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CADMIUM SOIL SORPTION AT LOW CONCENTRATIONS: II. REVERSIBILITY, EFFECT OF CHANGES IN SOLUTE COMPOSITION, AND EFFECT OF SOIL AGING

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Abstract. Desorption of Cd from two Danish soils (loamy sand, sandy loam) previously exposed to low concentrations of Cd was examined in terms of reversibility, effect of changes in solute composition, and effects of aging of the soils for extended time prior to accomplishing the desorption experiments. The loamy sand exhibited full reversibility of Cd sorption in 10^{-3} M CaCl_2 at pH = 6.0, while the sandy loam at the same conditions exhibited a partial irreversibility of the order of $1 \mu\text{g Cd g}^{-1}$ soil. However, this partial irreversibility was not caused by any strong binding of Cd since no irreversibility was observed in 10^{-2} M CaCl_2 at the same pH. Changing the solute composition with respect to Zn, CaCl_2 , pH and the presence of organic ligands (EDTA) caused significant desorption of Cd from the soils. The degree of desorption was proven with respect to variations in CaCl_2 and pH to be governed by the sorption equilibrium conditions independently of the previous distribution of Cd between soil and solute. Aging of the soil at a temperature of 1°C (after exposure to Cd) for 35 and 67 wk did not reveal any changes with respect to desorption of Cd at pH = 6.0 in 10^{-3} M CaCl_2 .

1. Introduction

The increasing Cd content of agricultural soils due to application of phosphate fertilizers, atmospheric deposition, and disposal of wastes such as sewage sludge and municipal compost (Tjell *et al.*, 1980) has in view of the potential toxicity of Cd to man through contamination of agricultural produce and drinking water given rise to extensive research on the soil chemistry of Cd. However, most of the reported investigations have dealt with excessive Cd concentrations (in excess of $20 \mu\text{g}$ ($0.18 \mu\text{mol}$) Cd g^{-1} soil or $100 \mu\text{g}$ ($0.9 \mu\text{mol}$) Cd dm^{-3} solute; Christensen, 1980) and hence are only of minor environmental pertinence. The few reported investigations on the soil chemistry of Cd at low concentrations (Christensen, 1984; Garcia-Miragaya and Page, 1978; Jarvis and Jones, 1980; Mayer, 1978) have revealed that soils have a high capacity for sorbing Cd, that equilibrium is approximately reached within 1 h, that the sorption capacity is highly dependent on pH, and that Ca in the solute may significantly compete for sorption sites.

Evaluation of the environmental problem of Cd addition to soils requires, besides the abovementioned knowledge, information on desorption of Cd from soils previously loaded with Cd. In the long term it is paramount, whether sorbed Cd is readily released from the soil by a decrease in solute Cd concentration or a change in solute composition, or if the soil binds Cd so firmly that the soil, from an environmental point of view, acts as a permanent sink for Cd. The development of firm bonds may however, from a theoretical point of view, require extended time. Hence the question on the effect of aging of the Cd loaded soils must be taken into consideration as well.

Several investigations (Blom, 1974; Ferrell and Price, 1978; Garcia-Miragaya, 1980;

Jarvis and Jones, 1980; John, 1971; Levy and Francis, 1976; Mayer, 1978; Navrot *et al.*, 1978, Riffaldi and Levi-Minzi, 1975; Singh, 1979; Singh and Sekhon, 1977; Tiller *et al.*, 1979) have examined the exchangeability of sorbed Cd by accomplishing desorption experiments with a specific extractant. However, applying most of these results to the actual problem of Cd addition to agricultural soils is difficult, since most of the investigations have been accomplished at excessive Cd concentrations. Furthermore, a variety of extractants has been employed including weak solutions of Ca salts and 1 N ammoniumacetate, and every investigation has used its own extraction procedure and hence defined 'exchangeability' in its own way. Only the approach by Mayer (1978) yields results of a type directly applicable to prediction of solute Cd concentrations in actual soil environments: The desorption experiments employed Cd free soil solutions and the results were expressed in terms of desorption isotherms. In the case of an acid forest soil loaded with low Cd concentrations full reversibility was observed (Mayer, 1978).

