Adsorption and Precipitation of Cadmium Affected by chemical Form and addition Rate of Phosphate in Soils Having Different Levels of Cadmium

Hyun Ho Lee[a], Vance N. Owens[b], Sungkyun Park[c], Jiwoong Kim[c], and Chang Oh Hong[a*]

[a]Department of Life Science and Environmental Biochemistry, Pusan National University, 1268-05, Miryang, 50463, Korea
[b]Plant Science Department and North Central Sun Grant Center, South Dakota State University, 1110 Rotunda Lane North, Brookings, SD 57007, USA
[b]Department of physics, Pusan National University, Busan 46241, South Korea

Previous study and Introduction

Application of phosphate (P) to Cd contaminated soils is the widely used remediation treatment to reduce the bioavailability of this metal. Many studies have been conducted on Cd immobilization with P materials in soil (Table 1).

Table 1. Selected reference on the phosphate affected mechanisms of cadmium immobilization

Primary mechanism for Cd immobilization	P materials	P addition rate	Cd concentration in soil	Reference
Adsorption (Adsorption of Cd by increase in pH and negative charge)	MPP	1,000 mg kg^{-1}	10 mg Cd kg^{-1}	Bolan, 2003
	CP, MP, RP, and SSP	500 g m^{-2}	5.81 mg kg^{-1}	Biling, 2008
	CP, DAP, DPP, FP, FSP, MPP, and RP	1,600 mg kg^{-1}	5.57 mg kg^{-1}	Hong, 2010
Precipitation (Substitution of Ca in hydroxyapatite, precipitation of $Cd_3(PO_4)_2$ and $CdCO_3$ in elevated soil pH condition)	Hydroxyapatite	15,000 mg kg^{-1}	6.0 mg kg^{-1}	Boisson,1999
	DAP	2,300 mg kg^{-1}	1,090 mg kg^{-1}	McGowen, 2001
	DPP	1,600 mg kg^{-1}	5.57 mg kg^{-1}	Hong, 2014
	DPP	16,000 mg kg^{-1}	5.57 mg kg^{-1}	Kim, 2015
Not clear (probably precipitation and adsorption by charge of soil pH, formation of Ca-Cd-phosphate, and ion exchange, co-precipitation of insoluble Cd phosphate mineral)	CP	20 mg kg^{-1}	18.6 mg kg^{-1}	Chen, 2000
	RP	100,000 mg kg^{-1}	295 mg kg^{-1}	Basta, 2001
	Hydroxyapatite	50,000 mg kg^{-1}	1.1 mg kg^{-1}	Seaman, 2001
	MPP	24 mg kg^{-1}	60 mg kg^{-1}	Dheri, 2007
	DAP, Hydroxyapatite, RP, and TSP	1,091mg kg^{-1}	1.5 mg kg^{-1}	Chen, 2007

RP; Rock phosphate, FP; Fused phosphate, FSP; Fused and superphosphate, SSP; single superphosphate, DAP; Diammonium phosphate, MPP; monopotassium phosphate, DPP; Dipotassium phosphate, CP; calcium phosphate, MP; magnesium phosphate, TSP; triple-superphosphate

Above the studies have reported that **P-induced immobilization of Cd in soils could be attri-buted to two primary factors**: (1) **Cd^{2+} adsorption** to soil particles induced by increase in pH and negative charge of soil and (2) **precipitation of Cd** in a variety of inorganic phosphate forms, such as $Cd_3(PO_4)_2$ and $CdCO_3$. However, several studies simply evaluated effect of P on Cd immobilization and did not clearly address mechanism of Cd immobilization with P in depth.

Materials and method

Soil characteristics

An upland soil was selected for this study from experimental field of *Pusan National University* (35°30'07" N and 128°43'16" E) Miryang, South Korea.

