

COMPUTED EQUILIBRIUM SPECIATION OF  
CADMIUM IN SOIL SOLUTIONS OF VARYING  
ORGANIC CONTENTS, pH, AND CO<sub>2</sub> CONCENTRATION

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ABSTRACT

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## ABSTRACT

Environmental impacts of trace metals depends on both total metal concentration and its chemical form. A thermodynamic equilibrium computer model, REDEQL.EPA, has been used to study Cd speciation in a soil solution environment. CO<sub>2</sub> equilibrium concentrations were found to be important in Cd speciation. At a soil solution pH of 5 and using nitrilotriacetate (NTA) as sole organic simulator, CO<sub>2</sub> levels below 10% show almost 80% of the Cd present as Cd-NTA. If 10% CO<sub>2</sub> levels are used and several organic simulators with stability constants of log K<sub>s</sub> ≤ 6.9, 37 and < 1% of the Cd is organically bound at pH's of 5 and 6, respectively. In contrast, if 0.035% CO<sub>2</sub> is used, 48 and 58% of the Cd is organically bound at pH's of 5 and 6, respectively. At soil solution pH's > 5-6, most Cd is precipitated as CdCO<sub>3</sub>. The model is only as accurate as the thermodynamic constants and metal or ligand input concentrations. Adsorption, redox reactions, kinetics, and more precise stability constants for organic materials are several areas which need further investigation.

## INTRODUCTION

The fate of heavy metals in the environment is of particular concern due to heavy metal containing wastes from increased use of oil shale and coal for fuels and increased disposal of urban and industrial sewage wastes on land.

Cadmium, present in many sludges (Hinesly et al., 1972) and phosphatic fertilizers (Williams and David, 1973), is particularly important due to its association with deleterious effects on human health (Lewis et al., 1969 and Schroeder, et al., 1965) and other environmental impacts (Lighthart and Bond, 1976; Lighthart, et al., 1977). Lee and Keeney (1975) reported that Cd added to soil by commercial fertilizers may be as much as 2150 kg annually in Wisconsin whereas a potential of 1700 kg could be added if wastewater sludges from all sewage treatment plants in the state were applied on land. Much of the current research in heavy metals is of a survey nature (Street et al., 1977).

Movement and availability of metal ions, such as Cd, in the soil solution depend primarily on the interactions of these ions with various soil constituents and/or elements comprising the solution. In order to predict the fate of such metals applied to soils, a better understanding of the chemical reactions governing their speciation in the soil solution is required. Since measurement of many equilibrium species in soil solutions is very difficult if not impossible, this paper presents results from a model incorporating inorganic and organic components for Cd speciation in simulated soil solutions with a thermodynamic equilibrium model and discusses factors which affect speciation of this metal. The results presented represent theoretical environments for well defined

systems, which may not apply in detail to a natural environment, however they clearly illustrate the type of information that is obtainable from equilibrium models and identify factors controlling speciation.

## EQUILIBRIUM MODEL

Research on trace metals in the environment has, until recently, assessed the total concentration of metal present. It is now obvious that the form of the metal species may be more important than total concentration for assessing environmental impact, however chemical species are difficult to measure directly (Sibley and Morgan, 1975). Equilibrium models may be used to compute the concentration of different species in prescribed systems on the basis of thermodynamic (stability constant) data.

Several chemical speciating equilibria programs are available for use in freshwater systems (Truesdale and Jones, 1974; Cumme, 1973; and Morel and Morgan, 1972), seawater (Morgan and Sibley, 1975) sewage outfalls (Morel et al., 1975), and acid rain and lake acidification (Morgan, 1975). The program used here, REDEQL.EPA, is a modified version of Morel and Morgan's (1972) REDEQL.2 whose computational details are available from Ingle et al., (1977). Chemical details are available in Morgan and Sibley (1975).

The model used in REDEQL.EPA assumes a fixed temperature of 25° C. Atmospheric CO<sub>2</sub> concentrations used were either 0.035 or 10%. Hydrogen ion concentrations (pH) ranged from 3-9, and metal and ligand values are as shown in Table 1. Soil solution inorganic ion concentrations were taken from Freid and Broeshart (1967). Since REDEQL.EPA does not contain thermodynamic data for fulvic or humic acid-metal complexes, either artificial organic compounds, eg. nitrilotriacetate (NTA), or organics such as tartrate, acetate, phthalate, or amino acids (where thermodynamic data is available for Cd) were used to simulate the soluble organic-metal complexes.

After metal and ligand inputs, the model then uses the Simplex iterative optimization computation to find the equilibrium concentrations, within a specified error, of all free metals, free ligands, metal-ligand complexes, and solid precipitates.

## RESULTS

Using an equilibrium  $\text{CO}_2$  concentration of 10%, no organic compounds (case 1) and the metals and ligands as listed in Table 1, the percent Cd species distribution and the negative log of  $\text{Cd}^{++}$  is shown at different  $\text{H}^+$  concentrations in Figure 1. At pH's below 4.5, almost 60% of the Cd is present as the free ion. The remaining Cd is bound with Cl (30%) or  $\text{SO}_4^{--}$  (10%). When the solution pH reaches 4.5,  $\text{CdCO}_3$  begins formation and rapidly increases as the dominant Cd species until approximately 100% of the Cd is accounted for as  $\text{CdCO}_3$  at pH 6.0. Free ion Cd concentration decreased from  $10^{-4}$  M at pH 4.5 to  $10^{-13}$  M at pH 9.0.

