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## EVALUATION OF FOUR CHEMICAL EXTRACTANTS FOR METAL DETERMINATIONS IN WETLAND SOILS

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**ABSTRACT:** Wetland soils (hydric soils) are unique in their chemical characteristics compared to upland soils. It is known that they are capable of removing a variety of wastes from polluted water entering the wetland including metals and potentially toxic heavy metals. When these metals are determined in wetland soils, it is necessary to use the proper chemical extractant(s). Four commonly used chemical extractants (Mehlich 1, Mehlich 3, 0.1M HCl, and DTPA) for soil fertility evaluation were selected to measure metal concentrations of three different wetland soils/spoils. Soil samples were collected from the constructed wetland cells which were lined with Abernathy silt loam topsoil and two different mine spoil materials [collected from active coal strip-mined sites in Alabama (pH 5.9) and Tennessee (pH 3.2)]. Mehlich 3 extracted the most zinc (Zn), iron (Fe), manganese (Mn), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), and aluminum (Al), while 0.1M HCl extracted more cadmium (Cd), copper (Cu), and lead (Pb). Extractants followed the same trend in removing quantities of the metals from the three soil/spoil materials, with DTPA generally extracting the least amount of the metal (the trend was Mehlich 3 > 0.1N HCl > Mehlich 1 > DTPA). However, DTPA removed larger quantities of metals from Tennessee spoil compared to Alabama spoil and topsoil, suggesting the higher effectiveness of DTPA under acidic conditions. Metal concentrations in plant tissue did not show a definite trend in correlation with metals extracted by the four chemical extractants.

## INTRODUCTION

Recent years have seen a widespread increase in the scientific awareness and public understanding of the value of wetlands as source, sinks, and transformers of a great number of chemicals and other pollutants. Wetlands are among the most important ecosystems on earth and are usually thought of as transition zones between terrestrial and aquatic areas which possess characteristics of both systems (1,2).

Hydric soils (soils formed by wetland conditions) have special characteristics relative to dry mineral soils. Soil color and mottling which indicate the duration and depth of soil saturation, reveal the hydric condition (3). Wetland soils receive, hold, and recycle nutrients and other elements which are continually washed from upland regions. Some of these nutrients may support a wide variety of aquatic vegetation (4). Due to the high organic matter content of wetland soils, they normally have a great capacity to complex or adsorb metals and organics, which is responsible for the wetland's potential for pollutant retention (5).

Since wetland soils are developed under anaerobic conditions and a wide pH range, many of the metals are in reduced form. Considering the above mentioned specific characteristics of hydric soils compared to upland soils, it is necessary to use the appropriate chemical extractants for the determination of metals in these soils.

Many chemical extractants exist for determination of metals in dry mineral soils (6,7,8,9). However, these extractants may not be suitable for wetland soils. The purpose of this study was to evaluate the suitability of the four most commonly used chemical extractants (Mehlich 1, Mehlich 3, 0.1M HCl, and DTPA) for the determination of metals in soils.

## MATERIALS AND METHODS

Nine constructed wetland cells with a sloping bottom (0 to 35 cm), each 7 x 16 m in size, were established in 1992. Three of the wetland cells were lined with 15 cm of coal mine spoil from Tennessee, three were lined with 15 cm of coal mine spoil from Alabama, and three cells were lined with topsoil from the study area (Abernathy silt loam). The replicated substrates in separate cells were saturated with water and planted with 18 plants each of the following aquatic species: cattail (*Typha latifolia*), maidencane (*Panicum hemitomon*), pickerelweed (*Pontederia lanceolata*),

and bulrush (*Scirpus validus*). These were planted in rows in each cell. Cells were kept wet by sprinkler irrigation for five weeks until the plants were established and then were flooded to the designed depth. It should be noted that the present study was part of a larger project with more objectives.

