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AN EXPERIMENTAL STUDY OF CADMIUM ION EXCHANGEABILITY*

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Abstract—A laboratory study of cadmium exchangeability revealed large differences in extractable cadmium which are dependent on the exchange solution being utilized. The standard exchange solutions employed in this study were: N $NaNO_3$, N NaOAc, N NH_4OAc, $NCaCl_2$, and 2N $CaCl_2$, in order of increasing Cd removal. An interpretation of the chemical behavior of Cd and an experiment with mixed sodium nitrate and acetate solutions suggest that cadmium carbonate, octavite, was precipitated when the sediments were saturated with Cd prior to the exchange experiments and that the quantities of Cd recovered in the acetate solutions were erroneously high because of the dissolution of the carbonate material. Dissolution of solid phases, the lack of pH buffering, and the possible formation of a complex hydroxyl chloride salt also made the Cd values obtained with the chloride solutions too high. Sodium nitrate exchange solutions minimize these problems and are thought to best represent the exchangeable cadmium in the sediment.

Key Words—Adsorption, Cadmium, Exchange, Ion, Sedimentary.

INTRODUCTION

Ion exchange is one of the important processes which control the distribution of major and trace elements among aqueous solutions and particulate phases. In water softening, for example, undesirable cations in solution are allowed to exchange with other cations adsorbed on an ion exchanger and thereby modify the chemical composition of the salts in the water. There are also many agricultural, chemical, and engineering processes which utilize this type of chemical reaction. Ion exchange, usually cation exchange, also has been suggested as one of the most important ways to modify the chemistry of sediments during halmyrolysis and diagenesis.

Adsorption and ion exchange have been of interest recently to those studying trace metals in sediments and an attempt has been made to evaluate the importance of the process in regulating the availability of trace metal pollutants in the hydrosphere. Adsorption by various substances such as hydrous manganese and iron oxides, apatite, clay, and organic debris was reported to be one of the most important mechanisms which, with precipitation as a sulfide or concentration by organisms, was responsible for the low concentrations of trace metals in seawater (Krauskopf, 1956). Kopp and Kroner (1973) suggested that cadmium, like zinc, was absorbed by hydrolyzate sediments or precipitated as a carbonate in the rivers and lakes of the United States. Adsorption on clays in soils also played a significant role in cadmium fixation in the experimental studies by John (1971). The surface soils studied were retaining 98.7%, 98.0% and 88.2% of the cadmium from solutions which contained 5, 10, and 100 ppm of the element, respectively. Clayey soils were also reported by Langerwerff and Brower (1972) to be capable of adsorbing significant amounts of cadmium. On the other hand, Förstner and Müller (1974) found that less than 10% of the cadmium in the Rhine River sediments was exchangeable. The bulk of trace metals in the Amazon and Yukon rivers was reported by Gibbs (1973) to be within crystalline silicate minerals (detrital) or co-precipitated with hydroxides, and ion exchange was not a very important process.

This paper reports an attempt to examine the influence of ion exchange extraction techniques on the exchangeability of cadmium. Previous accounts of adsorbed or exchangeable cadmium have overestimated its importance because standard methods using ammonium acetate were usually employed. The standard methods do not compensate for the considerable interaction between cadmium and a complexing ion such as acetate.

MATERIALS AND METHODS

The material used to study cadmium exchangeability was a sample of bulk bottom sediment collected from a small lake in the backmarsh area of Caminada Bay on the coast of Louisiana. The sample is typical of the clay-rich material found in the area and it contains more than 50% clay-sized material, approximately 8% organic carbon and plant debris, and the remainder is predominantly quartz. X-ray diffractograms of the clay fraction revealed the presence of poorly crystallized smectite, illite, kaolinite, and chlorite. Approximately 200 g of the sediment was freeze-dried, gently pulverized, and homogenized for use in the experiments.

