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토양에 유입된 카드뮴, 구리, 아연의 시간에 따른 분배 계수의 변화

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Aging Effects On Partitioning Coefficients of Cd, Cu, and Zn in Metal-spiked Soils

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ABSTRACT

Temporal changes of metal solubility have been repeatedly observed in soils equilibrated with metal salt solutions. This phenomenon is known as aging, yet factors that affect the degree of metal aging remain largely unexamined. In this study, we compared the extent of aging on metal partitioning depending on soil, metal, and metal loading. Five soils spiked with four levels of Cd (2.5-20 mg kg^{-1}), Cu, and Zn (50-400 mg kg^{-1}) salt solutions were aged in the laboratory up to 1 year. The partitioning coefficient (K_d) of each metal was calculated from the ratio of total to dissolved metal concentration in samples collected at times ranging from 1 day to 1 year. The highest K_d values for Cd, Cu and Zn were recorded in a Histosol, Andisol, and fine-textured Alfisol, respectively, whereas the lowest K_d was recorded for an Oxisol and coarse-textured Alfisol. For all soils, a pattern of increasing K_d with aging was evident for Cd and Zn, but not Cu. Rapid Cu sorption was limited when dissolved organic matter was high in soils. In highly-retentive soils, K_d values seemed to be insensitive to metal loading, although a longer period was required for the higher metal loadings to reach the same degree of metal aging as the lower loadings. In soils with low sorption capacity, the K_d values were determined more by metal loading than by aging. Therefore, marked differences can be expected in the degree of metal aging in spiked soils by the soil type, metal and amount of metal added.

Keywords : Aging, Dissolved organic carbon, Metal, Partitioning coefficient, Soil properties

요 약 문

금속이 염 용액 형태로 토양에 유입될 때, 그 금속의 용해도는 시간이 지남에 따라 감소하는 경향(aging)을 보이는데, 이러한 시간 의존성 외에 토양 내 금속 용해도의 변화에 영향을 미치는 또 다른 요인들에 대한 고찰은 아직 미비한 상태이다. 본 연구에서는 물리화학적 성질이 다른 5 종류의 토양 (히스토졸, 앤디졸, 옥시졸, 미세입자 알피졸, 조대입자 알피졸)에 여러 비율의 카드뮴(2.5-20 mg kg^{-1})/ 구리(50-400 mg kg^{-1})/ 아연(50-400 mg kg^{-1}) 염 용액을 혼합하여, 상온에서 1년 동안 토양의 성질, 금속의 종류, 금속의 농도에 따른 용해도 변화관찰을 시도하였다. 그 결과, 히스토졸에서는 카드뮴이, 앤디졸에서는 구리가, 미세입자 알피졸에서는 아연이 가장 높은 분배 계수를 보였고, 옥시졸과 조대입자 알피졸에서는 모든 금속들이 가장 낮은 분배 계수를 나타내었다. 또한, 카드뮴과 아연의 경우 토양의 종류와는 무관하게 시간에 따른 분배 계수의 증가를 보였지만, 구리의 경우 토양 내 유입된 후 일주일 부터는 이러한 경향성를 찾아보기 어려웠다. 구리는 토양의 유기물이 많을 경우에는 빠른 흡착성을 보이지만, 토양수에 녹아있는 유기물이 많을 경우에는 그 흡착 특성이 제한됨을 관찰하였다. 더욱이, 흡수력이 높은 토양의 경우 금속의 분배 계수는 유입된

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금속의 양과는 무관할 뿐만 아니라, 높은 농도로 처리된 토양의 금속 분배 계수가 낮은 농도로 처리된 토양의 분배 계수와 유사해지기 까지는 더 오랜 시간이 요구되는 반면, 낮은 흡수력을 가진 토양의 경우에는 시간보다는 금속의 초기 유입양이 분배 계수 결정에 더욱 큰 영향을 미치는 것으로 밝혀졌다. 본 연구를 통해, 토양에 유입된 금속의 용해도 변화는 시간 뿐만 아니라, 토양의 성질, 금속의 종류와 농도에도 상당히 의존함을 입증하였다.