In order to reach hydric conditions and allow the constructed wetlands to become stabilized, samples for chemical analysis were not collected for a year and a half. The first set of soil/spoil samples was collected in December 1993 and a second set in June 1994. These samples were air-dried, mixed, passed through a 2-mm mesh stainless steel sieve, and analyzed for pH (1:1 soil/water ratio). Soil/spoil samples were extracted for metal concentration analysis using the following chemical extractants: Mehlich 1 (0.05M HCl and 0.025M H<sub>2</sub>SO<sub>4</sub> at a 1:4 soil/solution ratio); Mehlich 3 (0.2N CH<sub>3</sub>COOH, 0.25N NH<sub>4</sub>NO<sub>3</sub>, 0.15N NH<sub>4</sub>F, 0.013N HNO<sub>3</sub>, and 0.0001M EDTA at a 1:10 soil/solution ratio); 0.1M HCl (at a 1:10 soil/solution ratio); and DTPA (diethylenetriaminepentaacetic acid at a 1:2 soil/solution ratio). Plant shoots were cut at water level in June 1994, dried, ground, and digested with sulfuric acid and hydrogen peroxide (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) mixture (10). All samples were then analyzed for metal concentrations using an inductively coupled plasma (ICP) emission spectrometer (Perkin-Elmer model 400). Metal concentrations in plant and soil-spoil samples were statistically evaluated by analysis of variance for randomized complete block design. Tukey's test was applied to treatment means at 0.05 probability level. The correlation coefficients (r) between metals extracted by each extractant and the amount removed by each plant were determined.

## RESULTS AND DISCUSSION

### Initial Levels of Metals in Soil/Spoil

Initial chemical analyses of the three soil/spoil types prior to saturation are presented in Table 1. Tennessee spoil had lower pH than topsoil and Alabama spoil, with a pH of 3.3 as compared to 5.5 and 5.9 respectively. Mehlich 3 extracted the largest quantity of Ca, Mg, Fe, Mn, Cu, and Al from topsoil. A similar trend was observed for Tennessee and Alabama spoils, with the inclusion of Zn and Ni. The 0.1M HCl extractant extracted the most Pb from all samples and K from topsoil and Alabama mine spoil, while DTPA extracted the least amount of all metals from the samples. Mehlich 3 and DTPA did not extract Pb from any of the soil/spoil materials. Cadmium and Cr were not detected in any of the extractants. Norval (11)

TABLE 1. Initial Metal Concentrations of the Three Soil/spoil Materials Prior to Saturation.<sup>a</sup>

Soil/spoil	pH	Extractant	Zn	Pb	Cd	Ni	Fe	Mn	Cu	Cr	Al	Ca	Mg	K	Na
mg/kg															
Top soil	5.5	Mehlich 1	3.2 <sup>a*</sup>	1.9 <sup>a</sup>	— <sup>‡</sup>	—	89.0 <sup>a</sup>	181.0 <sup>a</sup>	1.0 <sup>a</sup>	—	68.0 <sup>b</sup>	28.1 <sup>b</sup>	8.5 <sup>b</sup>	20.0 <sup>b</sup>	12.8 <sup>a</sup>
		0.1M HCl	6.2 <sup>a</sup>	2.9 <sup>a</sup>	—	—	91.0 <sup>a</sup>	199.0 <sup>a</sup>	1.8 <sup>a</sup>	—	298.0 <sup>a</sup>	37.9 <sup>b</sup>	9.1 <sup>b</sup>	69.0 <sup>a</sup>	16.0 <sup>a</sup>
		Mehlich 3	3.9 <sup>a</sup>	—	—	—	110.0 <sup>a</sup>	324.0 <sup>a</sup>	2.2 <sup>a</sup>	—	430.0 <sup>a</sup>	889.0 <sup>a</sup>	45.0 <sup>a</sup>	54.0 <sup>a</sup>	21.4 <sup>a</sup>
		DTPA	—	—	—	—	5.1 <sup>b</sup>	9.8 <sup>b</sup>	—	—	0.6 <sup>c</sup>	9.1 <sup>c</sup>	1.3 <sup>c</sup>	1.0 <sup>c</sup>	3.4 <sup>b</sup>
Alabama mine spoil	5.9	Mehlich 1	2.0 <sup>a</sup>	1.1 <sup>b</sup>	—	1.3 <sup>a</sup>	69.5 <sup>a</sup>	129.0 <sup>a</sup>	1.2 <sup>a</sup>	—	118.0 <sup>a</sup>	10.3 <sup>c</sup>	8.3 <sup>b</sup>	80.2 <sup>a</sup>	8.2 <sup>a</sup>
		0.1M HCl	2.9 <sup>a</sup>	8.8 <sup>a</sup>	—	2.0 <sup>a</sup>	76.5 <sup>a</sup>	130.0 <sup>a</sup>	1.8 <sup>a</sup>	—	128.0 <sup>a</sup>	709.0 <sup>b</sup>	149.0 <sup>a</sup>	125.0 <sup>a</sup>	9.5 <sup>a</sup>
		Mehlich 3	3.1 <sup>a</sup>	—	—	2.8 <sup>a</sup>	106.0 <sup>a</sup>	267.0 <sup>a</sup>	1.9 <sup>a</sup>	—	279.0 <sup>a</sup>	864.0 <sup>a</sup>	150.0 <sup>a</sup>	39.0 <sup>b</sup>	9.8 <sup>a</sup>
		DTPA	—	—	—	—	3.5 <sup>b</sup>	6.5 <sup>b</sup>	—	—	0.6 <sup>b</sup>	6.6 <sup>c</sup>	8.2 <sup>b</sup>	1.5 <sup>c</sup>	2.2 <sup>b</sup>
Tennessee mine spoil	3.3	Mehlich 1	4.2 <sup>b</sup>	2.3 <sup>a</sup>	—	3.1 <sup>b</sup>	221.0 <sup>a</sup>	169.0 <sup>a</sup>	2.1 <sup>a</sup>	—	214.0 <sup>a</sup>	20.8 <sup>b</sup>	12.3 <sup>b</sup>	37.6 <sup>a</sup>	2.3 <sup>a</sup>
		0.1M HCl	3.8 <sup>b</sup>	7.8 <sup>a</sup>	—	10.0 <sup>a</sup>	248.0 <sup>a</sup>	175.0 <sup>a</sup>	4.9 <sup>a</sup>	—	238.0 <sup>a</sup>	312.0 <sup>a</sup>	156.0 <sup>a</sup>	41.0 <sup>a</sup>	3.1 <sup>a</sup>
		Mehlich 3	21.0 <sup>a</sup>	—	—	20.5 <sup>a</sup>	413.0 <sup>a</sup>	199.0 <sup>a</sup>	5.2 <sup>a</sup>	—	359.0 <sup>a</sup>	368.0 <sup>a</sup>	165.0 <sup>a</sup>	54.0 <sup>a</sup>	5.2 <sup>a</sup>
		DTPA	6.5 <sup>b</sup>	—	—	8.1 <sup>b</sup>	117.0 <sup>b</sup>	49.0 <sup>b</sup>	2.8 <sup>a</sup>	—	1.6 <sup>b</sup>	7.9 <sup>c</sup>	10.7 <sup>b</sup>	2.3 <sup>b</sup>	1.1 <sup>b</sup>

