

ADSORPTION OF ARSENATE BY SOILS AND ITS RELATION TO SELECTED CHEMICAL PROPERTIES AND ANIONS¹

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ABSTRACT

We studied the retention of arsenate by four soils of Saskatchewan, Canada, and its relation to selected soil properties and anionic environments. The data indicate that As retention by the soils at the dilute As concentration range studied does not proceed through the precipitation of sparingly soluble arsenate compounds. Arsenate retention evidently proceeds through adsorption mechanisms. The adsorption maxima of the soils are not related to acidity and the contents of inorganic C, but are linearly related to amounts of ammonium oxalate-extractable Al and, to a lesser extent, to the contents of clay and ammonium oxalate-extractable Fe. Chloride, nitrate, and sulfate present at concentrations usually present in saline soils have little effect on the adsorption of As. Phosphate substantially suppresses As adsorption by the soils, and the extent of the suppression varies from soil to soil.

INTRODUCTION

Arsenic is a toxic and ubiquitous element in nature. Not only is it commonly present in rocks, minerals, soils, sediments, and waters, but it is also nearly always present in vegetation, atmospheric dusts, the tissues of mammals, fish, and crustaceans, and bread and milk (Rankama and Sahama 1950; Kingsley and Schaffert 1951; National Research Council of Canada 1978; Huang and Liaw 1978). Scientific evidence supports the view that arsenic is carcinogenic and that chronic arsenosis can result from low intake levels (Fishbein 1972; Penrose 1974).

Arsenic may accumulate in soils through the use of arsenical pesticides, application of fertilizers, irrigation, oxidation of volatile arsines in air, dust from the burning of fossil fuels, and disposal of industrial, municipal, and animal wastes (Sandberg and Allen 1975). Promotion of fertilizer application and irrigation farming practices and the use of land for waste disposal would

thus enhance the As inputs to soil environments. In view of the chemistry of soil As (Huang 1975; Walsh and Keeney 1975), the suitability of lands for waste disposal would highly depend on their abilities to retain pollutants, preventing them from entering the food chain through plant uptake and leaching to surface runoff and groundwater. Consequently, knowledge of the effects of soil properties and ionic environments on the chemistry of As retention in soils is urgently needed in planning waste disposal and land management.

The present work was initiated to examine precipitation or adsorption as the mechanism of the arsenate retention by the soils at As concentrations commonly encountered in contaminated soil solution and its relation to selected soil properties and anionic environments.

MATERIALS AND METHODS

Characteristics of soils

Four surface soils (Ap horizon) used in this study were obtained from Saskatchewan, Canada. The general descriptions of the soils are given by Moss (1965).

The pH values of soil pastes were measured with a Metrohm E436 potentiograph. The or-

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TABLE 1
 General properties of the soils

Soil	Clay minerals ^a	pH ^b	Fine clay, <0.2 μm	Coarse clay, 0.2-2 μm	Oxalate-extractable				
					Inorganic C	Organic C	Al	Fe ppm	
									Si

TABLE 1
General properties of the soils

Soil	Clay minerals ^a	pH ^b	Fine clay, <0.2 μ m	Coarse clay, 0.2-2 μ m %	Organic C	Inorganic C	Oxalate-extractable		
							Al	Fe ppm	Si
Orthic Dark Gray Carrot River	Coarse clay: ^c Qr, Vr, Mt + Nt, Mi, Kl + Hl, Fl Fine clay: Mt + Nt, Vr, Qr	7.0	0.3	7.7	2.96	nd ^d	540	910	150
Orthic Black Melfort	Coarse clay: Mi, Qr, Kl + Hl, Vr, Chl, Mt + Nt Fine clay: Mt + Nt, Mi, Vr, Kl + Hl, Chl	7.0	26.3	15.9	4.98	nd	1110	3790	560
Orthic Black Oxbow	Coarse clay: Qr, Mi, Fl, Chl, Kl + Hl, Mt + Nt, Vr Fine clay: Mt + Nt, Mi, Vr, Chl, Kl + Hl	7.5	13.9	9.9	2.03	0.34	680	1510	350
Low Humic Eluviated Gleysol Oxbow	Coarse clay: Mi, Qr, Fl, Chl, Mt + Nt, Kl + Hl, Vr Fine clay: Mt + Nt, Mi, Vr, Chl, Kl + Hl	5.9	6.6	8.3	2.49	nd	710	2640	170

^a Chl = chlorite; Fl = feldspar; Kl + Hl = kaolinite + halloysite; Mi = mica; Mt + Nt = montmorillonite + nontronite; Qr = quartz; Vr = vermiculite.