주제어 : 노화 현상, 수용성 유기 물질, 금속, 분배 계수, 토양 성질

1. Introduction

Once soluble forms of metals enter the soil environment, metal solubility decreases quickly as a result of spontaneous sorption processes in soils (McBride, 1989). Clay minerals, iron (Fe) and manganese (Mn) oxides, and organic matter (OM) are major sorptive phases in soils, and their roles in controlling solubility of added metals have been thoroughly examined. Soil pH is also of importance in determining metal solubility, since metals sorbed on surface sites of these adsorbents can be readily released as soil pH decreases by hydrogen ion exchange. On the other hand, solubility of metals may increase at higher pH due to enhanced dissolution of soil OM.

The degree of sorption on the organic and mineral components of soils also depends on the nature of the adsorbing metal, and the concentrations of competing metal ions. For example, copper (Cu) shows relatively higher affinity for metal (hydro)oxides and OM than either zinc (Zn) or cadmium (Cd). Therefore, under competitive conditions, Cu would preferentially sorb to the surfaces of these adsorbents, leaving significant portions of Zn and Cd weakly-bound to nonspecific sites or unbound (Kinniburgh et al., 1976; Stevenson, 1977), which would ultimately increase their bioavailability and toxicity. Luo and Rimmer (1995) reported a synergistic effect of metal toxicity on spring barley grown in soils spiked with Cu and Zn individually and in combination, and suggested enhanced Zn extractability and bioavailability with increasing soil Cu could be responsible for this synergistic phytotoxicity.

Another important factor that affects metal solubility in soils is aging. Reduced solubility of added metals typically occurs over time in soils, resulting in a gradual decrease in potential bioavailability and toxicity (McBride, 2000). Pedersen and van Gestel (2001) have shown large differences in the Cu extractability estimated by $CaCl_2$ and its toxicity on *Folsomia fimetaria*, when comparing freshly Cu-spiked soil with soil aged with Cu from 1 day to 12 weeks and with a soil contaminated with a comparable concentration of total Cu that had aged in the field for more than 70 years. Because of the importance of aging to metal toxicity, using soils spiked for a short time with metal salts to estimate biological endpoints of toxic metals has been criticized (Lock and Janssen, 2003a, b). Furthermore, there are also other concerns with using freshly metal-spiked soils for ecotoxicity studies, including a pH decline in soils as an immediate result of metal spiking (Stuczynski et al., 2003), and increased soil salinity from the added salt (Stevens et al., 2003). Nevertheless, a considerable body of investigation for evaluating metal toxicity is still conducted using freshly metal-spiked soils (Renella et al., 2003). It is important that a more through understanding of the impact of time, soil properties and metal loading level on the aging effect be obtained in order to interpret bioassays more realistically.

Therefore, in the present work, we attempted to evaluate the effect of time on the solubility of metals by testing different types of soil and metal, covering a wide metal concentration range over which toxic effects on soil microbial organisms and crops could be expected (White and Chaney, 1980; Kandeler et al., 1996; Giller et al., 1998). Five soils, possessing a wide range of pH, mineralogy, and OM content, were spiked with three metals (Cd, Cu, and Zn) and allowed to age for a year under laboratory conditions. Soil solution extracts collected at times ranging from 1 day to 1 year were analyzed for dissolved Cd, Cu, and Zn concentrations, and for chemical properties including pH, dissolved organic carbon (DOC) content, and electrical conductivity (EC). To facilitate comparison among the soils and the metals tested, and for the practical interest of predicting metal behavior in the soil environment, the results of this study were presented in terms of metal partitioning coefficients (K_d) estimated over the 1-year period of equilibration.

The findings of this study, therefore, should increase our understanding of the metal aging process in spiked-soils, and provide the basis for choosing a reasonable metal-equilibration period prior to conducting a laboratory bioassay, which might help to reduce the disparity between short-term laboratory-based and long-term field-based ecotoxicity studies for metals.

2. Material and Methods

2.1. Soil Characteristics

Five soils, including two Alfisols with different textures (an Arkport fine sandy loam and a Hudson silt loam, collected in Tompkins County, NY), an Andisol (Egmont series, New Zealand), a Histosol (Carlisle, Orange County, NY), and an Oxisol (Ap horizon of an Acrohumox, Brazil), were tested for the present study. The surface soils were collected, air-dried, mixed thoroughly, passed through a 2-mm stainless steel screen, and then stored in sealed plastic bins prior to use.

