometry (ICP-OES, Thermo, iCAP 6000 series)**

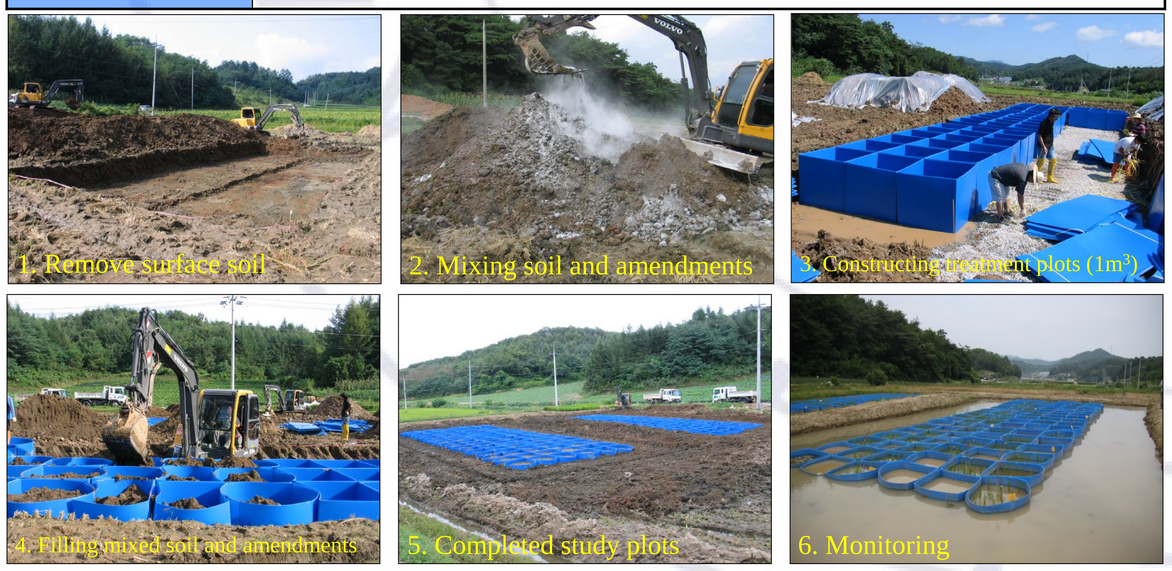

Figure 1. Process for constructing treatment plots

- ➢ **Mixing ratio of amendments: 1%, 3% (w/w)**
- ➢ **Crop: Rice**

Result

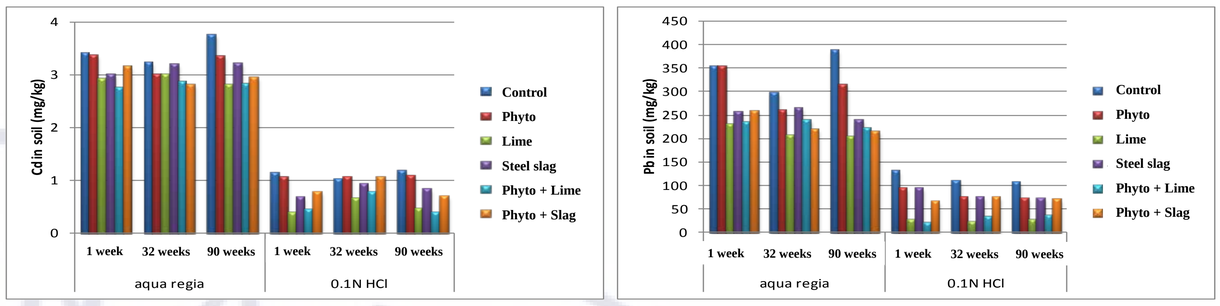

Figure 2. Concentration of heavy metals in soil with varied treatments.
(Two different extractants were used – aqua regia and 0.1N HCl)

Table 2. Heavy metal concentration in soil extracted with different extractants

Cd (mg/kg)	0.1M HCl			5mM DTPA			0.01M $CaCl_2$			1M NH_4NO_3		
	1 week	32 weeks	90 weeks	1 week	32 weeks	90 weeks	1 week	32 weeks	90 weeks	1 week	32 weeks	90 weeks
Control	1.15	1.03	1.18	0.562	0.468	0.523	0.126	0.114	0.084	0.121	0.109	0.103
Phyto	1.06	1.07	1.08	0.501	0.459	0.416	0.113	0.106	0.086	0.124	0.105	0.042
Lime	0.39	0.67	0.48	0.486	0.312	0.165	0.109	0.014	0.000	0.104	0.016	0.021
Steel Slag	0.68	0.92	0.85	0.491	0.410	0.358	0.086	0.015	0.000	0.113	0.011	0.008
Phyto + Lime	0.45	0.77	0.40	0.503	0.324	0.193	0.106	0.023	0.000	0.115	0.008	0.009
Phyto + Slag	0.78	1.06	0.70	0.506	0.488	0.327	0.094	0.031	0.000	0.109	0.013	0.011