If an organic compound is added to the above system, the Cd species distribution below pH 6 changes drastically, (Fig. 2, Case 2). Cadmium-nitrilotriacetate (NTA) has a stability constant of 11.9 and accounts for approximately 75% of the Cd. The remaining 25% of the Cd is either  $\text{Cd}^{++}$ ,  $\text{CdCl}_2$  or  $\text{CdSO}_4$ . Where no organic material is present (Fig. 1), approximately 60% of the Cd is present as  $\text{CdCO}_3$  at pH 5.0. In Figure 2 above pH 5.0, the percentage of Cd as  $\text{CdCO}_3$  rapidly rises to about 100% at pH 7.0. Free Cd ion concentrations are similar regardless as to whether NTA is present or not.

If all organic compounds with Cd formation constants in the program tableau are allowed to be present in the soil solution (Table 1, case 3), the importance of organic materials can readily be seen (Fig. 3).

Cadmium is almost totally present as Cd-DCTA ( $\log K = 21.6$ ) or Cd-EDTA ( $\log K = 18.2$ ). At pH's below 7, Cd-DCTA accounts for at least 90% of the Cd present with Cd-EDTA accounting for the remaining amount.

Cadmium as  $\text{CdCO}_3$  did not occur in this case. Free Cd-ion concentrations decreased from  $10^{-9}$  M at pH 7 to  $10^{-15}$  M at pH 10.0.

Since the thermodynamic constants for the Cd - NTA, -EDTA, or -DCTA are thought to be unrealistically high (See Stevenson, 1976) ( $\log K > 11$ ), these synthetic chelates were deleted and Cd speciation was determined on all remaining organic compounds (Fig. 4, case 4). Since Figure 4 looks strikingly similar to Figure 2, it must be surmised that the thermodynamic constants for picolinate ( $\log K = 5.1$  for a 1:1 metal-organic and  $\log K = 9.0$  for a 1:2 metal organic complex), the predominate Cd-organic species, are sufficiently high to complex a relatively large percentage of the Cd at pH's less than 5.5. At pH 5, Cd-picolinate accounts for approximately 75% of the Cd with the remaining 25% divided between  $\text{Cd}^{++}$  (7%),  $\text{Cl}^-$  (6%), tartrate (5%), phthalate (4%), and  $\text{SO}_4^{=}$  (3%). Above pH 5.5, the relative amount of Cd as Cd-picolinate decreases quickly while  $\text{CdCO}_3$  becomes the dominant Cd species.

In order to determine the effects of pH on the various Cd complexes over a wide range of stability constants, organic Cd complexes with a maximum  $\log K$  of 6.9 (regardless of stoichiometry) were used to compute the Cd distribution in Figure 5, (Table 1, case 5). It is obvious from the Cd distribution that the phthalate is not binding as much Cd as organic species with higher stability constants. At pH 5.0 phthalate is bound with approximately 28% of the Cd with the remainder of the Cd as  $\text{Cd}^{++}$  (26%),  $\text{CO}_3^{=}$  (18%),  $\text{Cl}^-$  (16%), acetate (9%),  $\text{SO}_4^{=}$  (3%). Cadmium

begins to bind with carbonate at pH 4.5 and increases to approximately 100% at pH 6.0. The absolute  $\text{Cd}^{++}$  present in this equilibrium solution decreases from  $10^{-4}$  M at pH 3 to  $10^{-13}$  M at pH 9.0.

To ascertain the effects of  $\text{CO}_2$  concentrations on Cd speciation, the same conditions were used as in Figure 5 (case 5) except with a 0.03% atmospheric  $\text{CO}_2$  level (Fig. 6, case 6). As in Figure 5, only organic-Cd complexes were used having stability constants ( $\log K$ ) less than 6.9. At this lower  $\text{CO}_2$  level, little difference from Figure 5 is noted for Cd speciation with the inorganics ( $\text{Cl}^-$  and  $\text{SO}_4^{--}$ ) but the percentage Cd bound with the organics increases. At pH 5.0, approximately 35% of the Cd is bound with phthalate and 13% Cd occurs as acetate. The organic bound Cd increases to a maximum of 43% (phthalate) and 15% (acetate) at pH 6.0. At a  $\text{CO}_2$  equilibrium level of 0.03%, a total of 48% Cd is organically bound at pH 5 and 58% is bound at pH 6, while a  $\text{CO}_2$  equilibrium level of 10% (Fig. 5) gives a maximum of 37% organically bound Cd at pH 5 and less than 1% Cd organically bound at pH 6. Cadmium carbonate does not begin to form until pH 6 at the lower  $\text{CO}_2$  levels. It is also interesting to note that the Cd free ion concentration is approximately  $1\frac{1}{2}$  orders of magnitude greater at the lower  $\text{CO}_2$  concentrations for a pH of 7 and above.

