Chemical speciation and solubility of arsenic, cadmium and lead in contaminated soil from abandoned mine tailing in Toyama prefecture, Japan

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INTRODUCTION

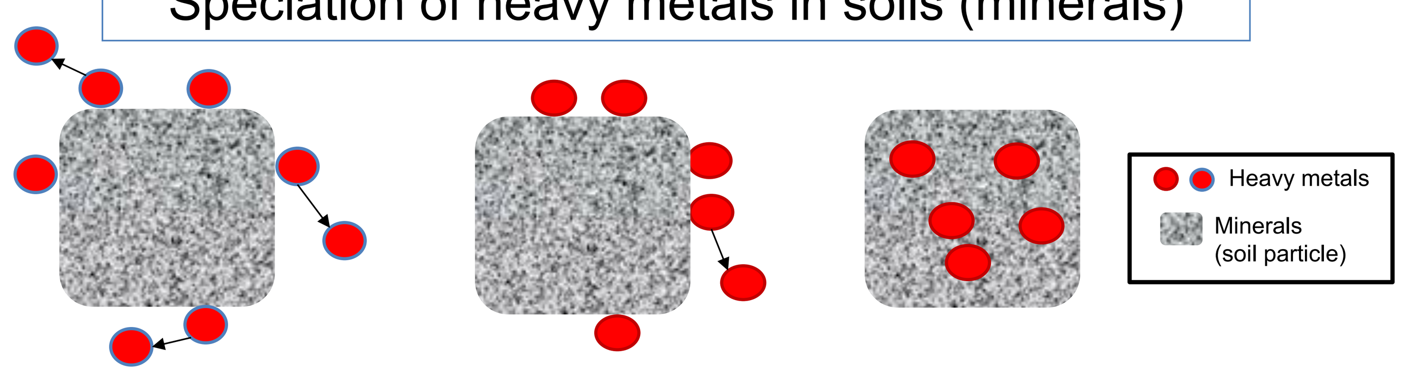
Contaminated soil (sink of heavy metals)

Transport to environment (groundwater, surface water, runoff)

Health and Environmental concern

Depends on surrounding environment especially for pH, ionic strength etc.

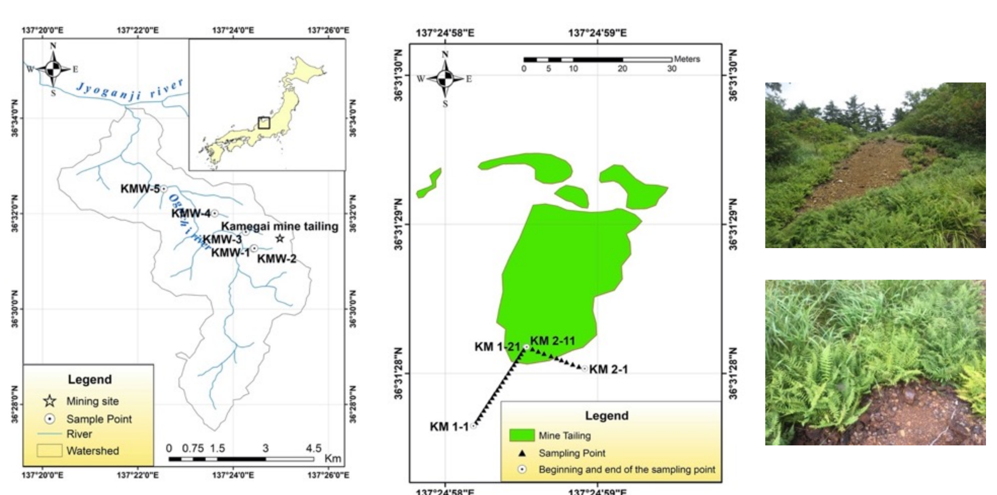
Speciation of heavy metals in soils (minerals)



Weak adsorption on minerals | Strong adsorption on minerals | Incorporation inside minerals

