行政院國家科學委員會專題研究計畫成果報告

重金屬在土壤中宿命與傳輸之模式探討及其應用於推算最大容許量之研究

The Application in Calculating the Maximum Permissible Amount from the Mathematical Modeling of the Fate and Transport of Heavy Metal in Soil

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1.中文摘要

台灣地區土壤重金屬污染防治，亟需建立一套合理的適當的土壤重金屬含量標準以做為一切土壤污染防治管制策略的基礎。國內近年來土壤之重金屬研究調查及建議標準值之資料甚豐。各研究均有其著重點、研究領域及研究範圍，互有關連但不相互重疊，惟如何更便利地以模型直接推算吸附量以推導出標準值再與目前國內現有已完成調查之暫訂土壤標準值相比較，如果兩者相差無幾，則此研究目的之一乃可提供另一種更簡易有效制訂參考值之方法。本計畫乃根據土壤-重金屬吸附實驗之數據以統計中逐步回歸方法，導出鉛的吸附分配常數和土壤物理-化學性質之間之關係模式。結果顯示本模式所導出在固定 pH 下，鉛的吸附分配常數和土壤中有機質含量有非常直接之相關性。

關鍵字：土壤、重金屬、有機質、分配常數、土壤標準

1. Abstract

The metal adsorption characteristics of fifteen Taiwan soils, exemplified by Pb (II), were evaluated using pH as the major variable. The greater adsorption was found for soils with a higher organic matter content at constant pH and metal concentration. To better understand the mechanism of adsorption, the experimental results for Pb (II) were tested in a partition coefficient model to relate the adsorption of the Pb (II) by the different soils with soil components. Partition coefficients obtained from experimental data were highly correlated with those calculated for a partition coefficient between lead and organic matter alone.

Keywords: Soil; Pb; Adsorption; Partition coefficient; Organic matter; Metal oxides

2. Introduction

In the soil environment, the mobility and the fate of metals is regulated via their partitioning between soil and soil solution [1]. The existence of trace metals in the solid phase is a result of a host reactions with the adsorption being the most important for trace metals. The interaction of metal ions with natural soil particles involves multiple mechanisms. This is because various species of the trace element can exist in solution due to complexation with organic and inorganic ligands. All species including free ion can be subject to ion exchange, nonspecific adsorption, (co)precipitation, and surface complexation [2]. Soil properties, such as clay; aluminum oxides; iron oxides; and manganese oxidess, are present in soils and including them is possible to develop an understanding of mechanisms for the adsorption of metals. In this study, we investigate the sorption of lead onto 15 soils collected in Taiwan. The influence of solution pH and of the concentrations of iron, manganese and aluminum oxides and of organic matter in the soil on Pb sorption were considered.

3. Materials and Experimental procedures

The 15 soil samples collected in Taiwan for this study are listed in Table 1. They represent a distribution of the major soil types present in Taiwan. The soils were air dried, and agglomerates were broken by hand and by using a wooden mallet. Particles larger than 2 mm were removed by sieving. All further tests were conducted on the less than 2-mm size fraction of the soils. Batch equilibration studies were conducted for lead (II) to each of the 15 soils. The soil suspensions were 1.00 ± 0.01 g per 100 mL. Ionic strength was maintained at 0.01 M with $NaNO_3$. We added lead nitrate at a concentration of $1x10^{-4}$ M. 10 to 12 pH values covering the range from 2.5 to 8.5 were used, and room temperature (25 ± 2° C) was maintained. The pH values of the samples were adjusted by adding NaOH or HNO_3 as required. Samples were shaken at 150 rpm on a reciprocating shaker for 24 hours. The pH values were determined after the 24 hours of shaking. The samples were then filtered through 25-mm diameter, 0.45-μm membrane filters. Lead concentration in the filtered solution were determined by AA.

4. Results and Discussion

1. Soil Characteristics

A summary of soil characteristics is presented in Table1.

2. Batch Equilibration

The most important factor in controlling the partitioning of a metal to soil is the solution pH [3]. The amount of Pb (II) adsorbed on the soil increases with pH (Figure 1). The high dependence of Pb adsorption on pH can be explained by the fact that pH will affect the surface charge of the adsorbent and the degree of ionization and the speciation of adsorbate [4].

The soils vary in their metal binding strength. Among all soil properties in our study, organic content appears to be the most important parameter in correlating to Pb adsorption. The range of adsorption is illustrated by comparison of the Tacha silty loam which displayed the greatest extent of metal adsorption of all the soils with Lichochen sand which has the least metal adsorption capacity (Figure 1).