#### DISCUSSION

The REDEQL.EPA equilibrium model can be successfully employed to calculate Cd speciation in complicated soil solution systems. We have shown in this paper that  $\text{CO}_2$  equilibrium concentrations could be very important in determining Cd speciation (Fig. 7). At a soil solution pH of 5 and using only NTA as an organic simulator source,  $\text{CO}_2$  levels below



approximately 10% show almost 80% of the Cd present as Cd-NTA. Obviously at higher pH's, smaller amounts of Cd would be organically bound, with  $\text{CO}_3^{=}$  complexation becoming increasingly important.

The thermodynamic values for Cd and naturally occurring organic matter (fulvic acids) while not presently in the program can be approximated by using a wide variety of organic materials for which the Cd stability constant is known. The importance of accurately knowing the Cd-organic log K constant is obvious from the large differences we obtained in Cd-speciation when a wide range of stability constants were used. Figure 8 shows  $\text{Cd}^{++}$  concentrations under the various calculated cases. Thus if the ionic species of Cd is considered to be the most harmful or toxic (to animals or microorganisms) form of Cd, then we can expect increasing toxic action at higher concentrations for lower soil solution pH's and with organic compounds of lower log K constants for Cd.

Several deficiencies occur in REDEQL.EPA. The equilibrium model is only as accurate as the thermodynamic constants and the concentration values used for metals and ligands. It is quite possible that an improved (more accurate) or expanded thermodynamic base will produce different answers. Stability constants for important complexes or solids may not be available. The assumption of an isothermal condition (25° C.) will produce errors of an unknown magnitude.

Since the soil solution is in a constant state of flux due to many variables of drying and wetting, microbial and plant root activity, and man made additives; the speciation, precipitation, or dissolution reactions may be too slow to reach an equilibrium in practical time intervals.

An adsorption model for aqueous metals with oxide surfaces and reduction-oxidation reactions are presently in the REDEQL.EPA program. Adsorption and redox were not used in the present study due to the highly complex nature of these models. Work is now being conducted on incorporation of redox and adsorption into the soil solution equilibrium.

Despite the above limitations, equilibrium models can be used to provide a first approximation of element speciation. The model allows us to analyze many elements under natural conditions and to investigate different chemical parameters and interaction between different processes on metal speciation.

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## REFERENCES

- Cumme, G.A. 1973 Calculation of chemical equilibrium concentrations of complexing ligands and metals: A flexible computer program taking into account uncertainty in formation constants. *Talanta* 20:1009-
- Fried, W. and H. Bruoeshart, 1967. The Soil-Plant System. Academic Press, New York. 156-158.
- Hinesly, T.D., R.L. Jones, and E.L. Ziegler. 1972. Effects of corn by applications of heated anaerobically digested sludge. *Compost Sci.* 13:26-30.
- Ingle, S.E., M. Schuldt, and D.W. Schults, 1977. A user's guide for REDEQL.EPA - A computer program for chemical equilibria in aqueous systems. Marine and Freshwater Ecology Branch, Corvallis Environmental Res. Lab., Corvallis, Oregon.
- Lee, K.W. and D.R. Keeney. 1975. Cadmium and zinc additions to Wisconsin soils by commercial fertilizers and wastewater sludge application, In: Water, Air, and Soil Pollution, 5 (1975):109-112.
- Lewis, G.O., H. Lyle, and S. Miller. 1969. Association between elevated heptic water-soluble protein-bound cadmium levels and chronic bronchites and/or emphysema, *Lancet* II:1330-1333.
- Lighthart, B., and H. Bond. 1976. Design and preliminary results from soil/litter microcosms, *Inteen. J. Environmental Studies.* 10:51-58.
- Lighthart, B., H. Bond, and B.G. Volk. 1977. The use of soil/litter microcosms with and without added pollutants to study certain components of the decomposer community. *Proc. of Collogua on Terrestrial Microcosms and Environmental Chemistry.* James M. Witt and J.W. Gillett editors. National Sci. Foundation. (in press)
- McDuff, R.E. and F.M.M. Morel. 1973. Description and use of chemical equilibrium program REDEQL.2. Tech. Rep. EQ-73-02. W.M. Keck Laboratory of Environmental Engineering Science, California Institute of Technology.
- Morel, F.M.M., and J.J. Morgan. 1972. A numerical method for computing equilibria in aguneous chemical systems. *Environ. Sci. Technol.* 6:58-67.
- Morel, F.M.M., J.C. Westall, C.R. O'Melia, and J.J. Morgan. 1975. Fate of trace metals in Los Angeles County wastewater discharge. *Environ. Sci. Technol.* 9:756-61.

Morgan, J.J. 1975. Potential chemical effects of atmospheric inputs to lakes. Presented at International Assoc. for Great Lakes Research Specialty Symposium, Geneva Park, Ontario, CANADA. October 1975.

Morgan, J.J., and T.H. Sibley. 1975. Chemical models for metals in coastal environments. Presented at Amer. Soc. Civil Engrs. Conference on Ocean Engineering, April 1975, at U. of Delaware, Newark, Delaware.

Schroeder, H.A. 1965. Cadmium as a factor in hypertension, J. Chron, Dis. 18:647-656.

Sibley, T.H. and J.J. Morgan. 1975. Equilibrium speciation of trace metals, In: Symposium Proceeding-International Conference on Heavy Metals in the Environment, V.1. Toronto, Ontario, CANADA, 319-338.

Stevenson, F.J. 1976. Stability constants of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$  complexes with humic acids. Soil Sci. Soc. Am. J. V.40:665-672.