Purpose: To elucidate the mobility of As, Pb and Cd in contaminated soil based on determine their chemical speciation analysis

MATERIALS AND METHODOLOGY



(a) Oguchi river catchment area with mine tailing and water sampling locations (b) soil sampling points (c) part of the mine tailing area (d) *Athyrium yokoscense* near mine tailing

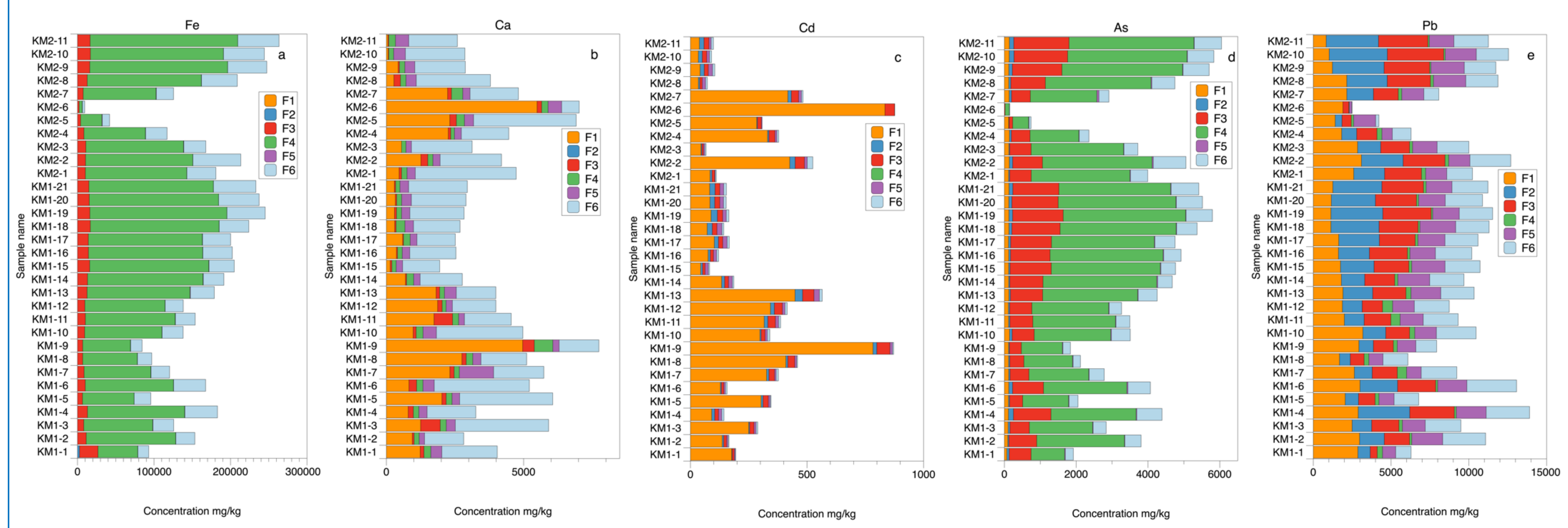
Soil samples were freeze dried and sieved by <63μm

- ✓ Sequential extraction procedure (SEP measured by ICP-OES, ICP-MS)
- ✓ X-ray adsorption fine structure (BL01B1 at SPring 8, Hyogo, Japan)
- ✓ X-ray diffraction