In the present study the release of Cd from two Danish soils loaded with low Cd concentrations (0.1 to 6 $\mu\text{g g}^{-1}$ soil and 1 to 50 $\mu\text{g Cd dm}^{-3}$ solute) was examined in terms of desorption isotherms caused by decreases in solute Cd concentrations and changes in solute composition. Furthermore, the effect of aging Cd loaded soils was investigated.

The sorption of Cd at low concentrations onto these soils and the effect of time, Cd load, pH, and Ca has previously been reported (Christensen, 1984).

2. Materials and Methods

2.1. SOILS

The soils consisted of a loamy sand and a sandy loam sampled in slightly weathered quaternary deposits (tills) in Jutland, Denmark at depths of 50 to 100 cm.

The soils were air dried and sifted through a 0.5 mm nylon mesh. Employing soil fractions less than 0.5 mm instead of less than 2.0 mm improved the precision from 11.5 to 3.6% (C.V) (Christensen, 1980) of batch Cd sorption experiments involving 1 to 2 g of soil.

The soil characteristics, as presented in Christensen (1984), were primarily determined by standard methods (Christensen, 1980).

2.2. CADMIUM LOADING OF SOILS

The soils were loaded with Cd by equilibrating 0.5 to 4 g of soil with solutes of preset Cd concentrations in 0.1 dm^3 polyethylene reactors, which were shaken for 20 hr. Cadmium (based on CdCl_2 standards) was added to the solutes as small volumes of 100 mg (900 μmol) Cd dm^{-3} of 10^{-2} M HNO_3 . A constant pH (6.00 ± 0.03) was maintained by adding small amounts of HNO_3 or NaOH . The solutes contained 10^{-3} M or 10^{-2} M CaCl_2 in the loading experiments.

Solute and soil were separated after equilibration by means of centrifugation corresponding to an equivalent particle diameter of 0.2 μm .

The solute Cd concentration was measured in order to control that the distribution of Cd between soil and solute was in accordance with previously determined sorption isotherms (Christensen, 1984). The separated solute was discarded. The equilibrium soil Cd concentration was calculated from the observed decrease in solute Cd concentration. In some cases, the soils were air dried prior to desorption.

2.3. DESORPTION EXPERIMENTS

The desorption experiments were accomplished analogously to the sorption experiments except that all Cd initially was present in the soil and the added solute of varying composition initially was free of Cd. The latter aspect was controlled analytically prior to the use of the desorbing solute. After equilibration for 20 hr at constant pH, soil and solute were separated and the solute Cd concentration determined. The final soil Cd concentration was calculated from the initial soil Cd concentration and the amount of Cd released to the desorbing solute.

2.4. AGING EXPERIMENTS

In order to examine if stronger binding of Cd to soil is developed during extended time of loading, reactors containing both soil and solute were stored at 1 °C after equilibration was accomplished as described for loading the soils with Cd. The reactors were shaken shortly each week. After 35 respectively 67 wk the reactors were weighed to control if any losses had occurred, pH was adjusted during a 20 hr period and the solute Cd concentration determined once again as a control. No significant long term (up to 67 wk) changes in equilibrium concentrations were observed (Christensen, 1984). The solute was discarded and the desorption experiments accomplished as previously described.

2.5. CADMIUM ANALYSIS

Solute samples, which were conserved by acidification, were buffered to pH 4 to 6 by addition of trisodium citrate, and Cd extracted by 1% DDDC (diethylammonium-diethyl-dithio-carbamate) in xylene prior to determination by flameless atomic absorption spectrophotometry (Perkin-Elmer 300S, HGA 72, deuterium background corrector). The apparatus was adjusted for highest sensitivity (Christensen, 1980). The precision of the Cd determination was estimated to 3% (C.V.). The Cd concentrations are expressed as Cd-total in the figures.