Characteristics of the soils were measured using the bulk control subsamples. Soil pH was determined in deionized water (1 : 2 w/v), and the organic matter (OM) levels of the soils were measured using the Walkley-Black method (Allison, 1965). Cation exchange capacity (CEC) of the soils was determined by an unbuffered $BaCl_2$ extraction method (Gillman, 1979), and the concentration of extractable Fe oxides was estimated by the Coffin method (Coffin, 1961). All the measurements are reported on a soil dry weight basis. Additional characteristics of the soils, for example, texture, and clay mineralogy, were taken from earlier publications (Van Raij and Peech, 1972; McBride, 2001; Jacobson et al., 2005) and are summarized in Table 1, along with the measured soil chemical properties.

2.2. Soil Preparation and Metal Analyses

Four stock solutions were made using $CdCl_2$, $CuSO_4$, and $ZnSO_4$ (reagent grade): (1) 50 mg L^{-1} of Cd and 1000 mg L^{-1} of Cu and Zn, (2) 25 mg L^{-1} of Cd and 500 mg L^{-1} of Cu and Zn, (3) 12.5 mg L^{-1} of Cd and 250 mg L^{-1} of Cu and Zn, and (4) 6.25 mg L^{-1} of Cd and 125 mg L^{-1} of Cu and Zn. A series of metal-spiked soils was generated by adding 100 mL of the

Table 1. Characteristics of five selected soils

	Hudson	Carlisle	Arkport	Oxisol	Egmont
pH	7.6	5.3	5.3	4.9	4.9
Organic matter (%)	6.1	38.0	3.5	6.5	2.6
CEC[†] (*meq* kg^{-1})	173	594	38	17	16 – 32
Extractable Fe oxides (mg kg^{-1})	6080	7840	2740	5900	4410
Texture analysis					
Sand (%)	9		77		
Silt (%)	68		16		
Clay (%)	23		7		
Clay mineralogy (by X-ray diffraction)					
Illite	*****		*******		
Chlorite	**		*		
Smectite	–		–		
Quartz	*		*		
Kaolinite				***	
Gibbsite				*	
Hematite/Goethite				*	
Allophane					***

[†] CEC: Cation exchange capacity.

each stock solution to 250 g of air-dried soil, which produced metal loadings of Cu and Zn of 50, 100, 200, and 400 mg kg^{-1}, and Cd of 2.5, 5, 10, and 20 mg kg^{-1}. In the case of the Oxisol and Egmont soils, however, there was not enough soil to create four different levels of metal loading, and therefore, only two metal loadings, the highest level (Cd 20 mg kg^{-1} and Cu and Zn 400 mg kg^{-1}) and the medium level (Cd 5 mg kg^{-1} and Cu and Zn 100 mg kg^{-1}) were prepared. Due to the limited available amounts of some soils, we were not able to prepare replicated soil columns.

After mixing, each of the metal-spiked soils was transferred to a plastic Büchner funnel, and allowed to equilibrate in the laboratory at 25°C. During the metal-equilibration period, appropriate amounts of de-ionized water were added to the samples to maintain constant soil moisture over time. Soil solution was collected repeatedly from the same soils by vacuum extraction at equilibrium times of 1 day, 3 days, 1 week, 1 month, 3 months, 6 months, and 1 year. To measure total metal concentrations in the soils after 1 year, a microwave-assisted HF digestion technique (EPA 3052) was used. The amount of Cd, Cu, and Zn in the soil digests as well as in the solution extracts was analyzed by inductively coupled plasma (ICP) emission spectrometry (SPECTRO CIROS CCD-ICP Spectrophotometer).

2.3. Soil Solution Characteristics

During the course of the first month, the solutions collected from the five soils treated with the highest metal loading (Cd 20 mg kg^{-1} and Cu and Zn 400 mg kg^{-1}) were characterized for pH, electrical conductivity (EC), and dissolved organic carbon (DOC) contents (Table 2). The EC measurement was carried out with an OAKTON conductivity meter at 25°C, and the DOC levels in the soil solutions were determined using persulfate oxidation/CO_2 analysis (OI Analytical model 1010 TOC/DOC autoanalyzer, College Station, TX).

3. Results and Discussion

The partitioning coefficient (K_d) of a metal was calculated by dividing the total soil metal content (mg kg^{-1}), measured after 1-year of aging, by the dissolved metal concentration (mg L^{-1}) in the soil solutions collected at the scheduled times in each soil. Metal loss over time was not considered in the estimation of the K_d values, since the total amounts of metals extracted in water by the successive extractions were negligible compared to the total metal contents remaining in the soils.

