

Chemical Forms of Cu, Zn, Ni and Co in Soil and Sediment of Ranau, Sabah

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ABSTRAK

Kajian ini dijalankan untuk menentukan taburan bentuk-bentuk kimia bagi Cu, Zn, Ni dan Co dalam sampel-sampel tanah dan sedimen yang diperolehi dari kawasan Lohan di Ranau, Sabah. Sampel-sampel tersebut diekstrak berturutan dengan 0.5 M KNO₃ untuk mengekstrak logam dalam bentuk yang mudah larut dan bertukar ganti, dengan 0.5 M NaOH untuk mengekstrak logam yang terjerap pada bahan organik, dengan 0.05 M Na₂EDTA untuk melarutkan logam dalam bentuk karbonat atau oksida, dan akhir sekali dengan 4 M HNO₃ pada suhu 80°C untuk melarutkan logam dalam bentuk mineral sulfida. Sebahagian besar logam-logam tersebut adalah dalam bentuk mineral sulfida dan hanya sebahagian kecil sahaja dalam bentuk yang mudah larut dan bertukar ganti.

ABSTRACT

This study was conducted to determine the distribution of the chemical forms of Cu, Zn, Ni and Co in the soil and sediment samples obtained from Lohan area in Ranau, Sabah. The samples were sequentially extracted with 0.5 M KNO₃ to remove soluble plus exchangeable metals, with 0.5 M NaOH to remove organically bound metals, 0.05 M Na₂EDTA to dissolve metals in oxide or carbonate form, and with 4 M HNO₃ at 80°C to dissolve metals in sulphide minerals. Most of the metals analysed were present as sulphide minerals with the exchangeable plus soluble fractions being very low.

INTRODUCTION

Metal cations in soils and sediments may be present in several different physicochemical forms:— (i) as simple or complex ions in soil solutions; (ii) as easily exchangeable ions; (iii) organically bound; (iv) occluded or co-precipitated with metal oxides, carbonates or phosphates and other secondary minerals; or (v) as ions in a crystal lattice of primary minerals (Viets, 1962; McLaren and Crawford, 1973; Soon and Bates, 1982). Metal cations present in soil in the first three forms are considered to be most available to plants, while the other forms are less available (Soon and Bates, 1982). Each

form, except for the most unavailable may presumably be estimated by an extraction procedure.

Sequential chemical extraction schemes have frequently been applied to fractionate trace metals in soils (Haq and Miller, 1972; McLaren and Crawford, 1973; Cottenie *et al.*, 1979; Garcia-Miragaya *et al.*, 1982) and sludge amended soils (Alloway *et al.*, 1979; Emmerich *et al.*, 1982; Sposito *et al.*, 1982; Soon and Bates, 1982). Reagents utilized were chosen on the basis of their selectivity and specificity towards particular physicochemical forms, although there may be overlapping in the forms extracted.

The objective of this study was to determine the distribution of the chemical forms of Cu, Zn, Ni and Co in soil and sediments from Lohan area in Ranau, Sabah using the sequential extraction procedure proposed by Sposito *et al.* (1982).

MATERIALS AND METHODS

The soil samples are as shown in Table 1. Soil samples S_1 is top soil taken from a former padi field, sample S_2 is a river sediment, while sample S_3 is a sediment taken from a mine tailing dam. All sampling sites are in the Lohan area in Ranau, Sabah. All samples were air-dried and sieved through a 2 mm sieve. Their main chemical characteristics are also shown in this table.

pH was measured in a 1 : 5 suspension using distilled water or 0.01 M CaCl_2 . Organic matter content was estimated by loss on ignition and the redox potentials (E_h) were measured using a platinum redox electrode. The total content of Cu, Zn, Ni and Co were estimated by x-ray fluorescence spectrometry (XRFS). The 'available' metals were extracted by DPTA (Lindsay and Norvell, 1978) and Cu, Zn, Ni and Co in the extracts were determined by atomic absorption spectrophotometry (Perkin-Elmer model 3030).

The four metals were fractioned with sequential extraction procedure described by Sposito *et al.* (1982). It consisted of placing a duplicate of 2 g sample of soil or sediment in a centrifuge tube and extracting sequentially according to the procedure outlined in Table 2.

The samples were equilibrated on an 'end for end' shaker, centrifuged, decanted and filtered through Whatman no. 42 filter paper after each extraction. The supernatant liquids were analysed by atomic absorption spectrophotometry (Perkin-Elmer model 3030) for Cu, Zn, Ni and Co using standards prepared in the solution of the extracting reagents. Corrections were then made to overcome the background interference.