3. Results and Discussion

3.1. REVERSIBILITY

The results of the reversibility experiments, *i.e.* experiments where salt matrix composition and pH are identical for both sorption and desorption, are presented in Figure 1 for both soils at pH = 6.0 in a 10^{-3} M CaCl_2 salt matrix and in Figure 2 for the sandy loam at pH = 6.0 in a 10^{-2} M CaCl_2 salt matrix. In both cases, the corresponding sorption isotherms (as reported previously; Christensen, 1984) are shown for evaluation

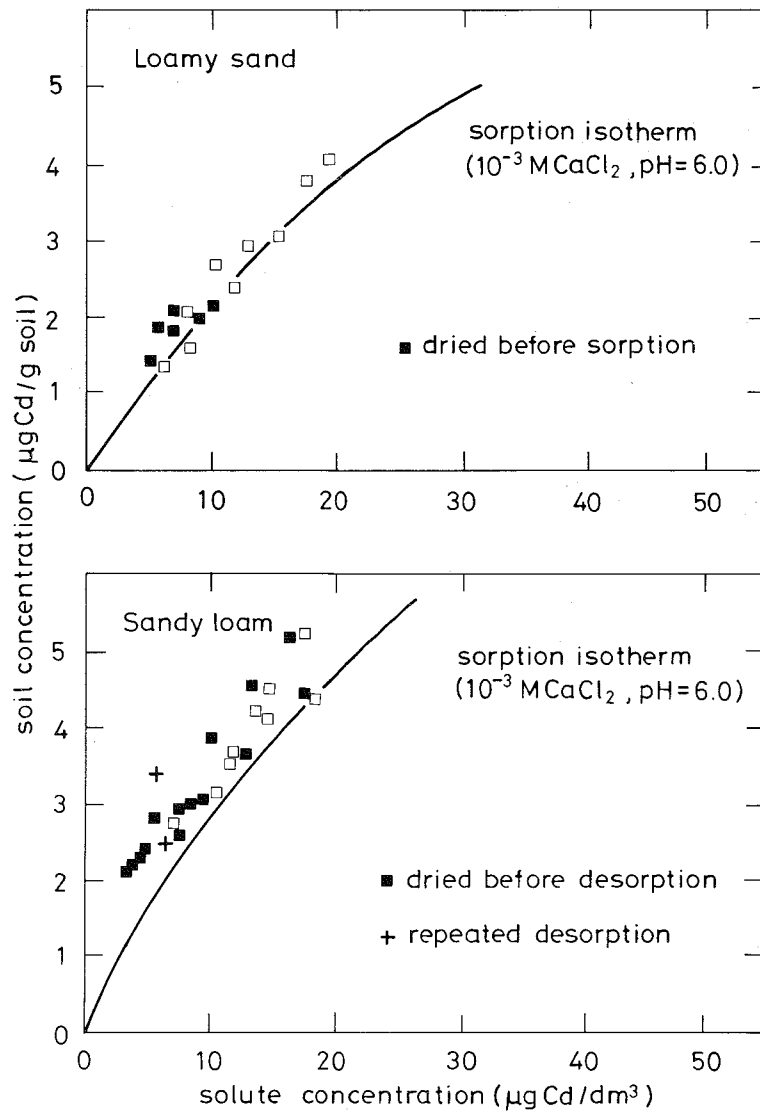


Fig. 1. Reversibility of Cd sorption in 10^{-3} M CaCl_2 at pH = 6.00 (Sorption (solid line) and desorption (points) experiments accomplished in identical salt matrix) (Sorption isotherm from Christensen, 1984).

of the data. For a fully reversible sorption process, the equilibrium distribution of Cd between soil and solute is independent of whether the amount of Cd initially is present in the soil or in the solute, and a single isotherm describes the equilibrium distribution. Full reversibility was observed in the case of the loamy sand in a 10^{-3} M CaCl_2 salt matrix (pH = 6.0) and the sandy loam in a 10^{-2} M CaCl_2 salt matrix (pH = 6.0). The location of the desorption equilibrium observations above the sorption isotherm for the sandy loam for a 10^{-3} M CaCl_2 salt matrix (pH = 6.0) indicated a partial irreversibility