<sup>a</sup> Data points represent the average of three replications.<sup>‡</sup> Not detectable

\* Means followed by the same letter in each column within each soil/spoil are not significantly different at the 5% level (Tukey's test).

reported that the 0.1M HCl extractant removed greater quantities of most of the metals compared with other extractants. However in this study, Mehlich 3 extracted the most of each metal from dry soil/spoil samples with the exception of K from topsoil and Alabama spoil. In general, with regard to the removal of metals from the three soil/spoil samples, extractants followed this order: Mehlich 3 > 0.1M HCl > Mehlich 1 > DTPA.

### **Plant Tissue Analysis**

Table 2 shows the metal analysis of plant tissue samples taken in June 1994. Maidencane significantly accumulated more Zn from topsoil and Tennessee spoil while removing the least amount of Mn from the same substrates and the least amount of Na from all materials. No significant differences were observed among the plants with regard to removing Pb, Cd, Ni, Cr, Cu, and Mg from all substrates. In general pickerelweed and maidencane were more efficient in removing most of the metals.

### **Metal Concentration in Soil/Spoil Sampled in December and June and Correlation with Plant Tissue Concentrations**

**Topsoil:** Mehlich 3 extracted higher quantities of Zn, Ni, Fe, Mn, Al, Ca, Mg, and Na from topsoil both in December and June. The 0.1M HCl extractant extracted more Pb, Cd, and Cu in both the December and June samples (Tables 3 and 4). All extractants removed very little or undetected amounts of Ni, Cr, Pb, and Cd from the topsoil. Extractants generally followed the order of: Mehlich 3 > 0.1M HCl > Mehlich 1 > DTPA with regard to removing most of the metals except for Pb, Cu, and Cd at both sampling times. However, statistically there were no significant differences among the Mehlich 3, 0.1M HCl, and Mehlich 1 extractants except for Al, Na, and K of which Mehlich 3 significantly extracted more in the June sampling. DTPA extracted more Pb from topsoil than Mehlich 3 and Mehlich 1 in both the December and June taken samples. A highly significant correlation ( $r = 0.99$  and  $0.97$ ) was observed between Mehlich 3 extractant and metal accumulation by maidencane and pickerelweed with regard to Mg (Table 5). Significant correlations were observed between the Mg extracted by 0.1M HCl and Mg accumulation by maidencane, pickerelweed, and bulrush. Calcium removal by Mehlich 3 showed a high correlation ( $r = 0.93$ ) with the Ca accumulation by cattail (Table 5). Surprisingly, large numbers of highly significant negative correlations were found between the accumulation of some metals in selected plant species and the amount of