RESULTS AND DISCUSSION

The distribution of the chemical forms of Cu, Zn, Ni and Co in the soil and sediment samples are shown in Table 3.

The total metal extracted is generally lower than the total metal content. This indicates that a proportion of each metal is present as more stable sulphide minerals or strongly associated with Mn and Fe oxides or silicate minerals. These require more drastic treatments.

The amount of Cu, Zn, Ni and Co extracted by KNO_3 is very small in all samples. Therefore there is only a small proportion of the metals in exchangeable and soluble form. This result is consistent with those obtained by Emmerich *et al.* (1982) and Sposito *et al.* (1982) for Cu, Zn and Ni in sewage sludge-treated soils. The amount of each metal is higher in the organically bound and carbonate or oxide forms. However, the amount is generally highest in the sulphide form extracted by HNO_3 . This indicates that a major proportion of the metals in the soil and sediment samples are present in less available forms. The availability of metals in the sulphide and carbonate or oxides forms is very low (Soon and Bates, 1982).

The amount of 'available' Cu, Zn, Ni and Co extracted by DPTA (see Table 1) shows the extracted fraction includes metals from more than one of the forms obtained by the sequential extraction. Eventhough it does not correspond to a combination of any two or three of those chemical forms, it does indicate that the exchangeable, soluble and organically bound forms of each metal contribute to the amount of 'available' metals. These forms are considered to be most available to plants (Cox and Kamprath, 1972; Soon and Bates, 1982).

There is poor correlation between the amount of metal extracted by NaOH and the organic matter content of the samples. However, there seems to be a decrease in NaOH extracted Cu and Zn as the organic matter content decreases. Organic matter is known to play an important role in binding Cu and Zn in soil (Schnitzer and Khan, 1972).

TABLE 1
Some important chemical characteristics of S₁, S₂ and S₃

Sample	pH		E _h (mv)	% organic matter	Total metal content (μg g ⁻¹)				*DTPA extractable metal (μg g ⁻¹)			
	H ₂ O	0.01 M CaCl ₂			Cu	Zn	Ni	Co	Cu	Zn	Ni	Co
Soil (S ₁)	6.5	6.0	479	4.38	100	400	1100	270	4.69	31.25	46.90	9.38
Sediment (S ₂)	6.2	6.1	489	1.39	770	600	600	130	28.91	15.63	7.80	8.59
Sediment (S ₃)	6.8	6.2	469	0.80	980	500	100	40	22.66	23.43	4.70	9.38

*DTPA = diethylenetriaminepentaacetic acid

TABLE 2
Order of sequential extraction and designated chemical forms extracted

Extractant	Extraction time	Chemical form extracted
1. 0.5 M KNO ₃	16 hours	exchangeable and soluble
2. 0.5 M NaOH	16 hours	organically bound
3. 0.05 M Na ₂ EDTA	6 hours	oxide or carbonate
4. 4.0 M HNO ₃ (80°C)	16 hours	sulphide

TABLE 3
Distribution of Cu, Zn, Ni and Co in the soil and sediments of the Lohan area

Sample	Amount extracted ($\mu\text{g g}^{-1}$)				Sum of metal extracted ($\mu\text{g g}^{-1}$)
	KNO ₃	NaOH	Na ₂ EDTA	HNO ₃	
COPPER					
S ₁	0.63	19.53	3.08	15.61	38.85
S ₂	0.44	16.40	83.35	629.99	730.18
S ₃	0.38	10.15	72.45	837.09	920.07
ZINC					
S ₁	0.38	31.24	46.75	62.22	140.59
S ₂	0.63	23.43	38.71	145.73	208.50
S ₃	0.50	15.62	30.94	103.98	151.04
NICKEL					
S ₁	3.75	46.86	15.44	604.11	670.16
S ₂	1.25	15.61	38.83	291.57	347.26
S ₃	1.25	15.60	15.32	20.74	52.91
COBALT					
S ₁	0.31	10.94	2.27	43.74	57.26
S ₂	0.38	10.93	6.79	31.23	49.33
S ₃	0.25	11.57	1.86	6.24	19.92

CONCLUSION

This study indicates that the chemical forms of Cu, Zn, Ni and Co in the soil and sediment samples include exchangeable and soluble, organically bound, oxide or carbonate and sulphide. Each metal is unevenly distributed in those forms. The various chemical forms, particularly the organically bound, exchangeable and

soluble forms, can contribute towards the amount of 'available' metal.

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