^b Soil: water paste.

^c Listed in decreasing order of abundance.

^d nd = not detectable.

ganic C of the soils was measured by determining total C (by dry combustion) and correcting for carbonates (Treadwell and Hall 1924). Inorganic C was determined by decomposing carbonates with dilute hydrochloric acid under reduced pressure in the presence of stannous chloride (Shaw 1931). The contents of the ammonium oxalate extractable Al, Fe, and Si of the soils were determined as described by McKeague (1978).

The <0.2 and 0.2 to 2 μm fractions of the soils were analyzed for crystalline clay minerals by x-ray diffraction after the removal of carbonates, organic matter, and sesquioxides (Jackson 1956).

The general properties of these soils are given in Table 1.

Time function of As removal from solution

A 0.5-g portion of soil samples was suspended into 40 ml of deionized distilled water in a 125-ml Erlenmeyer flask. The suspensions were shaken at $21.5 \pm 0.5^\circ\text{C}$ for 24 h. Ten milliliters of NaH_2AsO_4 solutions of 0.5 ppm and 10.75 ppm As were added to the 40-ml suspensions to make the 50-ml equilibrating solutions containing 0.10 ppm and 2.15 ppm As, respectively. The suspensions were then shaken for from 2 to 96 h under the same conditions. At the end of each reaction period, the suspensions were centrifuged and filtered by Millipore filters of 0.025- μm pore size. The determination of As was made on the filtrate by gas dispersion, followed by the arsenomolybdate blue method (Small and McCants 1961). The amounts of As removed from solution were determined from the differences between the initial and final As concentrations at the end of each reaction period. The removal of As from solution by the soils was rapid initially and then leveled off after a 24-h reaction period (Fig. 1). Further increase in the retention of As between the 24-h and 96-h reaction periods for all the soils studied became very small. In order to minimize surface abrasion of soil particles, all subsequent experiments on the reaction of As with soils were restricted to 24 h.

Ionic activity product

After the solutions had equilibrated for 24 h, pH values were determined. The concentrations of Al were determined by the aluminon method (Hsu 1963) with the addition of thioglycolic acid. Total Fe and ferrous Fe in the solution were

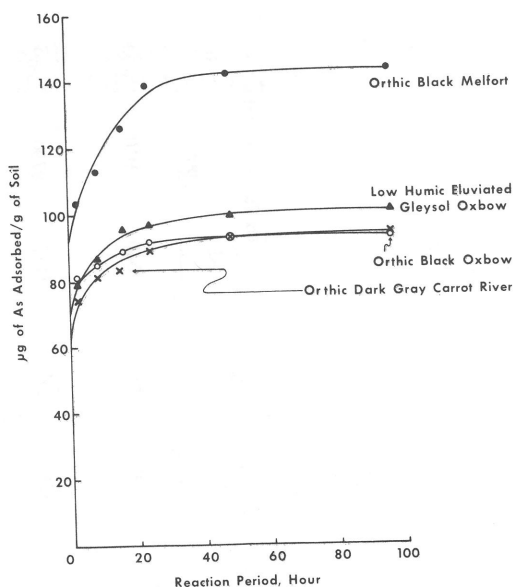


FIG. 1. The removal of As from solution by the soils as a function of time.

determined by the 1,10-phenanthroline (Jackson 1958) and bathophenanthroline (Ghosh et al. 1967) methods, respectively. The difference in the concentration between total Fe and ferrous Fe in the solution was taken to be ferric Fe. Calcium, Mg, Mn, and Pb were analyzed by atomic absorption spectroscopy, and Na and K by flame emission spectroscopy. Chloride and nitrate were determined by titrimetry and colorimetry, respectively (Jackson 1958). Sulfate was analyzed by the nephelometric method (Hamm et al. 1973). The concentrations of arsenate and arsenite were differentiated by the spectrophotometric method, which is based on the fact that arsenate, like phosphate, forms a blue complex with molybdate, but arsenite does not (Johnson and Pilson 1972).