TABLE 2. Metal Concentration in Tissue of Selected Aquatic Plants<sup>a</sup>

Soil/spoil	Aquatic plants	Zn	Pb	Cd	Ni	Fe	Mn	Cu	Cr	Mg	Ca	K	Na	Al
mg/kg														
Top soil	Cattail	38.0 b*	42.0 a	1.0 a	8.7 a	442.7 a	2445 a	5.0 <sup>a</sup>	3.3 a	829 a	6762 a	6269 b	2784 a	303 <sup>a</sup>
	Maidencane	73.0 a	32.0 a	1.0 a	13.0 a	367.0 a	395 b	2.3 <sup>a</sup>	10.7 a	490 a	1366 b	5869 b	604 b	236 <sup>a</sup>
	Pickerselweed	35.7 b	28.0 a	1.0 a	10.3 a	276.7 a	2311 a	3.3 <sup>a</sup>	7.3 a	1009 a	6225 a	9802 a	3413 a	208 <sup>a</sup>
	Bulrush	29.3 b	53.3 a	0.7 a	9.7 a	326.0 a	711 b	3.7 <sup>a</sup>	3.3 a	1192 a	1824 b	7078 b	3408 a	253 <sup>a</sup>
Alabama mine spoil	Cattail	51.3 a	30.3 a	1.7 a	10.7 a	711.0 c	1027 a	4.0 <sup>a</sup>	12.7 a	972 a	4996 a	9127 a	3674 a	399 <sup>c</sup>
	Maidencane	52.0 a	27.7 a	1.3 a	8.3 a	2312.0 b	598 b	5.0 <sup>a</sup>	11.3 a	702 a	2825 b	6217 a	845 c	1389 <sup>b</sup>
	Pickerselweed	70.7 a	36.3 a	2.7 a	15.3 a	3865.0 a	1736 a	9.0 <sup>a</sup>	13.3 a	1262 a	7535 a	10615 a	2289 b	2220 <sup>a</sup>
	Bulrush	36.0 a	22.3 a	2.0 a	6.7 a	436.0 c	510 b	5.3 <sup>a</sup>	4.3 a	1133 a	2172 b	6269 a	2277 b	270 <sup>c</sup>
Tennessee mine spoil	Cattail	43.7 b	35.7 a	2.0 a	5.7 a	193.7 a	660 <sup>ab</sup>	2.7 <sup>a</sup>	2.3 a	912 a	6770 <sup>ab</sup>	5040 a	1341 c	130 <sup>a</sup>
	Maidencane	172.0 a	23.3 a	2.0 a	2.0 a	272.0 a	174 b	3.7 <sup>a</sup>	4.0 a	630 a	1415 b	8135 a	375 d	199 <sup>a</sup>
	Pickerselweed	55.3 b	48.0 a	1.0 a	13.3 a	285.0 a	1319 a	6.3 <sup>a</sup>	8.3 a	1161 a	9404 a	9493 a	2064 b	215 <sup>a</sup>
	Bulrush	73.3 b	47.3 a	1.7 a	11.7 a	233.0 a	191 b	4.7 <sup>a</sup>	11.7 a	893 a	1566 b	9499 a	3216 a	152 <sup>a</sup>

<sup>a</sup> Data points represent the average of three replications.

\* Means followed by the same letter in each column within each soil/spoil are not significant at the 5% level (Tukey's test)

TABLE 3. Metal Concentrations of the Three Soil/spoil Materials as Determined by Four Extractants (December 1993).<sup>a</sup>