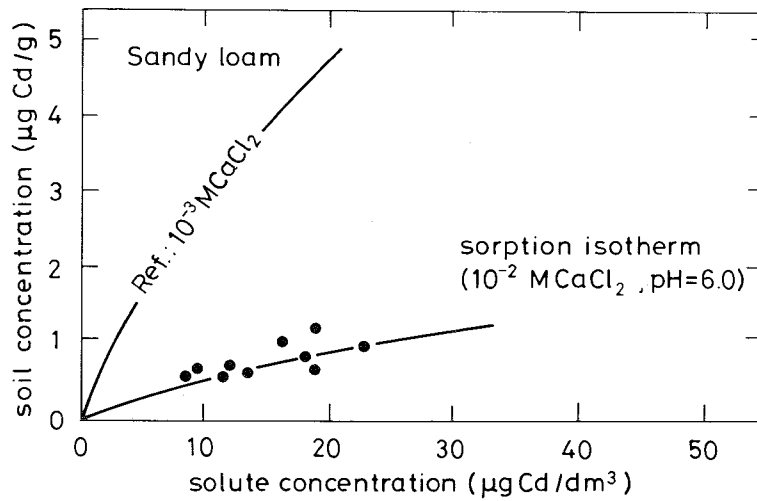


Fig. 2. Reversibility of Cd sorption onto a sandy loam in 10^{-2} M CaCl_2 at pH = 6.00 (Sorption (solid line) and desorption (points) experiments accomplished in identical salt matrix) (sorption isotherm from Christensen, 1984).

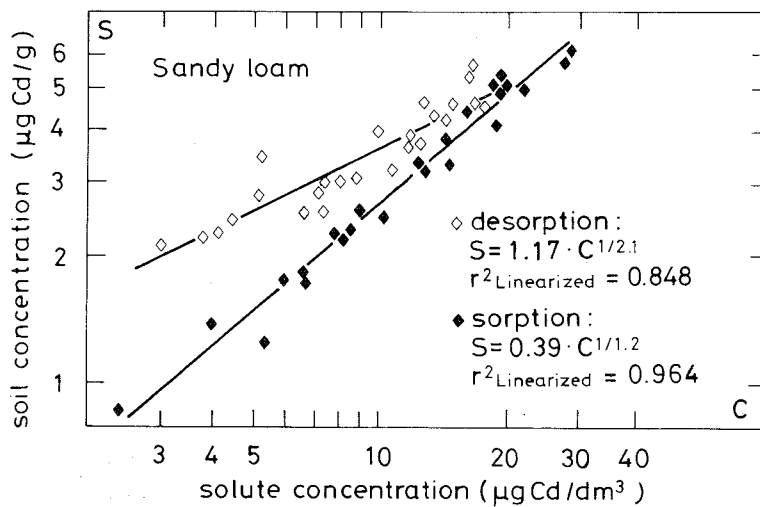


Fig. 3. Freundlich plot for sorption and desorption data for sandy loam in 10^{-3} M CaCl_2 at pH = 6.00 (The sorption data has previously been reported by Christensen, 1984).

of the sorption process at these conditions. A linearized Freundlich plot of both the desorption observations and the sorption observations (previously reported; Christensen, 1984) is presented in Figure 3. Statistical comparison of the regression lines show that the sorption and desorption isotherms are significantly different (z , slope = $6.76 > t(46)_{0.995} = 2.69$, where z , slope is the parameter for testing if the slopes are alike and $t(x)_f$ is the corresponding fractile, f , in a Student- t -distribution with x degrees of freedom, Hald (1952), but at solute equilibrium concentrations

above $10 \mu\text{g Cd dm}^{-3}$ solute the linearized isotherms seem to be parallel (z , slope = $= 0.09 < t(22)_{0.70} = 0.53$; z , intercept = $4.80 > t(22)_{0.995} = 2.84$).

The partial irreversibility observed for the sandy loam in a 10^{-3} M CaCl_2 salt matrix (pH = 6.0), approximately corresponding to $1 \mu\text{g Cd g}^{-1}$ soil, may be caused by sorption sites possessing higher free energy than the average sites. However, the free energy of these sites is not high enough to be attributed to specific sorption, since no irreversibility was observed when the sorption and desorption took place in a 10^{-2} M CaCl_2 salt matrix at the same pH.