The chemical properties of soil, such as pH, dissolved organic carbon (DOC) contents, and electrical conductivity (EC), can be temporarily altered by metal-spiking procedures, which also may have influenced the initial K_d values measured for metals in the present study. By analyzing soil solutions collected over the initial 1-month of the metal-equilibration period, we concluded that most changes in chemistry caused by metal spiking had dissipated within a month, and relatively stable chemical properties were regained since. The highest metal loading in this study caused a slight pH decline for all the metal-spiked soils, with the greatest pH change found for the two acidic soils, the Arkport and the Oxisol. Nevertheless, the pH values of all the metal-spiked soils recovered to those of the control (untreated) soils after a month of equilibration (Table 2).

Soil solutions collected 1 day following the metal spiking had the highest levels of DOC and EC, but these levels decreased gradually with time regardless of the soil type. A dramatic change in soil physical conditions might be partly responsible for the initially high DOC, as the soils used were air-dried before the addition of metal salt solutions. The Oxisol had the highest DOC among the soils tested, displaying a time-dependent decrease, whereas the Egmont had the lowest DOC, with little change over time. All of the metal-spiked soils reached EC values of less than 1.2 dS m^{-1} after a month of equilibration during which soil solution removed for analysis was replenished by de-ionized water (Table 2). An EC of 1.2 dS m^{-1} is considered the salinity threshold for metal-spiked soils appropriate for testing metal toxicity (Stevens et al., 2003). Since soil properties appeared stable after 1 month of equilibration, it is reasonable to assume that any increase of the K_d values seen after the first month is the likely result of aging processes of the added metals in soils.

Table 2. Soil solution analysis during the first month of the metal-equilibration period

	Equilibration period (d)[†]	Hudson	Carlisle	Arkport	Oxisol	Egmont
pH	1	7.64	5.27	4.65	4.32	4.98
	3	7.44	5.66	4.68	4.39	5.08
	7	7.63	5.36	5.07	4.48	5.17
	30	7.58	5.56	5.10	4.74	5.00
DOC (mg L^{-1})	1	243	306	419	1115	54.0
	3	94.9	192	334	681	40.5
	7	91.1	130	107	306	49.5
	30	93.0	124	81	165	35.2
EC (dS m^{-1})	1	4.25	3.70	4.54	4.56	0.747
	3	2.55	2.98	3.79	3.30	0.519
	7	1.61	1.32	1.43	1.82	0.631
	30	1.00	0.806	0.611	1.14	0.475

[†] Equilibration period is expressed as day.

Due to a limited amount of two of the soils, we were not able to prepare replicates for the metal treatments. Nevertheless, the consistency in estimated K_d values for successive sampling times indicated good reproducibility in dissolved metal analyses and allowed comparisons to be made among soils for different metals and metal concentrations in the present work.

3.1. Cadmium

The K_d values of Cd tended to increase with time regardless of soil type, but soil characteristics and Cd addition level affected the extent of increase significantly (Fig. 1). Four levels of Cd were tested in the Hudson, Carlisle (organic) and Arkport soils, but the water-extractable Cd concentration was often below the detection of limit of ICP (0.003 μM) in the lowest Cd treatment (2.5 mg kg^{-1}) of the Hudson and Carlisle soils, which allowed us to quantify K_d values only for the 5, 10 and 20 mg kg^{-1} Cd treatments in these soils.

Substantial differences in the K_d values were observed for different Cd loadings in the Hudson soil at the beginning of the aging experiment, but the K_d values of Cd converged and were much the same after 1 year regardless of loading. The equilibration time required to achieve these stabilized K_d values after Cd addition, however, increased with increasing total Cd contents in the soil. Specifically, 1 week was sufficient to stabilize the K_d value in the 5 mg kg^{-1} Cd treatment, whereas 3-month aging periods were needed for the 10 and 20 mg kg^{-1} Cd treatments to attain the same K_d value. The K_d values of Cd appeared to be little affected by the total Cd added (up to 20 mg kg^{-1}) in the Hudson soil after a certain period of aging. This behavior indicates that Cd sorption follows a near-linear (constant-partitioning) isotherm in this type of soil.

The Carlisle soil had the highest Cd K_d values among the soils tested, suggesting the importance of OM for the retention of added Cd in soils. The K_d values of Cd in the Carlisle soil also increased over time for all loading levels; however, unlike the Hudson, the final K_d value obtained at the highest Cd addition (20 mg kg^{-1}) was only about half of that at the 10 mg kg^{-1} level, indicating some dependency of Cd loading on Cd adsorption in the Carlisle soil.