Soil/spoil	pH	Extractant	Zn	Pb	Cd	Ni	Fe	Mn	Cu	Cr	Al	Ca	Mg	K	Na
mg/kg															
Top soil	5.8	Mehlich 1	2.14 a*	0.58 <sup>a</sup>	0.07 <sup>a</sup>	0.33 <sup>a</sup>	58.8 <sup>b</sup>	238.7 <sup>a</sup>	5.10 <sup>a</sup>	0.10 <sup>a</sup>	310.0 <sup>b</sup>	861.0 <sup>a</sup>	61.8 <sup>a</sup>	45.0 <sup>a</sup>	11.0 <sup>a</sup>
		Mehlich 3	3.10 <sup>a</sup>	— <sup>‡</sup>	0.06 <sup>a</sup>	0.65 <sup>a</sup>	188.0 <sup>a</sup>	367.0 <sup>a</sup>	1.20 <sup>b</sup>	0.37 <sup>a</sup>	530.0 <sup>a</sup>	989.0 <sup>a</sup>	75.0 <sup>a</sup>	65.0 <sup>a</sup>	18.5 <sup>a</sup>
		0.1M HCl	2.90 <sup>a</sup>	2.10 <sup>a</sup>	0.09 <sup>a</sup>	0.57 <sup>a</sup>	74.0 <sup>b</sup>	262.0 <sup>a</sup>	6.60 <sup>a</sup>	0.28 <sup>a</sup>	417.0 <sup>ab</sup>	953.0 <sup>a</sup>	72.0 <sup>a</sup>	49.3 <sup>a</sup>	16.8 <sup>a</sup>
		DTPA	0.11 <sup>b</sup>	1.00 <sup>a</sup>	0.01 <sup>a</sup>	0.04 <sup>a</sup>	4.3 <sup>c</sup>	18.8 <sup>b</sup>	0.78 <sup>b</sup>	0.02 <sup>a</sup>	0.3 <sup>c</sup>	9.6 <sup>a</sup>	0.3 <sup>b</sup>	0.7 <sup>b</sup>	3.7 <sup>b</sup>
Alabama mine spoil	6.6	Mehlich 1	1.20 <sup>a</sup>	0.35 <sup>b</sup>	0.00	1.50 <sup>a</sup>	80.0 <sup>b</sup>	169.0 <sup>a</sup>	4.10 <sup>a</sup>	—	209.0 <sup>b</sup>	764.0 <sup>a</sup>	141.0 <sup>a</sup>	32.2 <sup>a</sup>	16.0 <sup>a</sup>
		Mehlich 3	2.60 <sup>a</sup>	0.34 <sup>b</sup>	0.02 <sup>a</sup>	2.00 <sup>a</sup>	231.0 <sup>a</sup>	263.0 <sup>a</sup>	2.20 <sup>a</sup>	0.40 <sup>a</sup>	389.0 <sup>a</sup>	864.0 <sup>a</sup>	160.0 <sup>a</sup>	46.0 <sup>a</sup>	25.6 <sup>a</sup>
		0.1M HCl	2.20 <sup>a</sup>	4.90 <sup>a</sup>	0.03 <sup>a</sup>	1.60 <sup>a</sup>	166.0 <sup>ab</sup>	199.0 <sup>a</sup>	5.80 <sup>a</sup>	0.10 <sup>a</sup>	218.0 <sup>b</sup>	809.0 <sup>a</sup>	152.0 <sup>a</sup>	37.0 <sup>a</sup>	17.8 <sup>a</sup>
		DTPA	0.25 <sup>b</sup>	2.20 <sup>ab</sup>	0.01 <sup>a</sup>	0.30 <sup>a</sup>	16.4 <sup>c</sup>	55.0 <sup>b</sup>	3.10 <sup>a</sup>	0.01 <sup>a</sup>	0.9 <sup>c</sup>	8.6 <sup>b</sup>	9.8 <sup>b</sup>	2.5 <sup>b</sup>	3.8 <sup>b</sup>
Tennessee mine spoil	4.1	Mehlich 1	8.30 <sup>a</sup>	0.33 <sup>a</sup>	—	4.30 <sup>a</sup>	115.5 <sup>b</sup>	89.6 <sup>a</sup>	5.80 <sup>a</sup>	—	344.0 <sup>a</sup>	358.0 <sup>a</sup>	167.3 <sup>a</sup>	19.2 <sup>b</sup>	16.5 <sup>a</sup>
		Mehlich 3	9.70 <sup>a</sup>	0.35 <sup>a</sup>	—	6.70 <sup>a</sup>	361.0 <sup>a</sup>	161.0 <sup>a</sup>	2.70 <sup>a</sup>	0.40 <sup>a</sup>	459.0 <sup>a</sup>	468.0 <sup>a</sup>	215.0 <sup>a</sup>	50.0 <sup>a</sup>	24.0 <sup>a</sup>
		0.1M HCl	9.00 <sup>a</sup>	1.60 <sup>a</sup>	0.02 <sup>a</sup>	5.10 <sup>a</sup>	160.0 <sup>b</sup>	104.0 <sup>a</sup>	6.40 <sup>a</sup>	0.30 <sup>a</sup>	438.0 <sup>a</sup>	382.0 <sup>a</sup>	186.0 <sup>a</sup>	25.0 <sup>ab</sup>	18.5 <sup>a</sup>
		DTPA	7.20 <sup>a</sup>	2.40 <sup>a</sup>	0.05 <sup>a</sup>	4.40 <sup>a</sup>	117.5 <sup>b</sup>	52.6 <sup>b</sup>	5.00 <sup>a</sup>	—	0.6 <sup>b</sup>	8.9 <sup>b</sup>	17.7 <sup>b</sup>	2.3 <sup>c</sup>	5.3 <sup>b</sup>

<sup>a</sup> Data points represent the average of three replications.<sup>‡</sup> Not detectable

\* Means followed by the same letter in each column within each soil/spoil are not significantly different at the 5% level (Tukey's test).