Street, Jimmy J., W.L. Lindsay, and B.R. Sabey. 1977. Solubility and plant uptake of cadmium in soils amended with cadmium and sewage sludge. J. Environ. Qual., 6. No. 1:72-77.

Truesdale, A.H., and F.F. Jones. 1974. WATEQ, A computer program for calculating chemical equilibria of natural water. J. Research U.S. Geol. Survey 2:233-48.

Williams, C.H. and D.J. David. 1973. The effect of superphosphate on the cadmium content of soils and plants. Aust. J. Soil Res. 11:43-

TABLE 1: Tabulation of metal ligand concentrations (negative logarithm) used in the simulated soil solution for various cases calculated by REDEQL.EPA.

In All Cases

METALS  $Cd^{+2}$  3.87,  $Ca^{+2}$  1.70,  $Mg^{+2}$  1.70,  $K^{+1}$  3.00,  $Na^{+1}$  3.00,  $Fe^{+3}$  6.00,  $Al^{+3}$  6.00

LIGANDS  $CO_3^{-1}$  -2.00,  $SO_4^{-2}$  2.00,  $Cl^{-2}$  2.00,  $PO_4^{-3}$  6.00,  $NO_3^{-1}$  3.00

	CASES					
	1	2	3	4	5	6
acetate, acetylacetone, oxalate, salicylate, sulfosalicylate, phthalate.	-	-	2.97	2.97	2.30	2.30
tartrate, glycine, glutamate, arginine, ornithine, lysine, aspartate, alanine, methionine, valine, isoleucine, leucine, proline, picolinate.	-	-	2.97	2.97	-	-
nitrilotriacetate (NTA)	-	3.87	2.97	-	-	-
ethylenediaminetetracetate (EDTA), diaminocyclohexane-tetraacetate (DCTA)	-	-	2.97	-	-	-
atmospheric CO <sub>2</sub> (%)	10	10	10	10	10	.035

\*Each ligand was present at the given concentration.

## LIST OF FIGURES

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- Figure 7 Effects of CO<sub>2</sub> concentration on the Cd distribution in a simulated soil solution at pH 5.0 containing NTA.
- Figure 8 Free Cd-ion concentrations in a simulated soil solution containing the indicated organic compounds at 3% concentration.

Fig. 1. Cadmium speciation at indicated H-ion concentrations, atmospheric CO<sub>2</sub>, and organics.

