

Fractionation of Zn, Cu, Cr, and Ni in wastewaters, solids and in soil

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INTRODUCTION. -- The application of wastewaters and sludge to agricultural land as a means of disposing of the wastes has been practiced for many decades. Many recent reports (DOWDY and LARSON, 1975; LUND et al., 1976; PAGE, 1974; SCHALSCHA et al., 1978, 1979), and symposia, (including those edited by ELLIOT and STEVENSON, 1977, and MCKIM, 1978) indicate the value of these wastes in providing nutrients and soil amendments, but they also emphasize the potential hazard of heavy metals to crops and to animals and humans.

Because of the importance of heavy metals, a number of researchers have developed empirical methods for determining the chemical forms of these elements in waters, sludges and soils. MCLAREN and CRAWFORD (1973) developed a scheme for fractionating soil Cu into five fractions varying from soluble and exchangeable Cu to the Cu extracted only by destruction of clay lattice structures. SILVIERA and SOMMERS (1977) extracted Cu, Zn, Cd and Pb from sewage-treated soils with a sequence of reagents to determine KNO_3 , DTPA- and HNO_3 -extractable forms. STOVER et al. (1976) working with sludges developed a fractionation procedure using sequential extractions with KNO_3 , KF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA, and NHO_3 . SIMS and PATRICK (1978) used a scheme which fractionated Fe, Mn, Zn and Cu in soils into eight fractions varying from water soluble to residual forms.

The objectives of the research reported here were to use the procedure proposed by STOVER et al. (1976) to (i) fractionate the Zn, Cu, Cr and Ni in the suspended solids of untreated industrial and municipal sewage waters used for irrigating agricultural land and (ii) to determine if this procedure would give useful information as to the Zn, Cu, Cr and Ni fractions in soils irrigated for several

decades with these untreated water, comparing the results with those obtained in a control soil.

MATERIAL AND METHODS. — Samples of untreated domestic and industrial sewage water carried by the Zanjón de la Aguada canal (ZA-water), which collects two thirds of the wastewaters of the city of Santiago, Chile, were collected in plastic containers and immediately filtered to obtain the suspended solids (the sludge).

Soil samples were collected from a field under cultivation sampling four holes at the vertices of a 40-by 80-m quadrangular design (RIBLE et. al. 1976 and SCHALSCHA et. al., 1978). It was deemed sufficient to sample the effective root-zone and the 40 cm below so as to evaluate any possible metal movement down the soil profile. The soil samples were collected in plastic bags and stored at 4°C. Control samples were collected from a nearby agricultural area not subjected to irrigation with contaminated water.

After air-drying the soils were passed through a 2-mm sieve. The pH of the saturated soil paste, E.C. of the saturation extract, Cation-exchange capacity by saturating the soil with KCl, Organic-C by the Walkley-Black procedure, and texture by the Bouyoucus method, were determined.

Subsamples of the «sludges» and of each of the airdried soil samples were analyzed for total Zn, Cu, Cr and Ni by digesting the soil with a HNO₃-HClO₄ mixture and determining the metals by Atomic Absorption. A blank was run each time. All the soil samples were subjected to analysis by the STOVER et al. (1976) proposed fractionation procedure using the following sequence of reagent solutions: 1 M KNO₃; 0.5 M NaF (pH 6.5); 0.1 M Na₄P₂O₇; 0.1 M EDTA (pH 6.5; double extraction); and 1M HNO₃. After each extraction the residue was washed with distilled water. The Cu, Zn, Cr, and Ni extracted were determined using a Perkin Elmer model 360 Atomic Absorption Spectrophotometer. NaF was substituted for KF in this procedure. The somewhat smaller solubilizing effect of Al by NaF as compared to

TABLE 1. — *Some selected properties of soils studied (average of two samples).*

	Depth cm	pH	E.C. mmhos/cm x 10 ³	CEC meq/100g	Organic-C %	Texture*
Soils	0-5	7.0	0.82	23.0	2.8	SL
	5-40	7.3	0.76	27.6	1.8	SL
	40-80	7.7	0.82	35.5	0.5	SCL
Control	0-5	7.7	3.00	22.8	1.6	SL
	5-40	7.9	1.15	24.0	1.0	SL
	40-80	8.2	0.74	28.1	0.7	SL

* SL = Sandy Loam.