TABLE 4. Metal Concentrations of Three Soil/spoil Materials as Determined by Four Extractants (June 1994).<sup>a</sup>

Soil/spoil	pH	Extractant	Zn	Pb	Cd	Ni	Fe	Mn	Cu	Cr	Al	Ca	Mg	K	Na
mg/kg															
Top soil	5.4	Mehlich 1	1.45 a*	0.35 a	0.08 a	0.47 a	197.7 a	199.0 a	1.00 a	0.20 a	170.0 b	390.0 a	33.0 a	29.0 b	9.3 b
		Mehlich 3	2.70 a	— ‡	—	0.50 a	264.8 a	279.7 a	1.00 a	—	310.7 a	516.3 a	49.7 a	109.0 a	31.8 a
		0.1M HCl	1.92 a	0.93 a	0.17 a	0.49 a	260.1 a	240.9 a	1.88 a	0.28 a	223.0 <sup>ab</sup>	419.0 a	41.4 a	32.0 b	10.3 b
		DTPA	0.28 b	0.67 a	—	—	11.3 b	22.6 b	0.12 a	0.01 a	0.7 <sup>c</sup>	—	0.63 <sup>b</sup>	—	0.7 c
Alabama mine spoil	5.8	Mehlich 1	1.60 a	0.81 a	0.04 a	1.30 a	199.0 a	172.0 a	0.70 a	0.10 a	148.0 a	198.0 b	69.0 a	23.7 b	7.2 b
		Mehlich 3	2.70 a	—	—	1.60 a	277.7 a	234.7 a	1.00 a	—	220.2 a	451.8 a	88.5 a	79.3 a	32.7 a
		0.1M HCl	2.20 a	1.20 a	0.06 a	1.42 a	266.7 a	213.0 a	1.90 a	0.18 a	169.8 a	231.0 b	74.0 a	33.7 b	8.3 b
		DTPA	0.33 b	1.83 a	—	0.17 b	43.2 b	45.8 b	0.90 a	—	22.2 <sup>b</sup>	—	9.3 b	2.0 c	1.1 c
Tennessee mine spoil	4.5	Mehlich 1	2.90 a	0.94 a	0.05 a	1.15 a	183.0 a	21.0 b	1.90 a	0.07 a	200.0 a	161.0 b	57.0 a	32.7 b	7.2 b
		Mehlich 3	4.80 a	—	—	2.00 a	289.0 a	88.2 a	1.50 a	—	270.2 a	367.7 a	74.3 a	106.7 a	32.0 a
		0.1M HCl	3.90 a	1.50 a	0.10 a	1.70 a	201.0 a	36.7 b	2.20 a	0.10 a	228.0 a	176.0 b	64.3 a	35.0 b	9.5 b
		DTPA	2.67 a	1.83 a	—	1.00 a	57.7 b	31.0 b	1.30 a	—	270.2 <sup>a</sup>	—	5.2 b	3.2 c	1.7 c

<sup>a</sup> Data points represent the average of three replications.

‡ Not detectable

\* Means followed by the same letter in each column within each soil/spoil are not significantly different at the 5% level (Tukey's test).



TABLE 5. Correlation Coefficient (r) Between Chemically Extracted Metals From Topsoil and Metals Accumulated by Each Aquatic Plant.