Table 2. Selected physical and chemical Properties of the studied soil

Items		Concentration
pH (1:5 with H_2O)		6.7
Organic matter (g kg^{-1})		17.6
Total nitrogen (g kg^{-1})		1.05
Available phosphate (mg kg^{-1})		142
Exchangeable cation ($cmol_c$ kg^{-1})	K	0.42
	Ca	4.76
	Mg	0.93
	Na	0.38
Cation extractable capacity ($cmol_c$ kg)		6.85
Soil texture (%) *Sandy loam soil*	Clay	14.9
	Silt	25.7
	Sand	59.4

***Yongji* series (fine loamy, mesic family of Fluvaquentic Eutrudepts)**

Soil spiking

A Spiked artificially soil with $CdCl_2$ to give a total Cd concentration of 10, 100, 1,000 mg kg^{-1}

Incubation test

- Phosphate materials
  - K_2HPO_4, Dipotassium phosphate (DPP)
  - KH_2PO_4, monopotassium phosphate (MPP)
- Phosphate application rate
  0, 800, 1,600, and 3,200 mg P kg^{-1}
- Incubation condition
  Maintaining 70 % of water holding capacity and temperature for 25 ℃ during the 4 weeks

Cadmium – Equilibrium state analysis

- Input parameter
  - Soil pH (1:5 with H2O)
  - Ionic strength : $1/2\sum C_i Z_i$ (C. concentration, Z. valence)
  - Soluble cations : Cd^{2+}, Ca^{2+}, K^+, Mg^{2+}, Na^+, Al^{3+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+}, Si^{4+}
  - Soluble anions : PO_4^{3-}, Cl^-, SO_4^{2-}, NO_3^-, CO_3^{2-}
  - Dissolved organic carbon (DOC)
- Estimation
  Geochemical speciation model (*Visual MINTEQ* ver. 2.23)

X-ray analysis

- X-ray diffraction (XRD)
- X-ray photoelectron spectroscopy (XPS)

Statistical analysis

- Statistical analysis using the *Statistix* version 9.0

Research objectives

Previous studies were conducted in various conditions such as ***P materials***, ***addition rates of P***, and ***Cd concentrations*** in soil (Table 1). Therefore, we assumed that these various conditions could govern adsorption and precipitation of Cd in soil. Although a number of studies have examined Cd immobilization by P in soils, determining exact mechanism of Cd immobilization in various conditions has not been examined in detail. Therefore, the **objective** of this study was to **determine changes of Cd immobilization such as adsorption and precipitation in differently given conditions (form of inorganic P, addition rate of P, and Cd concentration in soil). The result of this study can help environmental scientist provide site specific-chemical immobilization technology for remediation of Cd contaminated soils with various conditions in the world.**

Results, Discussion, and Conclusion

Figure 1. Changes of (a); 1 M NH_4OAc extractable Cd concentration in soil, (b); pH of soil , and (c); negative charge of soil having different levels of Cd with addition of different rate of DPP (A) and MPP (B) after 6 weeks of incubation (*the same letter on the bar is not significantly different a P=0.05*).