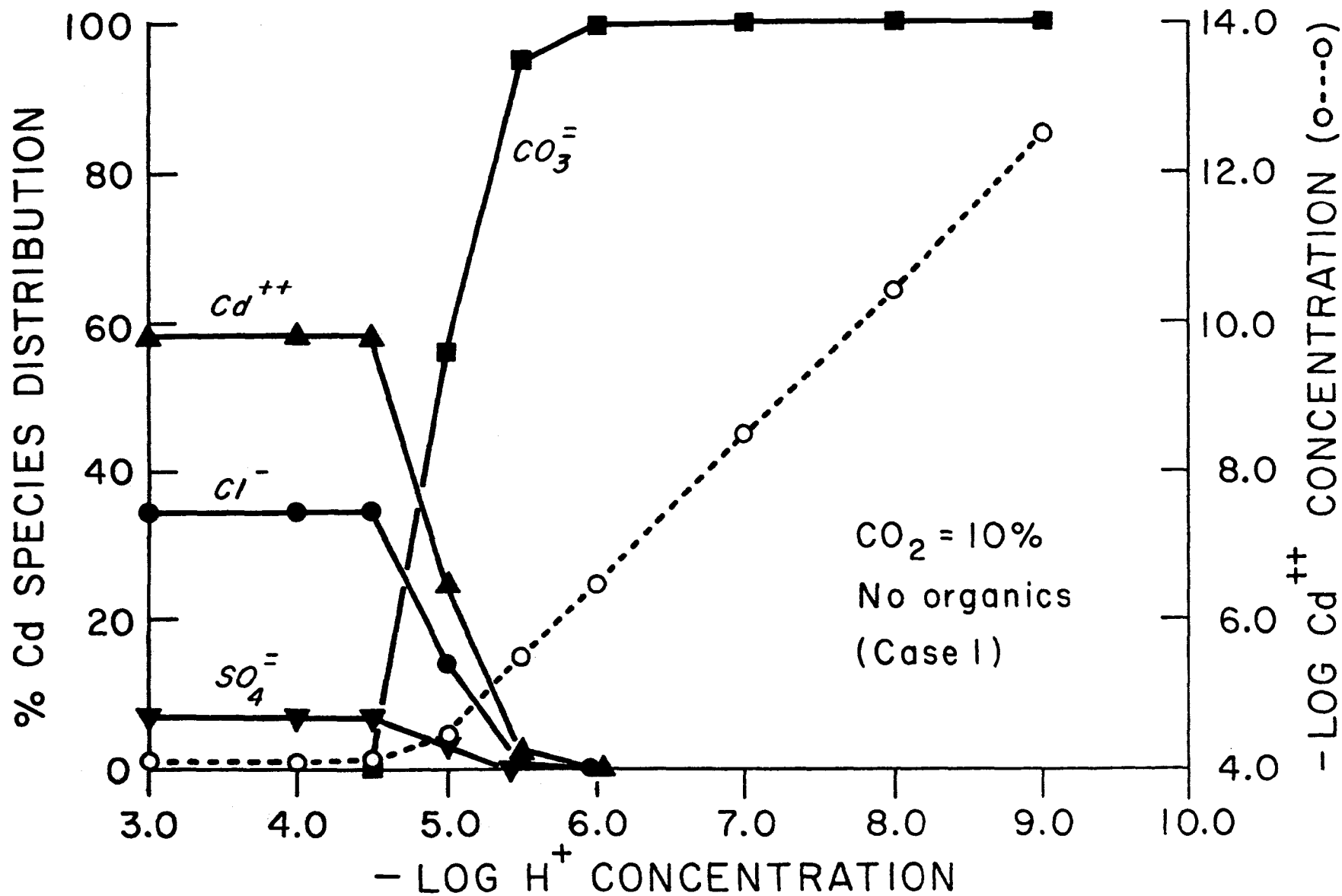


Fig. 2. Cadmium speciation at indicated H-ion concentrations, atmospheric CO<sub>2</sub>, and organics.

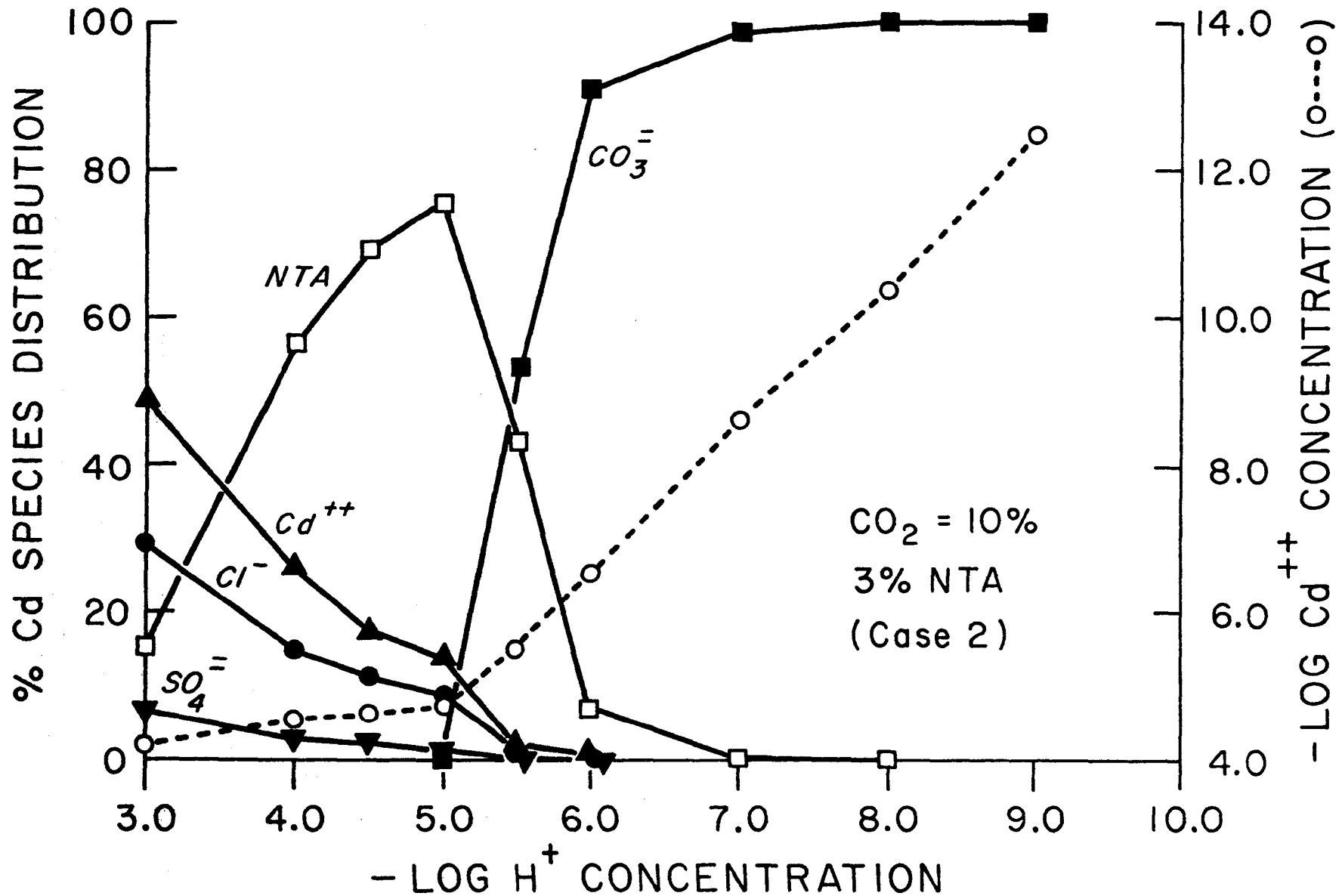




Fig. 3. Cadmium speciation at indicated H-ion concentrations, atmospheric CO<sub>2</sub>, and organics.