The activities of Al^{3+} , Fe^{3+} , Ca^{2+} , Mg^{2+} , and AsO_4^{3-} were computed from the analytical data and the pertinent equilibrium constants (Adams 1971; Hess and Blanchard 1976). The hydrolysis of cations and the formation of ion pairs were taken into consideration in the computation of ionic activities. The ionic activity products of $(\text{Al}^{3+})(\text{AsO}_4^{3-})$, $(\text{Fe}^{3+})(\text{AsO}_4^{3-})$, $(\text{Ca}^{2+})^3(\text{AsO}_4^{3-})^2$, and $(\text{Mg}^{2+})^3(\text{AsO}_4^{3-})^2$ were then calculated. Manganese and Pb were not present in detectable amounts in the equilibrated solutions.

Eadie-Hofstee plot of A

The initial concentrations of equilibrating solutions with soil samples were 0.145, 0.175, 0.215, 0.260, 0.300, 1.000, 1.450, and 2.150 ppm As. The ratio and equilibrating conditions were the same as those stated in the section "As Removal from Solution." The retention data of As by the soils were treated according to the rearranged Eadie-Hofstee plot of the Langmuir equation (Hofstee 1952; Syers et al. 1973)

$$\frac{x}{m} = b - \frac{x}{kc}$$

where

x/m is the mass of As adsorbed per unit mass of soil sample, $\mu\text{g/g}$

b is the adsorption maximum

k is the constant that may be

ing energy, $\text{ml}/\mu\text{g}$, and

c is the final concentration

$\mu\text{g/ml}$

The adsorption maxima of the soils were then calculated. The values

calculated in view of the limiting equation (Harter and Baker 1971)

Effects of anions on As

Amounts of NaNO_3 , Na_2CO_3 , and NaH_2PO_4 that cover the range

Comparison of the ionic activity

Soil or pure arsenates	Initial As concentration, ppm
Orthic Dark Gray Carrot River	2.15
Orthic Black Melfort	0.1
Orthic Black Oxbow	2.15
Low Humic Eluviated Gleysol Oxbow	0.1
Pure arsenates	2.15
	0.1

^a AlAsO_4 .

^b FeAsO_4 .

^c $\text{Ca}_3(\text{AsO}_4)_2$.

^d $\text{Mg}_3(\text{AsO}_4)_2$.

Eadie-Hofstee plot of As adsorption

The initial concentrations of As of the equilibrating solutions with soil samples were 0.100, 0.145, 0.175, 0.215, 0.260, 0.315, 0.465, 0.680, 1.000, 1.450, and 2.150 ppm As. The soil:solution ratio and equilibrating conditions were identical to those stated in the section "Time Function of As Removal from Solution." After equilibration, the retention data of As by the soil samples were treated according to the rearranged form (Eadie-Hofstee plot) of the Langmuir equation (Hofstee 1952; Syers et al. 1973)

$$\frac{x}{m} = b - \frac{x/m}{kc} \quad (1)$$

where

x/m is the mass of As adsorbed per unit weight of soil sample, $\mu\text{g/g}$

b is the adsorption maximum of As, $\mu\text{g/g}$

k is the constant that may be related to bonding energy, $\text{ml}/\mu\text{g}$, and

c is the final concentration of As in solution, $\mu\text{g/ml}$

The adsorption maxima of the soils for As were then calculated. The values of k were not calculated in view of the limitation of the Langmuir equation (Harter and Baker 1977; Sposito 1979).

Effects of anions on As adsorption

Amounts of NaNO_3 , NaCl , Na_2SO_4 , and NaH_2PO_4 that cover the range of values ex-

pected in soils were added to the equilibrating solutions. The concentrations of nitrate, chloride, sulfate, and phosphate of the 50-ml equilibrating solutions containing 0.10 and 2.15 ppm As as NaH_2AsO_4 were adjusted to range from $10^{-4}M$ to $10^{-2}M$. The soil:solution ratio and equilibrating conditions were the same as stated previously.