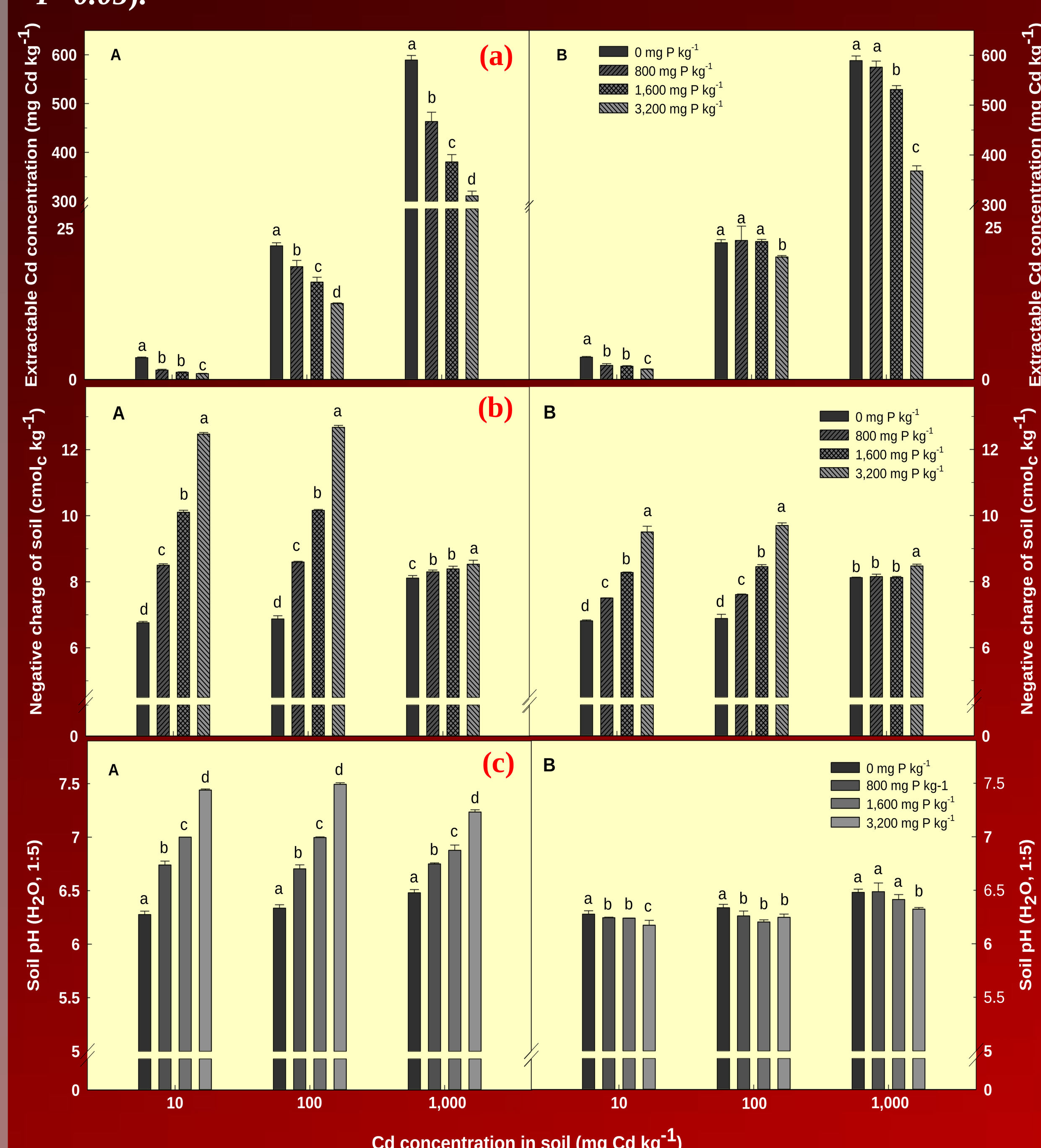


Figure 2. Expended XRD patterns for soil having 1,000 mg Cd kg^{-1} with addition of 3,200 mg kg^{-1} of DPP and MPP after 6 weeks of incubation.