The reversibility experiments show for the two experimental soils that Cd sorbed to the soils is for the predominant part easily desorbed in case of a decrease in solute Cd concentration. Only for the sandy loam in a dilute salt matrix (10^{-3} M CaCl_2 , pH = 6.0) the sorption-desorption process exhibits a slight irreversibility. This indicates that the experimental soils primarily act as a moderator temporarily storing significant amounts of Cd and equalizing the solute Cd concentrations, rather than as a permanent sink making added Cd environmentally unavailable.

3.2. EFFECT OF CHANGES IN SOLUTE COMPOSITION

The results of the desorption experiments elucidating the effect of changes in solute composition are presented in Figure 4 for both soils originally loaded with Cd at pH = 6.0 in a 10^{-3} M salt matrix. The desorbing solutes varied from the sorption salt matrix with respect to Zn content, Ca and chloride concentrations, pH and the presence of a complexing agent. For both soils the presence of $5 \text{ mg (76 } \mu\text{mol) Zn dm}^{-3}$ desorbing solute lowered the equilibrium isotherm about 25%, increasing the CaCl_2 concentration 10 items (10^{-3} M to 10^{-2} M) lowered the equilibrium isotherm about 50%, while lowering the pH two units (pH = 6.0 to pH = 4.0) or adding a significant amount of a strong complexing agent (10^{-2} M Na_2 EDTA) lowered the equilibrium isotherm more than 75%.

The presence of Zn in the soil solution in concentrations much higher than Cd (which is the most common situation) only slightly affects the ability of the experimental soils to retain Cd, indicating that Zn on an equivalent basis is not a strong competitor for sorption sites. The addition of significant amounts of EDTA is not directly of environmental pertinence, but is used as a model for the presence of organic compounds possessing the ability to complex Cd. The fact that EDTA does not remove all previously sorbed Cd from the soil may be due to soil sorption of Cd-EDTA complexes or the ability of the soil sorption sites to compete with EDTA for Cd.

The significant desorption of Cd caused by lowering the pH or increasing the CaCl_2 concentration of the saltmatrix is evidently governed by the sorption isotherm valid for Cd sorption at conditions identical to the desorption conditions. This is shown in Figure 5 which, in the case of the sandy loam, compares the desorption observations (Cd originally sorbed at pH = 6.0 in a 10^{-3} M CaCl_2 salt matrix) presented in Figure 4 with sorption isotherms (previously reported; Christensen, 1982) valid at pH = 6.0 in 10^{-2} M CaCl_2 and pH = 4.0 in 10^{-3} M CaCl_2 , respectively.

The experiments show for the two experimental soils that changes in the soil solute