The K_d values of Cd in the Arkport soil also increased with time, but they were lower for this coarse-textured soil than for the fine-textured Hudson and organic Carlisle soil for all Cd loadings. Furthermore, at the 10 and 20 mg kg^{-1} Cd treatments, the K_d values did not change much for the first 6 months, and then increased only slightly by the end of the experiment, suggesting little impact of aging on the partitioning of Cd when high concentrations of soluble Cd are introduced into this soil. In addition, the K_d values tended to decrease with increased Cd loading in the Arkport soil, displaying the highest K_d for the 2.5

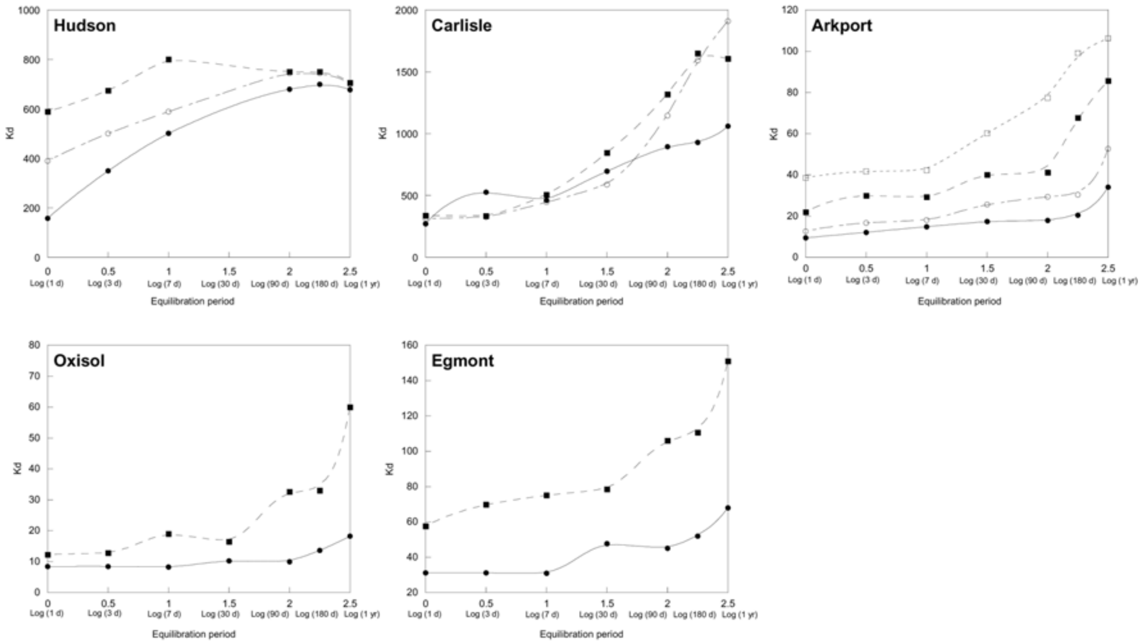

Fig. 1. The K_d values of Cd in five soils during the course of a year (Cd 20 mg kg^{-1} (●), 10 mg kg^{-1} (○), 5 mg kg^{-1} (■) and 2.5 mg kg^{-1} (□)).

mg kg^{-1} addition level and the lowest for the 20 mg kg^{-1} Cd treatment. This sensitivity of K_d values to the amount of Cd loaded suggests one of the following two explanations: (i) a one-year aging period might not be long enough to allow high concentrations of added Cd to react completely with all soil surfaces or (ii) unlike the Hudson soil, Cd sorption processes are non-linear (Langmuir-like) in the Arkport soil, a likely result of lower sorption capacity in this coarse-textured soil.

Despite higher OM content, the Oxisol showed lower K_d values than the Egmont for the same Cd loading. Presumably, the sorption sites of the OM in this acidic soil are occupied by Al^{3+} or Fe^{3+}, and thereby, not effective in retaining added Cd (Lopes and Cox, 1977). Furthermore, little time-dependent change in the K_d value was observed for the Oxisol treated with 20 mg kg^{-1} Cd, whereas a slight increase in the K_d value was found in the case of 5 mg kg^{-1} Cd treatment after 3 months of equilibration. The low soil pH and relatively high DOC contents probably also contributed to increased Cd solubility in the Oxisol. Therefore, the partitioning of Cd in the Oxisol soil appears to be largely determined by the amount of Cd initially introduced to the soil, but little by the duration of aging. The final K_d value for Cd was inversely related to the total Cd content in both the Oxisol and Egmont, suggesting nonlinear (Langmuir-like) Cd sorption behavior in these soils.