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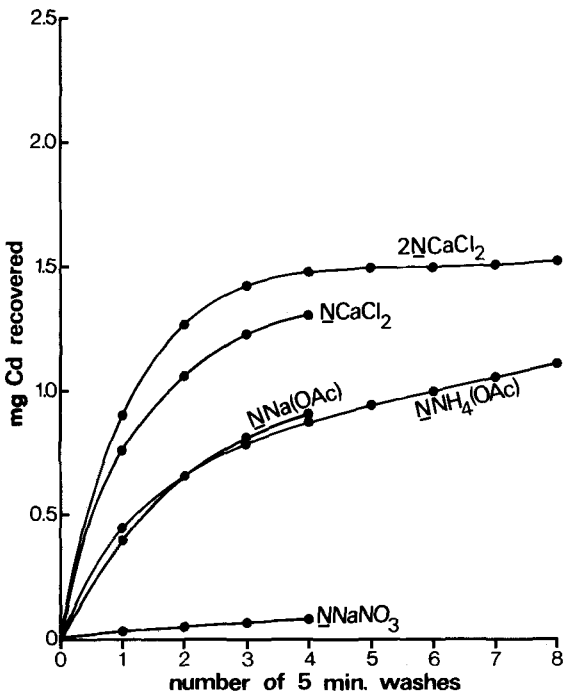


Fig. 1. Variation in the cumulative amount of exchangeable cadmium recovered by successive treatments with the ion exchange solutions indicated.

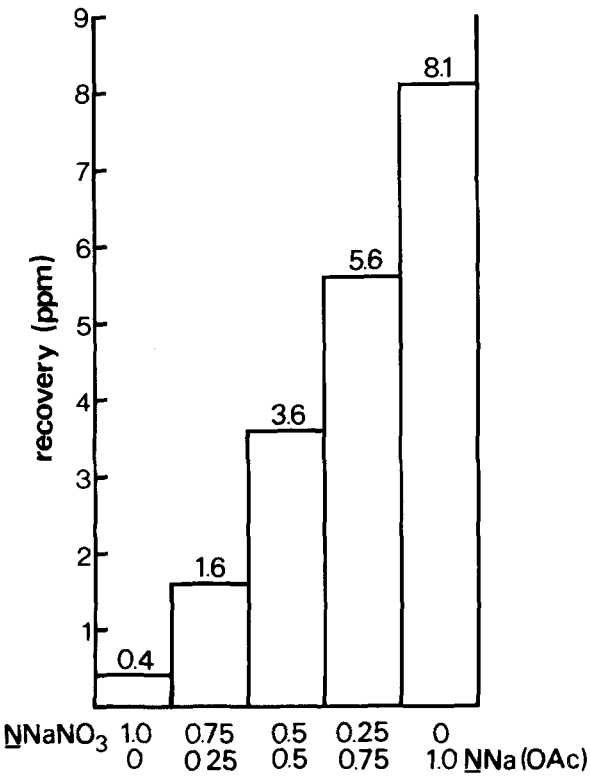


Fig. 2. Amount of exchangeable cadmium recovered with graded mixtures of sodium nitrate and sodium acetate.

Samples of the freeze-dried sediment were saturated with cadmium by overnight reaction with 50 ml of a 50 ppm Cd solution for each 2 grams of sediment. The Cd-clays were then centrifuged and the sediment residues subjected to repeated 5-minute washes with the cation exchange solutions identified below. The cadmium recovered in each wash solution was measured by atomic absorption techniques immediately after extraction.

The results of these treatments for each exchange solution are plotted as the cumulative amount of cadmium recovered versus the number of extractions (Figure 1). The solutions used were N NH_4OAc, N NaOAc, N $NaNO_3$, N $CaCl_2$, and 2 N $CaCl_2$ and the slurries formed with them had an initially neutral pH. Each value reported in Figure 1 is the average of four replications.

RESULTS

Inspection of Figure 1 reveals large differences in the cumulative quantity of cadmium recovered with each exchange solution. There are also large differences in the quantity removed between successive washes. In the first wash, the calcium chloride solutions removed almost twice as much cadmium as the sodium and ammonium acetate solutions. After eight washes the sodium nitrate had removed only a fraction of the amount removed by the acetate solutions. Cumulatively, the 2 N $CaCl_2$ extractant solution recovered approximately 11% more cadmium than the N $CaCl_2$ solution.