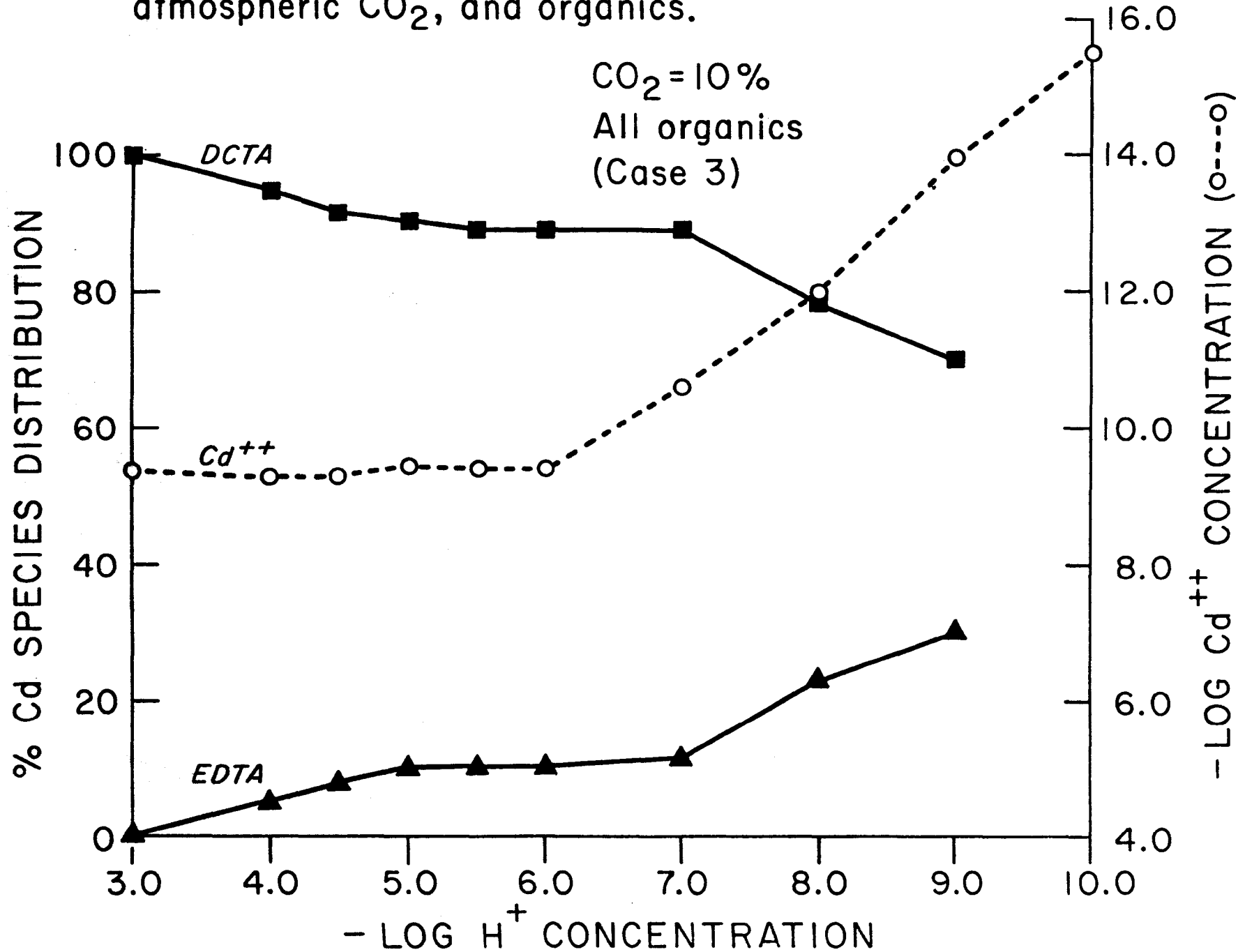


Fig. 4. Cadmium speciation at indicated H-ion concentration, atmospheric CO<sub>2</sub>, and organics.