3.2. Zinc

Like Cd, a pattern of increasing K_d values with time was evident for Zn (Fig. 2). Specifically, the Hudson soil appeared to have the greatest capacity to adsorb the added Zn over time, recording the highest K_d among the soils tested. The K_d values for all Zn addition levels displayed a similar time-dependent increasing pattern and reached much the same level by the end of the aging experiment. However, the K_d value for the highest Zn addition came close to those of the lower Zn treatments only after 6 months of aging, suggesting that longer equilibration times may be needed at the higher Zn level to obtain the same K_d observed for the lower levels. As with Cd, the K_d values of Zn in the Hudson soil appeared to be independent of total Zn added after a relatively long equilibration period.

The Carlisle soil also showed a tendency for K_d values of Zn to increase with time, but the final K_d values tended to be inversely related to the amount of Zn added, suggesting some degree of dependence of the

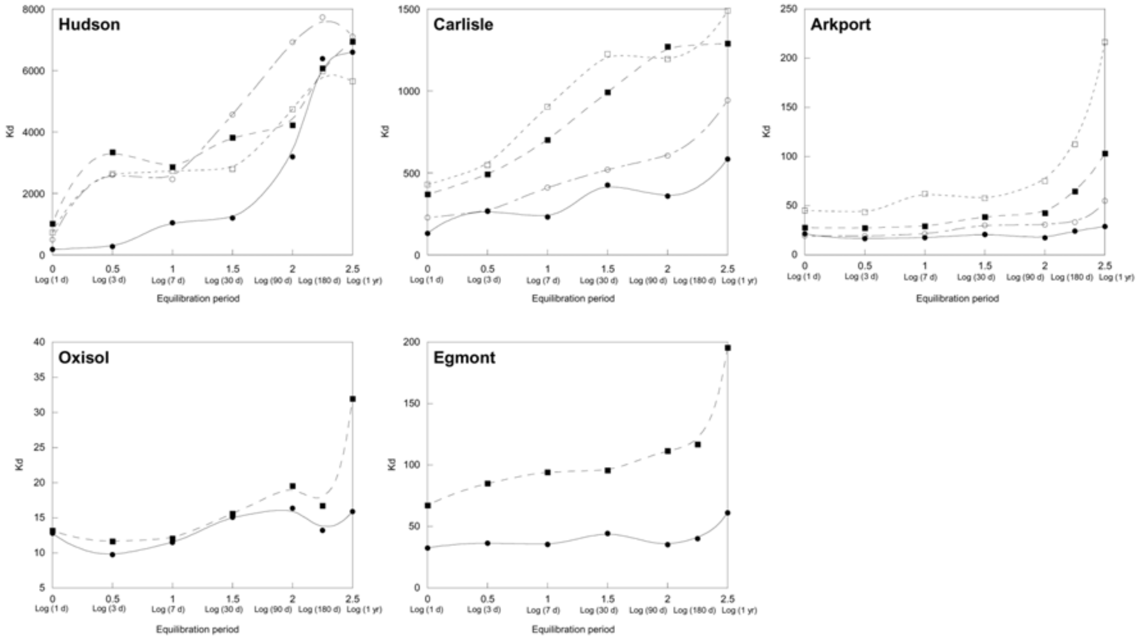

Fig. 2. The K_d values of Zn in five soils during the course of a year (Zn 400 mg kg^{-1} (●), 200 mg kg^{-1} (○), 100 mg kg^{-1} (■) and 50 mg kg^{-1} (□)).

K_d values on total Zn loadings. The K_d values for Zn in the Carlisle were significantly higher than those for the other soils, presumably due to higher levels of OM and extractable Fe oxides in this soil, yet lower than that of the Hudson which had the highest pH of the soils tested in this study. The difference in pH probably accounts for the ability of the Hudson mineral soil to sorb Zn more effectively than the organic soil at the same loadings, indicating the importance of pH in determining the degree of Zn sorption in soils over time.