SCL = Sandy Clay Loam.

KF was considered to be of no consequence given the high solution: solid ratio and the great excess of fluoride used (LINKE, 1958).

The main values of at least duplicate analysis of the four samples are presented in tables 1 and 2.

TABLE 2. — Total Cu, Zn, Cr and Ni and the percentage of each extracted by a sequence of extractant solutions from sludge and soil samples*.

Material	Soil depth cm	KNO ₃	NaF	Na ₂ P ₂ O ₇	% of total			Residual	Total mg/kg
					EDTA	HNO ₃	Sum		
COPPER (Cu)									
Sludge		16	9	15	28	12	80	20	428
	0.5	< 1	2	22	10	9	43	57	524
Soil	5-40	nd	2	22	10	30	64	36	553
	40-80	nd	< 1	16	10	42	69	31	472
	0.5	nd	nd	11	13	16	39	61	102
Control	5-40	nd	nd	14	9	17	40	60	99
Soil	40-80	nd	nd	17	8	18	43	57	113
ZINC (Zn)									
Sludge		-	5	52	13	5	77	23	497
	0.5	nd	nd	8	5	11	24	76	208
Soil	5-40	nd	nd	21	3	30	54	46	214
	40-80	nd	nd	8	2	36	46	54	175
	0.5	nd	nd	2	2	21	25	75	112
Control	5-40	nd	nd	2	2	23	27	73	94
Soil	40-80	nd	nd	2	2	27	31	69	102
CHROMIUM (Cr)									
Sludge		3	7	30	17	40	97	3	355
	0.5	nd	nd	40	nd	75	115	-15	23
Soil	5-40	nd	nd	nd	nd	97	97	3	9
	40-80	nd	nd	nd	nd	32	32	68	5
	0.5	nd	nd	nd	nd	39	39	61	7
Control	5-40	nd	nd	nd	nd	44	44	56	9
Soil	40-80	nd	nd	nd	nd	30	30	70	10
NICKEL (Ni)									
Sludge		33	25	4	21	4	87	13	51
	0.5	nd	nd	8	nd	nd	8	92	20
Soil	5-40	nd	nd	nd	nd	37	37	63	26
	40-80	nd	nd	nd	nd	45	45	55	24
	0.5	nd	nd	nd	nd	nd	nd	100	19
Control	5-40	nd	nd	nd	nd	nd	nd	100	19
Soil	40-80	nd	nd	nd	nd	nd	nd	100	18

* Data are averages for four samples from each soil depth and four samples of sludge (filtered residue) from four samples of untreated wastewater.

" Not detected.

RESULTS AND DISCUSSION. — STOVER et al. (1976) stated that the heavy metals extracted from sludges by the sequential described, were largely in the: exchangeable, absorbed, organically complexed, carbonate and sulfide forms, respectively. Because of the possibility of secondary precipitation and/or adsorption in one extractant and resolubilization in a subsequent extractant the identification of the indicated chemical forms of the elements with the quantities extracted is somewhat uncertain. This uncertainty is probably much greater in soils and undoubtedly increases with increase in the number of extractants used. However, insipite of the uncertainties, for convenience the names of chemical forms are in some cases used in presenting and discussing the results.

Data for the total Cu, Zn, Cr and Ni and the amount of these elements removed by sequential extraction from sludge and soils are presented in Table 2.