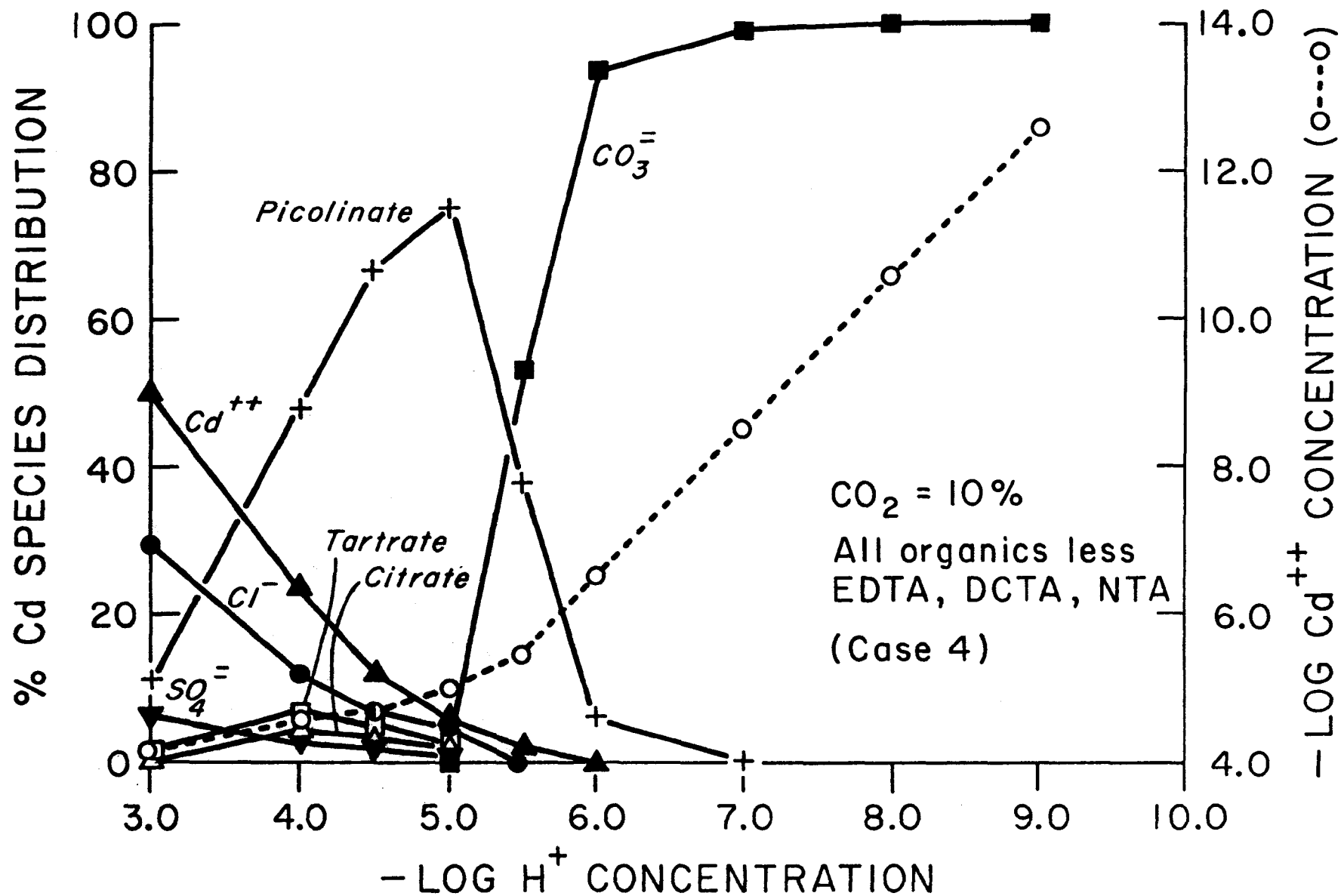


Fig. 5. Cadmium speciation at indicated H-ion concentrations, atmospheric CO<sub>2</sub>, and organics.