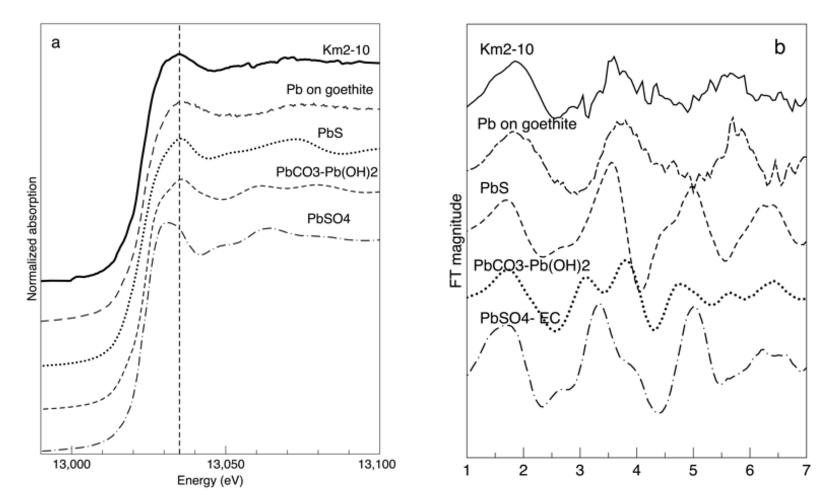
Sequential extraction procedure

Extraction steps	Reagent/ concentration/ pH	Soil phase
1	$MgCl_2$ (1M)	Exchangeable, F1
2	$CH_3COONa \times 3H_2O$ 1 mol l^{-1}, pH 5	Carbonates, F2
3	$C_2H_2O_4$ (about 10 g / L) + $C_2H_8N_2O_4$ (16.1 g / L), pH3	Iron and manganese oxides (amorphous), F3
4	$Na_3C_6H_5O_7$ (0.3 mol l^{-1}), $NaHCO_3$ (0.2 mol l^{-1}), $Na_2S_2O_4$ HCl, pH6.7	Reducible (e.g. iron and manganese oxides), F4
5	H_2O_2 (8.8 mol l^{-1}) + CH_3COONH_4 (1 mol l^{-1}), pH2	Oxidizable (e.g. organic matter and sulfides), F5
6	HNO_3 60% + HF 48%+ HCl 36%	Residual (non-silicate bound metals), F6