The slope of the curves differs significantly (Figure 1). The solutions containing the divalent calcium cations appear to reach a plateau most rapidly. However, additional Cd is being recovered by each subsequent extraction. After three washes, the bulk of the $CaCl_2$-extractable Cd has been removed, while the acetate solutions continued to extract relatively large amounts of the element even after eight washings. Sodium nitrate was the least effective in recovering cadmium and the differences between successive washes were so small that the reaction was assumed to be nearly complete after four washes. A slow reaction rate was ruled out because other experiments showed that there was no increase in recoverable cadmium even after 24 hours of contact with the sodium nitrate solution. In all cases, the cumulative amount of cadmium recovered by the repeated washes was less than 60% of the amount initially added. In other words, cadmium has been "fixed" in a nonexchangeable form by reactions occurring in these experiments.

DISCUSSION

Ion exchange is a surface chemical phenomenon which is influenced by a considerable number of variables. The distribution of ions in the exchange solution and the exchanger is modified by specific characteristics of the ions involved, the sediment to water ratios,

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the characteristics of the exchange substrate, and other factors discussed in detail by Wiklander (1964). It is difficult to express ion exchange equilibria in a strict thermodynamic sense.

In practice, most of the difficulties associated with the interpretation of ion exchange reactions with clay minerals are sidestepped by employing a standard procedure. Exchangeable alkali and alkaline earth elements and cation exchange capacity are functionally defined by the quantities of the element exchanged by a N NH_4(OAc) solution buffered at pH 7, or 8.2, and at a fixed solid to solution ratio.

If ammonium acetate is replaced by other extractant solutions, results similar to those illustrated in Figure 1 are to be expected, but the differences are seldom so great. The large differences in recoverable Cd and the tendency of the extracted Cd, in most cases, to continue to increase with additional washings suggest that processes other than simple cation exchange are involved.

Precipitation of a solid mineral form of Cd during the initial saturation phase of the experiment and subsequent dissolution in the exchange solutions is one possible way to produce results similar to those observed. Octavite, cadmium carbonate, is the most likely phase to be precipitated within this system under oxidizing conditions and a pH near 7. The presence of octavite would also help explain some of the differences illustrated in Figure 1 because the acetate ion has been reported to dissolve carbonates and affect ion exchange measurements in sediments and soils which contain calcite and other carbonates (Jackson, 1969). This assumption and the possible role of colloids in the supernatant solutions on the amount of exchangeable cadmium could not be verified because it was not possible to confirm by direct measurements the presence of such small quantities of the mineral or colloids.

In one experiment we were able to demonstrate that the amount of extracted Cd increased in proportion to the fraction of sodium acetate in a mixed sodium nitrate-sodium acetate solution. Ten Cd-saturated clay samples were prepared as previously outlined, and then subjected to a 5-minute wash with either N $NaNO_3$, N NaOAc, or their mixtures. Two were washed with a neutral solution containing 100% $NaNO_3$ and two others were extracted with a 100% NaOAc solution. The remaining samples were treated in pairs with 25:75, 50:50, and 75:25 mixtures of N NaOAc and N $NaNO_3$, respectively.

The results of the mixed solution experiment are illustrated in Figure 2. The presence of the complexing acetate ion, $C_2H_3O_2^-$, greatly increases the amount of Cd recovered in almost direct proportion to the concentration of the complexing ion. Note that in all cases, the intended exchange ion, Na^+, was at a 1 N concentration and that the initial sediment-cadmium systems probably contained $CaCO_3$, octavite. The differing extraction efficiencies of the sodium nitrate, sodium acetate, and ammonium acetate solutions are assumed to be due in large part to the dissolution of the $CaCO_3$ thought to be present and the resulting formation of the aqueous cadmium complex, $Cd(C_2H_3O_2)^+$. The cadmium-ligand aqueous stability constants for nitrate and acetate increase in the same order as the amount of Cd recovered (Figure 1). The respective constants are $10^{-0.6}$ and $10^{1.7}$ (Sillen and Martell, 1964).

The reactions involved in the $CaCl_2$ extractions are more difficult to explain. The divalent calcium ion should produce more exchangeable Cd than the solutions containing the univalent cations. The interaction of the chloride ion and the possible forms of solid cadmium cannot be evaluated clearly because of the scarcity of solubility data. The higher recovery with $CaCl_2$ could be related to changes in pH because the chloride solutions are not as well buffered as the acetate and nitrate ones.