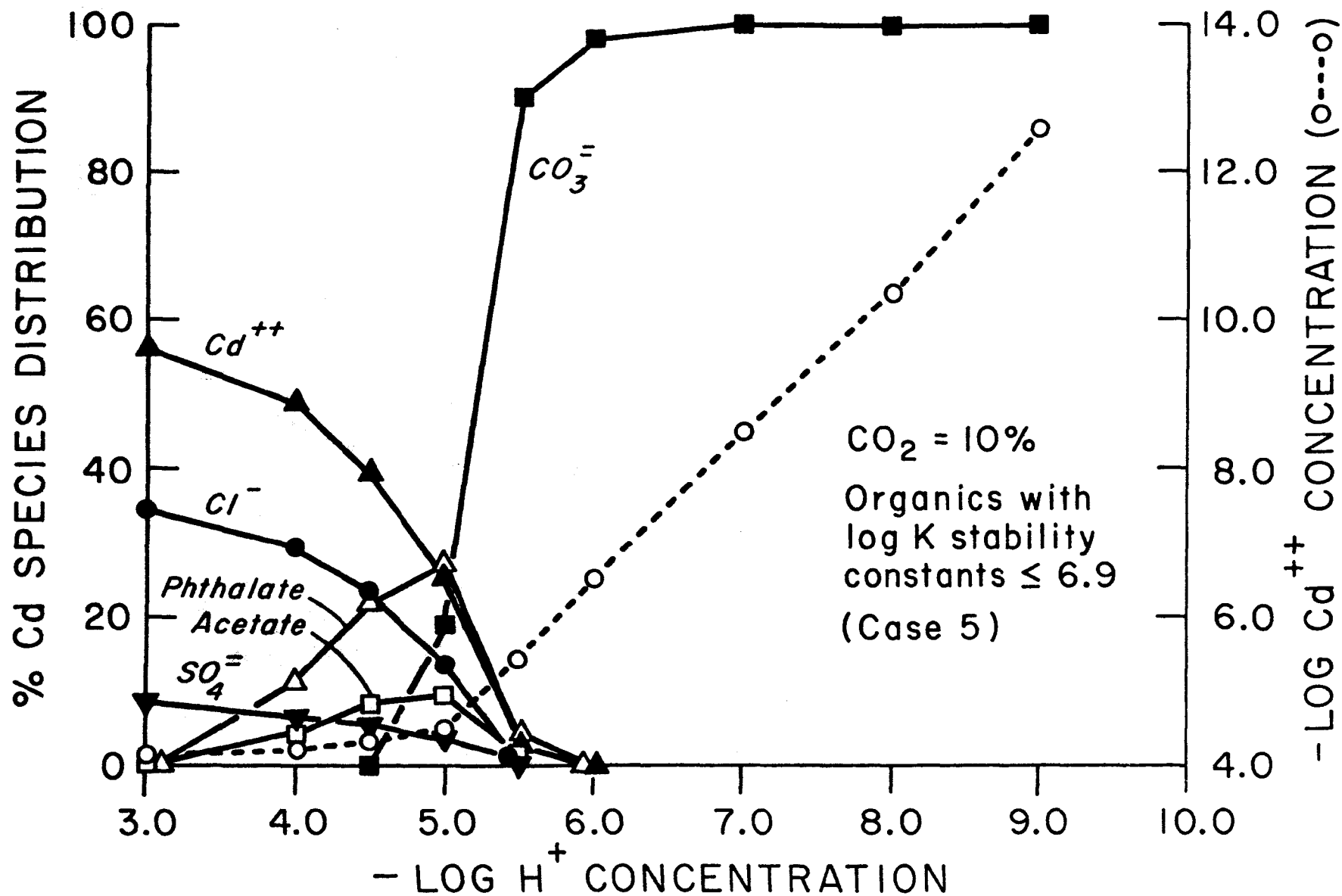
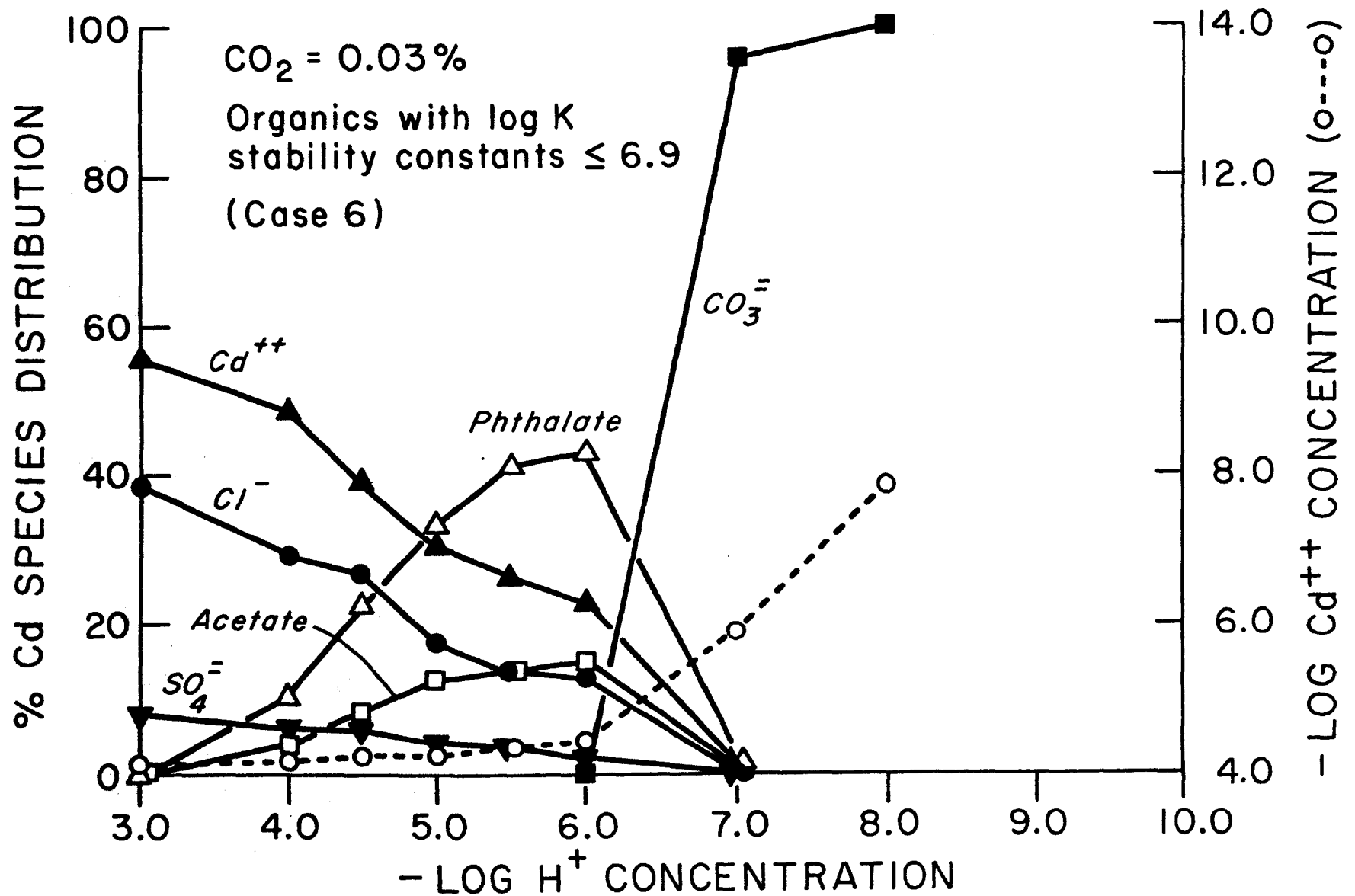


Fig. 6. Cadmium speciation at indicated H-ion concentrations, atmospheric CO<sub>2</sub>, and organics.



ig. 7. Effects of CO<sub>2</sub> concentration on the Cd distribution in a simulated soil solution at pH 5.0 containing NTA.