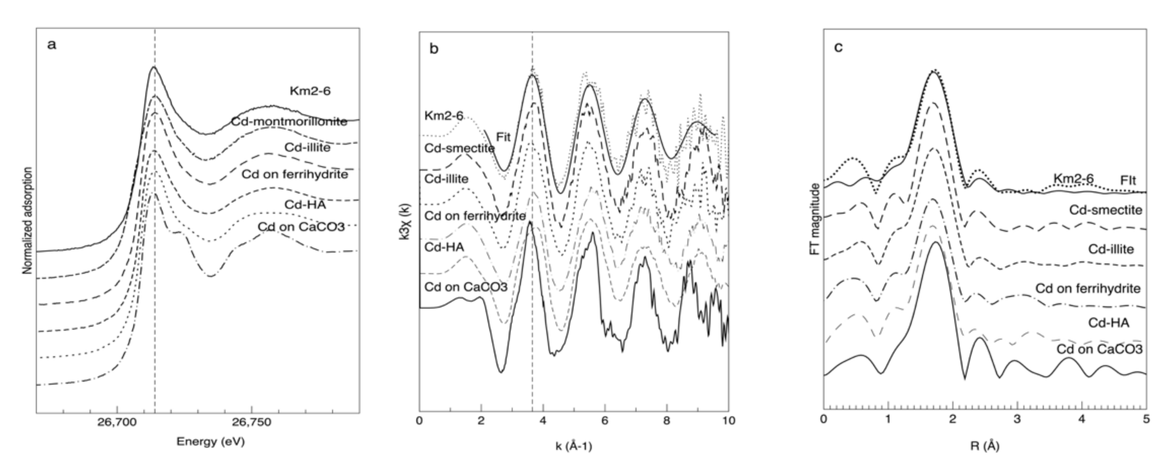
RESULTS



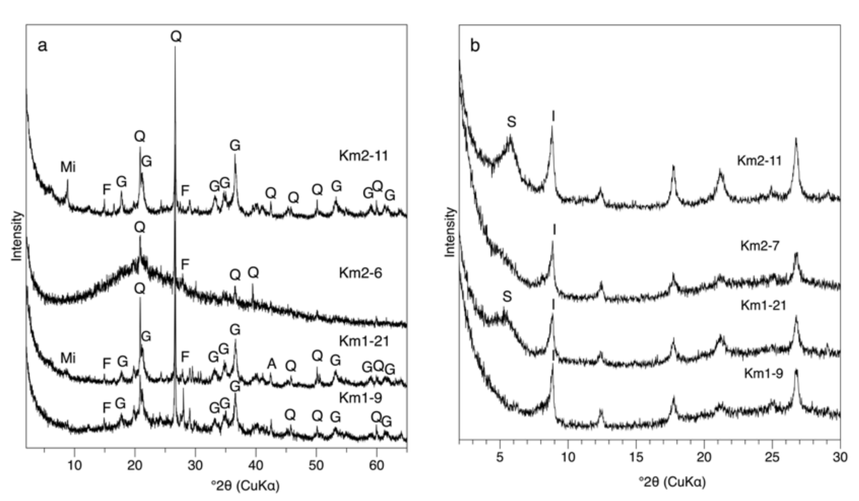
Results of sequential extraction procedure



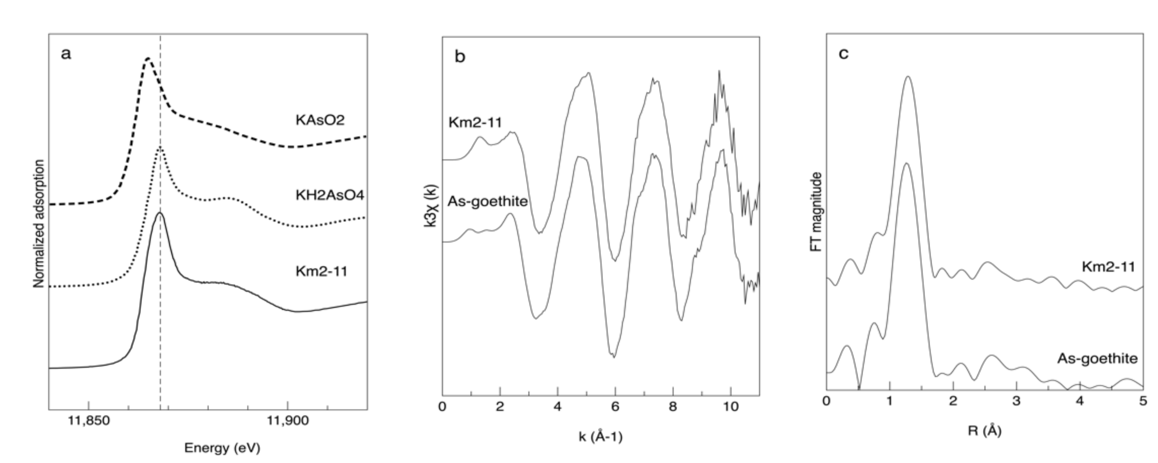
Pb (a) XANES and (b) EXAFS spectra in k spaces for km2-10 and related reference materials. Spectra in *k* spaces is presented as black line for km2-10. Fitting of the spectrum is Pb on goethite, PbS, $PbCO_3$-Pb$(OH)_2$ and $PbSO_4$.



Cd (a) XANES spectra for sample km2-6 and reference materials (Cd- montmorillonite, Cd on illite, Cd on ferrihydrite, Cd -humic substances and Cd on $CaCO_3$). Cd K-edge EXAFS spectra in (b) *k* and (c) *R* spaces for km2-6 and related reference materials. Spectra (b) in *k* and (c) *R* spaces are presented as dotted black line for km2-6 and black line for fit.