Extractants	correlated parameters for plant and soil	cattail	maidencane	pickerelweed	bulrush
Mehlich 3	Zn	-0.55	-0.68	-0.76	-0.95*
	Pb	~	~	~	~
	Cd	~	~	~	~
	Ni	~	~	~	~
	Fe	-0.76	0.34	0.58	0.18
	Mn	0.81	-0.92	-0.80	-0.51
	Mg	-0.55	0.99**	0.97*	0.58
	Cu	~	~	~	~
	Cr	~	~	~	~
	Ca	0.93	-0.84	-0.69	-0.22
	Na	0.31	-0.86	-0.17	-0.21
	K	-0.39	-0.98*	0.38	-1.00**
DTPA	Zn	0.44	-0.97*	-0.94	-1.21
	Pb	~	~	~	~
	Cd	~	~	~	~
	Ni	~	~	~	~
	Fe	-0.81	-0.83	-0.65	-0.91
	Mn	0.38	-0.99**	-1.00**	-0.89
	Mg	0.45	0.61	0.71	0.99**
	Cu	-0.87	-0.94	-0.94	-0.76
	Cr	~	~	~	~
	Ca	~	~	~	~
	Na	-0.61	0.98*	-0.17	0.52
	K	-0.94	-0.51	-0.42	-0.73
0.1M HCl	Zn	0.44	-0.97*	-0.94	-0.21
	Pb	-0.19	-0.91	0.24	0.64
	Cd	~	~	~	~
	Ni	~	~	~	~
	Fe	-0.99**	-0.22	0.06	-0.38
	Mn	-0.99**	0.40	0.18	-0.21
	Mg	0.01	0.90	0.95*	0.94
	Cu	-0.87	-0.76	-0.76	-0.94
	Cr	0.50	-0.21	-0.82	-0.76
	Ca	0.24	-0.93	-0.99**	-0.92
	Na	0.76	-1.00**	0.37	-0.69
	K	0.59	-0.68	0.99**	-0.45

\*\*, \* significant at the 0.01 and 0.05 probability levels

~ metals undetected in soil/spoil materials

the specific metal removed by a specific extractant. This indicates the inability of that specific extractant to be used to determine metal availability in a given spoil for a given plant.

**Alabama Spoil:** A trend similar to topsoil was found with regard to the extraction of metals from Alabama spoil. Mehlich 3 generally removed the most metal, followed by 0.1M HCl, Mehlich 1, and DTPA (Tables 3 and 4). DTPA extracted more Pb and Cu than Mehlich 3, but less Cu than Mehlich 1 (differences were not significant, however). Similar to the results for the topsoil, all extractants removed very small quantities of Cd, Ni, and Cr, indicating the much lower concentration of these elements in the soil/spoil materials. Zinc concentration in bulrush, Ni and Na concentrations in cattail, and Fe concentration in maidencane were significantly correlated with metal removed by Mehlich 3 extractant (Table 6). Calcium, Zn, and Pb levels in maidencane, Ni in cattail, and Mn in pickerelweed showed significant correlation with 0.1M HCl extractant. DTPA showed highly significant correlation ( $r = 0.98$ ) with Cu concentration in bulrush, and significant correlation ( $r = 0.95$ ) with Na concentration in cattail (Table 6). This suggests that for the Alabama spoil, these extractants can be used to determine available metal levels for those specific metal-plant combinations.

**Tennessee Spoil:** DTPA extracted the largest quantity of Pb in December compared to other extractants. DTPA also extracted more Cu in the December sampling than Mehlich 3. However, 0.1M HCl extracted most Cu in both sampling periods (Tables 3 and 4). Mehlich 3 was most effective for removal of most of the metals in both sampling periods, i.e. Zn, Ni, Fe, Mn, Al, Ca, Mg, K, and Na. In general, DTPA was more effective and removed greater quantities of metals from Tennessee spoil than from Alabama spoil or from topsoil. This may be due to the lower pH of the Tennessee spoil. The extractants removed the least amounts of Cd, Ni, and Cr, indicative of the lower concentration of these metals in the soil/spoil materials. Highly significant correlations were observed between quantities removed by Mehlich 3, and the Zn and K levels in pickerelweed, Ni in bulrush, and Ca in cattail (Table 7). Lead and Zn concentrations in bulrush, Cu in maidencane, and Cu in cattail showed highly significant correlations with 0.1M HCl. As for the Tennessee spoil, these extractants can be used to determine available metal levels for the above mentioned specific metal-plant combinations.

TABLE 6. Correlation Coefficient (r) Between Chemically Extracted Metals From Alabama Mine Spoil and Metals Accumulated by Each Aquatic Plant.