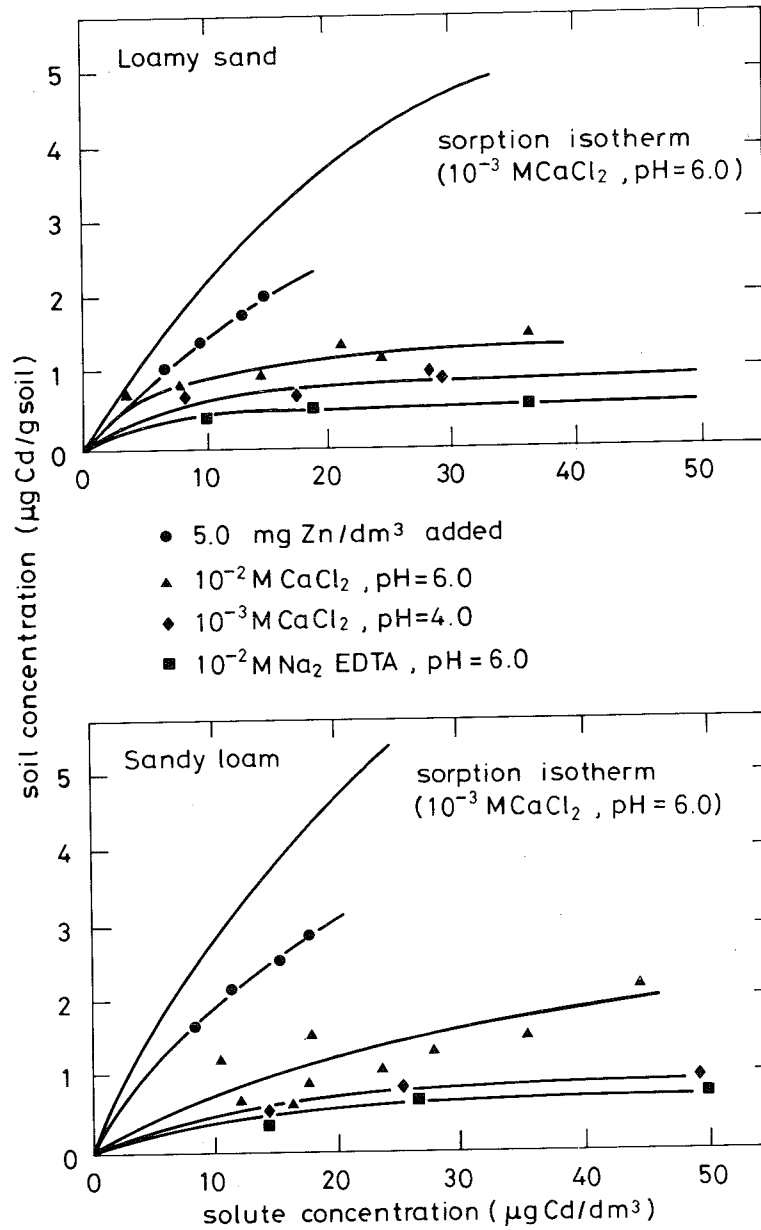


Fig. 4. Effects of various changes in solute composition on the desorption of Cd previously sorbed at pH = 6.00 in a 10⁻³ M CaCl₂ salt matrix (Sorption isotherm from Christensen, 1984).

composition, substantiated by changes in solute concentrations of Zn, EDTA, Ca and chloride, and in pH, cause significant desorption of previously sorbed Cd, and indicates that the equilibrium distribution of Cd between soil and solute, from an environmental point of view, is governed by the equilibrium isotherm valid for the specific solute