X- ray diffraction patterns of samples (Mi- mica, F- feldspar, Q- quartz, G- goethite, S- smectite, I- iliite)

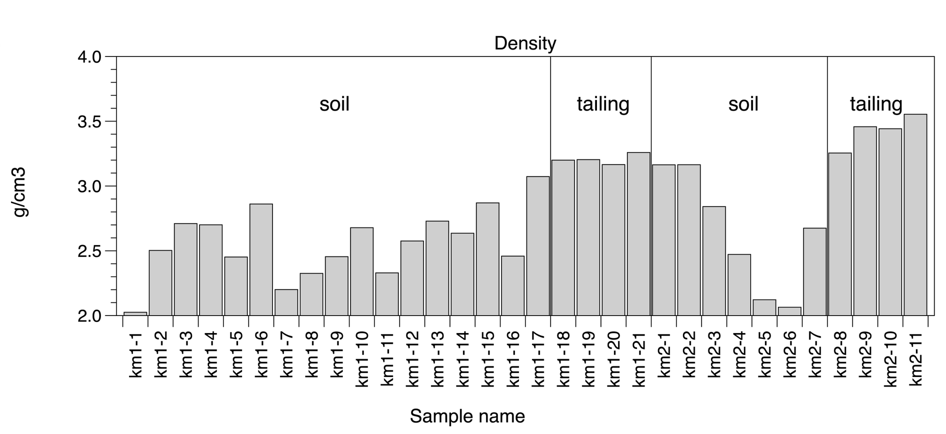


As (a) XANES spectra for sample km2-11 and reference materials ($KAsO_2$ and KH_2AsO_4), As k- edge EXAFS spectra in (b) k and (c) R spaces for km2-11 and related reference material which is As on goethite.

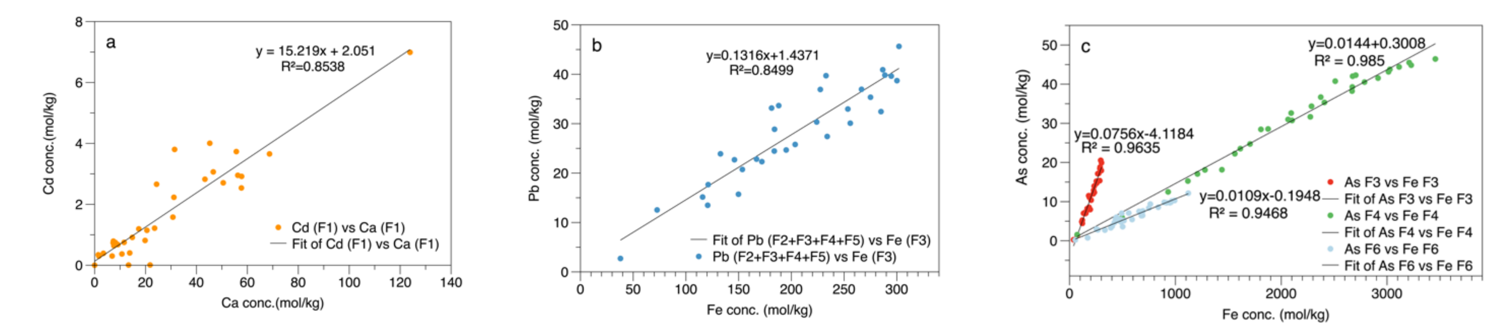
SEP results shown Fe mainly associated with F4. Fe in F3 and F6 were also detectable. Ca were mainly associated F1 and F6. Fe has positive correlation with density, but Ca has negatively correlated with density. Cd mainly associated with F1. As mainly associated with F4 following F3 and F6. Pb almost evenly associated with F1, F2, F3, F5 and F6.