Some Cu was extracted from the sludge by each extractant, but about one-fourth of the total was extracted in the EDTA reagent. The total Cu in the wastewater-treated soil was about four times that of the control soil. The wastewater treated soil accumulated measurable quantities of exchangeable Cu in the surface layer and measurable quantities of adsorbed Cu throughtout the profile, whereas the control soil had no detectable quantities of these forms at any depth. Also, the treated soil hag greater quantities of adsorbed Cu throughtout the profile, whereas the control soil had no detectable quantities of these forms at any depth. Also, the treated soil had greater quantities of organically bound Cu in the 0-to-5 cm and 5-to-40 cm depths. The overall effect of the Cu in the sludge has been to increase the quantities of the more reactive forms of Cu in the soil.

About half of the total Zn in the sludge was extracted by $\text{Na}_2\text{P}_2\text{O}_7$, but some Zn was extracted by each reagent. However about one-fourth of the total Zn was not removed from the sludge in the sequential extraction. The wastewater-treated soil had approximately twice the Zn content of the control soil. Also the amount of Zn extracted by $\text{Na}_2\text{P}_2\text{O}_7$ was much greater in the treated than in the control soil. Evidently the organically complexed Zn in the sludge has significantly increased the amount of this form of Zn in the treated soil. The amount of EDTA-extractable Zn has increased in the treated soil. The lack of exchangeable and adsorbed forms

in the treated soil indicates a continual transition from these forms to less active forms. Also, a much larger fraction of the total Zn was not extracted from the soils than from the sludge.

Most of the Cr in the sludge was extracted by the $\text{Na}_4\text{P}_2\text{O}_7$ and the HNO_3 extractants. As was the case with Cu and Zn some Cr was extracted in each reagent. The treated soil contained an increase in the organically complexed Cr only in the surface layer and increased quantities of HNO_3 -extracted Cr in the 5-to-40 cm depth as compared to the control which contained measurable amounts of Cr only in the HNO_3 reagent. Evidently the Cr added in the wastewater has accumulated mostly in the surface (the cultivated layer).

The amount of total Ni in the sludge was much less than the amounts of Zn, Cu or Cr and it was largely extracted in the KNO_3 , NaF and EDTA reagents. There was no Ni removed in any reagent in the sequential extraction of the control soil. The treated soil had a measurable amount of organically complexed Ni in the surface layer and measurable amounts of HNO_3 -extractable Ni in the 5-to-80 cm depth.

A comparison of the soil that has received ZA wastewaters for several decades with the control soil indicates that the wastewater increased the reactivity of each of the four elements in the soil. This statement assumes that the reactivity of the elements decreases with increase in the number of extractions in the sequential extraction with KNO_3 , NaF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA, and HNO_3 . In the cases of Zn and Cu, increases were found in the first three extraction and for Cr and Ni increases were found with $\text{Na}_4\text{P}_2\text{O}_7$ and HNO_3 .

The estimated amounts of Cu, Zn, Cr and Ni added to the soil through the use of the ZA waters over a one-year period would be, in kg/ha/yr: Cu=3.3; Zn=3.6; Cr=3.2 and Ni=0.4. These values were calculated from an annual water use of 2×10^4 m³/ha and 0.3 kg of sludge/m³ water (CORREA, 1978).

The fractionation procedure of STOVER et al. (1976) gives potentially useful information for the status of Cu, Zn, Cr and Ni in sewage sludge. The elements extracted by KNO_3 and NaF should be available to plants. The amounts extracted by $\text{Na}_4\text{P}_2\text{O}_7$ could react more slowly but become available as the sludge organic matter decomposes. The EDTA- and HNO_3 -extracted elements are probably not highly reactive.

The distribution of Zn, Cu, and Ni into various forms in the sludge filtered from the ZA wastewater was roughly comparable but not identical to those for the activated and trickle-filter sludges studied by STOVER et al. (1976). The information gathered about the fractions of these metals in soils show clearly that the procedure applied gives useful information. The absence of exchangeable and adsorbed forms of Zn, Cr and Ni indicates that leaching of metals should not be an environmental problem, provided that a nearly neutral soil pH is maintained. The small amounts of exchangeable and adsorbed Cu should not constitute a problem either. The proportion of the chemical forms of these metals in the sludge are quite different from those in the wastewater irrigated soils. The organic matter incorporated into the soil by wastewater irrigation could be the responsible factor in interpreting the high proportion of organically bound metals found. The difference with the proportion found in the control soil is quite noticeable.