RESULTS AND DISCUSSION

In all the soils studied, the values of $p\text{Al} + p\text{AsO}_4$, $p\text{Fe} + p\text{AsO}_4$, $3p\text{Ca} + 2p\text{AsO}_4$, and $3p\text{Mg} + 2p\text{AsO}_4$ at the lowest and highest initial concentrations of solution As were very much higher than their respective values for AlAsO_4 , FeAsO_4 , $\text{Ca}_3(\text{AsO}_4)_2$, and $\text{Mg}_3(\text{AsO}_4)_2$ (Table 2). Furthermore, the equilibrated solutions did not contain Mn and Pb in detectable amounts. At the detection limit, the ionic activity products of the equilibrated solutions of the system studied, $3p\text{Mn} + 2p\text{AsO}_4$ and $3p\text{Pb} + 2p\text{AsO}_4$, did not exceed the solubility products of $\text{Mn}_3(\text{AsO}_4)_2$ and $\text{Pb}_3(\text{AsO}_4)_2$ (Hess and Blanchard 1976). Therefore, the quantities of soluble Al, Fe, Ca, Mg, Mn, and Pb of the soils were not sufficient to precipitate the amounts of AsO_4^{3-} added. It is thus clear that the systems were much undersaturated in respect to the sparingly soluble arsenate compounds that may form in soils. This reveals that the retention of As by the soils did not proceed through precipitation reactions in

TABLE 2

Comparison of the ionic activity products to solubility products of sparingly soluble arsenate compounds of Al, Fe, Ca, and Mg

Soil or pure arsenates	Initial As concentration, ppm	$p\text{Al} + p\text{AsO}_4$	$p\text{Fe} + p\text{AsO}_4$	$3p\text{Ca} + 2p\text{AsO}_4$	$3p\text{Mg} + 2p\text{AsO}_4$
Orthic Dark Gray	2.15	25.82	72.74	30.92	32.62
Carrot River	0.1	27.35	84.44	33.90	35.56
Orthic Black	2.15	25.62	64.11	31.05	32.76
Melfort	0.1	27.77	71.45	34.66	36.47
Orthic Black	2.15	24.42	46.28	28.80	30.72
Oxbow	0.1	26.09	47.32	31.99	33.90
Low Humic	2.15	25.50	83.10	32.06	33.58
Eluviated Gleysol	0.1	27.36	84.76	35.27	36.60
Oxbow					
Pure arsenates		18.96 (Hess & Blanchard 1976) ^a	16.90 (Hess & Blanchard 1976) ^b	18.30 (Hess & Blanchard 1976) ^c	
		15.80 (Chukhlantsev 1956) ^a	20.24 (Chukhlantsev 1956) ^b	18.17 (Chukhlantsev 1956) ^c	19.68 (Chukhlantsev 1956) ^d

^a AlAsO_4 .

^b FeAsO_4 .

^c $\text{Ca}_3(\text{AsO}_4)_2$.

^d $\text{Mg}_3(\text{AsO}_4)_2$.

the systems. Hence, the depletion of As from solution apparently proceeded through the adsorption reactions of soil particles.

The adsorption data of As were then treated according to the rearranged form (Eadie-Hofstee plot) of the Langmuir equation (Fig. 2). This plotting emphasizes adsorption behavior at very low concentrations (Syers et al. 1973). The data (Fig. 2) show that in the lowest equilibrating As concentration range, as the As adsorption increased, the ratio of the amount of As adsorbed to the final concentration of solution As initially increased up to certain values, and thereafter the trend reverted. This indicates that an increasing proportion of As was adsorbed with increasing equilibrium concentration of As until the critical equilibrium concentration of As, which varied with soils, was reached. At this point, the adsorption isotherms reverted to the normal pattern. The inverse relationship at the lowest equilibrating As concentration range be-