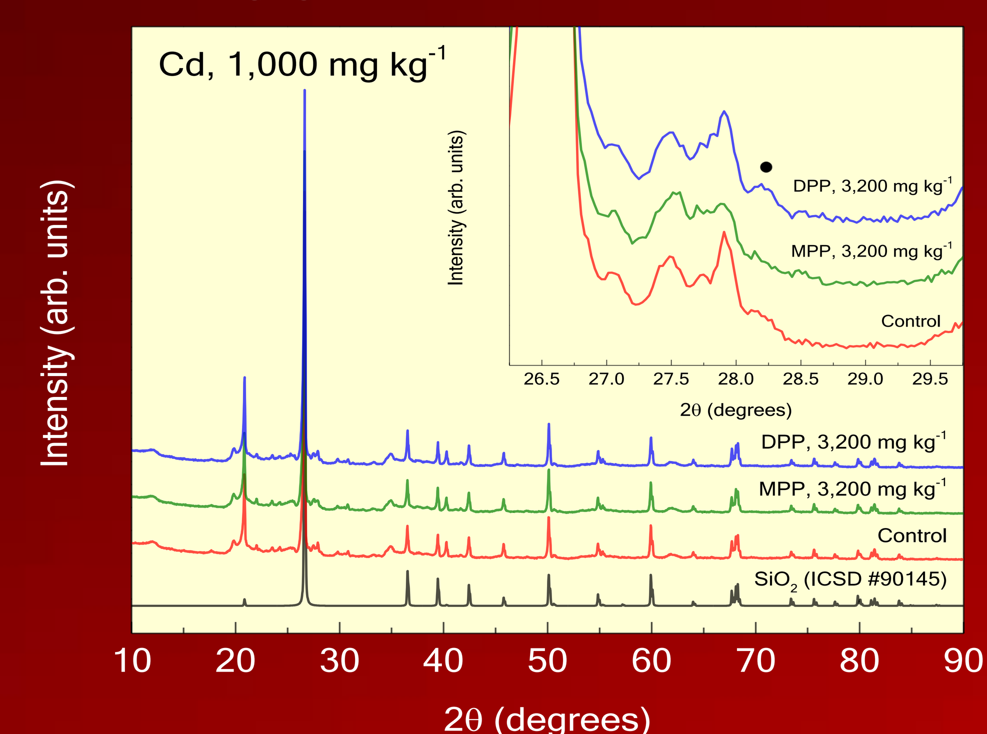
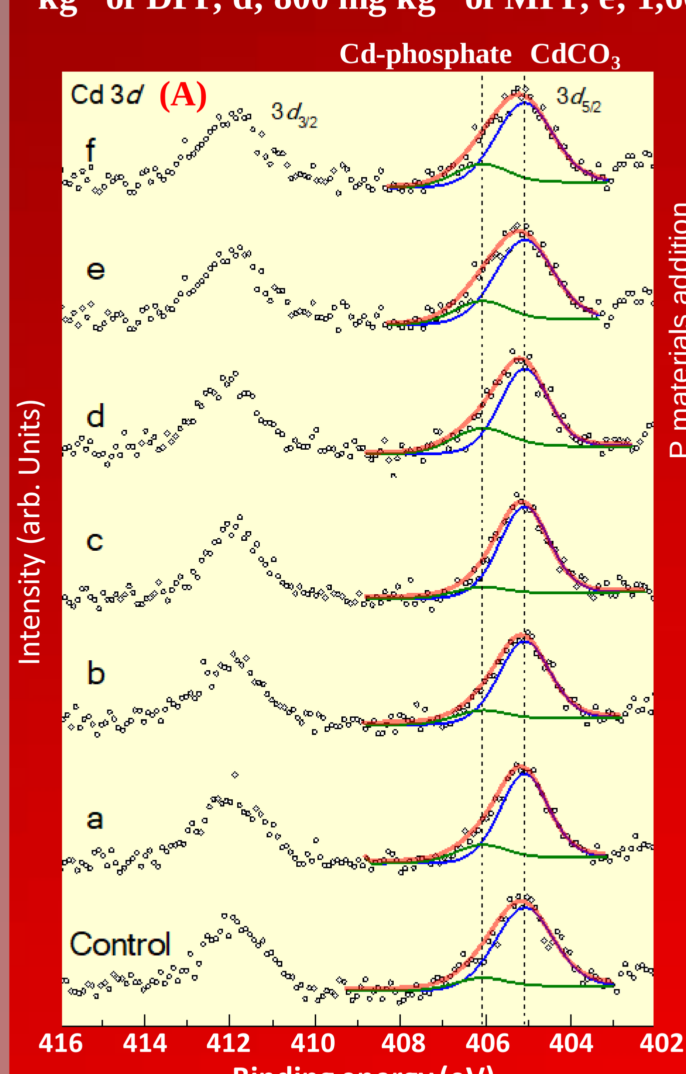


Figure 3. (A) Deconvolution of Cd $3d_{5/2}$ peak in XPS spectra for soil, and (B) Quantification of Cd compound of soil having 1,000 mg Cd kg^{-1} with addition of different rate of DPP and MPP 6 weeks of incubation (a; 800 mg kg^{-1} of DPP, b; 1,600 mg kg^{-1} of DPP, c; 3,200 mg kg^{-1} of DPP, d; 800 mg kg^{-1} of MPP, e; 1,600 mg kg^{-1} of MPP, f; 3,200 mg kg^{-1} of MPP).