Similar to the Carlisle soil, an inverse relation between the K_d values and Zn loading was also found in the Arkport, but with two noticeable differences: (i) the K_d values for the Arkport soil were much lower than those of the Hudson and Carlisle soils, and (ii) the K_d values at the lower Zn loadings increased over time, whereas those at the highest Zn (400 mg kg^{-1}) addition remained relatively constant. These trends were also seen in the Oxisol and Egmont soils, although the Egmont soil was better able to sorb Zn compared to the Oxisol for the same Zn loadings despite the same low pH as the Oxisol.

Lock and Janssen (2003b) suggested that aging would have more influence on Zn sorption and partitioning if soils have higher pH, and the results of the present experiment agree with their findings. More interestingly, a marked difference found in the K_d values depending on Zn loading in some of the soils tested in this study would also suggest a strong influence of loading on the process of Zn aging in soils, especially when there is a weak sorption tendency to begin with.

3.3. Copper

Compared to Cd and Zn, Cu showed a unique pattern of change in K_d values with time (Fig. 3). First, the time needed to reach a near-constant K_d value for a given Cu loading was shorter than for the other two metals. For example, in the Hudson and Carlisle soils, the K_d values for Cu displayed a time-dependent increase initially, but stabilized within one week of equilibration. Due to the nature of the metal, *i.e.*, strongly associated with soil OM, it might be that partitioning of the added Cu into OM occurs very rapidly and is little affected by subsequent aging processes. This agrees with results of isotope exchange experiments by McLaren and Crawford (1974), showing that the bulk of Cu adsorbed on OM is not labile after 1 day of equilibration.

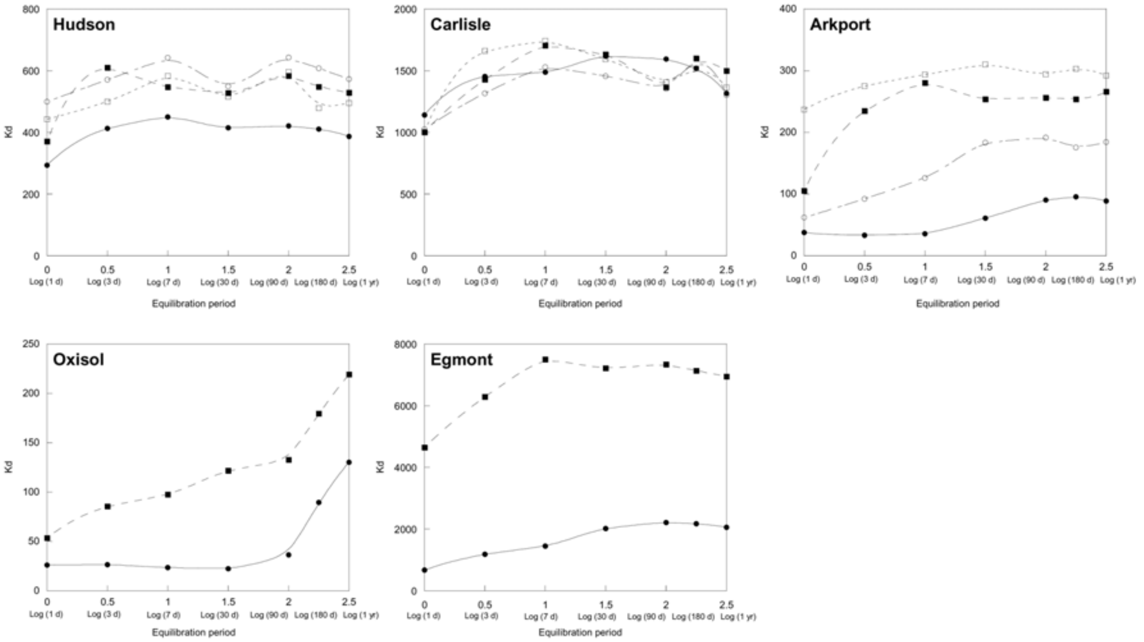

Fig. 3. The K_d values of Cu in five soils during the course of a year (Cu 400 mg kg^{-1} (●), 200 mg kg^{-1} (○), 100 mg kg^{-1} (■) and 50 mg kg^{-1} (□)).