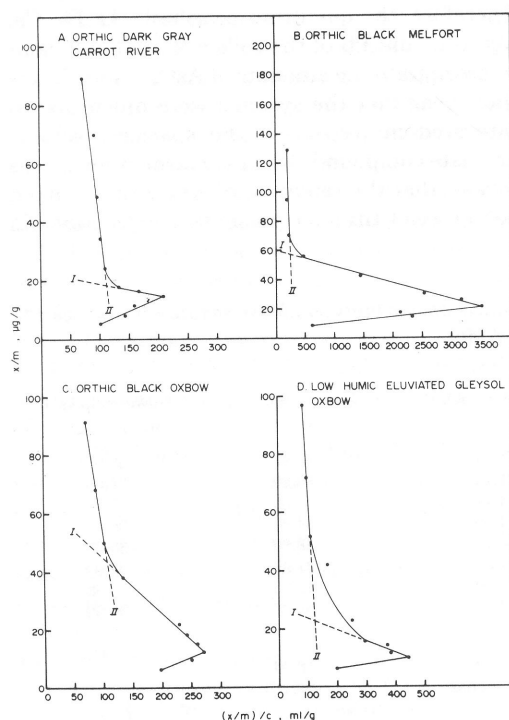


FIG. 2. Isotherms of As adsorption by the soils, using the rearranged form (Eadie-Hofstee plot) of the Langmuir equation; x/m is micrograms of As adsorbed per gram of soil sample, and c is micrograms of As per milliliter of the equilibrated solution. I and II stand for regions I and II, respectively.

TABLE 3

Arsenic adsorption maxima of the soils

Soil	Region I	Region II	Sum
	$\mu\text{g As/g soil}$		
Orthic Dark Gray	24	224	248
Carrot River			
Orthic Black Melfort	60	275	335
Orthic Black Oxbow	66	200	266
Low Humic Eluviated	28	242	270
Gleysol Oxbow			

TABLE 4

Correlation of arsenate adsorption maxima of the soils with their selected properties

Soil properties	Square of correlation coefficient, r^2	Significance, S
Oxalate extractable Al, ppm	0.997	0.001
Oxalate extractable Fe, ppm	0.850	0.077
Clay, %	0.901	0.050
pH	0.002	0.950
Inorganic C, %	0.058	0.759

low the critical point is attributed to competition from certain soil anions during the reaction period. In the higher concentration range beyond the critical point, each curve can be resolved into two straight-line components by a graphical method. Equation (1) may then be rewritten for the two straight-line regions as follows (Syers et al. 1973)

$$\frac{x}{m} = b^I - \frac{x/m^I}{k^I c} + b^{II} + \frac{x/m^{II}}{k^{II} c} \quad (2)$$

where superscripts I and II refer to region I (straight line corresponding to lower equilibrating As concentrations) and region II (straight line corresponding to higher equilibrating As concentrations).

The As adsorption maxima of the soils are summarized in Table 3. The As adsorption maxima were not found to be related to acidity and the contents of inorganic C (carbonates) at all but were linearly related to amounts of ammonium oxalate-extractable Al and, to a lesser extent, to the contents of clay and ammonium oxalate-extractable Fe (Table 4). The ammonium oxalate-extractable Al and Fe are poorly crystalline hydroxy-Al and hydroxy-Fe compounds of relatively recent weathering (Schwertmann 1964; Huang et al. 1977). Alumi-

Effect of nitrate, chloride,

Anions added to equilibrating solution	Orthic Ca
No treatment	Equilib
Nitrate: $10^{-4} M$	
$10^{-2} M$	
Chloride: $10^{-4} M$	
$10^{-2} M$	
Sulfate: $10^{-4} M$	
$10^{-2} M$	
Phosphate: $10^{-4} M$	
$10^{-2} M$	
No treatment	Equilib
$10^{-2} M$ anions:	
Nitrate	
Chloride	
Sulfate	
Phosphate	

num and Fe may be bonded hydroxyl bridging mechanism. Furthermore, these sesquioxides may be present as discrete colloids as coatings on planar surfaces of minerals, and as complexes with organic ligands, low molecular acids, and functional groups of humic acids of soils (Huang and Kozak 1977; Kodama 1977; Schwertmann and Kwong and Huang 1978; Huang et al. 1978). Table 4) indicate that these phosphorus and Fe compounds, and particularly, are closely associated with As by the soils. In addition, charges originating from exposed surfaces of micas, vermiculites, chlorites, and kaolinites present in soils (Table 1) may affect the adsorption of As by the soils. To examine the influence of adsorption of As by active soil cations, salts of nitrate, chloride, and phosphate were added individually to the soils in the systems. The chloride, nitrate, and sulfate to the equilibrating solution range from 10 000. Nevertheless, the adsorption of As by the soils did not vary significant

TABLE 5

Effect of nitrate, chloride, sulfate, and phosphate concentration on As adsorption by the soils