Pb (mg/kg)	0.1M HCl			5mM DTPA			0.01M $CaCl_2$			1M NH_4NO_3		
	1 week	32 weeks	90 weeks	1 week	32 weeks	90 weeks	1 week	32 weeks	90 weeks	1 week	32 weeks	90 weeks
Control	130.61	110.14	107.49	56.469	66.044	70.329	0.053	0.351	0.360	0.134	0.126	0.122
Phyto	94.81	76.24	72.56	57.582	62.891	61.377	0.048	0.312	0.306	0.123	0.109	0.111
Lime	28.20	24.14	27.65	51.264	23.322	21.097	0.043	0.098	0.000	0.118	0.115	0.107
Steel Slag	94.81	76.24	72.56	52.713	36.979	35.991	0.047	0.204	0.145	0.121	0.113	0.114
Phyto + Lime	20.99	35.49	37.15	49.871	29.566	26.584	0.051	0.239	0.000	0.123	0.116	0.106
Phyto + Slag	66.04	74.42	71.70	55.256	45.226	37.486	0.049	0.207	0.016	0.118	0.105	0.095

Table 3. Heavy metal concentration in soil extracted with sequential extraction

Cd (%)	1 week					32 weeks					90 weeks				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
Control	16.87	5.11	28.40	0.77	48.85	16.84	4.72	29.61	0.77	48.06	16.46	5.69	30.77	1.28	45.79
Phyto	16.72	5.09	28.72	0.79	48.68	12.59	4.49	30.05	0.78	52.09	12.40	4.71	28.95	0.78	53.17
Lime	7.02	4.01	20.95	1.45	66.57	6.04	4.06	24.52	1.86	63.52	6.31	4.76	22.42	1.32	65.18
Steel Slag	10.28	5.40	28.46	0.76	55.10	10.76	5.81	31.06	1.27	51.10	7.61	7.87	27.61	0.75	56.15
Phyto + Lime	7.06	4.64	22.63	1.55	64.12	6.85	4.20	25.55	1.51	61.89	5.61	3.95	21.45	1.52	67.48
Phyto + Slag	9.61	6.01	28.61	1.22	54.55	8.74	5.52	29.10	0.81	55.82	7.20	5.86	26.74	2.30	57.90

Pb (%)	1 week					32 weeks					90 weeks				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
Control	0.76	5.50	60.43	0.83	32.48	0.94	5.67	64.19	0.78	28.42	0.68	5.55	60.65	0.88	32.23
Phyto	0.72	5.44	62.68	0.84	30.32	0.37	4.47	63.30	0.77	31.10	0.50	4.69	60.67	0.79	33.35
Lime	0.03	2.18	50.73	0.55	46.51	0.04	1.98	53.78	0.60	43.61	0.06	2.46	53.29	0.70	43.49
Steel Slag	0.15	5.13	62.48	0.68	31.56	0.10	5.43	62.12	0.87	31.48	0.05	5.06	61.18	0.69	33.01
Phyto + Lime	0.06	2.61	53.47	0.61	43.26	0.04	2.52	55.07	0.70	41.67	0.03	2.03	49.03	0.61	48.29
Phyto + Slag	0.09	5.28	63.12	0.71	30.81	0.10	5.31	62.76	0.70	31.13	0.13	4.79	60.95	0.70	33.43

Table 4. Heavy Metal concentration in rice grain with varied treatments

	Control	Phyto	Lime	Steel Slag	Phyto + Lime	Phyto + Slag
	---------- mg/kg ----------					
Cd	0.098	0.041	0.026	0.030	0.023	0.045
Pb	0.222	0.061	0.049	0.050	0.039	0.048

Table 5. Calculated transfer factor (TF) of heavy metals from soil to plant

	Cd						Pb					
	0.1M HCl	5mM DTPA	0.01M $CaCl_2$	1M NH_4NO_3	F1 + F2		0.1M HCl	5mM DTPA	0.01M $CaCl_2$	1M NH_4NO_3	F1 + F2	
	---------- mg/kg ----------											
Control	1.18	0.523	0.084	0.103	16.46	5.69	107.49	70.329	0.360	0.122	0.68	5.55
Phyto	1.08	0.416	0.086	0.042	12.40	4.71	72.56	61.377	0.306	0.111	0.50	4.69
Lime	0.48	0.165	0.000	0.021	6.31	4.76	27.65	21.097	0.000	0.107	0.06	2.46
Steel Slag	0.85	0.358	0.000	0.008	7.61	7.87	72.56	35.991	0.145	0.114	0.05	5.06
Phyto + Lime	0.40	0.193	0.000	0.009	5.61	3.95	37.15	26.584	0.000	0.106	0.03	2.03
Phyto + Slag	0.70	0.327	0.000	0.011	7.20	5.86	71.70	37.486	0.016	0.095	0.13	4.79

Summary and Conclusion

- ➢ Application of chemical amendments showed higher efficiency (27-78%) of heavy metal stabilization than phytostabilization (8 - 27%)
- ➢ Result of sequential extraction showed that fraction 1 and 2 were decreased while fraction 4 and 5 were increased after treatment
- ➢ Heavy metal concentration in rice grain was also decreased after treatment indicating heavy metal immobilization in soil.
- ➢ Among different extraction methods, 0.01M $CaCl_2$ for Cd and 1M NH_4NO_3 showed the lowest transfer factor. However, correlation analysis between heavy metal concentration in soil extracted with varied extractants and rice should be conducted for selecting optimum extraction method

Reference

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