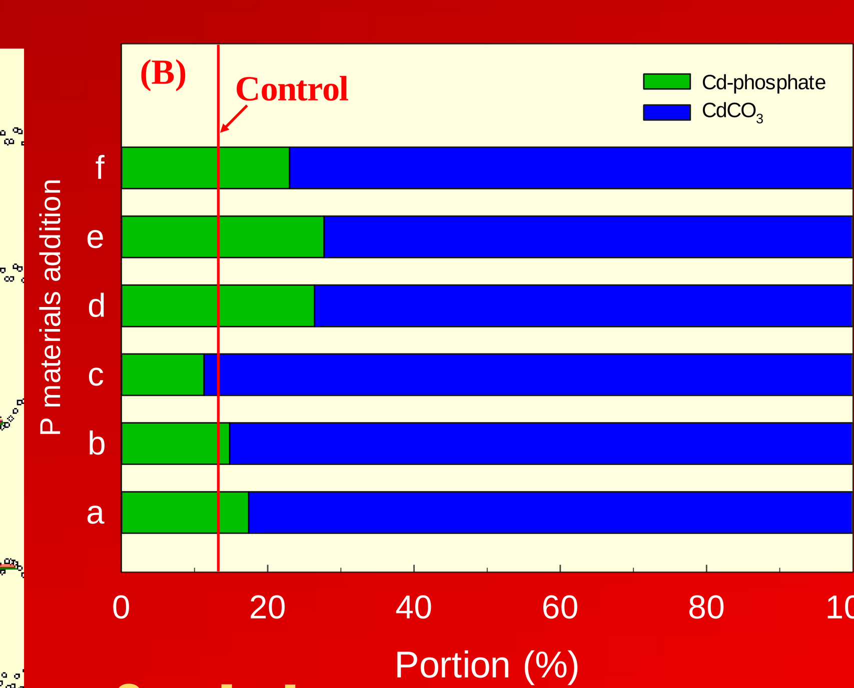
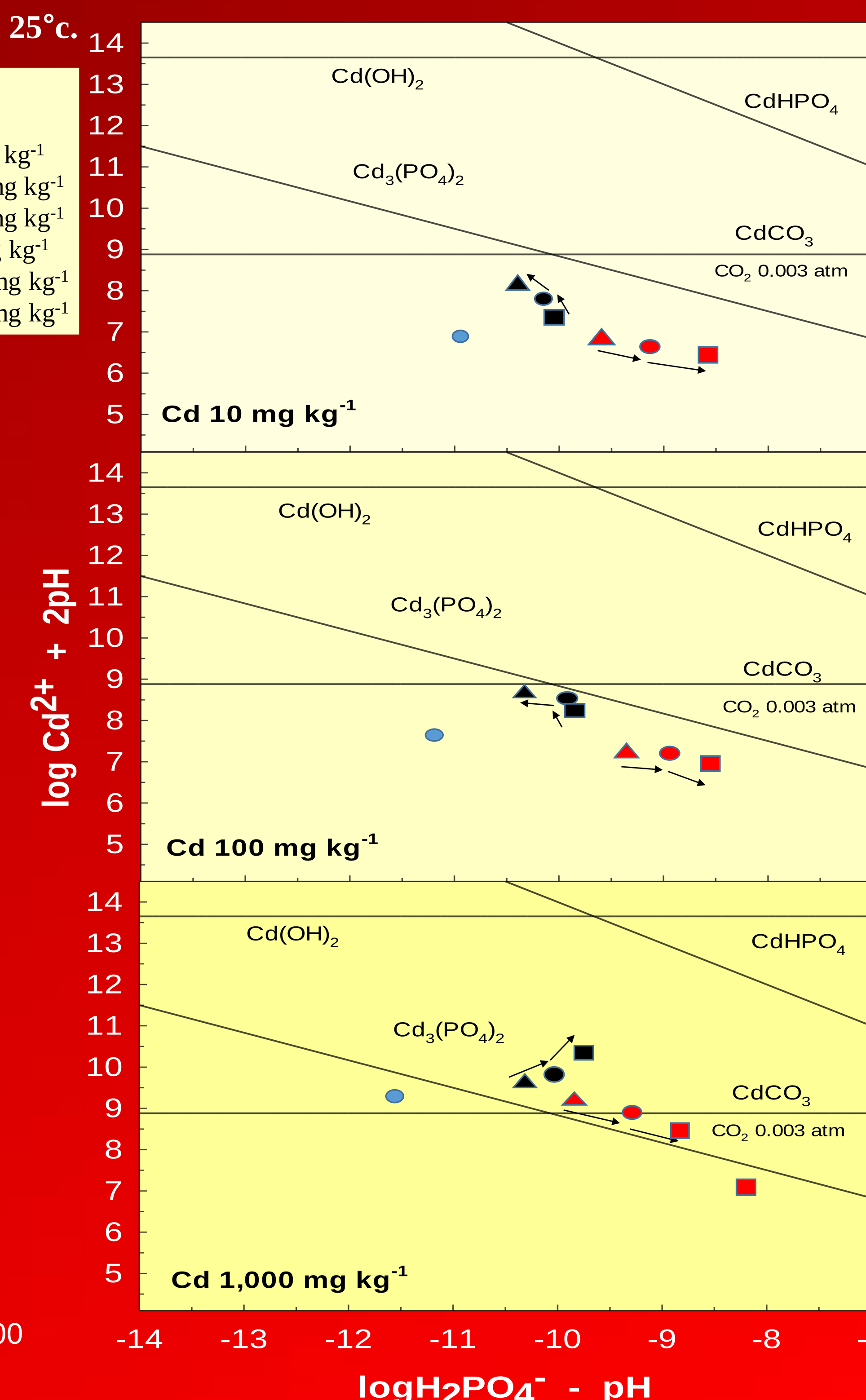