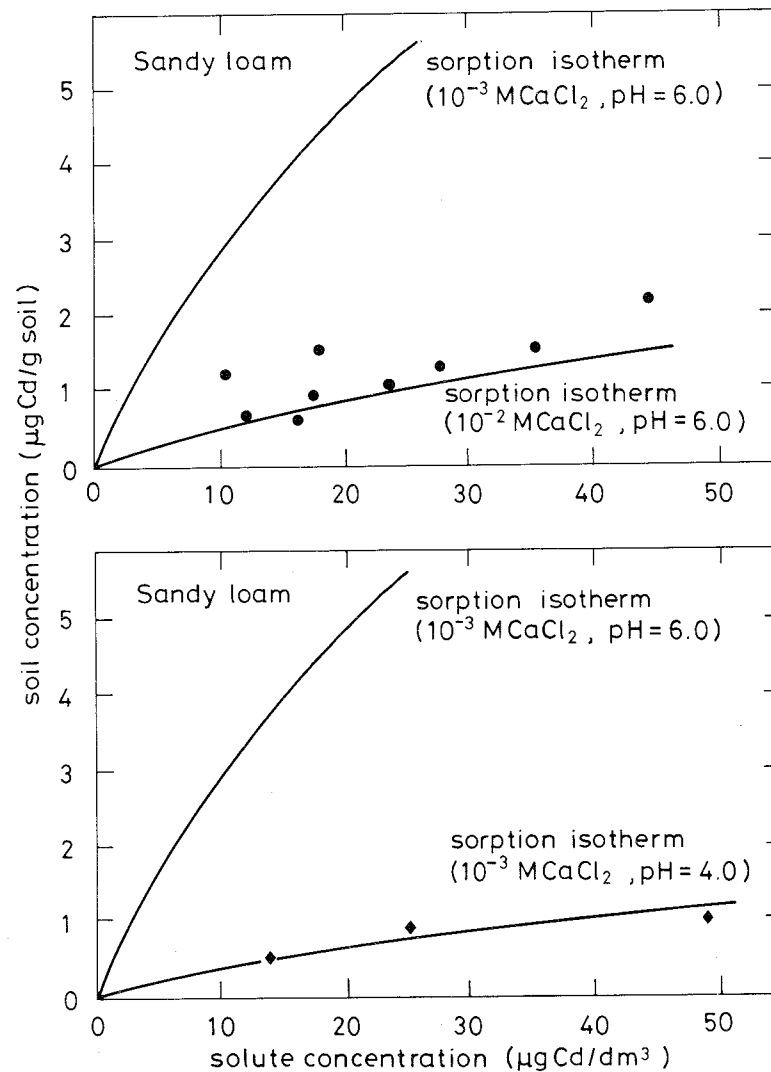


Fig. 5. Observations obtained by desorbing Cd (sorbed at pH = 6.00 in a 10^{-3} M CaCl_2 salt matrix) by changing the solute composition with respect to pH respectively CaCl_2 concentration (as shown in Figure 4) compared to sorption isotherms determined at conditions similar to the desorption conditions (previously reported; Christensen, 1984).

composition independently of the previous distribution of Cd. A fact that significantly simplifies prediction of the behavior of Cd in soils, but also emphasizes the importance of knowing the variations in soil solute composition, *e.g.* with respect to Ca and pH.

3.3. EFFECT OF SOIL AGING

The result of the reversibility experiments (a 10^{-3} M CaCl_2 salt matrix at pH = 6.0 was employed for both sorption and desorption) involving soils that have been exposed to

Cd for extended time in order to examine if a stronger binding was developed is presented in Figure 6.

The loamy sand exhibited no irreversibility after 35 wk of aging and hence no development of a stronger binding of Cd as a function of time. For the sandy loam the desorption observations were located above the sorption equilibrium isotherm as was the case for the desorption experiments accomplished without aging of the soil (as presented in