3. Partition Coefficients

The ratio of the Pb concentration in the soil to the concentration in the solution phase is defined by partition coefficient (K_d) which is a function of pH.

$$K_d = \frac{[C_s]_{Pb}}{[C_w]_{Pb}} \qquad (1)$$

These K_d values vary greatly from soil to soil. From Figure 2, the variation in K_d at fixed pH can obviously observed. This indicates that pH is the most important parameter, but it is not the only one.

As shown in Figure 2, the adsorption edge data (shown in Figure 1) were used to establish K_d values at fixed pH and plot log K_d versus pH for all 15 soils. We developed a general partitioning model for the sorption of Pb by soil surface substances at fixed pH to predict the partitioning of Pb to soil. of the variation of lead adsorption with measured soil properties was made. Clay content and surface area showed less relationship with adsorption. Based on a preliminary statistical analysis, the major adsorbing sites for binding Pb (II) are considered to be Fe_2O_3, Al_2O_3, Mn_2O_3, and organic matter. A typical reaction between lead and a sorption phase can be written as Equation 2:

$$\equiv S + Pb \leftrightarrow \equiv S - Pb \qquad (2)$$

$$K_{\equiv S-Pb} = \frac{[\equiv S - Pb]}{[\equiv S][Pb]} \qquad (3)$$

where $K_{\equiv S-Pb}$ is the conditional stability constant of this reaction; ≡S is a binding site onto iron, aluminum, manganese oxide and organic matter; ≡S-Pb is the quantities of lead sorbed by the binding site.

Therefore the partition coefficient is

where $[\equiv S_i]$ is site concentration of a particular class of sites.

$$K_d = \sum K_{\equiv S_i} - Pb[\equiv S_i] \qquad (4)$$

Equation 4 was applied to the lead adsorption data to obtain experimental partition coefficients for the Taiwan soils. These partition coefficients were regressed stepwise against site concentrations for the component considered: organic matter, iron oxide, aluminum oxide, and manganese oxide using Equation 4 to obtain conditional formation constants for each phase. Separate regression was done omitting one or more sorption phases. These formation constants were then used to calculate predicted partition coefficients. The results were listed in Table 2. Table 3 shows the comparisons of the results predicted by the model with the experimental data for three different pH values (3.0, 4.0, and 5.0). The single component that gives the best correlation is organic matter (R^2 = 0.941 for pH 4.0). A small improvement is obtained by including aluminum oxide (R^2 = 0.973 for pH 4.0) while only slight improvement is obtained with four components (organic matter, iron, aluminum and manganese oxide) (R^2 = 0.977 for pH 4.0). At each fixed pH, this model fits the experimental data very well by considering organic matter as the only sorption phase (R^2 > 0.900). The results indicate that organic matter is the most important of the single phase.

5. Summary and Conclusion

The result of adsorption edge study showed that Pb adsorption is highly pH dependent. Different soils have very different adsorption abilities. Among all soil properties, the organic matter plays a most important role in controlling lead sorption onto soils.

The adsorption coefficient, which is related to the percentage lead adsorbed, increases with rising pH values.

A model for the sorption of metal by soil surface properties at fixed pH was developed. The results show that the conditional partition coefficients were highly correlated to the organic matter content at a fixed pH.

6. References

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Table 1. *Soil properties

Soil Name	pH water	Clay (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO_2 (%)	OM (%)
Beichatianshan silty loam	3.9	44.5	1.095	1.374	0.055	8.3
Changhua loamy sand	3.5	16.1	0.121	0.079	0.001	0.8
Chiayi sandy loam	6.8	9.7	0.243	0.133	0.038	1.1
Guanyin sandy loam	5.6	9.5	0.638	0.443	0.017	2.3
Huwei loam	7.4	20.2	0.860	0.721	0.095	5.4
Jente clay loam	4.8	28.0	0.810	0.638	0.001	5.1
Kaohsiung silty loam	7.1	20.8	0.784	0.620	0.022	4.0
Keelung silty clay	6.6	27.1	0.917	0.748	0.021	5.5
Luzhu sandy loam	4.9	7.8	0.746	0.248	0.010	1.8
Tacha silty loam	5.8	13.6	0.584	0.410	0.003	11.2
Taichung silty loam	6.6	6.4	1.442	1.271	0.024	1.3
Tenchung silty loam	6.7	24.3	0.417	0.144	0.060	3.0
Lichochen sand	4.2	6.5	0.778	0.496	0.046	0.4
Yuenlin silty clay loam	5.7	34.2	1.029	1.154	0.042	6.7
Yunlin silty loam	6.9	9.5	0.505	0.161	0.009	1.6