Secondly, the K_d values of Cu seemed to be relatively independent of the amount of Cu added in the Hudson and Carlisle soils, where the level of OM was comparably high. The insensitivity of the K_d values to total soil Cu suggests that Cu sorption follows a near-linear (constant-partitioning) isotherm in soils having high OM and excess Cu sorption sites. On the other hand, in the Egmont soil, an allophanic soil with low OM, the K_d values of Cu and the equilibration time were strongly affected by Cu loading. Specifically, the K_d values were very different for the two Cu loadings, about 3.5 times higher for the 100 mg Cu kg^{-1} loading compared to the 400 mg kg^{-1} loading, indicating non-linear sorption behavior of Cu. One-week and one-month of equilibration were required to stabilize the K_d values for the 100 mg kg^{-1} and the 400 mg kg^{-1} Cu treatment, respectively. Nevertheless, the Egmont was the most efficient soil in adsorbing Cu, displaying the highest K_d value among all soils. The high K_d is attributed to chemisorption of Cu^{+2} on high surface-area non-crystalline alluminosilicates in the allophanic soil (Clark and McBride, 1984), limiting Cu solubility effectively in this acidic soil. In addition, the very low DOC in this soil (Table 2) would limit dissolution of Cu by organic complexation.

The K_d values of Cu in the Arkport and the Oxisol displayed a time-dependent increase with the exception of the 50 and 100 mg kg^{-1} treatments in the Arkport, where only 1 week of equilibration time was needed for stable K_d values. There was also an inverse relationship between the amount of Cu added and the K_d values for both soils. Aging affected the partitioning of Cu most evidently in the Arkport and the Oxisol soil, especially at higher loadings, yet K_d values at these higher loadings remained lower than those for the lower Cu loadings at all times. Thus, Cu follows a pattern of behavior like Cd and Zn; if a soil does not have enough adsorption sites for the added metal, metal loading and equilibration period become critical in determining the degree of Cu partitioning over time.

High initial DOC and low pH might be responsible for this delay of rapid Cu equilibration in the Arkport and Oxisol soils, through either inhibiting sorption of Cu on solid OM or desorbing bound Cu, or both. A strong influence of DOC on the amount of total dissolved Cu in soils has been also noted elsewhere (Benedetti et al., 1995; Temminghoff et al., 1997; Weng et al., 2002). The Oxisol in particular had the highest DOC levels at the beginning of the experiment among the soils tested (Table 2), but after 1-month equilibration period, the levels of DOC reduced to concentrations comparable to those in the other soils. Thus, DOC may have had a controlling influence on the K_d of Cu in these soils, with high DOC leading to lower K_d values. The ability of DOC to bring adsorbed Cu into solution could be partly responsible for the less evident role of aging in Cu sorption compared to Cd and Zn.

4. Conclusions

A range of soils selected for their widely different mineralogy, clay and OM contents were reacted with soluble Cd, Cu and Zn salt solutions over a 1-year time period. The Carlisle (organic) soil displayed high partition coefficient (K_d) values for Cd and Cu, indicating the importance of OM as a sorptive phase for these metals, whereas the highest K_d value of Zn was observed in the Hudson soil, where soil pH is relatively high. The Egmont soil, an allophanic mineral soil, was uniquely superior at adsorbing Cu at low pH, but did not effectively adsorb Cd or Zn.

The K_d values of Cd and Zn increased with aging to a different degree and rate determined by the soil type, metal and amount of metal added. In the most metal-retentive soils (e.g., the Carlisle soil and the fine-textured Hudson), the K_d value of each metal appeared to be insensitive to total amount added, possibly indicating a linear-sorption function for these soils. However, it was found that equilibration time required to reach a constant K_d increased with the amount of metal introduced. Conversely, in soils with weak metal sorption characteristics where much lower K_d values were observed (e.g., the coarse-textured Arkport and the highly-weathered Oxisol), K_d values only reached near-constant values for the lowest metal additions. Therefore, little aging effect of metals can be expected if high levels of metals are added to these soils.

In the specific case of Cu, K_d values stabilized at a very early stage of the metal-equilibration period, affected little by aging. Aging of Cu was only apparent either when high Cu was introduced to soils having low OM contents, or when elevated soil DOC levels were present initially as a result of wetting air-dried soils. Linear Cu sorption behavior was found in the soils with high OM levels, whereas non-linear behavior was reported in the allophanic mineral soil.

Thus, it can be concluded that metal aging occurs in spiked soils, most particularly in the case of soil with good sorbent characteristics, and more significant for Cd and Zn than Cu. Based on the results of the present study, it is recommended to equilibrate metal-spiked soils at least 1 month prior to conducting bioassays, with several cycles of leaching to remove excess salts and DOC until soil physicochemical conditions are stabilized.

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