XAFS results

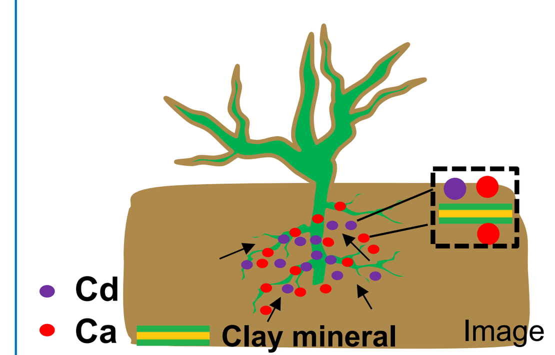
- •Cd- same with Cd on illite, smectite spectra
- •As- same with As on goethite
- •Pb- same with Pb on goethite

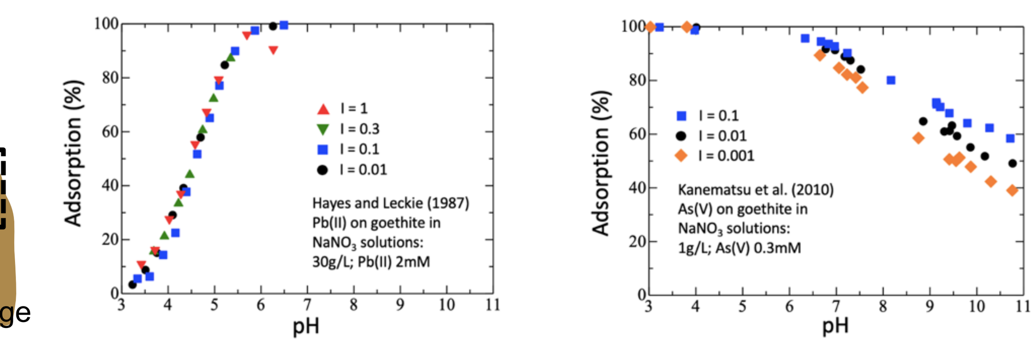


DISCUSSION



Correlation of (a) Cd and Ca (F1), (b) Pb and Fe (F3) and (c) As and Fe (F3)



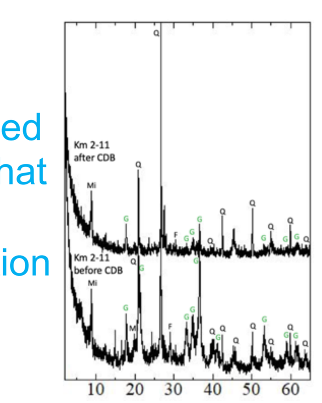


Exchangeable Cd on illite and smectite in soil.
Cd release to the plant because of that dried plant (Athyrium yokoscence, hebinonegosa) has high concentration of Cd

Iron (oxyhydr)oxides (goethite) -> main sorption for Pb in soil but it extracted mainly F2 and F3. The reagent of F2 was at pH5 and F3 was at pH3. Pb at these pH can desorb when crystalline Fe cannot release because of low pH (Usiyama and Fukushi 2016)

Iron (oxyhydr)oxides, amorphous forms -> main sorption for As in soil (Fukushi et al., 2007, Frommer et al., 2011, Suda and Makino et al., 2016, Xu et al., 2017)

F6 dissolved Goethite that left after CDB solution of step4



	Unit	kmw1	kmw3	kmw5
pH	(-)	7.6	7.8	7.6
Ionic strength	M	0.0012	0.0006	0.0007
As	μg/L	3.7	**12**	0.7
Cd	μg/L	0.03	<0.02	<0.02
Pb	μg/L	0.07	<0.01	<0.01

pH: neutral, slightly alkaline
Ionic strength: low
As. concentration exceed the environmental standard
Cd, Pb: low concentration

CONCLUSION

- ▪Cd adsorbed on clay minerals -> release from plant (Athyrium yokoscence).
- ▪As are mainly associated with the amorphous and crystalline iron oxides (goethite).
- ▪Pb are mainly associated with the crystalline iron oxides (goethite).
- ▪Cd on clay minerals will be released to environment only if soil transport to rivers which has high ionic strength.
- ▪As will be released to the environment if soil transport to rivers which has high pH.
- ▪Pb will be released to environment due to low pH.
- ▪River water survey around study area consistent with the dissolution behavior of Pb, As and Cd.

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