*organic matter: the Walkey-Black wet combustion method[5]; pH : in water solution [5]; particle size distribution: sedimentation method[5]; metal oxides: the ammonium oxalate extraction method [6]

Table 2. The observed and predicted K_D at PH 4.0 and 5.0

Soil name	pH 4.0		pH 5.0	
	Obs.K_d	Pred. K_d	Obs. K_d	Pred. K_d
Beichatianshan silty loam	203.5	196.9	417.6	499.9
Changhua loamy sand	18.6	21.2	51.2	59.4
Chiayi sandy loam	29.9	41.3	164.2	195.7
Guanyin sandy loam	83.4	81.8	575.8	506.9
Huwei loam	136.0	138.3	468.9	423.3
Jente clay loam	121.2	128.2	418.3	430.6
Kaohsiung silty loam	113.6	98.9	321.2	290.7
Keelung silty clay	142.6	146.1	493.0	456.9
Lichochen sand	11.9	28.5	136.7	122.8
Luzhu sandy loam	54.3	61.6	13.2	167.0
Tacha silty loam	243.3	256.2	797.9	774.8
Taichung silty loam	35.5	36.8	87.4	109.2
Tenchung silty loam	109.1	89.3	345.7	331.4
Yuenlin silty clay loam	189.2	181.9	631.5	673.9
Yunlin silty loam	53.5	39.4	127.0	109.1

Table 3. Comparison of R^2 for regression of experimental K_ds against predicted values.

Component Considered	R^2			
	natural pH	pH 3.0	pH 4.0	pH 5.0
OM	0.002	0.905	0.941	0.936
Fe	0.107	0.197	0.296	0.263
Al	0.425	0.154	0.345	0.182
Mn	0.510	0.107	0.121	0.074
OM & Al	0.543	0.923	0.973	0.972
OM, Fe & Al	0.584	0.926	0.976	0.975
OM, Fe, Al & Mn	0.586	0.929	0.977	0.975

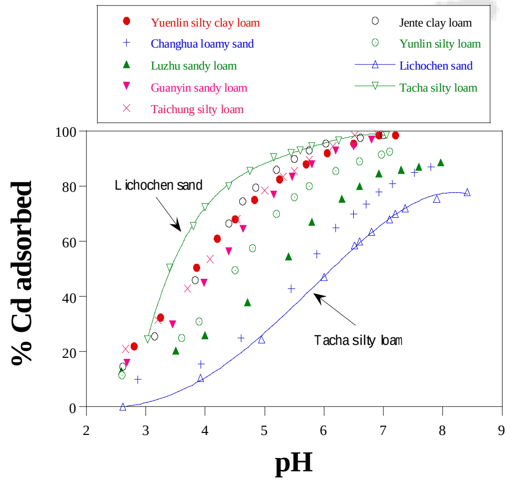

Figure 1. Adsorption of 1 x 10^{-4} M lead onto nine of fifteen Taiwan soils; soil:water = 1g/100 mL; I = 0.01 M $NaNO_3$; T=25° C.

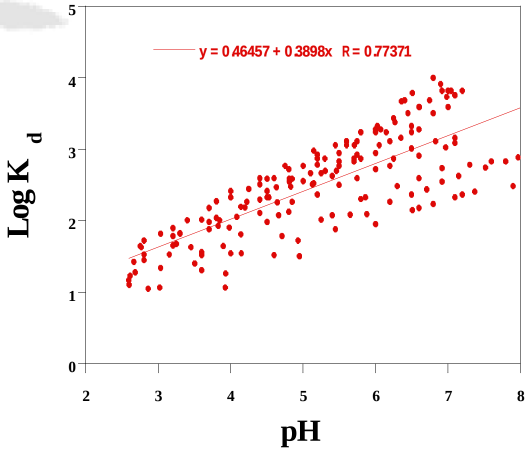

Figure 2. Log K_d as a function of pH for adsorption of Pb onto 15 Taiwan soils. soil:water = 1g/100 mL; I = 0.01 M $NaNO_3$ T=25° C.