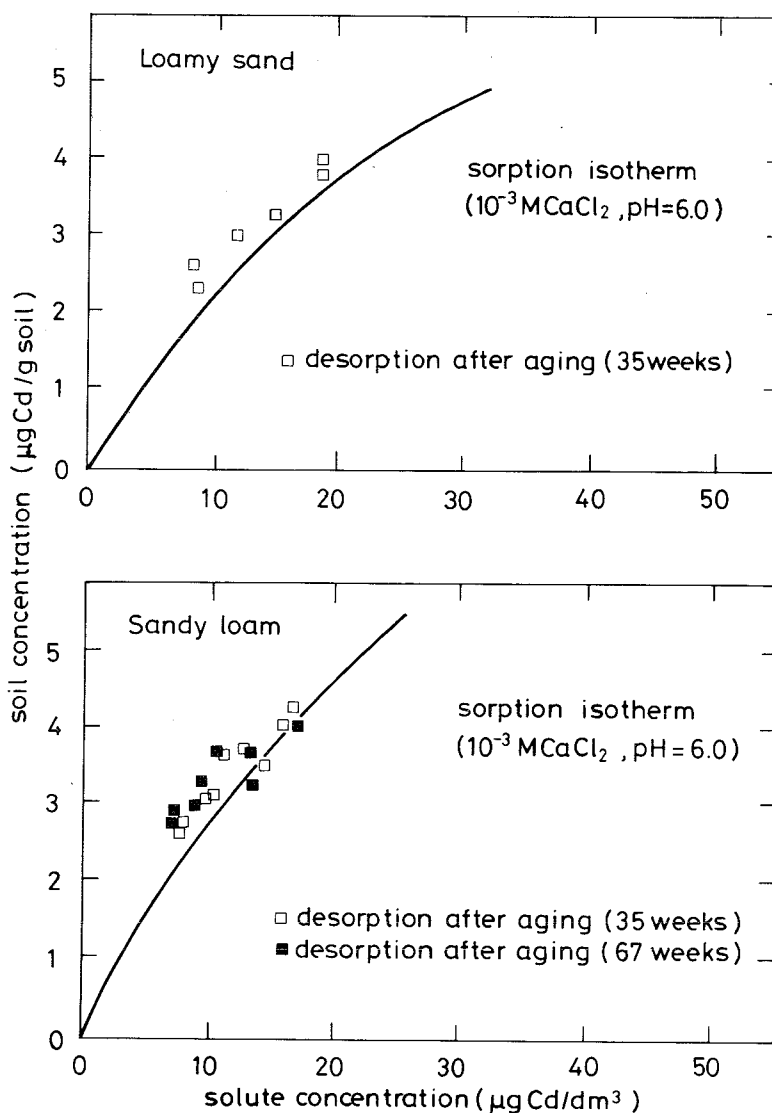


Fig. 6. Reversibility of Cd sorption in 10⁻³ M CaCl₂ at pH = 6.00 (Sorption and desorption experiments accomplished in identical salt matrix) after aging of Cd loaded soils (extended time, temperature: 1 °C) (Sorption isotherm from Christensen, 1984).

Figure 1). Comparison of desorption observations obtained with and without aging of the soil, by means of linearized Freundlich plots (confer Figure 3) show no statistically significant differences in terms of slope (z , slope = $0.71 < t(38)_{0.80} = 0.85$) or intercept (z , intercept = $0.13 < t(38)_{0.70} = 0.53$). This indicates that a stronger binding of Cd as a function of time was not developed for the sandy loam either. Figure 6 may give the impression that the partial irreversibility is not significant in case of the aged soils but comparison by means of the linearized Freundlich plot of the sorption observations (previously reported; Christensen, 1984) and the desorption observations including both 35 and 67 wk of soil aging reveals that at least for observations below $10 \mu\text{g Cd dm}^{-3}$ the observed partial irreversibility is statistically significant (the isotherms are parallel since z , slope = $0.72 < t(28)_{0.80} = 0.86$ and z , intercept = $82 > t(28)_{0.995} = 2.8$).

The aging experiments gave no evidence of the development of a stronger binding of Cd to soil as a function of time. The time span examined (35 and 67 wk) is from an environmental point of view fairly short and may be too short for a very slowly developing irreversibility to be significant. However, as long as a positive evidence for the development of a strong irreversibility of Cd soil sorption is not presented, the experimental soils must be considered to release previously sorbed Cd easily upon changes in soil solution composition independently of the time factor.

4. Conclusion

Based on desorption experiments with two soils previously exposed to low concentrations of Cd it is concluded that:

- For the loamy sand no irreversibility was observed, while the sandy loam exhibited a slight but weak irreversibility. This indicates that the experimental soils are no permanent sink for Cd.
- Increasing the soil solution concentrations of Zn, H^+ , Ca, or EDTA (as a model for organic ligands) significantly desorbed Cd from the soils.
- Aging of the soils after exposure to Cd gave no evidence of development of a stronger binding of Cd to soil, indicating that the often mentioned reversion of Cd in soil environments still lacks documentation.

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TABLE 1

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Characteristics of experimental soils

Soil parameters	loamy sand	sandy loam
Texture of <0.5 mm:		
% coarse sand (0.2-0.5 mm)	31.6	16.0
% fine sand (0.02-0.2 mm)	54.7	53.5
% silt (2-20 μm)	6.8	12.0
% clay (<2 μm)	6.2	18.0
% organic matter	0.7	0.5
pH (10^{-2} M CaCl_2)	6.0	6.5
CEC (meq. /100 g soil)	7.5	17.6
Metal content:		
Manganese (μg Mn/g soil)		
Dithionite-citrate	82	55
Hot 1:1 HNO_3 for 6 hours	74	110
Iron (μg Fe/g soil)		
Dithionite-citrate	2790	5560
Hot 1:1 HNO_3 for 6 hours	5800	15100
Zinc (μg Zn/g soil)		
Hot 1:1 HNO_3 for 6 hours	18	29
Cadmium (μg Cd/g soil)		
Hot 1:1 HNO_3 for 6 hours	0.03	0.035

Mineral composition of the clay fraction (X-ray analysis of sodium carbonate and dithionite + citrate pretreated clay fractions) of both soils is dominated by the 14-Ångström-minerals (montmorillonite, vermiculite, chlorite). Both contain some hydrous mica, kaolinite, and a little quartz, amphiboles and feldspar. The loamy sand contains relatively more chlorite and amphiboles, but less hydrous mica and interstratified vermiculite.

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