Extractants	correlated parameters for plant and soil	catrail	maidencane	pickere/weed	bulrush
Mehlich 3	Zn	0.83	-0.29	-0.74	0.99**
	Pb	~	~	~	~
	Cd	~	~	~	~
	Ni	0.97*	-0.61	0.82	0.90
	Fe	-0.93	0.99**	0.26	0.83
	Mn	-0.59	-0.06	0.93	-0.15
	Mg	-0.99**	0.57	0.34	0.63
	Cu	~	~	~	~
	Cr	~	~	~	~
	Ca	-1.00**	0.95*	0.40	0.56
	Na	0.95*	-0.95*	-0.83	-0.20
	K	-0.15	-0.26	-0.52	-0.02
DTPA	Zn	-0.07	0.68	-0.95*	0.40
	Pb	-0.39	-1.00**	0.96*	-0.90
	Cd	~	~	~	~
	Ni	0.28	-0.99**	-0.08	0.83
	Fe	0.44	0.08	-0.98*	0.50
	Mn	0.83	-0.28	-0.75	-0.19
	Mg	-1.00**	0.36	0.12	0.79
	Cu	~	-0.76	-0.79	0.98*
	Cr	~	~	~	~
	Ca	~	~	~	~
	Na	0.95*	-0.61	-1.00**	-0.73
	K	-0.59	0.86	-0.23	0.71
0.1M HCl	Zn	-0.90	0.97*	-0.21	-0.60
	Pb	0.39	1.00**	-0.96	0.90
	Cd	~	~	~	~
	Ni	0.97*	-0.61	0.82	0.90
	Fe	-0.96*	0.68	0.81	0.30
	Mn	-0.16	-0.51	1.00**	-0.59
	Mg	-0.94	0.72	0.52	0.46
	Cu	-0.87	0.19	0.14	0.65
	Cr	-0.24	0.93	-0.44	-0.87
	Ca	-0.99**	0.97*	0.46	0.51
	Na	0.86	-0.41	-0.97*	-0.87
	K	0.71	-0.37	0.93	-0.58

\*\*, \* significant at the 0.01 and 0.05 probability levels

~ metals undetected in soil/spoil materials

TABLE 7. Correlation Coefficient (r) Between Chemically Extracted Metals From Tennessee Mine Spoil and Metals Accumulated by Each Aquatic Plant.

Extractants	correlated parameters for plant and soil	cattail	maidencane	pickere weed	bulrush
Mehlich 3	Zn	0.60	-0.12	1.00**	0.56
	Pb	~	~	~	~
	Cd	~	~	~	~
	Ni	-0.41	-0.50	0.90	0.98*
	Fe	0.12	0.66	0.51	-1.00**
	Mn	0.02	-0.78	-0.75	0.94
	Mg	0.91	-0.38	0.87	-0.61
	Cu	~	0.87	0.62	-0.92
	Cr	~	~	~	~
	Ca	0.95*	-0.91	0.20	0.22
	Na	0.58	0.23	0.03	-0.67
	K	-0.54	0.35	0.99**	-0.95*
DTPA	Zn	0.51	-0.01	1.00**	0.64
	Pb	0.48	0.08	0.57	-0.82
	Cd	~	~	~	~
	Ni	-0.41	-0.50	0.90	0.98*
	Fe	-0.64	1.00**	-0.28	-0.66
	Mn	0.54	-0.99**	-0.31	0.62
	Mg	0.99**	-0.61	0.71	-0.38
	Cu	~	~	~	~
	Cr	~	~	~	~
	Ca	~	~	~	~
	Na	-0.94	-1.00**	0.95	0.90
	K	-0.54	0.35	0.99**	-0.95*
0.1M HCl	Zn	-0.49	0.86	0.49	0.98*
	Pb	0.03	-0.57	-0.90	1.00**
	Cd	~	~	~	~
	Ni	-0.24	-0.33	0.80	0.93
	Fe	-0.92	0.91	-0.68	-0.25
	Mn	0.10	-0.83	-0.70	0.91
	Mg	0.84	-0.98*	0.05	0.34
	Cu	-0.50	1.00**	0.14	-0.61
	Cr	~	~	~	~
	Ca	1.00**	-0.71	0.51	-0.12
	Na	0.22	-0.16	0.42	-0.33
	K	-0.03	0.78	0.91	-0.98*

\*\*, \* significant at the 0.01 and 0.05 probability levels

~ metals undetected in soil/spoil materials

### CONCLUSIONS

The results of this study showed the complexity and dynamics of metal removal by aquatic plants and chemical extractants from hydric (wetland) soil. Even though there is an apparent lack of a universal extractant for removal of metal or metal nutrient determinations under differing conditions, a number of extractants have been studied and compared for extraction of metal from dry (upland) soils (12,13,14,15,16). However, the search for an appropriate extractant for routine metal determination of hydric soils is warranted. Mehlich 3 was clearly the most effective in extracting most of the metals in this study, although it did not have the highest correlation with uptake levels in the selected plants. Similar studies with more plant species will help in selection of more appropriate chemical extractants for the extraction of metals and metal nutrients from hydric soils.

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