Figure 4. Cadmium solubility diagram of soil solution with different level of Cd at different addition rate of DPP and MPP after 6 weeks of incubation at 25°c.



Conclusion

Results of incubation study clearly demonstrated that ***chemical forms of P***, ***addition rate of P***, and ***inherent Cd level*** in soil affected adsorption and precipitation of Cd in soil. In 10 and 100 mg kg^{-1} of Cd levels, DPP and MPP similarly increased negative charge of soil and decreased extractable Cd concentration(Fig. 1). **Immobilization of Cd might be mainly attributed to negative charge induced Cd adsorption in soil with relatively low Cd levels (< 100 mg kg^{-1}).** In XRD pattern, for 1,000 mg kg^{-1} of Cd level soil added with 3,200 mg kg^{-1} of DPP, a diffrac-tion peak revealing to the presence of a novel Cd compound, $Cd(H_2PO_4)_2$,was observed(Fig. 2). In addition, XPS analysis and modeling for saturation index for Cd minerals proved that formation of poorly crystallized or amorphous $CdCO_3$ and $Cd_3(PO_4)_2$ in soil having 1,000 mg kg^{-1} of Cd level with addition of both DPP and MPP. **Precipitation of $Cd(H_2PO_4)_2$ and formation of poorly crystallized or amorphous $CdCO_3$ and Cd-phosphate might be a dominant mechanism to immobilize Cd besides Cd adsorption in soil with relatively high Cd levels (1,000 mg kg^{-1}).**

부산대학교
PUSAN NATIONAL UNIVERSITY