CONCLUSIONS

When sediments are treated in the laboratory with very dilute cadmium solutions almost all of the element can be removed from solution. Attempts to determine the fraction of the "fixed" cadmium that is exchangeable are strongly influenced by the extractant solution utilized. There is a strong suggestion that anion complexing and its effect on the solubility of solid phases, such as cadmium carbonate (octavite) is more dominant than cation exchange in determining the amount of Cd released. Values for exchangeable cadmium reported in the literature could include a significant quantity of aqueous $Cd(C_2H_3O_2)^+$ which might produce an incorrect evaluation of the ion exchange process in controlling the distribution of cadmium.

Cation exchange solutions utilizing sodium nitrate should be considered for use in the determination of the exchangeability of Cd and similar trace metals. Sodium nitrate has produced results which we think are more indicative of cation exchange, particularly when a sparsely soluble solid phase such as octavite is suspected to be present. The values obtained with sodium nitrate are considerably lower than the exchangeable Cd extracted with acetate and chloride solutions and are more like the quantities reported by Förstner and Müller (1974) with a similar noncomplexing solution.

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REFERENCES

Engler, R. M. Brannon, J. M., Rose, J. R. and Bigham, G. N. (1974) A practical selective extraction procedure for sediment characterization. Symposium on Chemistry of Marine Sediments, ACS Nat. Mtg., Atlantic City, N.J.

Förstner, U. and Müller, G. (1974) *Schwermetalle in Flussen und Seen*: Springer Verlag, Heidelburg, 225 pp.

Gibbs, R. J. (1973) Mechanisms of trace metal transport in rivers. *Science* **180,** 71–73.

Jackson, M. L. (1969) *Soil Chemical Analysis:* University of Wisconsin, Madison, Wis., 895 pp.

John, M. K. (1971) Influence of soil characteristics on adsorption and disorption of cadmium. *Environ. Lett.* **2,** 173–179.

Kopp, J. F. and Kroner, R. C. (1973) Trace metals in waters of the United States: A five-year summary of trace metals in rivers and lakes of the United States (October 1, 1962–September 30, 1967). U.S. Dept. Inter. Fed. Water. Pollut. Control Adm., Div. Pollut. Surv., Cincinnati, Ohio, 75 pp.

Krauskopf, K. B. (1956) Factors controlling the concentrations of thirteen rare metals in sea water. *Geochim. Cosmochim. Acta* **9,** 1–32.

Langerwerff, J. V. and Brower, D. L. (1972) Exchange adsorption of trace quantities of cadmium in soils treated with chlorides of aluminum, calcium and sodium. *Soil Sci. Soc. Am. Proc.* **36,** 734–737.

Perhac, R. M. (1973) Sorption and extraction of cadmium from natural materials. Abstracts with Proceedings, GSA 1972 mtg., GAAPBC 5(7), 776.

Sillen, L. G. and Martell, A. E. (1964) *Stability Constants of Metal-Ion Complexes*: Spec. Publ. No. 17, London, The Chemical Society, Burlington House, W.I. 223 pp.

Wiklander, L. (1964) Cation and anion exchange phenomena. In *Chemistry of the Soil* (Edited by Bean, F. A.), Chapter 4. American Chemical Society Monograph, pp. 163–205.

Резюме- Лабораторное изучение обменной способности кадмия обнаружило большие различия в экстрагируемых количествах кадмия,что зависит от раствора, применяемого при обмене.Стандартными обменными растворами,которые использовались при этих исследованиях,были:N.$NaNO_3$,N.NaOAc,N.NH_4OAc,N.$CaCl_2$,и 2N. $CaCl_2$,чтобы увеличить отщепление кадмия.Интерпретация химического поведения Cd и опыт со смешанными растворами азотно-натривой соли и ацетата показали, что карбонат кадмия,октавит,осаждался,в то время как отложения были насыщены кадмием еще до экспериментов обмена и что количество Cd,обнаруженное в ацетатном растворе,было завышено в результате растворения карбонатного материала.Растворение твердых фаз,недостаточное буферное действие pH и возможное образование гидроксильной хлоридной соли также вызывают слишком высокое извлечение Cd.Обменные растворы азотно-натриевой соли сводят к минимуму эти проблемы и,предполагается,правильно определяют обменное количество кадмия в отложениях.

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