Anions added to equilibrating solution	Orthic Dark Gray Carrot River	Orthic Black Melfort	Orthic Black Oxbow	Low Humic Eluviated Gleysol Oxbow
As adsorbed, $\mu\text{g/g}$				
Equilibrating As concentration: $1.33 \times 10^{-6} M$ (0.10 ppm)				
No treatment	5.0	8.4	6.6	
Nitrate: $10^{-4} M$	5.8	9.2	6.2	6.6
$10^{-2} M$	5.2	9.4	6.4	6.4
Chloride: $10^{-4} M$	4.4	8.6	6.6	7.0
$10^{-2} M$	5.0	9.4	6.0	6.4
Sulfate: $10^{-4} M$	5.8	9.4	6.2	6.2
$10^{-2} M$	5.2	9.4	6.2	6.0
Phosphate: $10^{-4} M$	4.2	3.2	2.0	6.2
$10^{-2} M$	3.8	0.8	0.6	5.6
				3.4
Equilibrating As concentration: $2.87 \times 10^{-5} M$ (2.15 ppm)				
No treatment	89.6	139.0	91.6	
$10^{-2} M$ anions:				96.6
Nitrate	87.4	137.6	99.4	
Chloride	87.8	136.6	94.4	105.9
Sulfate	86.4	134.2	91.4	106.9
Phosphate	77.0	78.8	78.8	110.3
				76.7

num and Fe may be bonded together by the hydroxyl bridging mechanism (Jackson 1965). Furthermore, these sesquioxides components may be present as discrete colloidal precipitates, as coatings on planar surfaces and edges of clay minerals, and as complexes with a series of inorganic ligands, low molecular weight organic acids, and functional groups of humic substances of soils (Huang and Kozak 1970; Schnitzer and Kodama 1977; Schwertmann and Taylor 1977; Kwong and Huang 1978; Huang 1980). The data (Table 4) indicate that these poorly ordered Al and Fe compounds, and particularly Al components, are closely associated with the adsorption of As by the soils. In addition, the positive charges originating from exposed crystal edges (Huang 1980) of micas, vermiculites, smectites, chlorites, and kaolinites present in the clay fractions of soils (Table 1) may also contribute to the adsorption of As by the soils (Table 4).

To examine the influence of anions on the adsorption of As by active soil components, sodium salts of nitrate, chloride, sulfate, and phosphate were added individually with arsenate to the soils in the systems. The molar ratio of chloride, nitrate, and sulfate to arsenate added to the equilibrating solution ranged from 100 to 1000. Nevertheless, the adsorption of As by the soils did not vary significantly with increased

concentration of chloride, nitrate, and sulfate (Table 5). Phosphate, however, substantially suppressed the adsorption of As, and the extent of suppression varied significantly from soil to soil. The observed impact of added phosphate on the As adsorption (Table 5) is consistent with the interpretation that the deviation from the normal adsorption pattern at the lowest equilibrating As concentration range (Fig. 2) is attributable to anion competition. It may be inferred from the present findings that the retention of As by the soils and the subsequent retardation of As movement by the active soil components would not be particularly sensitive to variations in the levels of chloride, nitrate, and sulfate commonly present in saline soils, but would be very significantly affected by the extent of the application of phosphate fertilizers and the phosphate concentration of wastes disposed on the land.

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DETERMINATION OF ABSORPTION SPECTRA

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Rec

We conducted this extraction for preclean and for concentrating t was effective in removing percent HOAc without of Cu and Zn from bot out by adjusting the pH APDC precipitate form using a phase separation this technique were in concentration technique

INTRODUCTION

Precleaning of reagents and metals for analysis are often micronutrient research. A technique for these purposes is the roldine dithiocarbamate-metone system (APDC-MIBK) used chloroform, instead of M to extract several trace metals Zn, from acid ammonium acetate. He found that the reducing agent hydrochloride and the complexing agent phosphate, 0.1 M citrate, and not interfere with the extracting solutions of 0.5 to 1.0% inhibited the extraction of several metals. Sanzalone (1973) reported the MIBK system was highly effective in extracting Cu from hydroxylamine extracts of soils and sediments. (1974) found this system suitable for the extraction and concentration of several metals including Cu and Zn, in the dithiocarbamate extracting solution.

The objectives of the present study were to assess the usefulness of the APDC-MIBK system for concentrating Cu and Zn from soils and 2.5% HOAc and for removing contamination from these solutions.