From an agricultural point of view no easily available metal forms are present in soils. However, the slow conversion of some organically bound metal by microbiological activity simultaneously with a possible moderate solubilization of carbonates and sulfides by chemical and/or microbial action, is quite feasible. Metal plant uptake should therefore be taking place. This is corroborated by field observation of crops grown on these soils where no trace metal deficiency or metal phytotoxicity symptoms are detectable.

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SUMMARY. — The suspend solids (sludge) from the municipal wastewater from the City of Santiago, Chile, and soil samples from a field that had been irrigated with the wastewater for several decades and from a field that has not received wastewater (control) were analyzed for total, Zn, Cu, Cr and Ni and for the amounts of these elements removed in a sequential extraction with KNO_3 , NaF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA and HNO_3 solution. Some of each element was removed by each extraction from the sludge. Compared to the control soil the wastewater-treated soil showed more reactive forms of these elements.

RÉSUMÉ. — On a fait le dosage de Zn, Cu, Cr et Ni total et les quantités déplacées par une procédé d'extraction successive avec solutions de KNO_3 , NaF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA et HNO_3 respectivement dans solides (boue) suspendues dans l'eau municipal de refus de Santiago, Chili et dans sols arrosés avec la même corte d'eau par plusier dizaines des anés. Dosages similaires ont été faites dans sols contrôl. On a trouvé que toutes les solutions deplacent une partie de chaque élément. Le partage de ces éléments dans les sols est différent mais, les sols arrosés avec d'eau d'refus, contient une plus grand quantité des ions que le sols utilisés de contrôl.

ZUSAMMENFASSUNG — Es wurde der Gesamtgehalt and Zn, Cu, Cr und Ni im festen Anteil des Schlammes der Abwässer von Santiago, Chile und auch die mittels einen Folge von Lösungen (KNO_3 , NaF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA und HNO_3) herausgelösten Teilmengen jener Elemente bestimmt. Die Untersuchung erstreckte sich auf Proben der mit diesen Abwässern berieselten Ackerböden sowie auf Kontroll-böden. Es ergab sich für die Schlammproben, dass alle Extraktionslösungen einen gewissen Teil der Metalle herauslösen. Die Verteilung dieser Elemente in Ackerböden untercheidet sich von jener der Schlammproben.

Aber die mit Abwässern beriselten Böden, verglichen mit unverseuchten Bödenproben, haben höhere Gehalte der untersuchten Elementen.

RESUMEN. — Se determinó el contenido de Zn, Cu, Cr y Ni total y las cantidades removidas por extracción secuencial con soluciones de: KNO_3 , NaF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA y HNO_3 respectivamente, en los sólidos suspendidos (lodos) de aguas de desechos de Santiago, Chile y en suelos regados con estas aguas por varios decenios. Determinaciones similares se efectuaron en suelos controles. En los lodos, todos los extrayentes remueven parte de cada elemento. En los suelos es diferente, pero se aprecia que el suelo regado con aguas de desecho, contiene mayor cantidad de formas reactivas que el suelo control.

RIASSUNTO. — Si misurò il contenuto totale di Zn, Cu, Cr e Ni nei solidi sospesi nelle acque comunali inquinate di Santiago del Cile e dei campioni di suoli irrigati con queste acque da varie decine di anni e il contenuto rimosso mediante un procedimento estrattivo con soluzioni di KNO_3 , NaF, $\text{Na}_4\text{P}_2\text{O}_7$, EDTA e HNO_3 ; determinazioni simili sono state fatte in suoli controllo. Si è trovato che nei solidi sospesi, tutte le soluzioni rimuovono una parte di ogni elemento. La distribuzione di questi elementi nel suolo è differente, ma si può osservare che i suoli irrigati con acque inquinate, contengono gli elementi in forme più reattive rispetto ai suoli di controllo.

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